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A novel method to study the reversibility of aromatic substitution reactions

Aria, Porus Soli, Ph.D.

City University of New York, 1991

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A NOVEL METHOD TO STUDY THE REVERSIBILITY OF AROMATIC SUBSTITUTION REACTIONS

by

Porus S. Aria

A dissertation submitted to the Graduate Faculty in Chemistry in Partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

1991

Approval Page

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

1/22/91
Date

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1/23/91
Date

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Abstract

A NOVEL METHOD TO STUDY THE REVERSIBILITY OF AROMATIC SUBSTITUTION REACTIONS

by

Porus S. Aria

Mentor: Professor Leonard H. Schwartz

Optically active 2,2'-dicarbomethoxy-9,9'-bianthryl (**1**) has been observed to racemize in the presence of phenyl and benzyl radicals. This racemization process is suggested as a means of studying the reversibility of radical addition to an anthracene ring. It is suggested that addition of the radical forms a σ-complex that has a lower rotational energy barrier between the central C-9, C-9' carbon atoms than the starting bianthryl **1**. Reversal of the addition step would result in recovery of racemized **1** if the bond rotation in the σ-complex were competitive with the reversal step. No racemization was observed in the absence of the radical source. The racemization was reduced or completely prevented by the presence of radical inhibitors. These results are interpreted to mean that the radical adds reversibly to the anthracene ring of **1**.

The phenyl radical was generated by the thermal decomposition of (1) phenylazotriphenylmethane (PAT) at 50° C, (2) benzoyl peroxide at 80° C and (3) diphenylmercury at 180° and 200° C in bromobenzene. The benzyl radical was generated by the thermal decomposition of dibenzylmercury at 160°, 130°, 100° and 50° C in bromobenzene and the *m*-fluorobenzyl radical was generated by the thermal decomposition of bis(*m*-fluorobenzyl)mercury at 160° and 130° C.

Initial rates of racemization and the order with respect to each reagent was determined. Arrhenius parameters for the racemization of bianthryl **1** in the presence of dibenzylmercury were determined.

Methyl-2-α–naphthyl-3-nitrobenzoate (**51a**) was observed to racemize in the presence of KF in 18-crown-6 solution of acetonitrile at 83° and 100° C. These results suggests that the fluoride ion adds reversibly to biaryl **51a**.

Acknowledgements

Throughout my tenure as a graduate student there have been many people who have aided me in one way or another and for whose services I am grateful. However to thank everyone is, in effect, not to thank anyone, and therefore I make special mention only of those who have been most instrumental to the success of my graduate education.

I thank Professor Leonard H. Schwartz for inspiration, patience and guidance. I enjoyed the freedom to persue research as I desired, even when results came slowly. His pain-staking effort to correct this manuscript is greatly appreciated.

I would like to express my appreciation to Professors Herbert Meislich, Jack Morrow and Howard Haubenstock, the members of my thesis committee for their criticisms and suggestions.

I would like to thank the following persons: Professor Theodore Axenrod for introducing me to high field NMR techniques and Professor Samuel Wilen for introducing me to the "art" of resolving optical isomers. Mr Hugo Schimatz for making many special pieces of apparatus and for teaching me glass blowing. Mr Ramsey Pal for keeping the NMR's running and the staff at the Rockefellar University for recording the mass spectra during the course of my work.

A special note of thanks is also due to Jim Scaffidi. As my friend and roommate, we shared many meaningful discussions and

therapeutic diversions that made the good times memorable and the bad times tolerable.

My family has been consistently supportive and warmly encouraging all these years. This usually taken for granted devotion is very much appreciated and thanked.

Finally I thank the Chemistry Department of The City College of New York for their financial support.

In loving memory of my father

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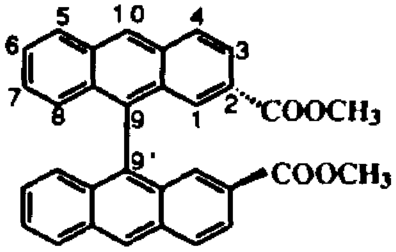
Chapter 1

Introduction

A new method has been developed to probe the reversibility of addition of radicals and nucleophiles to aromatic substrates. Optically active 2,2'-dicarbomethoxy-9,9'-bianthryl (1) has been observed to racemize in the presence of various radicals. This process is suggested as a means of studying the reversibility of radical addition to an anthracene ring.

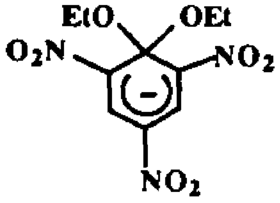


1

This thesis explores the racemization of biaryls as a probe for studying the reversibility of addition of various radicals and nucleophiles to aromatic systems. To place this method in perspective, some familiarity with the current methods used to study reversibility of addition to aromatic substrates is necessary.

1.1. Reversibility of Aromatic Substitution Reactions

The ideal approach for studying the reversibility of aromatic substitution reactions would involve the isolation or spectroscopic determination of the σ-complex and a study of its decomposition. Except for numerous investigations of relatively stable Meisenheimer complexes, e.g., **2**, which result from nucleophilic addition to an aromatic ring containing at least two strongly electron withdrawing groups,[1] these studies are relatively rare.



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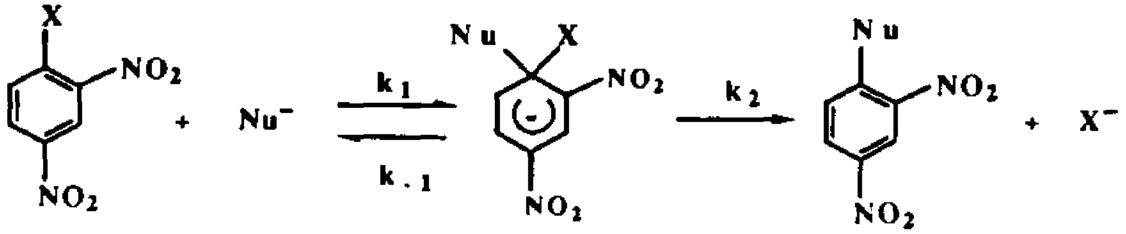
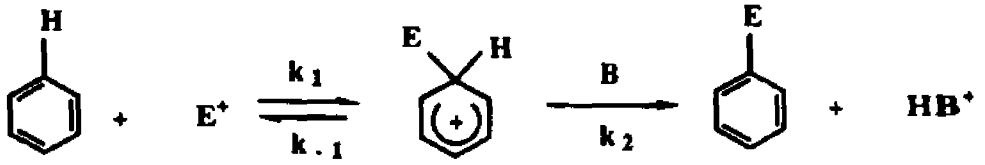
The generally accepted bimolecular mechanism for nucleophilic aromatic substitution (S_NAr) is shown in Scheme I.



Scheme I. S_NAr Mechanism.

Reversibility studies on activated aromatics (those containing at least two electron withdrawing groups) have shown that the rate-determining step is dictated by the nucleophile, the leaving group and the solvent used.[2]

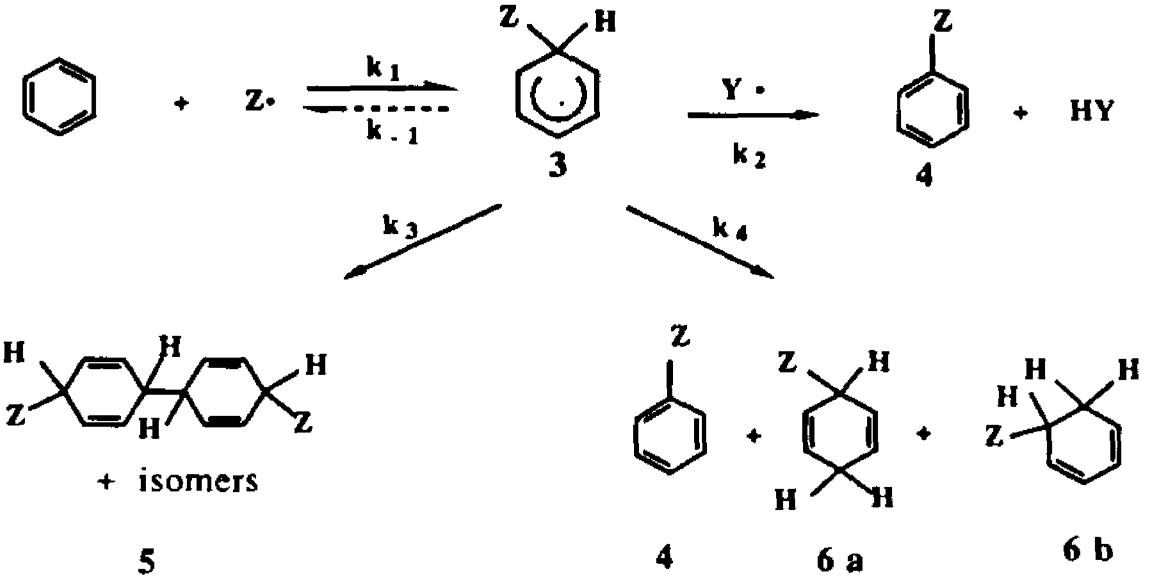
The most common method for studying the reversibility of addition of radicals and electrophiles to aromatic rings involves the use of kinetic isotope effects. The generally accepted mechanism for electrophilic aromatic substitution is shown in Scheme II.



Scheme II. General Mechanism for Electrophilic Aromatic Substitution

The relative magnitudes of k_{-1} and $k_2[B]$ vary considerably. As k_{-1} gains in importance compared to $k_2[B]$, the kinetic isotope effect (using C_6D_6) should increase. Electrophilic aromatic substitution reactions have been extensively studied using kinetic isotope effects.[3] Typically an equimolar mixture of C_6H_6 and C_6D_6 or other such pair of aromatic substrates is studied. The substitution products C_6H_5E and C_6D_5E are determined quantitatively and an isotope effect is reported as a ratio of C_6H_5E to C_6D_5E. With electrophilic aromatic substitution reactions, assuming the mechanism in Scheme II, such an isotope effect, if of sufficient magnitude, allows the conclusion that the formation of the σ-complex is reversible.

The reversibility of radical attack on aromatic substrates in homolytic substitution reactions has been the subject of numerous reports.[4,5,6] A general mechanism for homolytic aromatic substitution is shown in Scheme III. For some systems, cyclohexadienyl compounds **6** and/or dimers **5** or products derived from the dimers have been isolated, while from others, only the simple substitution product **4** has been obtained.[5] Many of the previous studies of the reversibility of addition of radicals to aromatic compounds have involved the use of kinetic isotope effects.[7,8] Often an equimolar mixture of C_6H_6 and C_6D_6, or other such pair of aromatic substrates is studied. The substitution products C_6H_5Z and C_6D_5Z are determined quantitatively and an isotope effect is reported as a ratio of C_6H_5Z to C_6D_5Z.



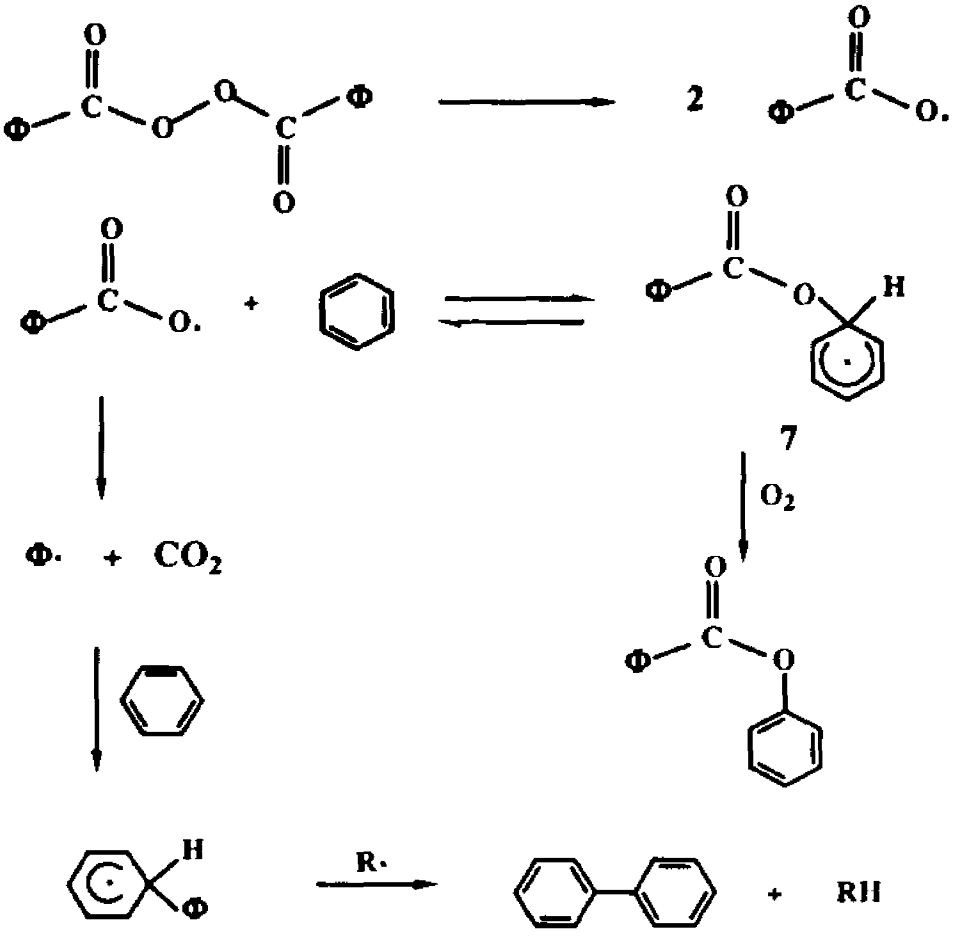
Scheme III. General Mechanism for Homolytic Aromatic Substitution

If no isotope effect is observed, then the first step of the mechanism in Scheme III is rate determining and the addition is claimed to be irreversible. Minisci and coworkers, recently showed that the addition of the phenyl radical to pyridine rings is irreversible.[9] No isotope effect was observed, which was interpreted to mean that the first step in the mechanism of Scheme III is rate determining. In the same paper,[9] a significant kinetic isotope effect was reported for isopropyl and α-tetrahydrofuranyl radicals, indicating that the C-H bond is broken in the rate determining step. The addition of these radicals was claimed to be reversible.

With homolytic aromatic substitution reactions, the observance of an isotope effect alone does not allow a conclusion to be made concerning the reversibility of the first step (Scheme III). Additional information is necessary because of the complexities found in homolytic aromatic substitution. Consider, for example, that the σ-complex (3) (Scheme III), is formed irreversibly and is competitively oxidized to substitution product (4) (step 2 and/or 4) or transformed to dimers (5) (step 3). Steps 2 and 4, which involves the breaking of the C-H (C-D) bond, could exhibit appreciable primary isotope effects, while step 3 would exhibit, at best, a small secondary isotope effect. Thus the irreversibly formed σ-complex would lead to the formation of a greater amount of C_6H_5Z than C_6D_5Z. The excess deuterated σ-complex would ultimately be involved in the formation of dimers, leading to a partitioning of the deuterium between different products (4 enriched in H, 5 enriched in D). Since more of the C_6H_5Z than C_6D_5Z would be formed, an isotope effect might be reported and reversibility of addition mistakenly claimed. The additional information that is necessary before proper conclusions can be drawn concerning the reversibility of radical addition is an accurate material balance (often not possible with radical reactions). This would establish whether competing pathways are present which can partition the σ–complex with isotopic discrimination. As an alternate approach, one could isolate without enrichment, the residual C_6H_6 and C_6D_6 and compare their relative amounts to that of the starting mixture. If unchanged, addition of Z• to the aromatic could be concluded to be irreversible. To obtain either type of necessary data could involve considerable experimental difficulties. In a particularly careful study involving the addition of phenyl radicals to benzene, Eliel and coworkers[7c] showed that an isotope effect, as measured by the product deuterium content, was not due to reversible addition but was due to the side reactions of the irreversibly formed σ-complex.

Kinetic isotope data must be treated with caution. A small isotope effect could result from reversible addition, or could be due to a second order effect such as change in hybridization at the reacting carbon. To illustrate the interpretive difficulties involved, Sakurai and Hosomi[10] have attributed an isotope effect of 1.5, observed in a homolytic silylation reaction, as being due to a second-order effect. Denny and Klemchuk,[11] on the other hand, interpreted a smaller isotope effect of 1.32 from a homolytic intramolecular aromatic substitution reaction as being due to reversible addition. This interpretation has been questioned.[12] Kaboyashi and coworkers have attributed isotope effects from 1.12 to 1.57 as originating from reversible addition.[13]

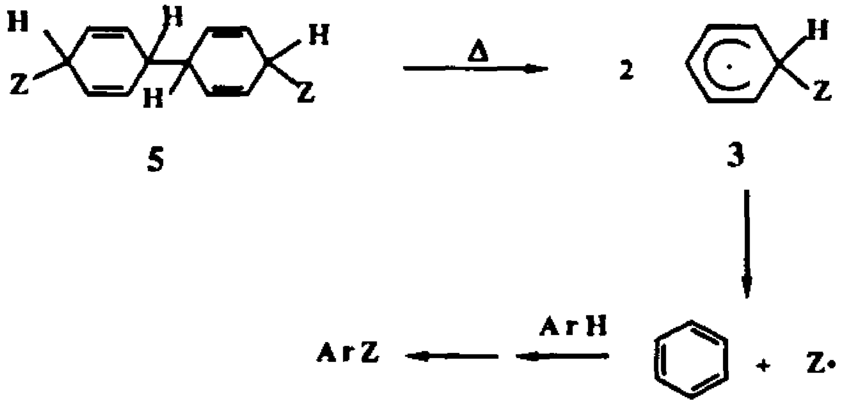
Another general method for studying reversibility involves the use of trapping agents to prevent the σ-complex from reverting to starting material. Consider the reaction of benzoyl peroxide with benzene (Scheme IV).[12]



Scheme IV. Reaction of Benzoyl Peroxide with Benzene

In the absence of oxygen, the major product is biphenyl. Phenyl benzoate is obtained in 13% yield. In the presence of oxygen (trapping agent), the yield of biphenyl drops significantly and the yield of phenyl benzoate increases correspondingly. These results have been used as evidence for the reversible addition of the benzoate radical (PhCOO•) to benzene. With oxygen present, the σ-complex 7 is trapped as phenyl benzoate. In the absence of oxygen, the removal of the hydrogen from this complex is relatively slow, which allows both the reversal of the first step and the irreversible decomposition of PhCOO• to Ph• to occur. Various other oxidizing agents have been used in similar studies.[14] It is generally assumed in using this method of studying reversibility that the trapping agent does not alter the exact nature of the attacking radical or the reaction pathway. These assumptions, which are difficult to verify, weaken the reliability of the method.[15]

Another method for studying the reversibility of radical addition involves generating the σ-complex by some means other than the attack of the radical on an aromatic substrate, and investigating the products that results. This is illustrated in Scheme V.



Scheme V. Thermal Decomposition of Dimer 5.

Dimer 5 is thermally decomposed in the presence of an aromatic substrate (ArH) known to react with the radical Z•. The isolation of ArZ is an indication that the σ-complex 3 decomposes to Z•. Since this step is the reversal of the addition step which would form the σ-complex, the isolation of ArZ is taken to indicate that in the case of addition of Z• to benzene, the σ-complex is formed reversibly. This method must be interpreted with great care, since the temperature necessary to convert the dimer **5** to the σ-complex **3** is generally significantly higher than the temperature employed for the corresponding substitution reaction of Z•. In a number of cases, employing such a method, reversibility of radical addition to an aromatic substrate has been claimed, in spite of the fact that the temperature used to decompose the cyclohexadienyl precursor was above the temperature of the corresponding aromatic substitution reaction.[16] It would appear that a negative result, i.e., failure to observe ArZ (Scheme V) has more significance than a positive result.[7b]

Based on the preceeding discussion, it can be seen that to establish unequivocally the reversibility of radical addition to an aromatic substrate can be a difficult task. There is a need for a simple and more easily interpretable general method.

This thesis offers the racemization of biaryls as a probe for studying the reversibility of addition to aromatic substrates.

At this point a brief discussion of atropisomerism is in order.

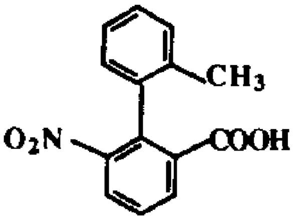
1.2. Atropisomerism

Atropisomerism has been defined by Kuhn[17] as isomerism caused by 'freezing' the internal rotation about a single bond. The first example of stable isomers due to restricted rotation was discovered by Christie and Kenner.[18] They resolved 2,2'-dinitro-6,6'-

diphenic acid. Since then many biphenyl derivatives have been resolved into optical isomers.[19] The term atropisomerism, in its original meaning, was phrased to cover the optical isomers of biphenyls. Hindered biphenyls can exist as enantiomers because the two benzene rings are not coplanar. With unsymmetrically substituted rings the plane passing through the pivotal bond and one of the benzene rings cannot be a σ–plane.

The major factor responsible for atropisomerism (restricted rotation) in biphenyls is the bulkiness of the ortho substituents.[20] Other biaryls exhibit similar properties. In bianthryls, benzo-benzo interactions and the interactions of the 2,2'-substituents (or H) are the major contributors to the rotational barrier.[19a] The rotational barriers of these compounds have been determined by measuring the rate of racemization of the optically active biaryls.

The steric effect of the ortho substituents is not the only factor which can influence the optical stability of a biaryl. Adams and coworkers[21] found that the optical stabilities of biphenyls **8**-**10** are in the order **10** > **9** > **8**. However on steric grounds, one would predict the optical stability to be **8** > **9** ~ **10**, since the van der Waals radii are in the order $CH_3 > NO_2 > COOH$.



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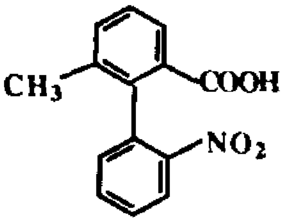

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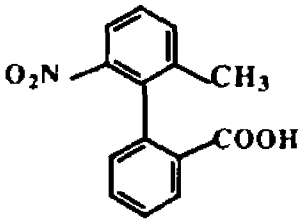
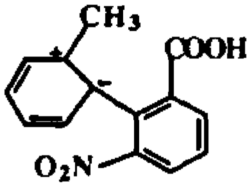


10

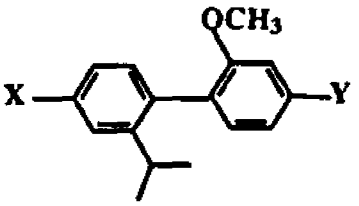
Baddeley[22] proposed a special type of structural influence to explain these results. It was suggested that out-of-plane bending about the pivotal C-1, C-1' bond could facilitate racemization by reducing the steric strain in the rotational transition state. The ease of this bending should depend on the electron density at the pivotal carbon atoms e.g., structure **11**. The greater the electron densities at the pivotal carbon atoms the more sp^3 character they would exhibit, and thus the greater the bending they could accomodate.



11

The electron densities in the upper rings of compounds **8-10** are in the same order as the rates of racemization.

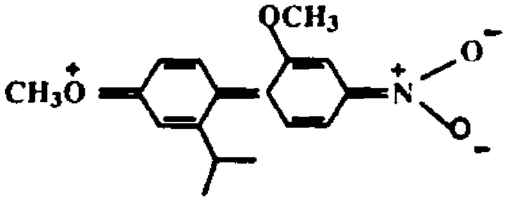
Oki and Yamamoto[23] reported the effects of para-substituents on the energy barrier to racemization of 2-isopropyl-2'-methoxy-biphenyl (**12**). They postulated that the effects of the substituents on the rotational barrier in biphenyls can be interpreted in terms of resonance stabilization and out-of-plane bending of the axis bond in the transition state.



12

	X	Y	ΔG≠
12a	H	H	19.2
12b	OCH_3	NO_2	18.2
12c	OCH_3	OCH_3	18.0

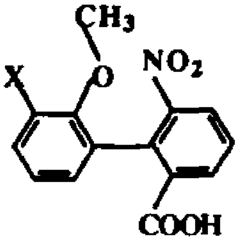
The lower rotational barrier in **12b**, may be explained in terms of resonance stabilization of the transition state due to the contribution of canonical structure **13**. The two electron donating methoxy groups in the case of **12c** increase the π-electron density at the 1,1'-positions, which makes the out-of-plane bending of the axis bond easier. This lowers the energy barrier to rotation compared to **12a**.



13

Harris and Ling[24] also have proposed that the dependance of the racemization rates of various optically active 2,2'-diiodobiphenyls on the para-substituents could be interpreted on the basis that the axis bond is bent out-of-plane of the benzene rings in the transition state.

In 1934, Chien and Adams[25] found that a substituent at the 3'-position of 2-carboxy-2'-methoxy-6-nitrobiphenyl (**14**) can considerably reduce the rate of racemization. The magnitude of the effect was found to be dependent on nature of the 3'-substituent.



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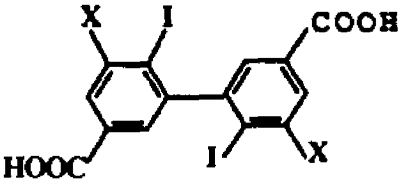
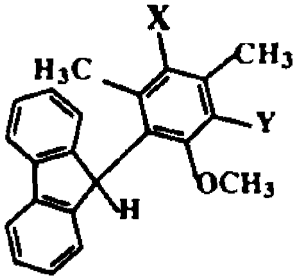


15a X = H
15b X = I

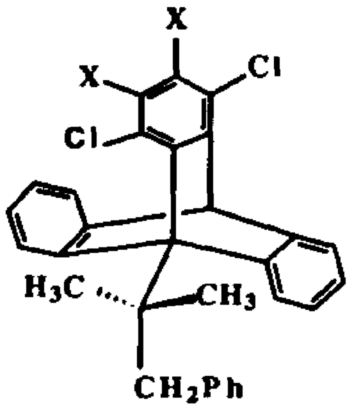
The origin of this effect was not understood at that time. In 1950 Rieger and Westheimer[26] found that 2,2'-diiodo-5,5'-dicarboxybiphenyl (**15a**) racemizes 30,000 times faster than 2,2',3,3'-tetraiodo-5,5'-dicarboxybiphenyl (**15b**), the enthalpies of activation ($\Delta G^{\neq}$) being 21.0 kcal/mol and 27.0 kcal/mol, respectively. Their pioneering work on molecular mechanics[26] revealed the origin of the retarding effects of the meta substituents, which is now called the "buttressing" effect. In the normal planar transition state for racemization, the ortho groups bend away from each other to relieve the steric strain. The presence of a group on the adjacent meta position, prevents the bending to some extent by "buttressing" the ortho-substituent, thus raising the transition state energy. The ground state in these compounds is essentially free of strain, and the buttressing does not appreciably affect the ground state energy. A buttressing effect that increases the energy barrier to racemization is refered to as a positive buttressing effect. The buttressing effect on the energy barrier to internal rotation about a sp^2-sp^2 single bond is generally positive, because the ground state of the molecule is not much affected by the introduction of a meta-substituent. However, with internal rotation about an sp^2-sp^3 or sp^3-sp^3 bond, the situation is somewhat different because the ground state usually suffers from congestion. If a substituent is introduced in the neighborhood of a congested site, it would increase the congestion and would increase the ground state energy. Since the energy barrier to rotation is the difference in energies between the ground state and the transition state, it is possible that the buttressing effect either raises or lowers the energy barrier.

Oki and coworkers observed a positive buttressing effect in 9-arylfluorenes (**16**).[27] The rotational barrier increased in the series **16c** > **16b** > **16a** .



16a X = Y = H
16b X = Br; Y = H
16c X = Y = Br

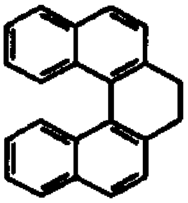
In a series of 9-(1,1-dimethyl-2-phenylethyl)triptycene derivatives (**17**),[28] the tetrachloro derivative **17a** has a lower rotational barrier than the dichloro derivative **17b**. This result shows a reverse or negative buttressing effect.



17a X = Cl
17b X = H

The *peri*-substituents in 9-*t*-alkyltriptycenes (**17**) play an important role in determining the energy barrier to rotation.[29] The 9-*t*-alkyltriptycenes (**17**) constitute a highly congested system. A substituent at a *peri*-position increases the congestion so that the C_9-C_{alkyl} bond is forced to bend away from that *peri*-substituent. This bending should affect the ground state energy. The larger the bending, the less stable should be the ground state, due to distortion of normal bond angles. If this feature is retained during the rotation process, the blocking groups (9-substituent and the *peri*-substituents) do not pass each other simultaneously. This should cause the energy barrier to decrease. Hence the negative buttressing effect originates from the fact that the transition state for rotation is less destabilized than the ground state upon introduction of the buttressing substituent.

It has been reported by Colter and Clemens,[30] that 9,10-dihydro-3,4,5,6,-dibenzophenanthrene (**18**) and 1,1'-binapthyl (**19**) racemize more rapidly when they form a charge transfer (CT) complex with electron acceptors, compared to their neutral molecular states.



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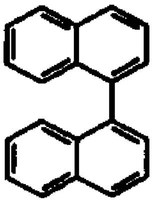
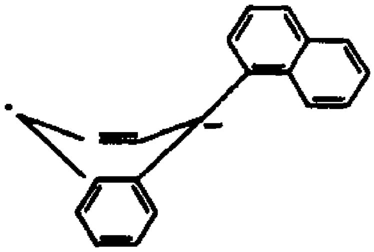


19

It was presumed that this effect is related to the radical ion character of the CT complex.[31] Ito and Hatano[32] reported the radical ions of **18** and **19** racemizes more rapidly than the corresponding neutral compounds, without the cleavage of the 1,1'-bond. Although the cause of this effect is not explained by the authors, it is conceivable that the resulting radical ion is present in a boat conformation such as **20**. This would lead to consecutive benzo-benzo interactions as opposed to simultaneous interactions as in **19** thus resulting in a lower rotational barrier.



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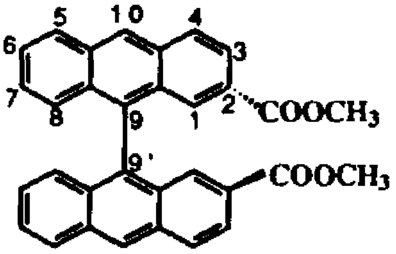
Racemization of 1,1'-binapthyl (**19**) is also hetrogeneously catalyzed by active carbons and carbon black,[33] Raney nickel[34] and platinum.[35] The heterogeneous catalysis on various carbon surfaces, has been suggested to occur via adsorption on relatively large graphitic planes.[36] Such adsorption would lead to a planar state which accounts for the racemization. Adsorption to form a planar molecule is unlikely on the more irregular surface of nickel and platinum. It was suggested that in these cases racemization occurs by rapid reversible electron transfer.

Crawford and Smyth suggested that electrophilic attack of a proton on an aromatic ring could lead to racemization of biphenyls.[37] In various series of chiral biphenyls, with constant blocking substituents, electron-donating groups were found to enhance the racemization rate while electron-withdrawing groups reduced it. It was argued that electron-donating groups would enhance the protonation of the ring, causing the pivotal carbon to be tetrahedral (sp^3), thereby reducing the rotational barrier. However, it should be pointed out that the racemization solutions were not acidic, and no attempt was made to correlate the racemization rates with the acidity of the medium.

1.3. Radical Catalyzed Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1)

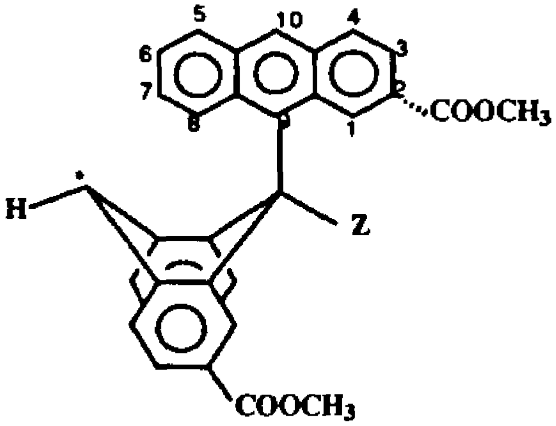
It has been established in our laboratory[38] that various radical systems catalyze the racemization of 2,2'-dicarbomethoxy-9,9'-bianthryl (**1**).



1

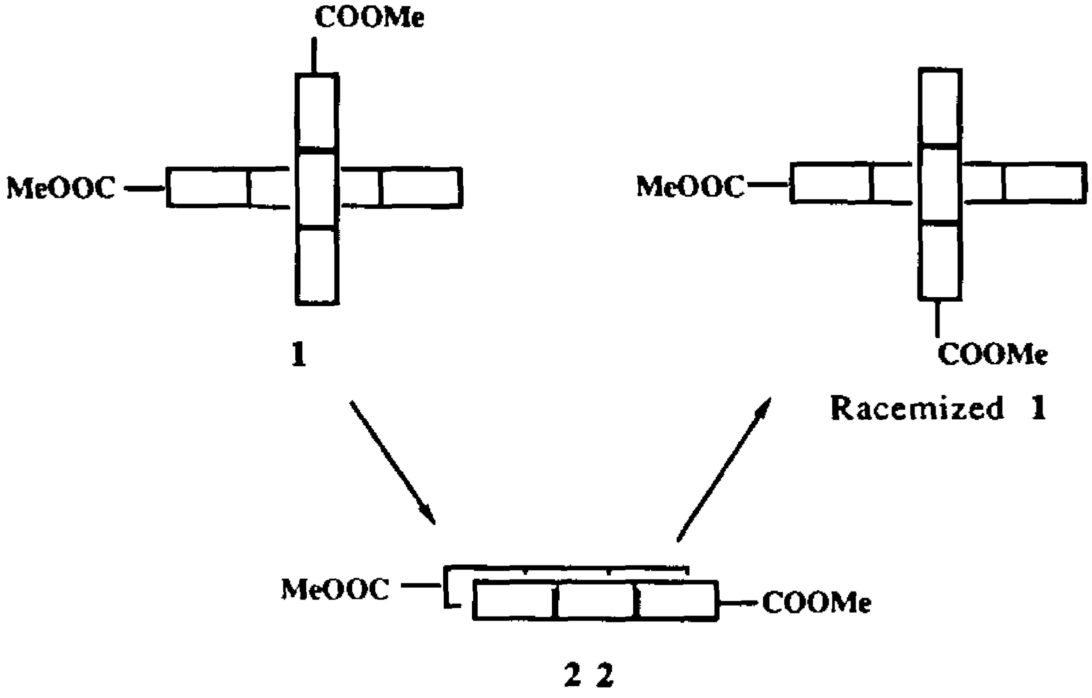
For example, heating bianthryl **1** in the presence of phenylazotriphenylmethane (PAT), a source of phenyl radicals in bromobenzene at 50 °C resulted in the recovery of partially racemized **1**.[39] A control experiment, without the radical source, showed no racemization.

To explain these results, it has been postulated that reversible addition to the aromatic system occurs via a cyclohexadienyl intermediate (σ-complex), e.g. **21**.



2 1

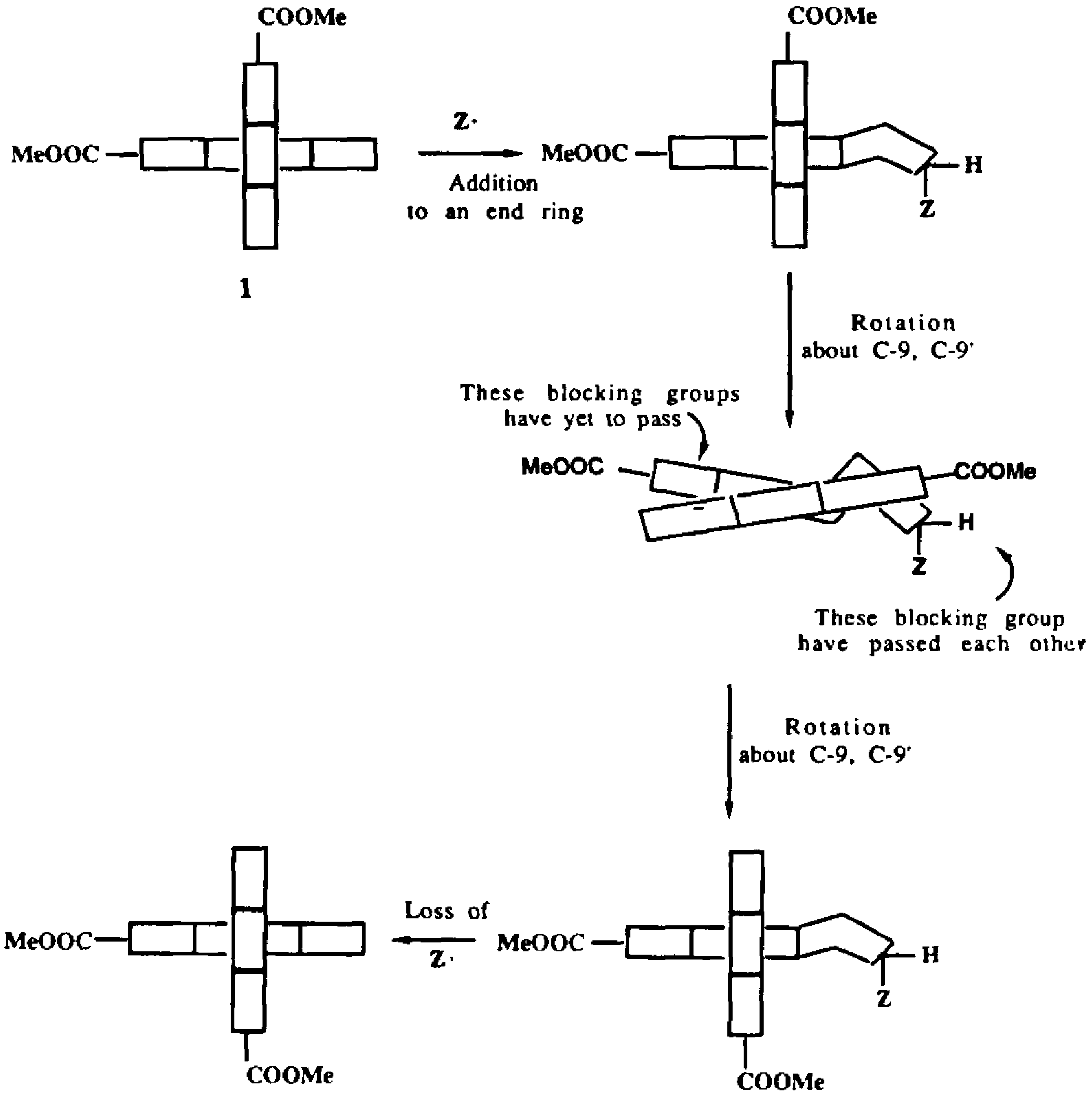
Structure **21** arises by the radical Z• attacking the C-9 position of bianthryl 1. The attachment of a radical to any other carbon of the anthracene ring would also distort that anthracyl unit from planarity due to the conversion of one of the carbons (the one which is bonded to the radical) from a trigonal sp^2 to a tetrahedral sp^3 arrangement. As a result, the rotational barrier about the pivotal bond (C-9, C-9') should be lowered due to a decrease in the number of simultaneous steric interactions in the rotational transition state. These arguments are illustrated in Schemes VI, VII and VIII.



Scheme VI. Simultaneous Interaction of Blocking Groups in the Racemization of Bianthryl **1**.

Scheme VI shows the rotational process in the starting bianthryl **1**. In the transition state (**22**), both sets of blocking groups pass each other simultaneously, resulting in a large energy barrier.

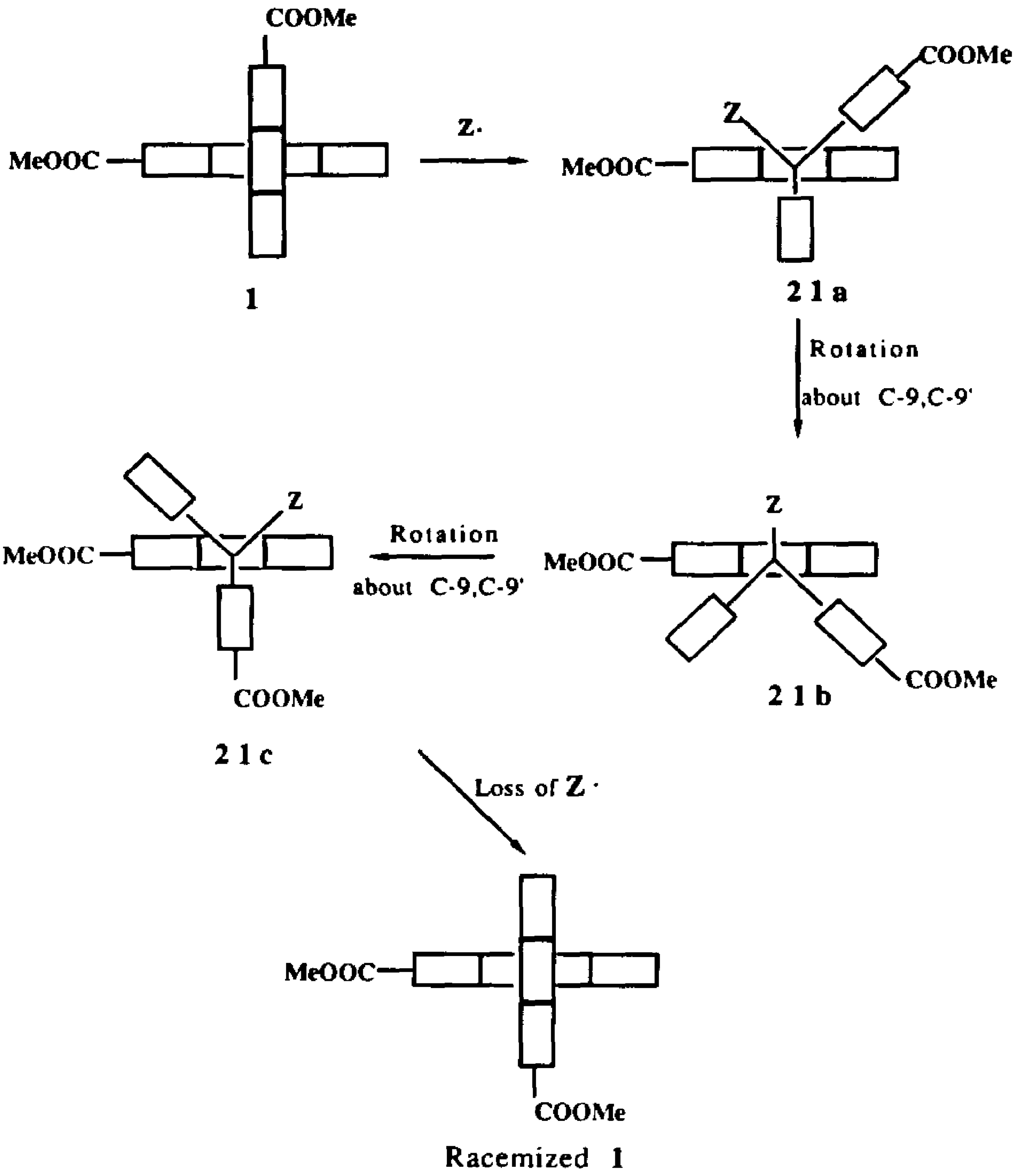
Scheme VII shows the addition of the radical (Z•) to an end ring of bianthryl **1**. The rotational process now involves a non-planar anthracyl unit. As shown, the two sets of blocking groups do not pass each other simultaneously. This results in a reduced overall rotational energy barrier. Subsequent loss of the radical would result in racemized starting material.



1

Racemized 1

Scheme VII. Sequential Interaction of Blocking Groups in the Racemization of a Cyclohexadienyl Intermediate Obtained from Addition of a Radical Z• to the End Ring of Bianthryl 1.



Scheme VIII. Sequencial Interaction of Blocking Groups in the Racemization of a Cyclohexadienyl Intermediate Obtained from the Addition of a Radical Z• to C-9 in Bianthryl 1.

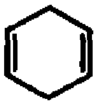
Scheme VIII shows the addition of a radical to the C-9 position to give the σ-complex **21**. Here again, the two sets of blocking substituents do not pass each other simultaneously during the rotational process. There are two consecutive benzo-benzo interactions instead of two simultaneous benzo-benzo interactions. This should result in a reduced rotational energy barrier and enhance the rotation between the two portions of the σ-complex. If the rotational process is competitive with the reversal step, the loss of the radical would result in racemized starting material.

The recovery of racemized bianthryl **1** would be an indication of reversible addition. The racemization of bianthryl **1** could thus serve as a general probe for the study of reversibility of addition to an anthracene system.

This thesis explores the racemization of biaryls as a general probe for studying the reversibility of addition of radicals and nucleophiles to aromatic systems. The recovery of racemized starting material is taken to indicate reversible addition. No matter what type of attacking reagent is used, the intermediate σ-complex should have a lower rotational barrier than the starting biaryl.

1.4. Structure and Conformation of Dihydro Aromatic Compounds.

The ring which is attacked by a radical in bianthryl **1** will probably not remain planar. Compounds of similar carbon framework were also shown to exist in non-planar geometries. The prefered geometries of 1,4-dihydrobenzene (**23**), 1,4-dihydronaphthalene (**24**), 9,10-dihydroanthracene (**25**) and their derivatives, have been the source of many investigations and the center of considerable controversy.[40] The key disagreement is whether the dihydro aromatic ring is planar or boat shaped.



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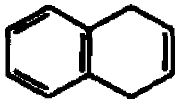

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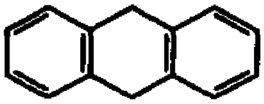
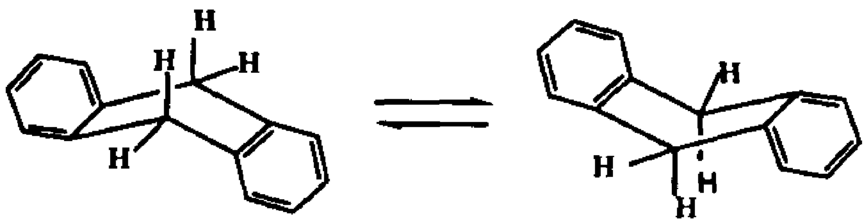


25

Although Drieding models strongly suggest the boat conformation for **23**-**25**, vibrational spectroscopy[41] has indicated a planar structure for 1,4-dihydrobenzene (**23**). While conflicting electron diffraction studies exist,[42] the experimental results involving NMR[43] seem to confirm the planar structure for **23**. On the other hand, 9,10-dihydroanthracene (**25**) was found to exist in a puckered conformation in the solid state[44] with a "folding angle" (the angle between the planes containing the benzene rings) of 145°. Solid-state ^{13}C NMR data have also provided support for a boat conformation.[45] In solution, the anticipated boat-to-boat interconversion (**26** ⇌ **26**') has never been demonstrated by dynamic NMR approaches, and this has been attributed to a very low barrier to interconversion.[46]



26

26'

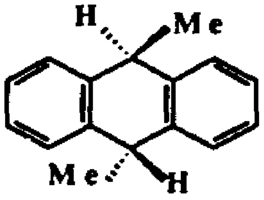
The preferred location of a substituent on C-9 in **26** has also been the subject of debate, but NMR experiments employing nuclear overhauser enhancement (NOE) have established the pseudoaxial position as the geometry of choice.[40]

The 1,4-dihydronaphthalene system (**24**) has received the least amount of attention. NMR data have suggested a boat conformation for monosubstituted derivatives, but with less puckering than in the 9,10-dihydroanthracene (**25**) series.[40]

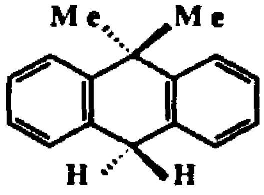
Thus, experimental evidence suggest a trend toward planarity in the series **25** < **24** < **23**. Planar structures have not generally been suggested for **25** or its derivatives.

Theoretical studies involving ab initio[47] (Gaussian 76 series program, using 3-21G basis set), molecular orbital[48] (MINDO/3, MNDO) and molecular mechanics[49] (MM1, MMP1 and MM2) calculations have all indicated an energy minimum corresponding to the planar structures for **23-25**.[50] However, the potential energy surface is quite flat. The energies required for 20° distortion from planarity for **23-25** are about 1 kcal/mol or less and decrease in the order **23**>**24**>**25** due to the interplay of angle strain and torsional effects.

MM1/MMP1 force field studies on monosubstituted derivatives of **23-25** gave somewhat steeper energy wells, and all exhibit optimum geometries that are non-planar.[51] The distortion from planarity increases with steric bulk of the substituent. In contrast to earlier suggestions of a boat-to-boat equilibrium, all the monosubstituted 1,4-dihydrobenzenes studied have a single energy minimum in which the substituent occupies a pseudoaxial position. The monosubstituted 1,4-dihydronaphthalene and 9,10-dihydroanthracene derivatives exhibit two distinct energy minima, but the pseudoaxial conformation is much more stable than the pseudoequatorial form in each case.



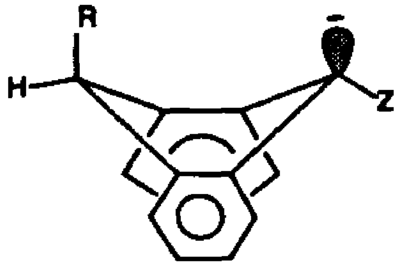
27



28

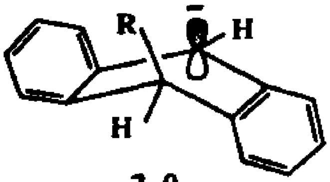
Dalling and coworkers[52] studied 9,10-dihydroanthracene and several of its methylated derivatives by solution and solid state ^{13}C NMR. Clearly, **27** and **28** exist as boat conformations in the solid state since separate resonances were observed for pseudoaxial and pseudoequatorial methyl groups. In solution, however, only single methyl signals were observed, even at -70°C, and this was attributed to a rapid boat-to-boat inversion process. Molecular mechanics calculations using MM2 and MMP1 force fields predicted three minima in the case of **27** and **28**: two boat and one planar.[53]

9,10-dihydroanthracene mono anion (**29**) has long been regarded as a boat-shaped molecule with sp^3 hybridization at the anionic center.[54]



29

However, in the light of proton[55] and carbon[56] NMR data, the structure would appear to be best viewed as sp^2 hybridized with substituents (e.g., *t*-Bu) causing some degree of puckering in the central ring (**30**).



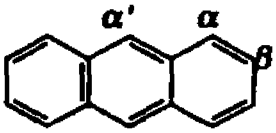
30

The "*para*" carbons showed a substantial upfield shift (even with *t*-Bu) which was attributed to extensive delocalization (which of course, decreases with ring puckering since the benzene rings lose their coplanarity).

MNDO calculations[57] have shown that the anions derived from 9-alkyl-9,10-dihydroanthracenes (**30**) may be considered as planar or almost planar structures with hybridization of the anionic center very close to sp^2. The driving force for the flattening is presumably a delocalization of the negative charge formally located on the "benzylic" carbon atom. As the anionic center hybridization becomes closer to sp^2, the overlap of it's *p*-orbitals with the π-orbitals of the benzene rings becomes more important. This effect is strong enough to cause complete planarity in the unsubstituted case (30; R=H). The addition of substituents, however, introduces a repulsive interaction between the R group and the *peri*-hydrogen atoms on the aromatic rings.

1.5: Relative Reactivities of α ', α and β Sites in Anthracene.

The three different types of position in anthracene are illustrated in **31**. It is well known that the α' (C-9, C-10) sites of anthracene are the most reactive.[58]



31

The order of reactivity calculated by MO calculations[59,60] is $\alpha' > \alpha > \beta$.. Experimental results are consistent with the theoretical studies. For homolytic phenylation, the partial rate factors for the α', α and β positions were found to be 684:48:11 respectively.[61] Recently, the partial rate factors of 6.6:3.6:1.3 were obtained for the α', α and β positions, in the isopropylation of anthracenes.[62]

Chapter 2

2.1 The Phenyl Radical

The details of the addition of the phenyl radical to aromatic substrates is presently unsettled.[4,5,6] There is considerable evidence that the addition of the phenyl radical is not reversible.[7,9] There is also contrary evidence that the addition is reversible.[8, 67]

The formation of the phenylcyclohexadienyl radical (σ–complex), from the reaction of the phenyl radical with benzene is well established. The phenyl radical shows small differences in reactivity in competitive reactions and is considered to be a relatively reactive carbon radical.[63] However, calculations suggest a somewhat greater stability.[64] Competitive studies using phenyl radicals generated photolytically and from the thermal decomposition of phenylazotriphenylmethane (PAT) have suggested that rate constants for the attack of the phenyl radical on an aromatic substrate (ArH) to be of the order of 10^6 $M^{-1}s^{-1}$, a value smaller than expected if the process is diffusion controlled (ca 3 X 10^9 $M^{-1}s^{-1}$).[65] Direct measurement of the rates of the reaction of the phenyl radical generated by laser flash photolysis of iodobenzene or benzoyl peroxide in Freon 113 at 25°C[66] with benzene, toluene or chlorobenzene revealed rate constants of 0.45, 1.7 and 1.2 X 10^6 $M^{-1}s^{-1}$ respectively which are smaller than expected for a diffusion controlled process.

This discrepancy can be explained by postulating that the attack by the phenyl radical on the aromatic substrate is reversible. Reversibility can significantly slow phenylation rates at elevated temperatures. Louw and Rothiuzen[67] proposed that the observed low rate of toluene phenylation found by other workers in high temperature gas phase reactions was due to reversibility. In their own experiments, they found that ortho phenylation of both chlorobenzene and cyanobenzene is less favored at high temperatures (400-500 °C) than at low temperatures (100 °C). This was interpreted as being due to reversibility. It was argued that ortho phenylation should be more reversible than meta and para phenylation. On the basis of their measured temperature dependance of products in liquid-phase reactions, Henriquez and co-workers[68] suggested that addition is reversible above 100°C. Phenylation of C_6H_6 was approximately 50% faster than C_6D_6 at 450°C using diphenyldiketone (benzil) as the phenyl radical source.[69] A similar effect was observed at 1000 K,[70] providing further evidence that the addition is reversible in the gas phase.

However at low temperatures (liquid-phase) the addition was claimed to be irreversible by Minisci and co-workers.[9] No isotope effect was observed in the addition of the phenyl radical to pyridine. This was interpreted to mean that the first step in the mechanism of Scheme III (p 4) is rate determining, and hence the addition is irreversible.

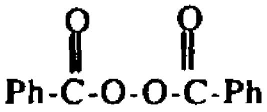
Theoretical studies of the phenylation process has confirmed the classical mechanism (Scheme III, p 4). A MNDO study of the addition of the phenyl radical to benzene has suggested the process to be strongly exothermic and therefore to have an early transition state. Reversibility becomes unlikely under such conditions.[71] Reversibility is related to the enthalpy of the radical addition. It increases as the addition becomes less exothermic by increasing the stability of the attacking radicals according to the sequence Ph < Me < primary alkyl < secondary alkyl < tertiary alkyl < benzyl.

2.2 Phenyl Radical Precursor

In this study, the phenyl radical was generated from three sources; phenylazotriphenylmethane (PAT, **32**), benzoyl peroxide (**33**) and diphenyl mercury (**34**).

$Ph\text{-}N{=}N\text{-}CPh_3$

32



$Ph\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}Ph$

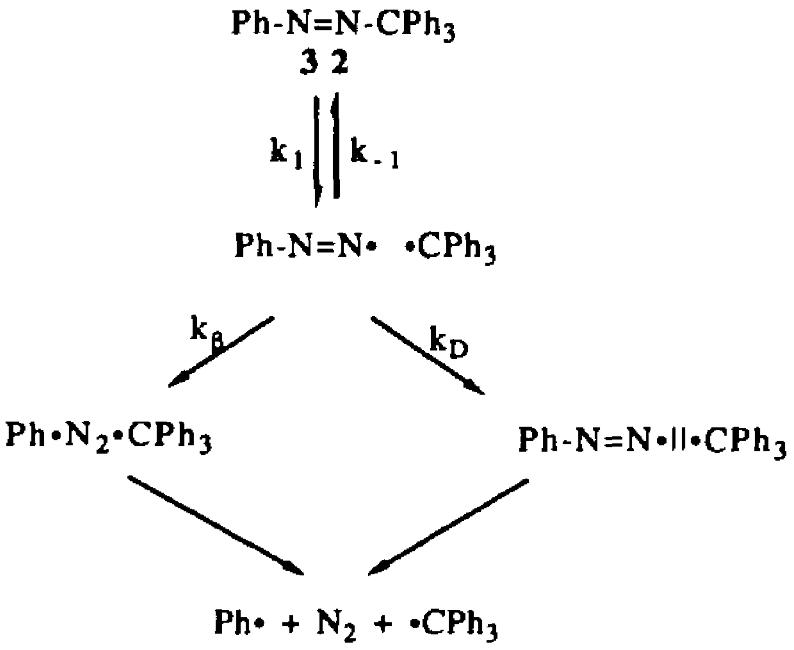
33

$Ph\text{-}Hg\text{-}Ph$

34

Azo compounds decompose thermally by two pathways, consecutive C-N cleavage (one bond scission) and simultaneous C-N (two-bond scission).[72] Phenylazotriphenylmethane (**32**) is an example of an azo compound which decomposes by a stepwise one-bond scission (Scheme IX).

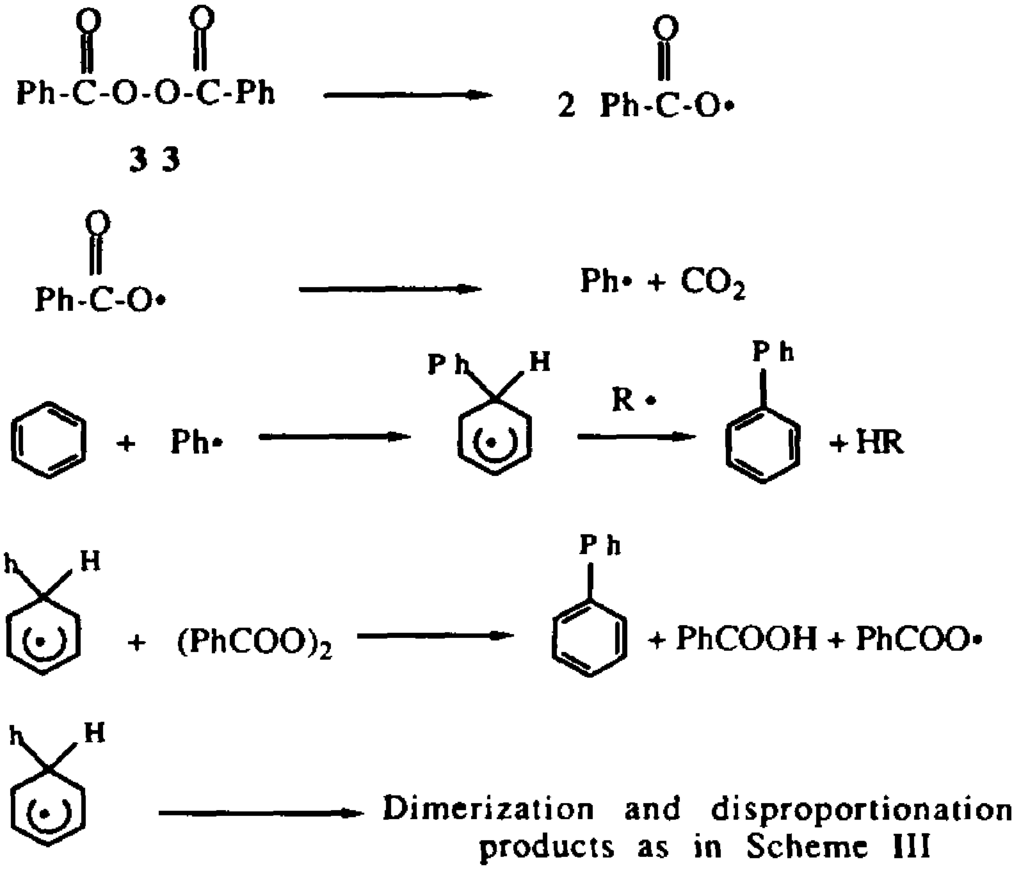
^1H, ^{13}C and ^{15}N CIDNP has provided compelling evidence for the one-bond scission mechanism shown in Scheme IX and the formation of the phenyldiazenyl radical (Ph-N=N•) from the decomposition of PAT.[73]



Scheme IX. Stepwise Decomposition of PAT.

Pryor showed that the decomposition rate of PAT decreases with increasing viscosity in a series of *n*-alkane solvents.[74] The decomposition rate also decreases when the solution of PAT is decomposed under high pressure in several hydrocarbon and aromatic solvents.[75] Kinetic data[75b] for the decomposition of PAT and its p-NO_2 derivative in *n*-alkane solvents suggests that K_β/K_D is significant and that β scission (K_β) of the initially formed phenyldiazenyl radical is an important cage reaction and becomes more important as increasing the viscosity of the solvent retards diffusion (K_D). In aromatic solvents K_β/K_D is insignificant, and β scission (K_β) is apparently not an important cage process. It is suggested that these observations reflect stabilization of the phenyldiazenyl radicals by aromatic solvents.

The decomposition of benzoyl peroxide (33) in benzene proceeds according to the sequence shown in scheme X.



Scheme X. Decomposition of Benzoyl Peroxide in Benzene.

The first step in this reaction sequence is rate determining.[76] At low peroxide concentration, this step is first order, but at higher peroxide concentrations the reaction order increases, indicating the process involves induced decomposition of the peroxide.[76] Kinetic studies of the decomposition of benzoyl peroxide in benzene have indicated three possible contributions, spontaneous decomposition of the peroxide which is a first-order process and fission of the O-O bond, which is induced by the attack of the σ-complex on the peroxide. The latter may show first-order or three-halves order depending on the nature of the termination step.

The homolysis of the peroxy bond initially gives rise to benzoyloxy radicals (Ph-COO•) which may loose CO_2 to give the less stable phenyl radical (Ph•). The benzoyloxy radical may itself attack the arenes. The formation of *o*- and *p*-arylbenzoates from the attack of Ph-COO• on toluene and anisole suggests that the benzoyloxy radical has some electrophilic character.[77] This is confirmed by earlier observations of the rates and orientation of aroyloxylation by benzoyl peroxide-$CuCl_2$ mixtures on PhX substrates in CH_3CN.[78]

Since the phenyl radical is not the primary product of the decomposition of benzoyl peroxide, and it has been demonstrated that reactive aromatic substrates like anthracene trap the benzoyloxy radical before the secondary cleavage,[79] the use of benzoyl peroxide as a source of the phenyl radical in this project may not allow for an unambiguous explanation of results. This will be discussed later.

Diphenyl mercury ($HgPh_2$, **34**) decomposes thermally to give Hg^{o} and Ph•. Previous work on the thermal decomposition of mercury compounds[80] suggests the process to be first-order[81] and can be categorized into two groups with regards to the activation energy and mechanism of decomposition. On one hand the dialkyl mercury compound has an activation energy of decomposition less than that determined by the sum of the first and second Hg-C bond dissociation energies ($E_a < D_1 + D_2$). In this case, the decomposition occurs stepwise as seen in equations 1 and 2. Dimethyl mercury, diethyl mercury and dibenzyl mercury are examples of such a stepwise decomposition process.

$$\text{R-Hg-R} \longrightarrow \text{R}\bullet + \text{R-Hg}\bullet \; ; \Delta H_1 = D_1 \qquad (1)$$

$$\text{R-Hg}\bullet \longrightarrow \text{Hg}^{\circ} + \text{R}\bullet \; ; \Delta H_2 = D_2 \qquad (2)$$

$$E_a < D_1 + D_2$$

The first step is rate-determining, and the second step is fast because of the low bond dissociation energy of the second Hg-C bond in R-Hg.

On the other hand, there are mercury compounds (e.g. diisopropyl mercury and diphenyl mercury) for which the activation energies of the first-order decomposition are approximately equal to the sum of the first and second bond dissociation energies (i.e. $E_a \sim D_1 + D_2$). This suggests a simultaneous rupture of both the Hg-C bonds (eq 3).

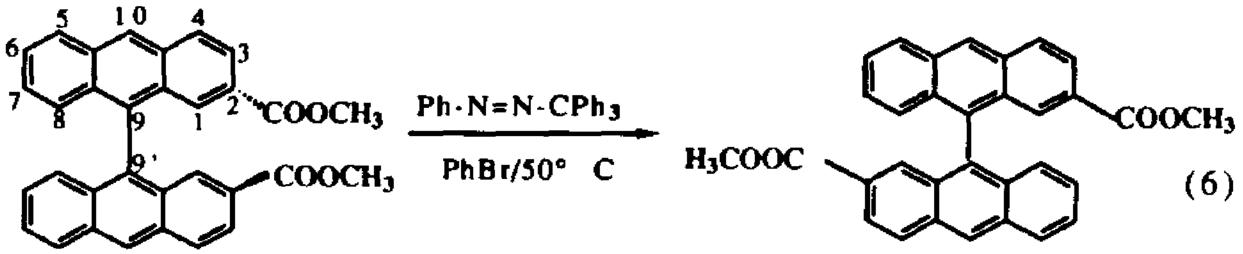
$$\text{R-Hg-R} \longrightarrow \text{R}\bullet + \text{Hg}^{\circ} + \text{R}\bullet \qquad (3)$$

$$Ea \sim D_1 + D_2$$

Diphenyl mercury is an example of simultaneous cleavage process. It has a high activation energy (Ea = 68 ± 4 Kcal/mole).[82]

2.3 Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) In The Presence of Phenyl Radicals Derived from Phenylazotriphenylmethane (PAT).

The reaction of optically active 2,2'-dicarbomethoxy-9,9'-bianthryl (**1**) with varying concentrations of PAT in bromobenzene at 50 ± 0.1 °C resulted in the recovery of partially racemized bianthryl (**1**) (eq. 6).



(+)-1 (±)-1

(6)

The reactions were carried out in sealed tubes, degassed by the freeze pump thaw process. The rotations of the reaction solutions decreased as a function of time. No racemization was observed in the absence of PAT. Table I summarizes the percentage racemization as a function of reaction time and PAT concentration. The percentage racemization calculated from the rotations of the reaction solutions was comparable to the percentage racemization of the recovered bianthryl **1** (p 39).

Table I. Percent Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) as a Function of Reaction Time and [PAT]

Rx. Time (h)	Bianthryl 1[a] : [PAT]							
	1 : 15		1 : 10		1 : 7.5		1 : 5	
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
0	0	0	0	0	0	0	0	0
0.25	4.3%	4.5%	3.4%	3.4%	2.2%	2.5%	1.6%	1.6%
0.50	6.9%	6.9%	5.3%	5.4%	4.0%	4.0%	3.1%	2.9%
1.00	10.3%	-	8.5%	-	6.7%	-	5.4%	-
2.00	15.0%	-	13.3%	-	10.0%	-	8.5%	-
3.00	17.2%	-	15.4%	-	11.8%	-	9.6%	-

[a] [Bianthryl] = 0.0064 M

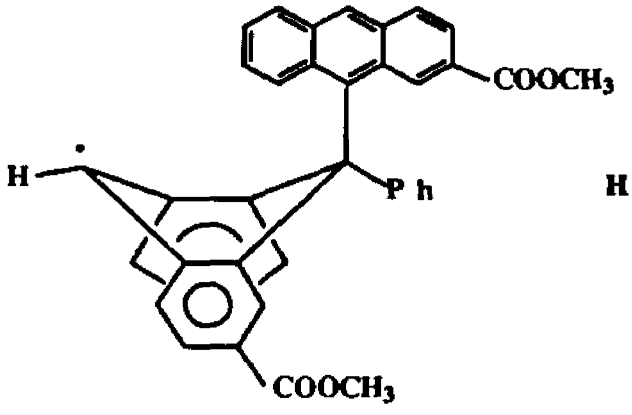
The recovery of partially racemized bianthryl **1** is taken to indicate that the addition of the phenyl radical to bianthryl **1** is reversible. The addition of the phenyl radical to bianthryl **1** results in a cyclohexadienyl complex (σ-complex), e.g., see section 1.3, p 19, which has a lower rotational energy barrier than bianthryl **1**.

No racemization was observed without the radical source. The racemization of **1** was totally inhibited (100% inhibition) by phenyl thiol, a radical scavenger.[83] Dicyclohexylphosphine (DCHP) was less effective and inhibited the racemization to the extent of 71% after a reaction time of 1 h. Addition of triphenylmethane as a H atom donor inhibited the racemization by 12% after 1 h reaction time.

The trityl radical ($Ph_3C\bullet$, **35**) formed by the decomposition of PAT is a relatively stable and hindered radical. To rule out the possibility of the trityl radical contributing to the racemization of **1**, bianthryl **1** was treated with trityl radicals generated by the reaction of trityl chloride and mercury in bromobenzene.[84] No racemization was observed at 50° C. These results suggests that the phenyl radical is the attacking species that causes the racemization of **1** via reversible addition.

2.4 Recovery And Investigation of Products From The Reaction of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) With PAT.

The fate of various possible radical intermediates should depend on the other group present on the carbon atom to which the phenyl radical has added. A radical such as **36**, from attack at C-9 on bianthryl **1**, should not easily yield a homolytic substitution product since a "leaving group" is not present. On the other hand radical **37**, from attack at C-10 can form a homolytic substitution product by C-10 hydrogen abstraction.



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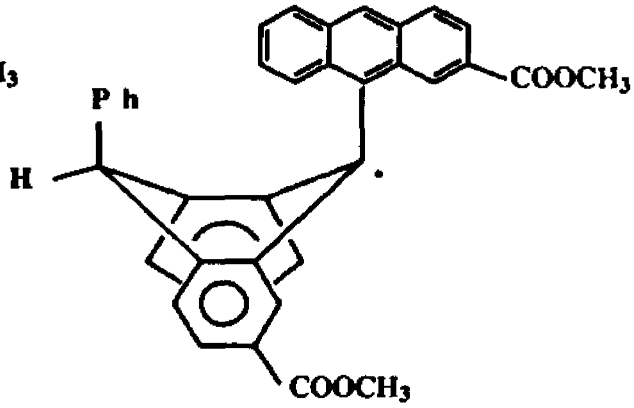
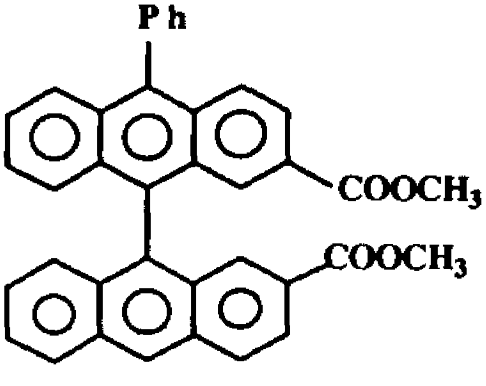


37

Bianthryl **1** (0.075g, 0.159 mmol, $[\alpha]_D$ = +130.3°) was heated with 10 equiv. of PAT (0.5596g, 1.60 mmol) in 25 mL of bromobenzene at 50 ± 0.1°C in a sealed tube (degassed by the freeze pump thaw process) for 25 h. The reaction solution was 17.5% racemized. Bromobenzene was distilled off (35°C, 1 torr) and the residue was purified by column chromatography followed by preparative TLC to give 0.0212g (28.8% recovery) of starting bianthryl **1** ($[\alpha]_D$ = +102°, 21.5% racemized.) along with two phenylated products. The two phenylated products (**38** and **39**) were characterized by ^1H, ^{13}C and homonuclear decoupling NMR and high resolution MS. The products were identified as 2,2'-dicarbomethoxy-10-phenyl-9,9'-bianthryl (**38**) (0.0408g, 45.4% recovery, $[\alpha]_D$ = 88.2°) and 2,2'-dicarbomethoxy-10,10'-diphenyl-9,9'-bianthryl (**39**) (0.0117g, 11.8% recovery, $[\alpha]_D$ =67.9°).



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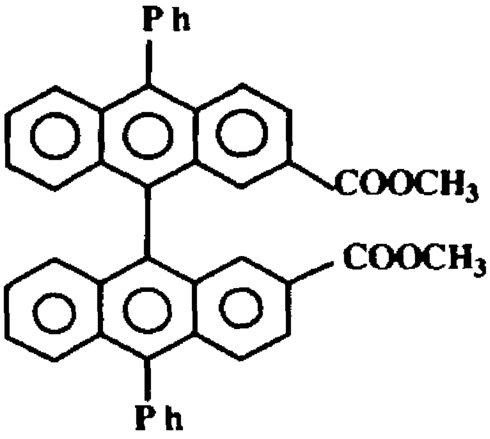


39

These results suggest that C-10 in bianthryl **1** is the site of attack by the phenyl radical. It should be pointed out that racemization of bianthryl **1** could occur from attack at any other carbon via reversible addition, but product formation occurs from the attack at C-10.

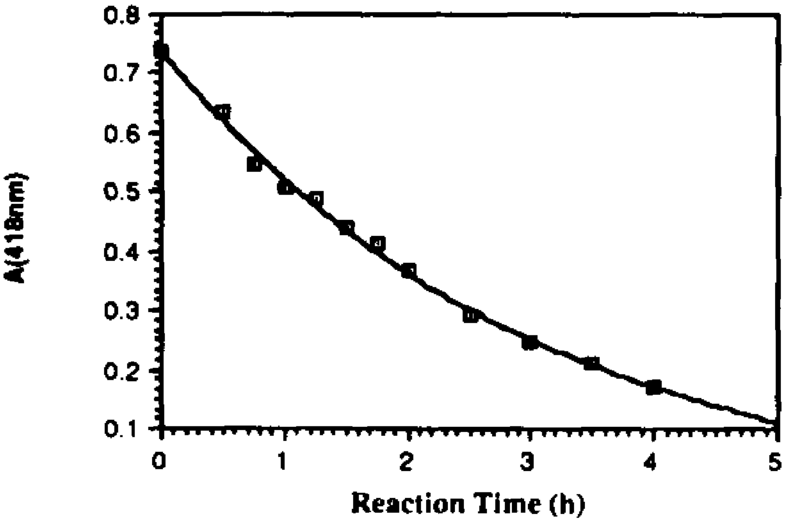
2.5 Decomposition Rate of PAT in Bromobenzene at 50°C.

Neuman and Lockyer[75b] reported the first-order rate constant for the decomposition of PAT in benzene at 50°C as $1.37 \times 10^{-4}\ s^{-1}$. This corresponds to a half-life ($t_{1/2}$) of 1.4 h. Pryor showed that the decomposition rate of PAT decreases with increasing viscosity of the solvent.[74] The decomposition rate of PAT is therefore expected to be lower in bromobenzene than in benzene based on the viscosities of the solvents.

The decomposition of PAT in bromobenzene at 50 ± 0.1°C was monitored via the absorbance of the azo linkage (-N=N-), which has an absorbance maximum at 418 nm ($\varepsilon \sim 115$). Samples (~35 mL) of a

0.0064 M solution of PAT in bromobenzene were placed in pyrex ampules, degassed by the freeze pump thaw process and sealed under vacuum (1 mm Hg). The absorbance was measured on a HP 8452A UV-Vis spectrophotometer as a function of reaction time and is plotted in Figure 1.

Figure 1. PAT Decomposition at 50°C

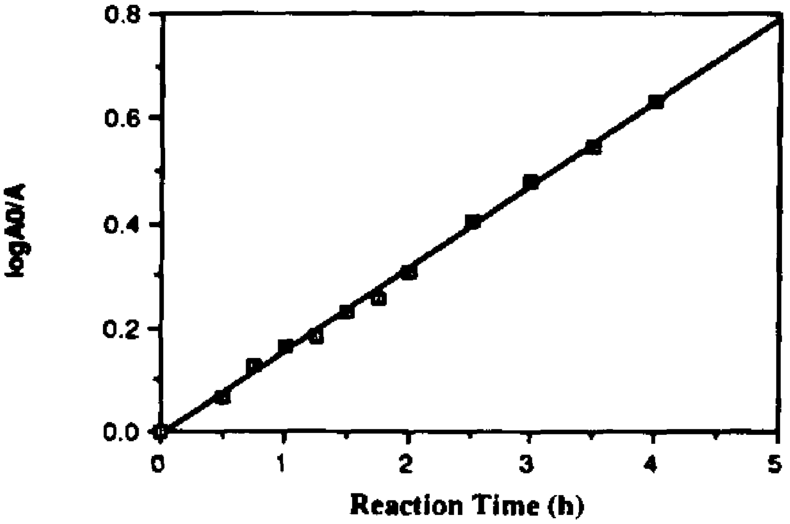


A first order plot of log A_o/A versus reaction time (Figure 2), where A_o is the absorbance at t = 0 and A is the absorbance at time t is a straight line passing through the the origin with slope = k = 4.4 X 10^{-5} s^{-1} (0.1588 h^{-1}) (Figure 2). This is consistent with the first-order rate equation, eq. 7.

$$\log A_o/A = kt \qquad (7)$$

$$t_{1/2} = \log 2/k \qquad (8)$$

Figure 2. First-order Plot for PAT Decomposition at 50°C.



The half-life ($t_{1/2}$) from eq. 8 is calculated as 1.895 h. This is in agreement with the observed % racemization of 1 which plateaus out after ~3.0 h (see Figure 3, p 43).

2.6 Racemization Kinetics and Order of the Reaction.

The rate of racemization of bianthryl 1 could depend on a number of rate constants:

(1) The rate of decomposition of PAT

(2) The rate of addition of the phenyl radical to the bianthryl

(3) The rate of reversal of addition

(4) The rate of rotation about the pivotal C-9, C-9' bond in the σ-complex.

(5) The rate of conversion of the σ-complex to substitution products.

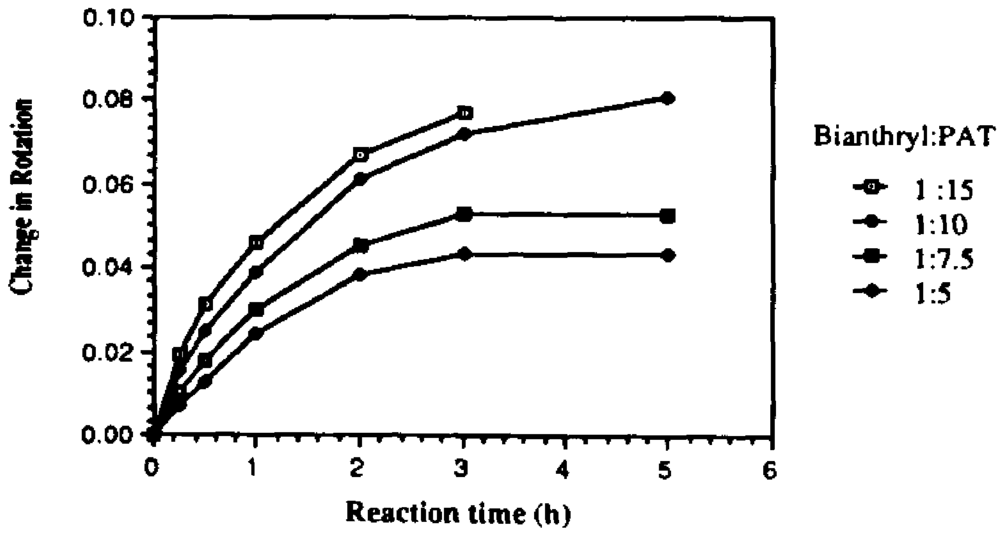
The kinetics can be analyzed by following the change in rotation of the reaction solution with time according to eq 9 because of a linear relationship between concentration and rotation (α).

$$d\alpha = \alpha_0 - \alpha_t = k \text{ X } t \qquad (9)$$

where α_0 = rotation at $t = 0$ and α_t = rotation at time t.

A series of racemization experiments were carried out to determine the initial rate (k) and establish the order of the reaction with respect to bianthryl **1** and PAT. In one series, [bianthryl **1**] was held constant (0.0064 M) as the [PAT] was varied. In another series, [bianthryl **1**] was varied as [PAT] was kept constant (0.064 M). Each series was repeated twice. Figure 3 shows the plots of change in rotation (α_0 - α_t) versus reaction time with [bianthryl **1**] constant.

Figure 3. Change in Rotation for the Reaction of Bianthryl **1** with Varying Ratios of PAT at 50 °C.



Initial rates (k) were calculated as $(\alpha_0 - \alpha_t)/t$ at $t = 0.25$ h and are summarized in Tables II and III.

Table II. Initial Rates as a Function of [PAT]

Bianthryl : [PAT]	[PAT] M	k (h^{-1})	
		Run 1	Run 2
1 : 15	0.096	0.076	0.080
1 : 10	0.064	0.052	0.060
1 : 7.5	0.048	0.040	0.044
1 : 5.0	0.032	0.028	0.028

$k = (\alpha_0 - \alpha_t)/t$ at $t = 0.25$ h
[Bianthryl] = 0.0064 M

To obtain the order of the reaction with respect to PAT, the ratios of the initial rates (Table II) is compared to the ratios of [PAT]. For example, when the [PAT] is doubled (the concentration is changed from 1:5 to 1:10 or from 1:7.5 to 1:15) the initial rate is expected to double if the rate equation is first-order in PAT. It increases by a factor of 1.9 ± 0.1 (Run 1), which is concluded to be first-order in PAT.

To determine the order of the reaction with respect to bianthryl **1**, initial rates were obtained by varying [bianthryl 1], keeping [PAT] constant (Table III). By comparing the ratios of the initial rates to the ratios of [bianthryl **1**], the order of the reaction with respect to bianthryl **1** was determined to be first-order.

Table III. Initial Rates as a Function of [Bianthryl 1]

Biananthryl 1 : PAT	**[Bianthryl 1] M**	**k (h^{-1})**	
		Run 1	**Run 2**
2 : 10	0.0128	0.100	0.108
1.5 : 10	0.0096	0.080	0.084
1 : 10	0.0064	0.052	0.060

[PAT] = 0.064 M
$k = (\alpha_0 - \alpha_t)/t$ at t = 0.25 h

Consider the following rate equation (eq. 10),

$$d\alpha/dt = k[\text{bianthryl } \mathbf{1}]^x[\text{PAT}]^y \qquad (10)$$

where x is the order of the reaction with respect to bianthryl **1** and y is the order with respect to PAT. By making a run at two different initial concentrations of one component, say PAT, the other remaining constant, i.e., bianthryl **1**, the data will enable the determination of the order of the reaction with respect to that component. Let the two rates and the initial concentrations be k_1, $k_2$and $[\text{PAT}]_1$, $\text{PAT}]_2$. The [bianthryl **1**] is constant.

Then, $$k_1 = k[\text{bianthryl } \mathbf{1}]^x[\text{PAT}]_1^{\,y} \qquad (11)$$

$$k_2 = k[\text{bianthryl } 1]^x[\text{PAT}]_2^y \qquad (12)$$

Dividing eq. 11 by eq. 12 gives eq. 13 and taking logarithms we get eq. 14.

$$\frac{k_1}{k_2} = \frac{[\text{PAT}]_1^y}{[\text{PAT}]_2^y} \qquad (13)$$

$$\log k_1 - \log k_2 = y\{\log [\text{PAT}]_1 - \log [\text{PAT}]_2\} \qquad (14)$$

Similarly, keeping [PAT] constant and varying [bianthryl 1], we get eq.15

$$\log k_1 - \log k_2 = x\{\log [\text{bianthryl } 1]_1 - \log [\text{bianthryl } 1]_2\} \qquad (15)$$

Figures 4 A and 4 B are plots of eq. 14 for run 1 and run 2. The slopes (y) are equal to 0.91 and 0.96 respectively, with an average slope of 0.94 ± 0.03, which is the order of the reaction with respect to PAT.

Figure 4 A. Plot of Equation 14 (Run 1)

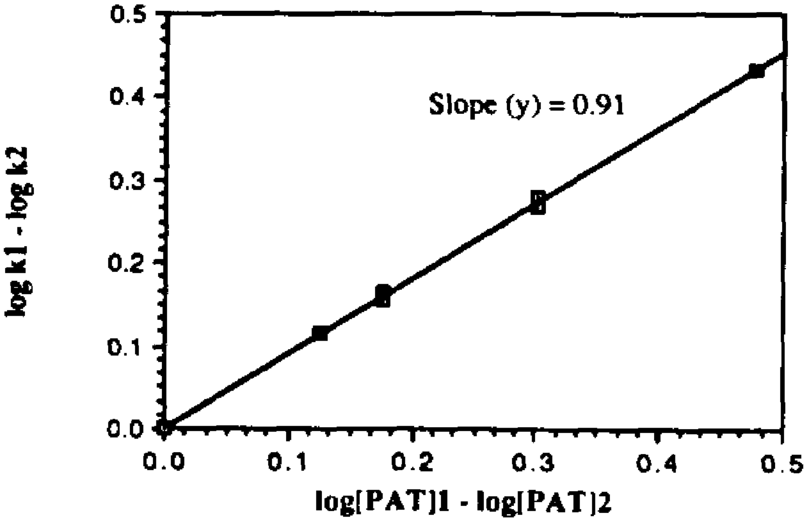
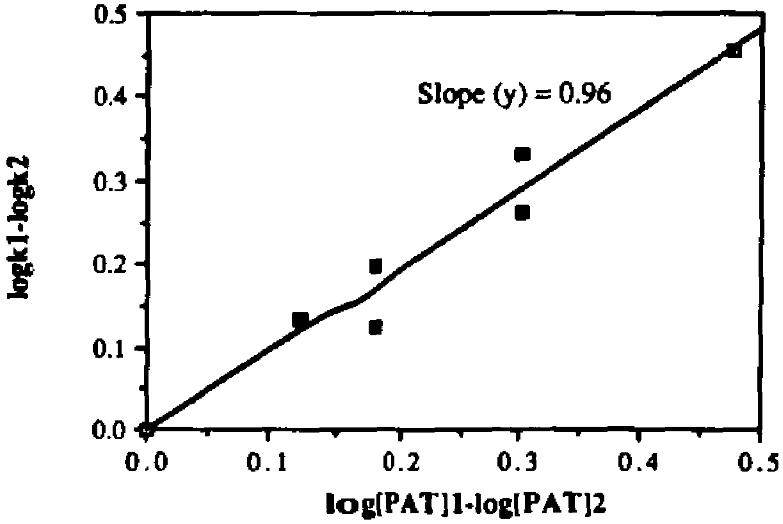


Figure 4 B. Plot of Equation 14 (Run 2)



Figures 5 A and 5 B are plots of eq. 15. The slopes (x) are equal to 0.96 and 0.84 for run 1 and run 2 respectively. The average slope of 0.90±0.06 suggests the reaction to be first order with respect to bianthryl 1.

Figure 5 A. Plot of Equation 15 (Run 1).

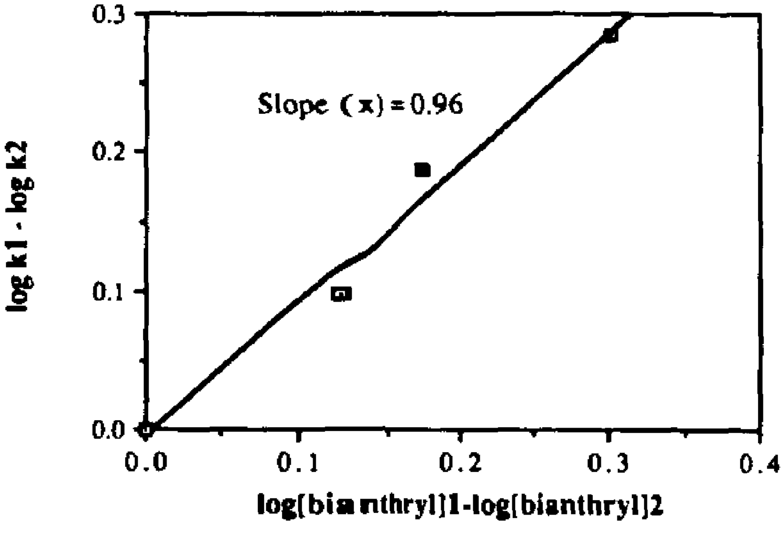
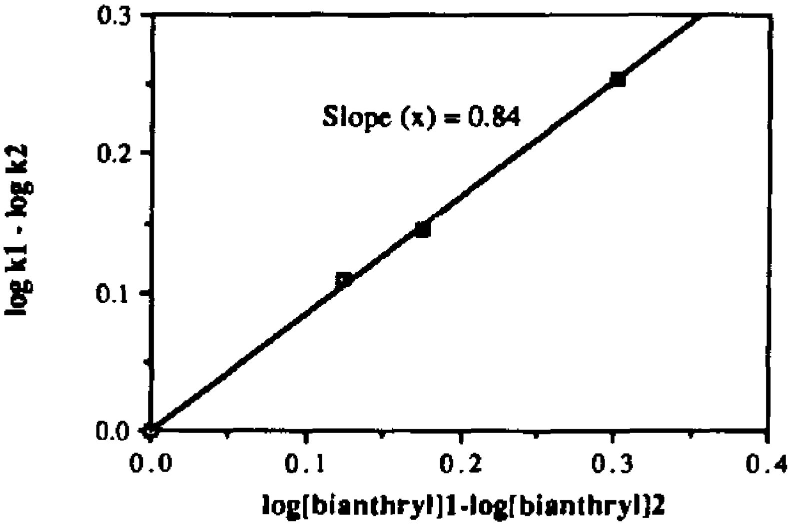


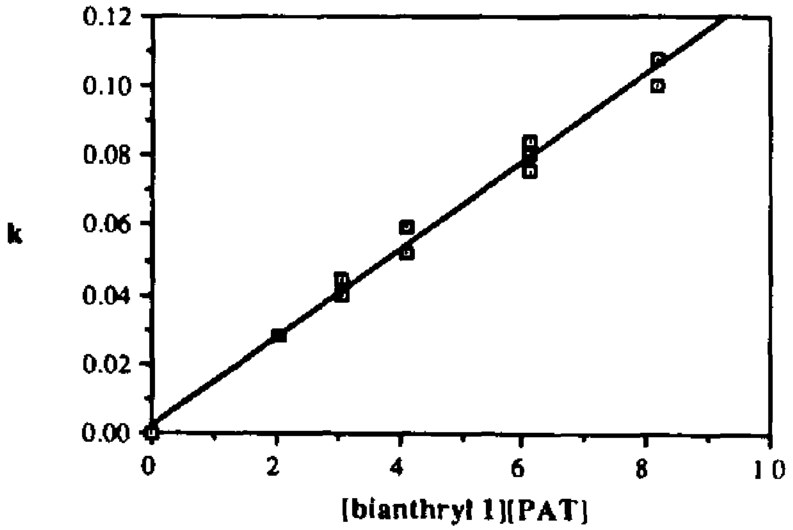
Figure 5 B. Plot of Equation 15 (Run 2)



The rate expression is therefore first-order in PAT and bianthryl **1**.

Figure 6 shows a plot of initial rate (k) versus [bianthryl **1**][PAT], which is a straight line through the origin with a slope (rate constant) of 1.27 X 10^5 $M^{-1}h^{-1}$.

Figure 6. Plot of Initial Rate (k) versus [bianthryl 1][PAT].



2.7 Racemization of Optically Active 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the Presence of Benzoyl Peroxide in Bromobenzene at 80°C.

The homolysis of benzoyl peroxide initially leads to benzoyloxy radicals (PhCOO•), which may decompose further to give the less stable phenyl radicals (Ph•). The phenyl radical is therefore not the primary product of decomposition of benzoyl peroxide. Naphthalene gives two isomeric naphthylbenzoates on treatment with benzoyl peroxide at 80° and 100°C, but very little phenyl naphthalene.[85] It has also been demonstrated that anthracene traps the benzoyloxy radical before the secondary cleavage when it undergoes reaction with benzoyl peroxide at 80°C.[79] Therefore thermolysis of benzoyl peroxide is not a useful source of phenyl radicals for polybenzenoid systems, as the decarboxylation of PhCOO• to give Ph• is a minor process compared to its attack on the aromatic system.

The reaction of optically active 2,2'-dicarbomethoxy-9,9'-bianthryl (1) with 5 equiv. of benzoyl peroxide in bromobenzene at 80°C for 3 h resulted in the recovery of partially racemized bianthryl (1), benzoylated products and very little of the phenylated product. After 3 h, the reaction solution was 11% racemized. The recovered bianthryl was 12.8% racemized. The recovery of benzoylated bianthryls as the major product and very little of the phenylated products suggests that the PhCOO• attacks the bianthryl before it undergoes secondary cleavage to give Ph•. The recovery of partially racemized bianthryl (1) suggests that the addition of the benzoyloxy radical is reversible.

No racemization was observed without the radical source. The racemization of bianthryl 1 was totally inhibited by phenyl thiol, a radical inhibitor. These results further suggest that the PhCOO• is the attacking species that causes the racemization of bianthryl 1 via reversible addition.

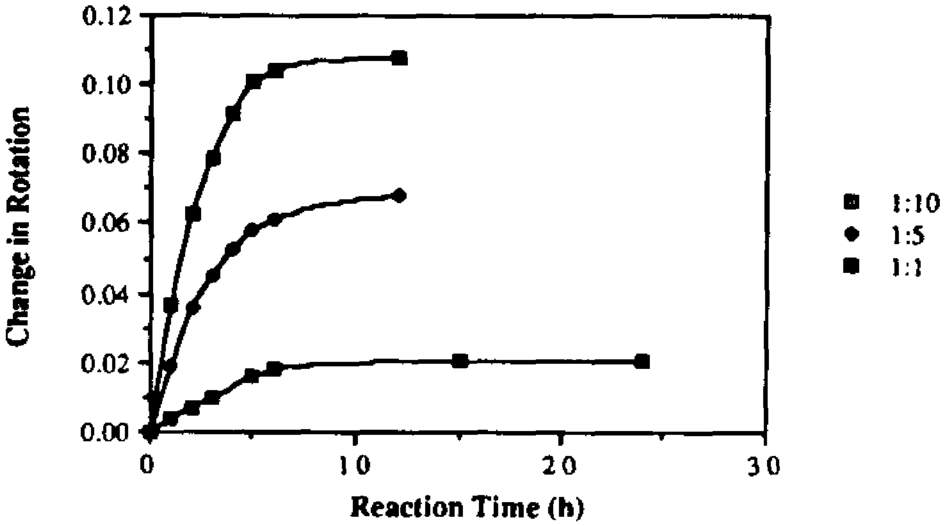
The % racemization depends on $[(PhCOO)_2]$ and is summarized in Table IV.

Table IV. Percent Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) as a Function of Time and [(PhCOO)$_2$]

Time h	Bianthryl 1 : [PhCOO)$_2$]					
	1 : 10		1 : 5		1 : 1	
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
0	0	0	0	0	0	0
1	8.1%	8.0%	4.1%	4.4%	0.9%	0.9%
2	13.7%	13.7%	7.8%	8.1%	-	1.5%
3	17.0%	17.2%	9.8%	10.0%	-	2.2%
4	20.0%	20.2%	11.5%	11.5%	-	-
5	22.0%	22.2%	12.6%	12.6%	3.4%	3.5%
6	22.7%	22.8%	13.5%	13.3%	-	3.9%
12	23.5%	23.9%	14.8%	14.6%	-	-
15	-	-	-	-	4.5%	4.6%
24	-	-	-	-	4.5%	4.6%

A plot of change in rotation ($\alpha_0 - \alpha_t$) versus reaction time is shown in Figure 7 for different concentrations of benzoyl peroxide.

Figure 7. Change in Rotation for the Reaction of Bianthryl 1 with Varying Ratios of Benzoyl Peroxide at 80 °C.



Initial rates (k) are calculated as $(\alpha_0 - \alpha_t)/t$ at t = 1 h and are summarized in Table V.

To obtain the order of the reaction with respect to benzoyl peroxide, the ratio of the initial rates are compared to the ratio of the concentrations of benzoyl peroxide. For example, changing the concentration of [$\mathrm{PhCOO})_2$] from 1:5 to 1:10, the initial rate is expected to double if the rate equation is first-order in benzoyl peroxide. It increases by a factor of 1.95 which is concluded to be first-order.

Table V. Initial Rates as a Function of $[(PhCOO)_2]$

Bianthryl:$(PhCOO)_2$	$[(PhCOO)_2]$ M	$k(h^{-1})$	
		Run 1	Run 2
1:10	0.064	0.037	0.038
1:5	0.032	0.019	0.020
1:1	0.0064	0.004	0.004

The order of the reaction can also be determined from eq. 16.

$$\log k_1 - \log k_2 = n\{\log [(PhCOO)_2]_1 - \log [(PhCOO)_2]_2\} \qquad (16)$$

where n is the order of the reaction with respect to benzoyl peroxide, k_1 and k_2 are initial rates corresponding to two concentrations of benzoyl peroxide. Plots of eq. 16 (Figures 8A and 8B) give straight lines passing through the origin with slopes (n) equal to 0.97 for run 1 and 0.99 for run 2 respectively. The average slope is 0.98 ± 0.01 suggests the reaction to be first order with respect to benzoyl peroxide.

Figure 8 A. Plot of Equation 16 (Run 1)

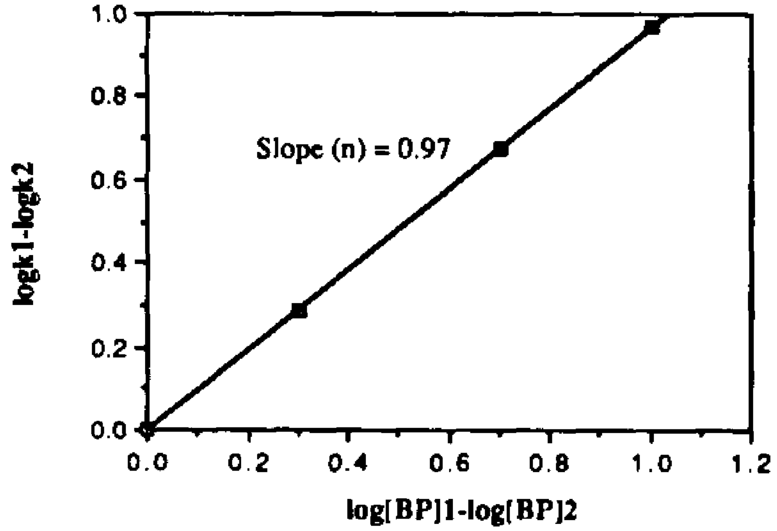
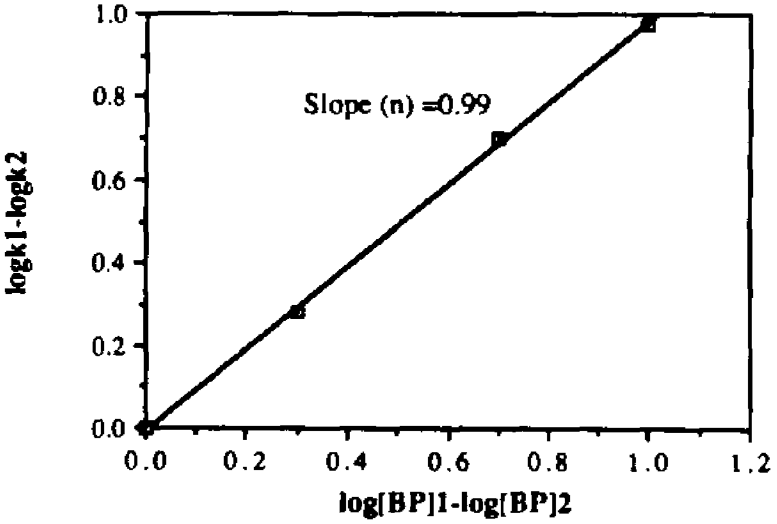
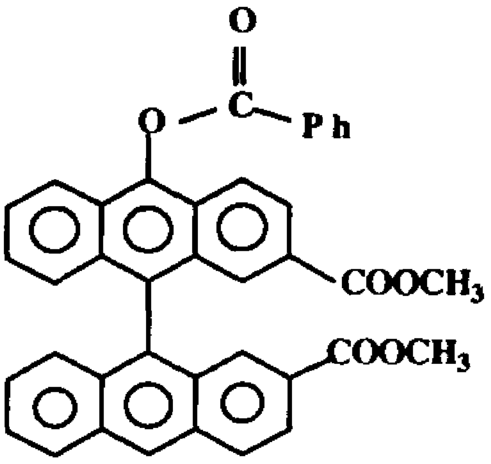


Figure 8 B. Plot of Equation 16 (Run 2).

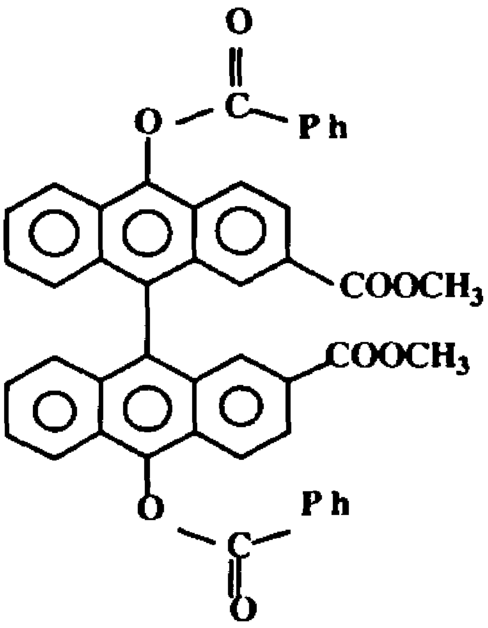


2.8 Recovery and Investigation of Products from the Reaction of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) with Benzoyl Peroxide at 80°C in Bromobenzene.

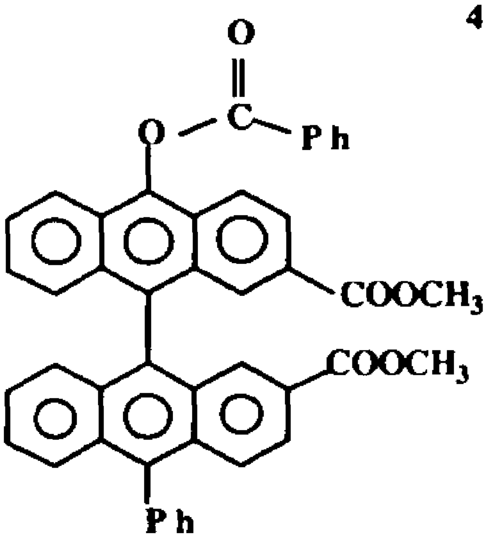
Optically active 2,2'-dicarbomethoxy-9,9-bianthryl (**1**) ; $[\alpha]_D$ = -152° (0.060g, 0.128 mmol) was heated with 10 equiv of $(PhCOO)_2$ (0.309 g, 1.28 mmol) in 20 mL of bromobenzene at 80°C in a sealed tube (degassed by the freeze pump thaw process). After 20 h, the reaction mixture was 30.7% racemized. Bromobenzene was distilled off (35°C, 1 mm Hg) and the residue was purified by column chromatography (silica gel; 2:1 PhH-$CHCl_3$) followed by preparative TLC (silica gel, benzene) to give three fractions containing the bianthryl moiety. None of the fractions consisted of the starting bianthryl (**1**). They all contained benzoylated products. The benzoylated products were identified as 2,2'-dicarbomethoxy-10-benzoyl-9,9'-bianthryl (**40**), 2,2'-dicarbomethoxy-10,10'-dibenzoyl-9,9'-bianthryl (**41**) and 2,2'-dicarbomethoxy-10-benzoyl-10'-phenyl-9,9'-bianthryl (**42**). The three products **40**-**42** were characterized by ^1H, ^{13}C, COSY and homonuclear decoupling NMR and high resolution MS. The formation of these products suggests that the benzoyl radical (PhCOO•) attacks the bianthryl (**1**) before the secondary cleavage to the phenyl radical. Also, as observed with the phenyl radical, the site of attack is C-10.



40 (10.5%)



41 (20.0%)



42 (16.4%)

Since no starting bianthryl (**1**) was isolated with 10 equiv of $(PhCOO)_2$ after 20 h reaction time, the reaction was repeated with 5 equiv of $(PhCOO)_2$ and a reaction time of 3 h. The reaction solution was 11.0% racemized. Bromobenzene was distilled off (35°C, 1 mm Hg), and the residue was purified by column chromatography followed by preparative TLC to give 0.0267g (44.5% recovery) of starting bianthryl 1 ($[\alpha]_D$ = -131.7°, 12.8% racemized) along with mono benzoylated product 42 (0.0135g, 18.0% yield).

These results suggest that the benzoyloxy radical racemizes the bianthryl (1) via reversible addition. Also it suggests that C-10 in bianthryl 1 is the site of attack by the benzoyloxy radical. This is consistent with the relative reactivities of the positions in anthracene.[61,62]

2.9 Racemization of Optically Active 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the Presence of Diphenylmercury (34).

Diphenyl mercury (Ph_2Hg, 34) decomposes on heating to give mercury and two phenyl radicals by simultaneous cleavage of both C-Hg bonds (eq. 17).

$$\text{Ph-Hg-Ph} \longrightarrow \text{Ph}\bullet + \text{Hg}^{0} + \text{Ph}\bullet \qquad (17)$$

$$Ea \sim D_1 + D_2 \sim 68 \pm 4 \text{ Kcal/mole}$$

The activation energy for the first-order decomposition is approximately equal to the sum of the first and second bond dissociation energies (i.e., $E_a \sim D_1 + D_2 \sim 68 \pm 4$ Kcal/mole), and the Arrhenuis frequency factor ($\log A = 16\ s^{-1}$) is abnormally high. This behavior led to the suggestion that in the case of diphenylmercury, the primary step determining the activation energy is the simultaneous rupture of both the C-Hg bonds.[82] The rate of decomposition can be calculated from eq. 18 (Table VI). The half-life ($t_{1/2}$) can be calculated from equation 19 (Table VI).

$$k = A\, e^{-E_a/RT} \qquad (18)$$

$$t_{1/2} = \frac{\ln 2}{k} \qquad (19)$$

Table VI. Rates and Half-lives of Decomposition of Ph_2Hg (34) in the Gas Phase.

Temp. °C	k s^{-1}	$t_{1/2}$ (days)
180°	1.19×10^{-17}	6.75×10^{11}
200°	2.93×10^{-16}	1.37×10^{10}

The reaction of optically active 2,2'-dicarbomethoxy-9,9'-bianthryl (1) with 5 equiv. of Ph_2Hg (34) in bromobenzene at 200° and 180°C resulted in the recovery of partially racemized bianthryl 1. The reactions were carried out in sealed tubes, degassed by the freeze pump thaw process. The racemization of bianthryl 1 could not be followed by measuring the rotations of the reaction solutions as they turned dark in color. The reaction solutions were worked up to isolate partially racemized bianthryl 1. The percent racemization as a function of reaction time at 200° and 180°C is summarized in Tables VII and VIII, respectively.

Table VII. Percent Racemization as a Function of Reaction Time at 200°. Bianthryl 1 : Ph_2Hg = 1 : 5.

Reaction time(h)	$[\alpha]_D$	% Racemization	$\log \alpha_0/\alpha$
0	+92.0°	0	0
48	+69.7°	24.2%	0.120
75	+60.0°	34.8%	0.186
95	+57.8°	37.2%	0.202
121	+51.5°	44.0%	0.252
140	+40.3°	56.2%	0.358
160	+36.0°	60.9%	0.407

Table VIII. Percent Racemization as a Function of Reaction Time at 180°. Biantlryl 1 : Ph_2Hg = 1 : 5.

Reaction time(h)	$[\alpha]_D$	% Racemization	$\log\alpha_0/\alpha$
0	-152.0°	0	0
100	-107.1°	29.5%	0.152
140	-93.1°	38.8%	0.213
200	-75.5°	50.1%	0.302
240	-67.1°	55.8%	0.355

For every molecule of Ph_2Hg (**34**), two phenyl radicals are formed. Since the half-life of decomposition of Ph_2Hg (**34**) is very high (Table VI), only 3.6 X 10^{-8}% and 8.0 X 10^{-10}% of the Ph_2Hg will have decomposed after 240 h (10 days) at 200° and 180°C, respectively, yet after 240 h, 55.9% of bianthryl **1** is racemized at 180°. Considering the molar ratio of bianthryl **1** to Ph_2Hg (**34**) used in the experiment (1:5), the maximum number of phenyl radicals in solution after 240 h at 180° was 8.0 X 10^{-11}. This caused 56% of the bianthryl molecules to racemize. In this case, each phenyl radical appears to have added reversibly to at least 7.0 X10^9 bianthryl molecules during its life-time, thus providing evidence that the phenyl radical catalyses the racemization of bianthryl **1**. This calculation does not include a correction for the thermal racemization process (p 62).

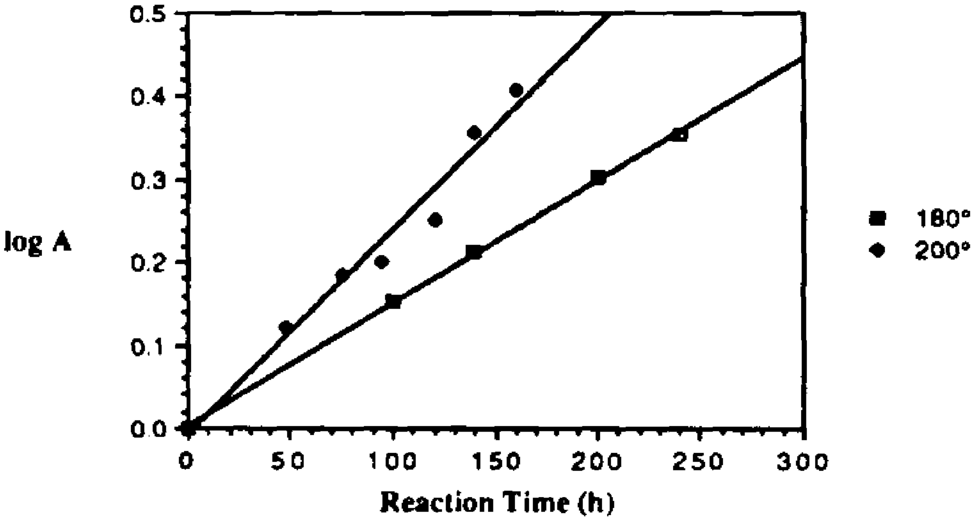
A first order plot of log $[\alpha_0]/[\alpha]$ versus reaction time (Figure 9, $A = [\alpha_0]/[\alpha]$), where $[\alpha_o]$ is the specific rotation of bianthryl **1** at $t = 0$ and $[\alpha]$ is the specific rotation at time t, is a straight line passing through the origin with slope equal to k (eq. 20).

$$\log \frac{[\alpha_0]}{[\alpha]} = kt \qquad (20)$$

The slopes (k) obtained at 200° and 180°C are $6.9 \times 10^{-7}\ s^{-1}$ ($0.0025\ h^{-1}$) and $4.2 \times 10^{-7}\ s^{-1}$ ($0.0015\ h^{-1}$) respectively. The rates for the thermal racemization of bianthryl **1** at 200° and 180°C in bromobenzene was calculated from the Arrhenius parameters (Ea = 39±0.5 kcal/mol; ln A = 11.1 ± 0.2)[92] as $9.20 \pm 0.30 \times 10^{-8}\ s^{-1}$ and $1.45 \pm 0.05 \times 10^{-8}\ s^{-1}$ respectively. The racemization process is faster in the presence of Ph_2Hg compared to the thermal racemization process suggesting that the phenyl radical catalyzes the racemization of bianthryl **1** via reversible addition.

A straight line passing through the origin for a first-order plot (Figure 9) was not observed when PAT and $(PhCOO)_2$ was used as a radical source (Figures 3 and 7). This deviation from a straight line in the case of PAT and $(PhCOO)_2$ might be the result of a competitive radical termination step where two phenyl radicals combine to form biphenyl. The radical termination step depends on the concentration of radicals in solution. Since PAT decomposes relatively easily at 50°C ($t_{1/2}$ = 1.8 h), there is an appreciable concentration of phenyl radicals formed in solution and so dimerization is favorable in comparison to attack of bianthryl **1**. In the case of Ph_2Hg (**34**), the concentration of phenyl radicals is negligible compared to bianthryl and this minimizes the probability of a phenyl radical colliding with another phenyl radical to form biphenyl. At any given reaction time, the change in [Ph•] is very small and may be assumed to be a constant and hence an apparent first-order rate is observed.

Figure 9. First-order Plots for the Reaction of bianthryl **1** : Ph_2Hg = 1 : 5 at 200° and 180° C.



The racemization of bianthryl **1** is essentially completely inhibited in the presence of phenyl thiol (PhSH) a radical inhibitor (Table IX). The 1 : 0 : 10 value represents the thermal process and within experimental error equal to the 1 : 5 : 10 value.

Table IX. % Racemization in the Presence of PhSH at 180°.

	Bianthryl : Ph_2Hg : PhSH		
Reaction Time	**1 : 5 : 0**	**1 : 5 : 10**	**1 : 0 : 10**
140 h	38.8%	6.5%	5.0%

Chapter 3

3.1 The Benzyl Radical.

The benzyl radical ($PhCH_2\bullet$) is relatively stable compared to other alkyl radicals. Few reactions, other than dimerization and H-abstraction, have been reported. The absence of homolytic aromatic substitution by the benzyl radical on benzene compounds has been attributed to an unfavorable thermochemistry.[86] However, benzyl radicals will attack aromatic compounds like anthracene,[87] where formation of the intermediate adduct involves less loss of stabilization energy.

No substitution has been observed for the reaction of benzyl radicals with protonated and unprotonated pyridines, bibenzyl is the only reaction product.[9] The low addition enthalpy in this case determines the high value of k_{-1} ($k_{-1} >> k_2[B]$ and no substitution product is observed (eq. 21).

$$PhCH_2\bullet + ArH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \bullet ArHCH_2Ph \xrightarrow[k_2]{B\bullet} ArCH_2Ph + HB \qquad (21)$$

Reversibility mainly depends on the enthalpy of the radical addition; it increases as the addition becomes less exothermic as the stability of the attacking radical increases. Thus the relatively stable benzyl radical adds reversibly to a benzene substrate.

Dibenzylmercury [$(PhCH_2)_2Hg$] has been extensively used as a thermal source of benzyl radicals in solution. The rate determining step appears to be the homolysis of one of the C-Hg bonds (eq. 22) rather than a simultaneous rupture of both the C-Hg bonds. This is based on a "normal" Arrhenius A factor and an activation energy lower than the energy required to break both of the C-Hg bonds.[88]

$$(PhCH_2)_2Hg \longrightarrow PhCH_2\cdot + PhCH_2Hg\cdot \qquad (22)$$

$$PhCH_2Hg\cdot \longrightarrow PhCH_2\cdot + Hg \qquad (23)$$

Further evidence for this mechanism has been demonstrated by Jackson and Agirbas.[89] They compared the decomposition rates of unsubstituted, monosubstituted and disubstituted dibenzylmercurials. For a one-bond cleavage mechanism, cleavage of a particular C-Hg bond should only be significantly affected by the aryl group forming the incipient benzylic radical. This assumes that there is no significant effect by a substituent "X" on the stability of the radical *p*-X-$C_6H_4CH_2Hg\cdot$. The CH_2 group should form an electronic barrier to the transmission of electronic effects from the para substituent to the mercury atom, and the odd electron will be in an sp orbital,[89] which is unsuitable for hyperconjugation. The expected rates of decomposition of $(ArCH_2)_2Hg$, $ArCH_2HgCH_2Ar'$ and $(Ar'CH_2)_2Hg$ should be $2k_a$, k_a+k_b and $2k_b$, respectively,[89] with the mono substituted compound decomposing at the arithmetic mean of the rates of unsubstituted and disubstituted compounds. Simultaneous rupture of both the C-Hg bonds depends on the strengths of the two types of bonds. This leads to the expectation that the monosubstituted compound should decompose at the geometric mean of the rates of the unsubstituted and disubstituted compounds (geometric mean of two numbers x and y is $\frac{\sqrt{x^2+y^2}}{2}$).

Jackson and Agirbas measured the rates of decomposition with dibenzylmercury, *p*-methoxydibenzylmercury and bis-(*p*-methoxybenzyl)mercury in octane at 140.2°C.[89] The rates of decomposition are shown in Table X.

Table X. Rates of Decomposition of $XPhCH_2HgCH_2PhY$ in Octane at 140.2 °C.

X	Y	10^5 k (s^{-1})
H	H	7.63
H	MeO	17.9
MeO	MeO	28.6

The rate of decomposition of *p*-methoxydibenzylmercury (17.9 X 10^5 s^{-1}) is close to the arithmetic mean of the unsubstituted and disubstituted compounds (18.1 X 10^5 s^{-1}), but significantly different from the geometric mean (14.8 X 10^5 s^{-1}).

Jackson and coworkers reported the Arrhenius parameters for the decomposition of dibenzylmercury in octane (logA = 14.38±0.20 and Ea = 34.91±0.38 kcal/mol).[90] The rates of decomposition of dibenzylmercury (k) and the half lives ($t_{1/2}$) are calculated from equations 24 and 25 at various temperatures and are summarized in Table XI.

$$k = A\,e^{-E_a/RT} \qquad (24)$$

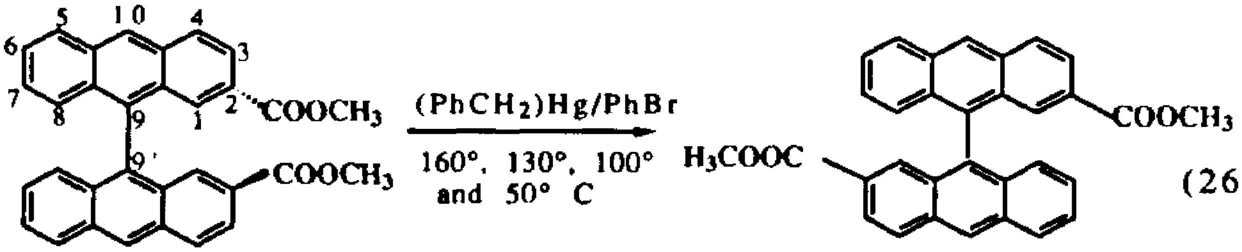
$$t_{1/2} = \frac{\log 2}{k} \qquad (25)$$

Table XI. Rates of Decomposition and Half lives of $(PhCH_2)_2Hg$ in Octane.

Temp. °C	k (s^{-1})	$t_{1/2}$ (h)
160°	5.8×10^{-4}	0.33
130°	2.4×10^{-5}	7.93
100°	8.5×10^{-7}	226
50°	5.8×10^{-10}	331,967

3.2 Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) with Dibenzylmercury in Bromobenzene.

The reaction of optically active 2,2'-dicarbomethoxy-9,9'-bianthryl (**1**) with varying concentrations of dibenzylmercury resulted in the recovery of partially racemized bianthryl **1**. No racemization has been observed in the absence of dibenzylmercury at temperatures as high as 190°C.[92] The reactions were carried out in sealed tubes degassed by the freeze pump thaw process at 160°, 130°, 100° and 50°C.



(+)-1 (±)-1 (26)

The percent racemization decreased as the concentration of dibenzylmercury was lowered. This is summarized for the reaction at 160°C in Table XII.

Table XII. Percent Racemization as a Function of $[(PhCH_2)_2Hg]$ at 160°C. Reaction time 40 h.

Bianthryl:$(PhCH_2)_2Hg$	$[(PhCH_2)_2Hg]$ M	% Racemization
1 : 0	0	0
1 : 10	6.4×10^{-3}	77.4%
1 : 5	3.2×10^{-3}	64.9%
1 : 1	6.4×10^{-4}	41.0%
1 : 0.50	3.2×10^{-4}	31.3%
1 : 0.33	2.1×10^{-4}	26.8%
1 : 0.25	1.6×10^{-4}	23.0%
1 : 0.20	1.3×10^{-4}	18.1%
1 : 0.10	6.4×10^{-5}	12.4%
1 : 0.066	4.3×10^{-5}	9.5%
1 : 0.050	3.2×10^{-5}	6.9%
1 : 0.033	2.1×10^{-5}	3.5%

[Bianthryl] = 6.4×10^{-4} M

The percent racemization also depends on the reaction time and the temperature. Table XIII shows the dependence of the percent racemization of bianthryl **1** on the reaction time and concentration of dibenzylmercury at 160°C.

Table XIII Percent Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the Presence of Dibenzylmercury as a Function of Reaction Time at 160°C in Bromobenzene

Time (h)	Bianthryl 1 : $(PhCH_2)_2Hg$					
	1 : 5		1 : 1		1 : 0.2	
	Run 1	Run 2	Run 1	Run 2	Run1	Run 2
0	0	0	0	0	0	0
0.25	21.2%	21.1%	9.7%	9.4%	3.0%	3.2%
0.50	34.1%	34.0%	14.8%	13.5%	5.9%	5.9%
0.75	42.1%	42.2%	19.5%	17.4%	8.5%	8.7%
1.00	46.1%	46.1%	23.2%	21.1%	11.3%	11.5%
1.25	51.5%	51.4%	26.5%	-	13.8%	14.0%
1.50	-	-	28.4%	-	-	-
1.75	-	-	30.2%	-	-	-
2.00	58.5%	-	31.1%	-	14.0%	-
3.00	61.5%	-	35.5%	-	16.1%	-
24.0	65.9%	-	40.9%	-	18.1%	-

The racemization of bianthryl **1** was totally inhibited in the presence of the radical scavengers phenylthiol and dicyclohexylphosphine. Triphenylmethane (a H atom donor) inhibited the racemization process to the extent of 30% after 1 h reaction time. The racemization of bianthryl **1** was not affected by the presence of oxygen. These results suggest that the benzyl radical is the attacking species that causes the racemization of **1** via reversible addition.

The plot of change in rotation ($\alpha_0 - \alpha_t$) versus reaction time at 160°C is shown in Figures 10 A and 10 B.

Figure 10 A. Change in Rotation as a Function of Reaction Time for the reaction of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) with Dibenzylmercury at 160° C.

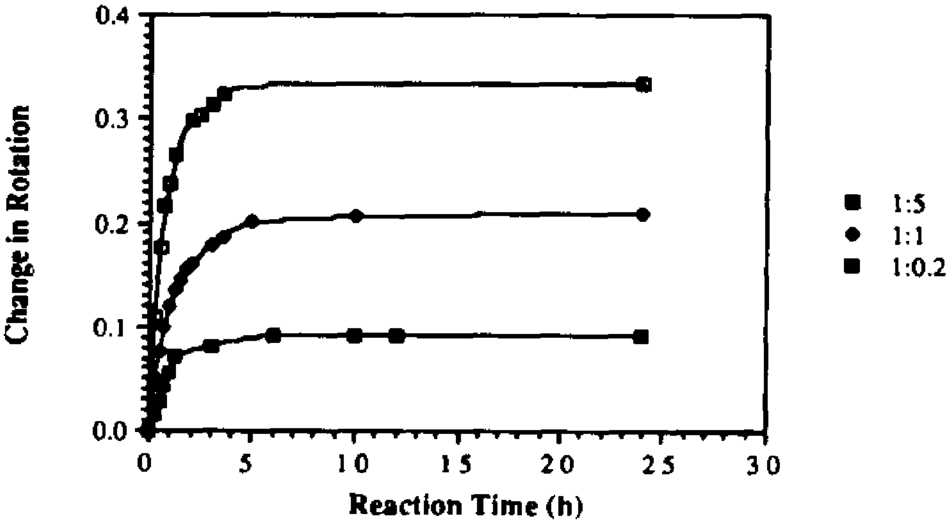
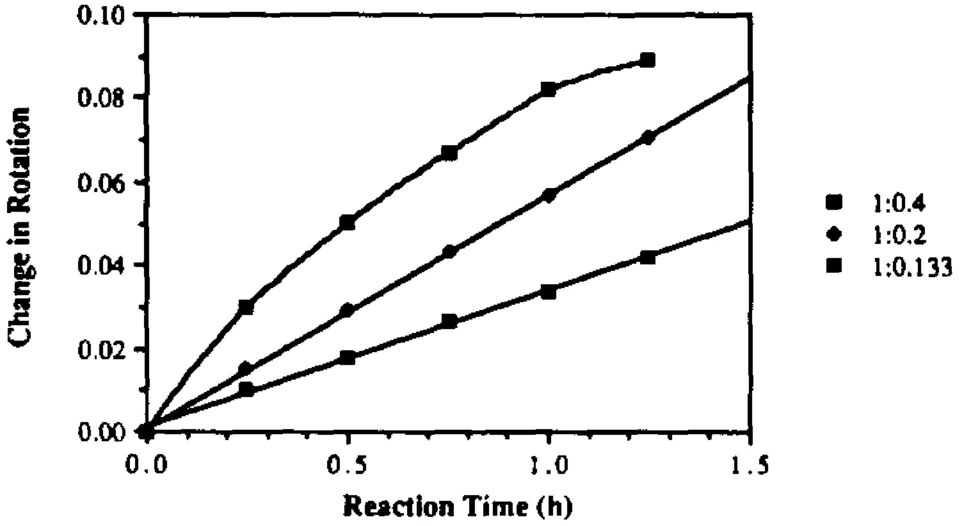


Figure 10 B. Change in Rotation as a Function of Reaction Time for the reaction of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) with Dibenzylmercury at 160° C.



As the concentration of dibenzylmercury is lowered, the plot of change in rotation versus reaction time gives a straight line (Figure 10 B) indicating a first order reaction.

A series of racemization experiments was carried out to determine the initial rates (k) and establish the order of the reaction with respect to bianthryl 1 and $(PhCH_2)_2Hg$. In one set, [bianthryl 1] was held constant (0.0064 M) as the $[(PhCH_2)_2Hg]$ was varied. In another set, [bianthryl 1] was varied as the $[(PhCH_2)_2Hg]$ was kept constant. Each set was repeated to duplicate results.

Initial rates were calculated as $(\alpha_0 - \alpha_t)/t$ at $t = 0.25$ h and are summarized in Table XIV for the reactions in which [bianthryl 1] is kept constant and $[(PhCH_2)_2Hg]$ is varied at 160°C.

Table XIV. Initial Rates as a Function of [$(PhCH_2)_2Hg$] at 160°C.

Bianthryl:$(PhCH_2)_2Hg$	[$(PhCH_2)_2Hg$] M	k_{expt} (h^{-1})	
		Run 1	Run 2
1 : 5.0	0.0320	0.435	0.432
1 : 1.0	0.0064	0.200	0.192
1 : 0.4	0.00256	0.116	0.120
1 : 0.2	0.00128	0.060	0.057
1 : 0.13	0.00085	0.036	0.033

At lower concentrations of dibenzylmercury, a reaction order of approximately one is observed. For example, when the concentration ratio was changed from 1:0.2 to 1:0.4 the rate increased by a factor of 1.93 (0.116/0.060). The rate would be expected to double if the reaction was first order since the [$(PhCH_2)_2Hg$] was doubled. An order less than first-order in dibenzylmercury is observed when the initial rates are compared at higher concentrations of dibenzylmercury. For example, when the concentration ratio was changed form 1:0.4 to 1:1 which corresponds to an increase in [$(PhCH_2)_2Hg$] of 2.5, the rate would be expected to increase by a factor of 2.5 if the reaction was first-order. It actually increased by a factor of 1.72, which corresponds to an order of 0.6 as $(2.5)^{0.6} = 1.73$. Another example of a lower order in $(PhCH_2)_2Hg$ can be seen when the

[$(PhCH_2)_2Hg$] was increased 5 times, from a concentration ratio of 1:1 to 1:5. The rate would be expected to increase 5 times if the reaction was first order in dibenzylmercury. It increased by a factor of 2.2, which corresponds to a half-order as $5^{1/2} = 2.2$.

The order of the reaction can also be determined from equation 27.

$$\log k_1 - \log k_2 = n\{\log [Bz_2Hg]_1 - \log [Bz_2Hg]_2\} \qquad (27)$$

k_1 and k_2 are initial rates corresponding to the two concentrations of dibenzylmercury (Bz_2Hg), and n is the order of the reaction with respect to dibenzylmercury.

Figure 11 A. Plot of Equation 27 (Run 1)

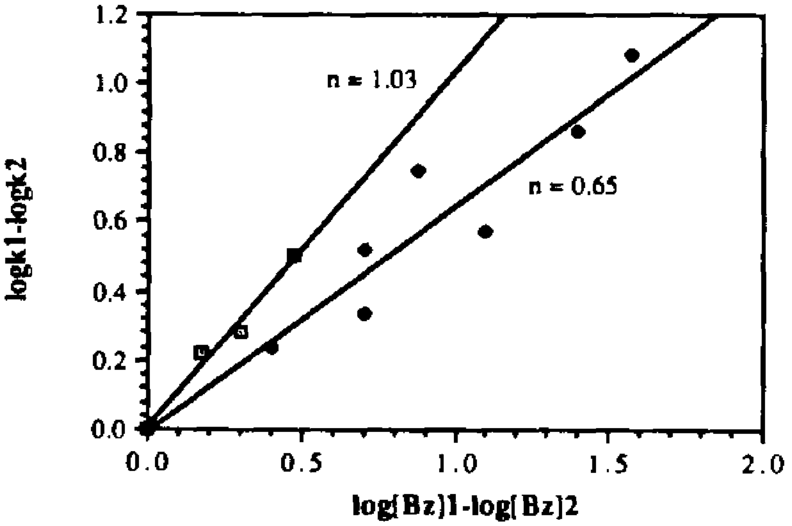
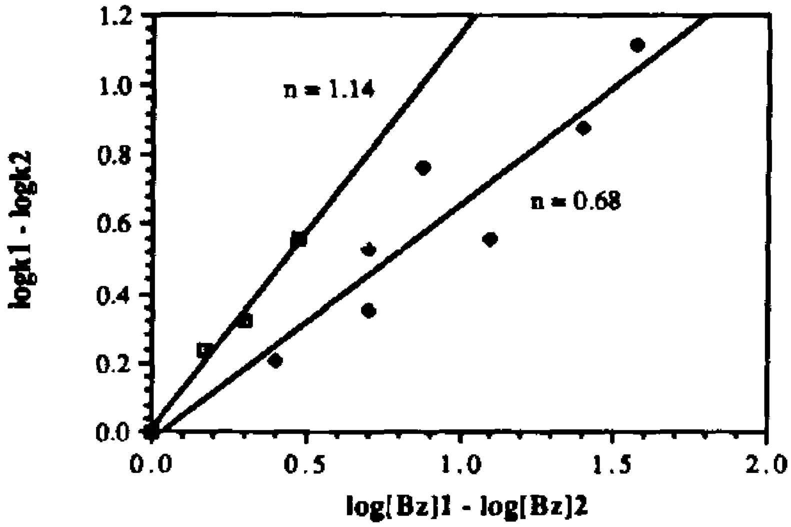


Figure 11 B. Plot of Equation 27 (Run 2)



A plot of equation 27 (Figures 11 A and 11 B for run 1 and run 2 respectively) gives two straight lines, one with an average slope (n) = 1.09±0.06 for low concentrations of dibenzylmercury and the other with an average slope (n) = 0.66±0.01 for higher concentrations of dibenzylmercury. A radical combination step to give bibenzyl may contribute to the lower order observed at higher concentrations of $(PhCH_2)_2Hg$. As the concentration of the benzyl radical increases, the probability of the benzyl radical colliding with another benzyl radical increases compared to attack on the bianthryl **1**, thus lowering the overall order with respect to dibenzylmercury.

Tables XV and XVI summarize the initial rates obtained when the $[(PhCH_2)_2Hg]$ is held constant and the [bianthryl 1] is varied.

Table XV. Initial Rates as a Function of [Bianthryl 1] at 160°C, with [$(PhCH_2)_2Hg$] 0.0064 M.

Bianthryl:[$(PhCH_2)_2Hg$]	[Bianthryl 1] M	k (h^{-1})	
		Run 1	Run 2
2.0 : 1	0.0128	0.348	0.344
1.5 : 1	0.0096	0.212	0.212
1.0 : 1	0.0064	0.200	0.192
0.75 : 1	0.0048	0.134	0.132
0.50 : 1	0.0032	0.100	0.096

Table XVI. Initial Rates as a Function of [Bianthryl 1] at 160°C with [$(PhCH_2)_2Hg$] 0.032 M

Bianthryl 1 : [$(PhCH_2)_2Hg$]	[Bianthryl 1] M	k (h^{-1})
2.0 : 5	0.0128	0.726
1.5 : 5	0.0096	0.602
1.0 : 5	0.0064	0.434
0.75 : 5	0.0048	0.322
0.50 : 5	0.0032	0.244

Plots of equation 28 (Figures 12 A, 12 B and 12 C) gives straight lines with an average slope (n) of 0.85 ± 0.02 which is the order of the reaction with respect to bianthryl **1**.

$$\log k_1 - \log k_2 = n\{\log [\text{Bianthryl } \mathbf{1}]_1 - \log [\text{Bianthryl } \mathbf{1}]_2\} \qquad (28)$$

where k_1 and k_2 are initial rates corresponding to the two concentrations of bianthryl **1** and n is the order of the reaction with respect to bianthryl **1**.

Figure 12 A. Plot of Equation 28. Data from Table XV (Run 1).

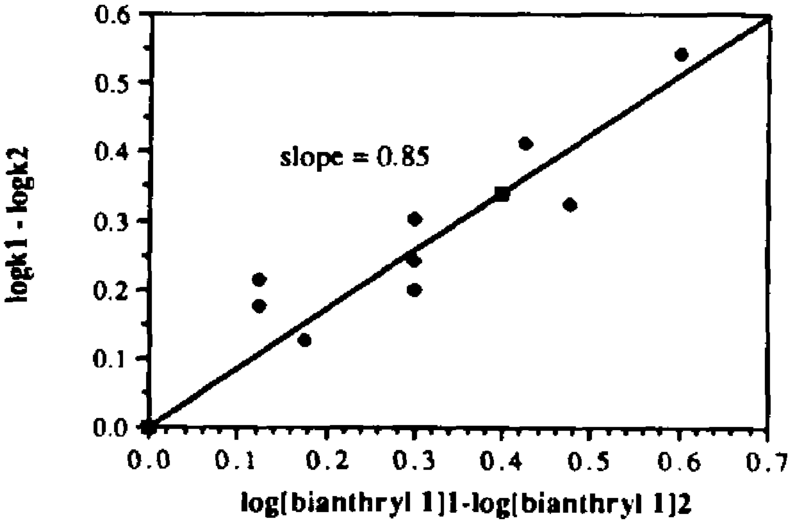


Figure 12 B. Plot of Equation 28. Data from Table XV (Run 2).

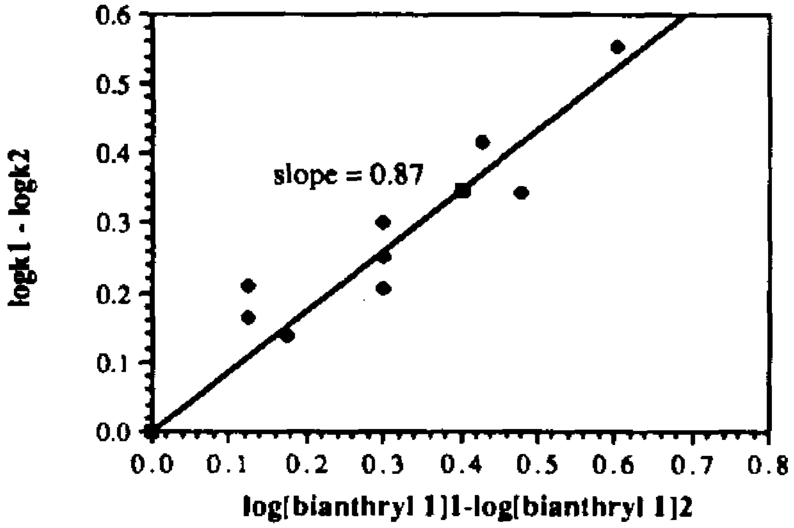
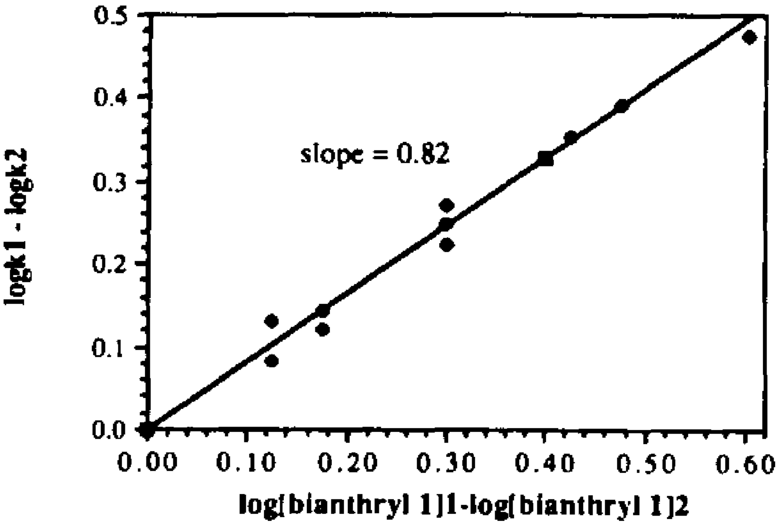


Figure 12 C. Plot of Equation 28. Data from Table XVI



3.3 Recovery of Racemized Bianthryl 1 From The Reaction with Dibenzylmercury in Bromobenzene at 160°C.

Optically active 2,2'-dicarbomethoxy-9,9'-bianthryl (1) (0.075g, 0.159 mmol, $[\alpha]_D$ = -151.1°) was heated with 10 equiv. of dibenzylmercury (0.6104g, 1.59 mmol) in 25 mL of bromobenzene at 160°C in a sealed tube degassed by the freeze pump thaw process for 10 h. The reaction solution was 74% racemized. The reaction solution was filtered to recover 0.3185g of Hg (99.5% recovery) indicating that all of the dibenzylmercury had decomposed. Bromobenzene was distilled off (35°C, 1 mm Hg), and the residue was purified by column chromatography followed by preparative TLC to give 0.0286g (38.1% recovery) of racemized bianthryl (1) ($[\alpha]_D$ = -42.0°, 72.2% racemized). This shows that the % racemization calculated from the rotation of the reaction solution is an accurate measure of the actual % racemization.

3.4 Reaction of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) with Dibenzylmercury in Bromobenzene at 130°, 100° and 50°C.

The decomposition of dibenzylmercury to give benzyl radicals is slower at 130°C compared to 160°C, and this trend is observed for the racemization of bianthryl 1. However, the time of observable racemization is longer, and the final racemization is greater than that observed at 160°C. For example, at 130° the final racemization is 83.2% after 75 h for the molar ratio of bianthryl **1** : $(PhCH_2)_2Hg$ = 1 : 5, whereas at 160°C, the percentage racemization almost remains constant after 3 h at 61.5% (see Figure 10, p 71). Table XVII shows the percent racemization as a function of reaction time and concentration of dibenzylmercury at 130°C. The percentage racemization increases with reaction time and the concentration of $(PhCH_2)_2Hg$.

Table XVII. Percent Racemization as a Function of Reaction Time and $[(PhCH_2)_2Hg]$ in Bromobenzene at 130°C.

Reaction Time (h)	**Bianthryl 1 : $(PhCH_2)_2Hg$**		
	1 : 5	**1 : 1**	**1 : 0.2**
0.0	0.0	0.0	0.0
1.0	8.8%	2.5%	0.8%
2.0	14.9%	5.9%	1.7%
3.0	20.0%	7.4%	-
5.0	30.0%	12.0%	3.7%
10.0	49.3%	21.0%	8.0%
13.0	55.2%	26.0%	-
15.0	-	-	11.0%
16.0	61.0%	29.0%	-
19.5	68.2%	-	-
20.5	-	-	14.7%
25.0	-	-	17.1%
26.0	76.0%	-	-
55.0	81.9%	56.0%	-
59.0	-	-	29.9%
75.0	83.2%	59.4%	32.0%

Figure 13 shows the change in rotation versus reaction time at 130°C.

Figure 13. Change in Rotation of Bianthryl **1** with Different Ratios of Dibenzylmercury at 130° C.

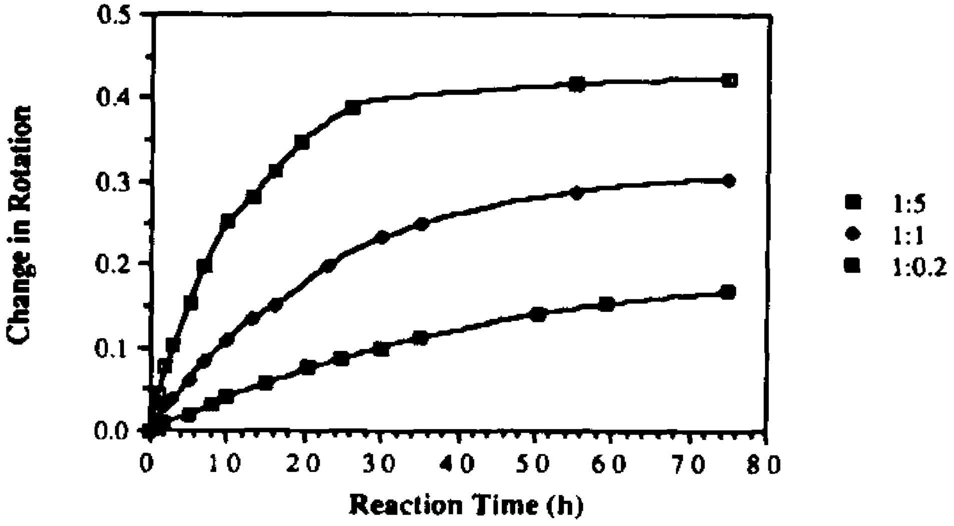
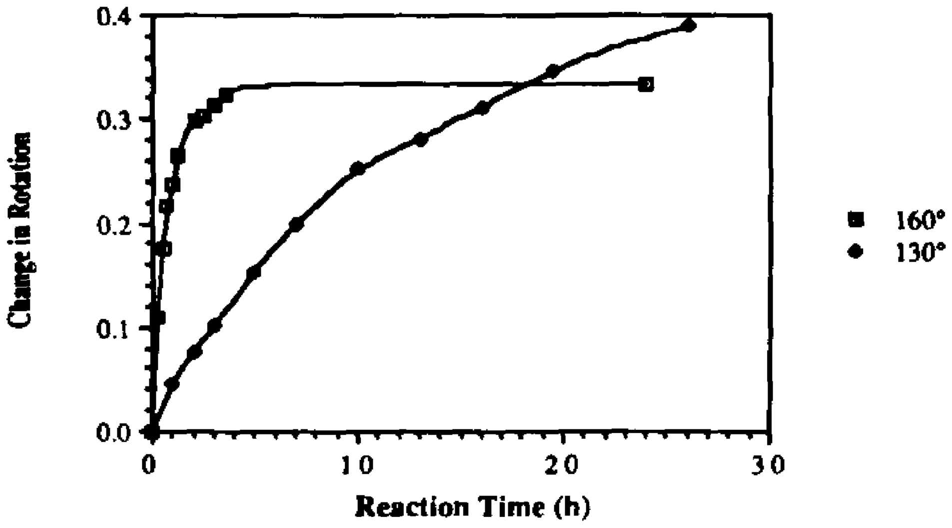


Figure 14 compares the change in rotation of bianthryl **1** at 160° and 130°C for bianthryl **1** : $(PhCH_2)_2Hg$ = 1 : 5.

Figure 14. Change in Rotation of Bianthryl 1 at 160° and 130° for Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 5.



As seen in Figure 14, the racemization rate is slower at 130° than at 160°C. This is expected since the decomposition of dibenzylmercury to give benzyl radicals is slower at 130°C. However, the final percentage racemization is greater at 130°C. Since the concentration of benzyl radicals generated in solution at any given time is lower at 130°C, the termination step, which is second order in benzyl radical will not compete as well with the addition to bianthryl 1, which is 0.66-1.0 order (p 74).

This trend is also observed at 100°C. The reaction of optically active 2,2'-dicarbomethoxy-9,9'-bianthryl (1) with dibenzylmercury at 100°C in bromobenzene resulted in extensive racemization. No racemization was observed under comparable conditions without the radical source.[92] The racemization rate is slower than at 160°C and

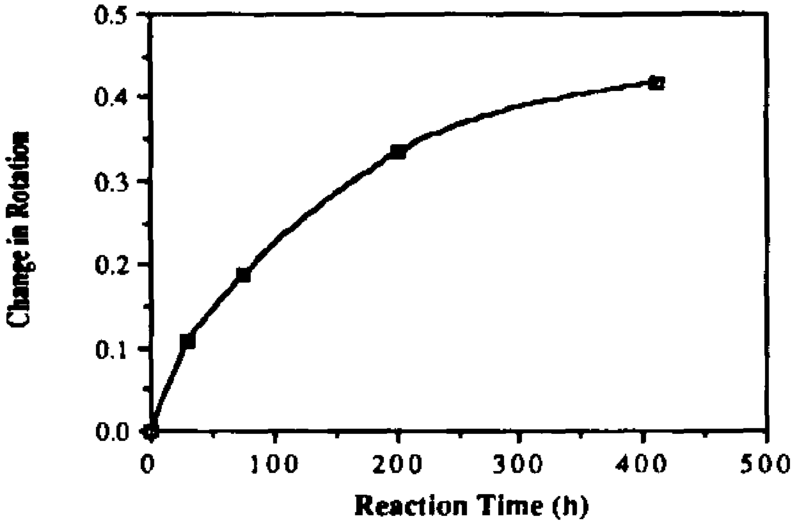
130°C as expected from the half-lives of decomposition of dibenzylmercury at these temperatures (p 67). After 410 h (approximately two half-lives) the bianthryl 1 racemized to the extent of 82.1%. The results are summarized in Table XVIII.

Table XVIII. Percentage Racemization as a Function of Reaction Time at 100°C. Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 5.

Reaction Time (h)	% Racemization
0	0
30	21.2%
75	36.7%
200	65.8%
410	82.1%

A plot of change in rotation (α_0-α_t) versus reaction time at 100°C is shown in Figure 15.

Figure 15. Change in Rotation of Bianthryl 1 in the Presence of Dibenzylmercury at 100°C.



The reaction of optically active 2,2'-dicarbomethoxy-9,9'-bianthryl (**1**) with dibenzylmercury at 50°C in bromobenzene also resulted in the recovery of bianthryl **1** which was substantially racemized. These results were not expected as the half life ($t_{1/2}$) for the thermal decomposition of dibenzylmercury in *n*-octane at 50°C is calculated to be 37.9 years! No racemization was observed without dibenzylmercury. To rule out the possibility that the mercury compound, i.e., dibenzylmercury may be responsible for the observed racemization instead of the benzyl radical, bianthryl **1** was reacted with diethylmercury, which has a very high half-life in the gas phase ($t_{1/2}$ = 4.1 X 10^{19} years at 50° C).[82a] After 820 h only 7.8% of the bianthryl **1** had racemized in the presence of diethylmercury as opposed to 42.8% racemization observed in the presence of dibenzylmercury. The phenyl group in dibenzylmercury should not have a great influence on the mercury atom since an insulating CH_2 group is present. It would be expected that dibenzylmercury and diethylmercury would interact similarly with bianthryl **1**, specially at a lower temperature. The results thus suggest that the benzyl radical rather than the mercury compound is responsible for the observed racemization. These results are summarized in Table XIX.

Table XIX. Percent Racemization at 50°C.
Bianthryl 1 : R_2Hg = 1 : 5

Reaction Time (h)	$(PhCH_2)_2Hg$	Et_2Hg
0	0	0
228	33.9%	2.03%
435	39.4%	2.0%
620	40.0%	3.5%
820	42.8%	7.8%

For every molecule of $(PhCH_2)_2Hg$, two benzyl radicals are formed. Since the half-life of decomposition of $(PhCH_2)_2Hg$ is 37.9 years, only 0.123% of the $(PhCH_2)_2Hg$ will have decomposed after 820 h at 50°, yet after 820 h, 42.8% of bianthryl **1** is racemized at 50°. Considering the molar ratio of bianthryl 1 to $(PhCH_2)_2Hg$ used in the experiment (1 : 5), the maximum number of benzyl radicals in solution after 820 h at 50° was 1.23×10^{-2}. This caused 42.8% of the bianthryl molecules to racemize. In this case, each benzyl radical appears to have added reversibly to at least 3480 bianthryl molecules during its life-time, thus providing evidence that the benzyl radical catalyses the racemization of bianthryl **1**.

Figure 16 shows the change in rotation versus reaction time for the reaction at 50°C for the ratio bianthryl **1** : $(PhCH_2)_2Hg$ of 1 : 5 and Figure 17 compares the change in rotation of bianthryl **1** at 100° and 50°C for bianthryl **1** : $(PhCH_2)_2Hg$ = 1 : 5.

Figure 16. Change in Rotation of Bianthryl 1 in the Presence of Dibenzylmercury at 50° C.

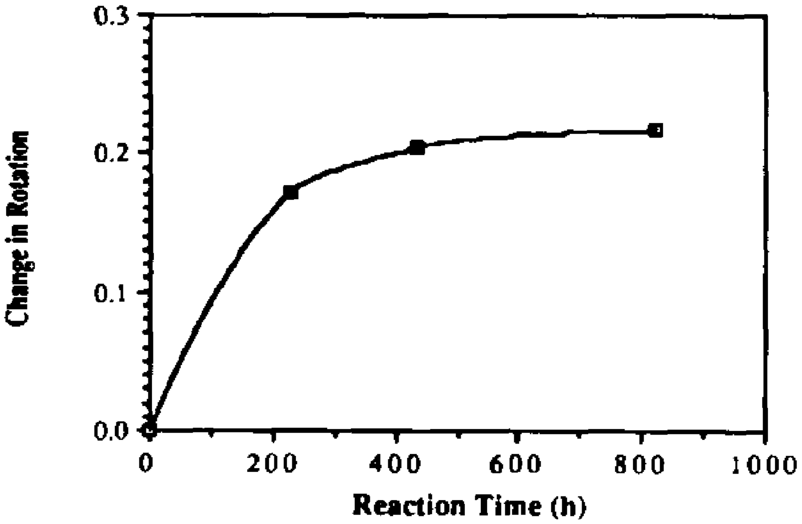
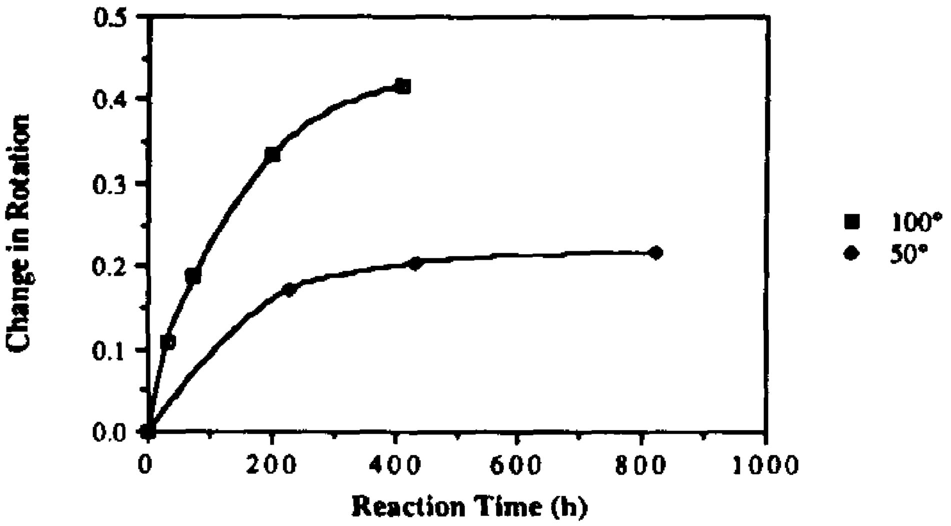


Figure 17. Change in Rotation of Bianthryl 1 in the Presence of Dibenzylmercury at 100° and 50° C.



3.5 Arrhenius Parameters for the Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the presence of Dibenzylmercury

Reaction rates are sensitive to temperature changes. An often quoted rule-of-thumb in the organic laboratory is that raising the temperature by 10°C will result in a doubling of the reaction rate. While this generalization is only occasionally accurate, it does illustrate the importance of temperature as a variable that influences reaction rates.

The temperature dependance of the rate constant is described within the accuracy of the experimental data by the Arrhenius equation (29).

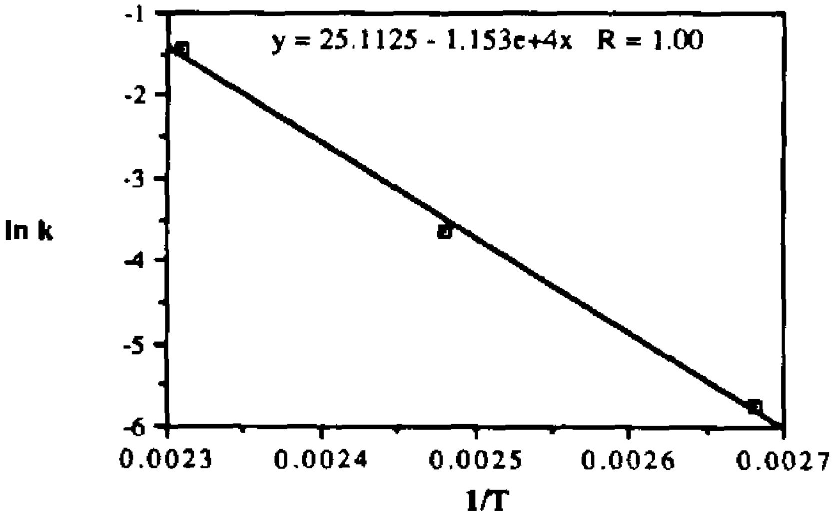
$$k = A\, e^{-E_a/RT} \qquad (29)$$

where A is the pre-exponential factor, E_a is the activation energy, R is the gas constant and T is the absolute temperature. The values of the empirical constants A and E_a are usually found graphically from the logarithmic form of the Arrhenius equation (30)

$$\ln k = \ln A - \frac{E_a}{RT} \qquad (30)$$

A graph of ln k versus 1/T gives a straight line with slope $-E_a/R$ and intercept ln A (Figure 18).

Figure 18. Arrhenius Plot for the Racemization of Bianthryl 1 in the Presence of Dibenzylmercury.



The racemization data for bianthryl 1 and dibenzylmercury at 160° C, 130° C and 100° C is plotted in Figure 18. The intercept ln A, is equal to 25.1 ($\log_{10} A = 10.9$) and the slope -Ea/R, is equal to $-1.153.X10^4$. The activation energy (E_a) for the racemization process is calculated to be 22.8 kcal/mole.

2,2'-Dicarbomethoxy-9,9'-bianthryl (1) has a high optical stability. The interactions of the pairs of hydrogens at the 1,1' and 8,8' positions in the transition state create a sizeable barrier to the rotation around the 9,9' pivotal bond. Koukotas[91] estimated a minimum activation energy (E_a) of 43 kcal/mol in dimethyl phthalate. This estimate was based on the absence of thermal racemization after 6 h at 200°C. More accurate Arrhenius parameters have recently been determined for the thermal racemization of bianthryl **1** in bromobenzene in our laboratory.[92] The values obtained were $\log_{10} A = 11.1 \pm 0.2$ and $Ea = 39.0 \pm 0.5$ kcal/mol.

Thus reversible addition of the benzyl radical to bianthryl **1** to form a cyclohexadienyl intermediate (σ-complex), e.g., **21** (p 19) considerably reduces the rotational barrier about the pivotal bond (C-9, C9') due to a decrease in the number of simultaneous steric interactions in the rotational transition state.

3.6 Reaction of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) with Bis-(*m*-fluorobenzyl)mercury in bromobenzene.

Substituent effects on free radicals reactions are influenced by polar, resonance and steric factors.[90] Jackson and coworkers[90] studied the kinetics of decomposition of substituted dibenzylmercury compounds in octane solution. The first-order rate constants obtained by them, did not correlate well with any of the polar substituent constants, σ, σ^+ or σ^-. Plots of log k against σ however showed that the *meta*-substituents lie close to a line with slope -0.6, indicating that there is in fact a significant polar influence on the decomposition reaction. They interpreted this as being due to the destruction of the partial negative charge on the benzylic carbon atom on going from the ground state to the transition state in the reaction in equation 31.

$$XC_6H_4\overset{\delta-}{C}H_2\text{-}\overset{\delta+}{Hg}\text{-}CH_2C_6H_4 \longrightarrow XC_6H_4CH_2\bullet + \bullet HgCH_2C_6H_4X \qquad (31)$$

The points for the *para*-substituents lie above the *meta*-line. Since both electron-withdrawing and electron-donating substituents were involved, this could not be explained by the polar effect. The enhancement of the rate was attributed to the stabilization of the benzylic radical produced by conjugating groups, whether electron-withdrawing or electron-donating.

Bis-(*m*-fluorobenzyl)mercury was synthesized from the corresponding Grignard reagent and $HgCl_2$. Jackson reported the Arrhenius parameters log A = 14.38 and Ea = 35.24 kcal/mol for the decomposition of bis-(*m*-fluorobenzyl)mercury in octane.[90] The half-lives ($t_{1/2}$) calculated at 160°C and 130°C are 1.19 h and 12.15 h, respectively. The decomposition of bis-(*m*-fluorobenzyl)mercury is thus slower than that of the unsubstituted dibenzylmercury. Table XX compares their half-lives.

Table XX. Half-lives of Dibenzylmercury and Bis-(*m*-fluorobenzyl)mercury in octane.

	$(PhCH_2)Hg$	$(m\text{-}FC_6H_4CH_2)_2Hg$
$t_{1/2}$ at 160°	0.33 h	1.19 h
$t_{1/2}$ at 130°	7.93 h	12.15 h

The reaction of 2,2'-dicarbomethoxy-9,9'-bianthryl (**1**) with bis-(*m*-fluorobenzyl)mercury in bromobenzene resulted in the recovery of partially racemized bianthryl **1**. As expected from the half-lives, the racemization rate is slower than in the presence of dibenzylmercury. No racemization was observed without the radical source at temperatures as high as 190°C.[92] The racemization process was completely inhibited by phenylthiol a radical scavenger. Thus, in the reaction of bianthryl **1** with bis-(*m*-fluorobenzyl)mercury, the $m\text{-}FC_6H_4CH_2\cdot$ causes the racemization of bianthryl **1** via reversible addition.

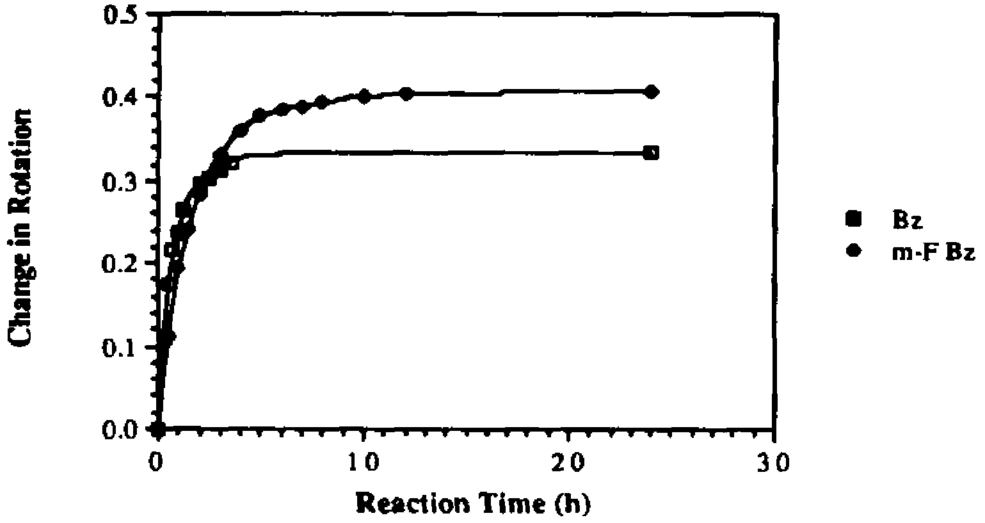
Table XXI shows the percentage racemization as a function of reaction time at 160°C. The final % racemization was 81.0% after 10 h.

Table XXI. Percentage Racemization at 160°.
Bianthryl 1 : (m-$FC_6H_4CH_2)_2Hg$ = 1 : 5.

Reaction Time (h)	% Racemization
0.0	0.0
0.5	22.7%
1.0	38.9%
1.5	48.4%
2.0	57.2%
3.0	66.7%
4.0	72.3%
5.0	75.9%
6.0	77.5%
7.0	78.1%
8.0	79.1%
10.0	80.7%
12.0	81.0%
24.0	81.0%
48.0	81.0%

Figure 19 compares the change in rotation versus reaction time at 160°C for the reaction of bianthryl 1 with dibenzylmercury and bis-(*m*-fluorobenzyl)mercury (1:5 molar ratio).

Figure 19. Change in Rotation versus Reaction Time at 160°C for the Reaction of Bianthryl 1 with Dibenzylmercury and Bis-(*m*-fluorobenzyl)mercury (1:5 molar ratio).



As seen from Figure 19, the racemization rate is slightly faster for the reaction with dibenzylmercury as expected from their calculated half-lives, and the final % racemization is 65.9% for the reaction with dibenzylmercury compared to 81.0% for the reaction with bis-(*m*-fluorobenzyl)mercury.

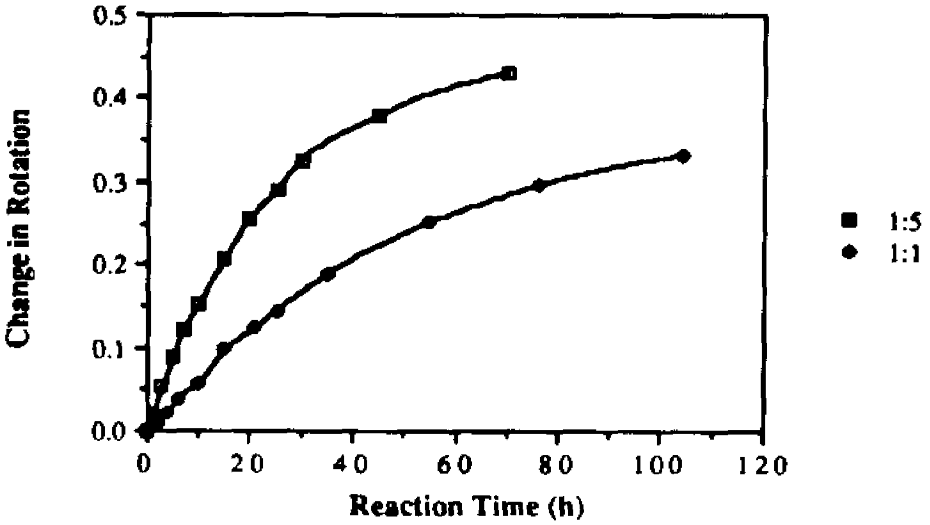
The reaction at 130°C also follows the same trend. Table XXII shows percentage racemization as a function of reaction time for the ratios of bianthryl **1**: bis-(*m*-fluorobenzyl)mercury.of 1 : 5 and 1 : 1.

Table XXII. Percentage Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl 1 in the Presence of Bis-(*m*-fluorobenzyl)mercury at 130°C.

Bianthryl 1:$(m\text{-}FC_6H_4CH_2)_2Hg$ 1:5		Bianthryl 1:$(m\text{-}FC_6H_4CH_2)_2Hg$ 1:1	
Time (h)	% Racemization	Time (h)	% Racemization
0.0	0.0	0.0	0.0
3.0	3.3%	2	1.6%
5.0	10.4%	4.0	4.5%
7.0	23.8%	10.0	11.4%
10.0	30.0%	15.0	19.3%
15.0	40.6%	21.0	24.5%
20.0	50.4%	25.0	28.2%
25.0	56.9%	35.0	37.1%
30.0	64.2%	55.0	49.5%
45.0	75.0%	76.0	58.4%
70.0	84.8%	104.0	65.5%

Figure 20 shows a plot of change in rotation (α_0-α_t) versus reaction time for the reaction at 130°C.

Figure 20. Change in Rotation of Bianthryl 1 in the Presence of Bis-(*m*-fluorobenzyl)mercury at 130°C.

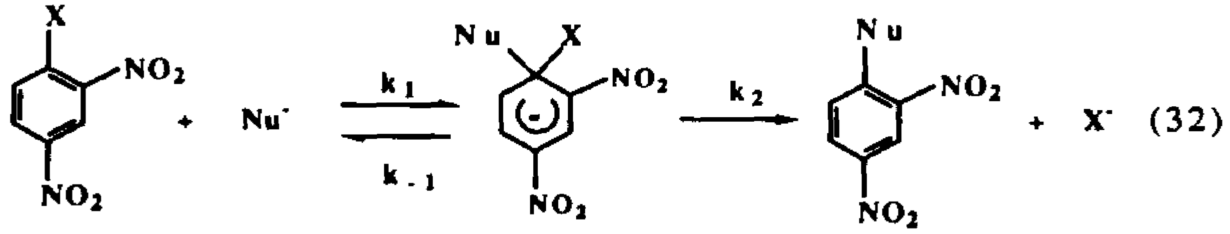


Chapter 4

4.1 Nucleophilic Aromatic Substitution.

Nucleophilic aromatic substitution is generally observed in aromatic or heteroaromatic compounds carrying a nucleofugic (leaving) group with activation by a strong electron-withdrawing group (e.g., a nitro group) in a conjugable position with respect to the carbon carrying the nucleofugic group.[1a]

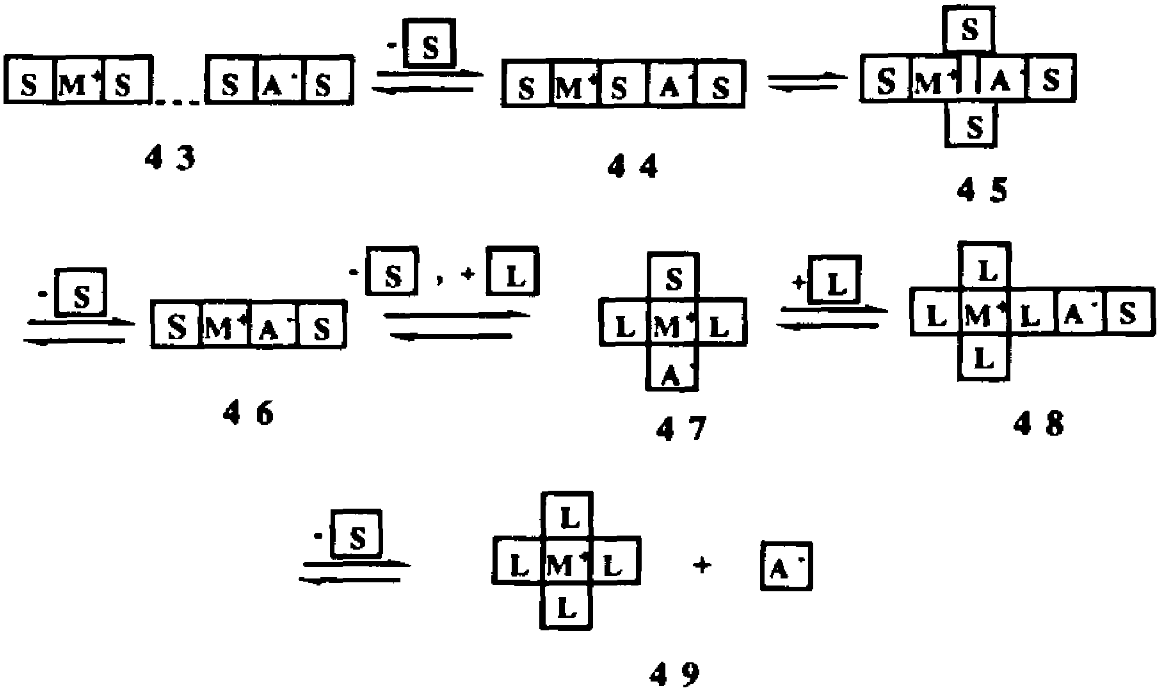
Bunnett[93] has provided strong evidence for a two-step pathway for nucleophilic aromatic substitution (eq. 32) using the "elemental effect", i.e., the variation in rate of substitution as the leaving group is varied.



For many reactions of this type, the rate does not depend on the carbon-nucleofugic group bond energy. The fluoro derivative is typically much more reactive than its chlorine, bromine or iodine analogs, contrary to what would be expected on the basis of bond energies if the C-X bond is broken in the rate-limiting step.

The first step (eq. 32) has generally been found to be rate-limiting.[94] Several properties of the nucleophile, such as basicity, polarizability, degree of solvation and interactions between the nucleophile, nucleofuge, substrate moiety and solvent influence the reactivity. In order to understand the leaving group sequence F > Cl > Br > I, consider a small low-polarizable reagent such as the methoxide ion. The factors determining its reactivity are (a) its ability to bond to a positive center, which is well represented by its basicity and (b) repulsions between the negative charge on the nucleophile and the electronic cloud of the leaving group and the substrate framework in the vicinity of the site of substitution. According to this approach, the fluoro derivative is more reactive than other halo derivatives because, owing to the small radius of fluorine, repulsion is minimized. With the other halogens as leaving groups, the repulsion is more important, as the other halogens are larger, with the consequence that there is a larger interaction zone between the incoming nucleophile and the leaving group. However, when the nucleophile is larger, softer and more polarizable, like the thiophenoxide ion, it can efficiently make the new bond at a larger distance, thus minimizing this repulsion. Highly polarizable nucleophiles can easily distort their bonding electrons forward towards the site of substitution so as to avoid bringing the rest of the molecule close enough to cause excessive repulsion.[95] In agreement with this concept, the nitro group is an extremely good leaving group, much better than fluorine, when a more polarizable reagent like thiophenoxide is used. Similar interpretations can be given for other leaving groups.

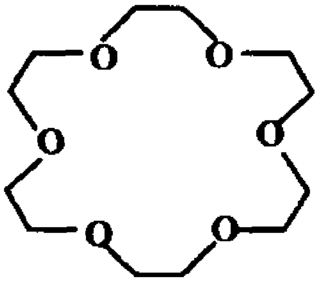
Ionic nucleophiles can exist in a variety of forms ranging from separately-solvated ions (**43**), solvent-separated ions (**44**), loose and tight ion-pairs (**45**), contact ion pairs (**46**) or complicated aggregates of three, four or more contact ion pairs[96] (Scheme XI).



Scheme XI. Ion-Pair Solvation and Complexation Effects.[96]
(S=solvent, M^+=cation, A^-=anion, L=ligand)

Separately solvated ions (**43**) predominate in good solvating solvents. In less polar solvents, contact ion pairs and associated aggregates become more significant. Upon addition of complexing agents like crown ethers or cryptands these species are converted more or less into ligand-separated ion pairs (**48**).[97] In the case of crown ether complexes a metal cation-anion contact always can occur from the open faces of the ring plane (**47**). Direct cation-anion pairing is expected to be weaker or absent if a more shielding cryptands are used (ligand-solvated cation, **48**). However, completely unsolvated, so-called "naked anions" (**49**), are never generated with crown ethers or crytands. Ion-pairing still occurs, forming complexed ion pairs. Totally isolated naked anions exist only in the absence of any species suited for interaction, e.g., under gas phase conditions.[98]

Weakly solvated, almost "naked" anions formed by complexation in solvents of low polarity differ essentially in two respect from their solvated ionic species.[98] (a) On account of their smaller size they possess a higher effective charge and (b) they do not have a (tight) solvation shell that must be broken or removed in the course of a reaction. The anion is already in a state prepared for a reaction, it is activated.[99] This can lead to a drastic increase in the rate constant for a given reaction, and has been demonstrated by numerous examples, ranging from simple nucleophilic substitutions on saturated or unsaturated carbon atoms, to C-C bond formations, eliminations, additions, oxidations, reductions and many others.[99] The fluoride ion was generally known for its difficulties to undergo a nucleophilic substitution in protic solvents.[100] Owing to its high charge density it is surrounded by a thick and tight solvation shell in highly polar solvents in which inorganic fluorides readily dissolve. In less polar solvents, where the anion would be less solvated, the high lattice energy prevents solubilization. However, poorly solvated fluoride ion (naked fluoride), generated by complexation, reacts as a strong (hard) base and as a more effective nucleophile compared to its higher solvated analogs. 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-crown-6) (**50**) is an effective agent for the solubilization of KF in polar and non-polar, aprotic organic solvents.[101] A comparison of the hydrophilic, electronegative cavity size of 18-crown-6 (2.6-3.2 Å) and the diameter of the unsolvated K^+ (2.66 Å) confirm the excellent 'fit' of K^+ into the 18-crown-6 cavity.[102]



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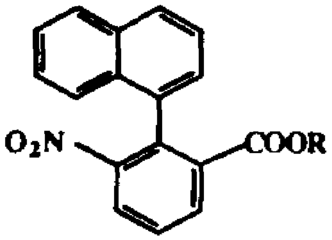
This solubilized fluoride ion (naked fluoride) reacts with a wide variety of organic substrates under relatively mild conditions. Less than 5% of the reaction takes place without the 18-crown-6 under identical conditions.

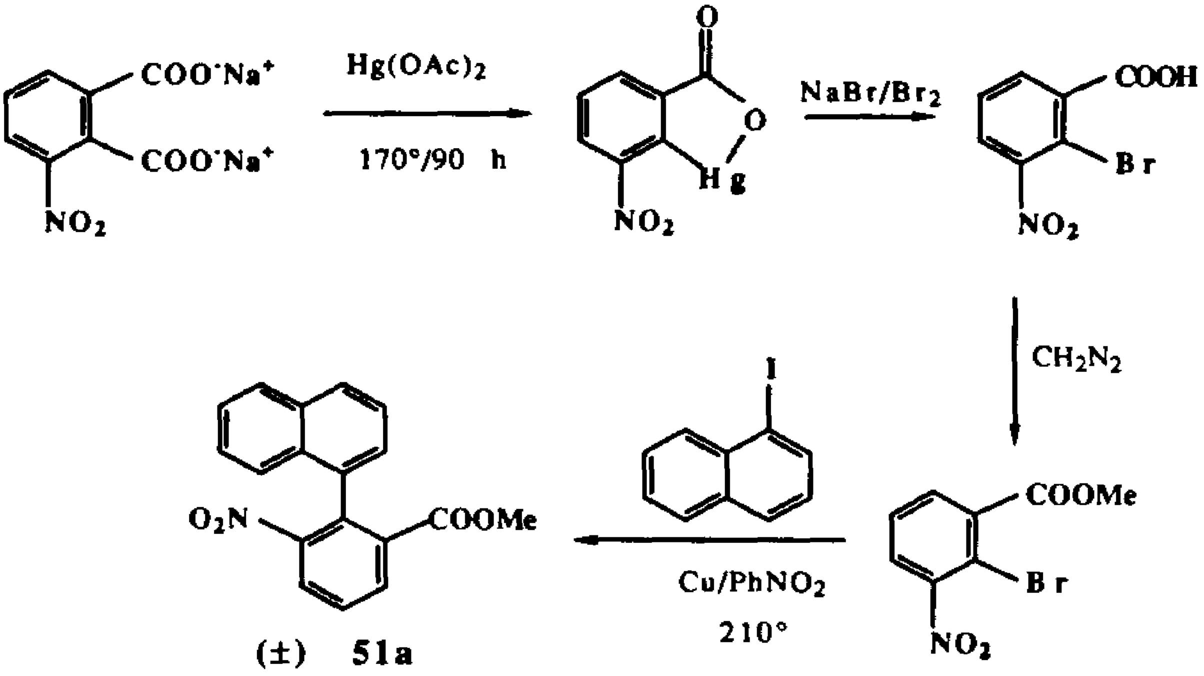
In this study, chiral biaryl methyl-2-α-naphthyl-3-nitrobenzoate (**51a**) was used as the aromatic substrate to study the reversibility of aromatic nucleophilic substitution reactions. The racemization of the biaryl (**51a**) was used as a probe to study the reversibility of addition of the fluoride ion to aromatic substrates. The recovery of racemized starting material would indicate reversible addition.



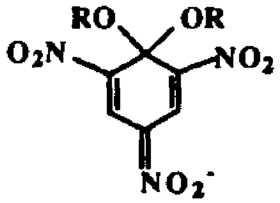
5 1
(a) $R=CH_3$
(b) $R=H$

(±)-Methyl-2-α-naphthyl-3-nitrobenzoate (**51a**) was synthesized according to Scheme XII. Acidic hydrolysis yielded (±)-**51b** which was resolved with (-)-quinine to obtain optically active acid **51b** and then esterified with diazomethane to get optically active methyl-2-α-naphthyl-3-nitrobenzoate (**51a**).

Scheme XII. Synthesis of (±)-Methyl-2-α-naphthyl-3-nitrobenzoate (51a)



Anionic σ-complexes form as a stable or transient species from covalent addition of nucleophiles to electron-deficient aromatic or heteroaromatic substrates. These have been known since 1900 when Jackson[103] proposed structure **52** for the red-colored species resulting from the reaction of picryl ethers with potassium alkoxides.



52

The first chemical evidence for such a structure was obtained in 1902 by Meisenheimer[104] and compounds of this type are now commonly referred to as "Meisenheimer" complexes.[105] The attachment of a nucleophile to any one of the carbons of the activated benzene ring of biaryl **51a** should distort the phenyl unit from planarity due to the conversion of one of the carbons (the one which is bonded to the nucleophile) from a trigonal sp^2 to a tetrahedral sp^3 arrangement. As a result, the rotational barrier about the pivotal bond should be lowered due to the decrease in the number of simultaneous steric interactions in the rotational transition state. This should enhance the rotation between the two portions of the Meisenheimer complex. These arguments were illustrated for 2,2'-dicarbomethoxy-9,9'-bianthryl (1) in Schemes VI, VII and VIII (pp 20-22). If the rotational process is competitive with the reversal step, the loss of the nucleophile would result in racemized starting material.

4.2 Racemization of Methyl-2-α-naphthyl-3-nitrobenzoate (51a) in the Presence of KF and 18-Crown-6 in Refluxing Acetonitrile (83°C).

The reaction of optically active methyl-2-α-naphthyl-3-nitrobenzoate (**51a**) with 2 equiv of KF solubilized in an acetonitrile solution of 18-crown-6 (1.5 equiv/equiv of KF) at 83° under a nitrogen atmosphere resulted in the recovery of partially racemized biaryl (**51a**). Table XXIII shows the percentage racemization as a function of reaction time.

Table XXIII. Percentage Racemization of Methyl-2-α-naphthyl-3-nitrobenzoate (51a) in the Presence of KF/18-Crown-6 in Refluxing CH_3CN

Reaction Time (h)	% Racemization		log $[\alpha_0]/[\alpha]$	
	Run 1	Run 2	Run 1	Run 2
0	0	0	0	0
25	5.3%	5.2%	0.024	0.023
100	23.6%	18.5%	0.117	0.089
240	38.9%	38.9%	0.214	0.214

In the absence of KF, methyl-2-α-naphthyl-3-nitrobenzoate (**51a**) was observed to racemize thermally in acetonitrile at 83°. The extent of thermal racemization was less compared to the racemization observed when KF was present. Table XXIV shows the thermal racemization of methyl-2-α-naphthyl-3-nitrobenzoate (**51a**) in refluxing acetonitrile as a function of reaction time.

Table XXIV. Thermal Racemization of Methyl-2-α-naphthyl-3-nitrobenzoate (51a) in Refluxing CH_3CN

Reaction Time (h)	% Racemization		log $[\alpha_0]/[\alpha]$	
	Run 1	Run 2	Run 1	Run 2
0	0	0	0	0
75	9.5%	8.8%	0.044	0.040
150	13.2%	16.6%	0.062	0.079
240	26.3%	25.3%	0.133	0.127

First order plots of log $[\alpha_0]/[\alpha]$ versus reaction time for the racemization of methyl-2-α-naphthyl-3-nitrobenzoate (**51a**) with and without KF/18-crown-6 at reflux are shown in Figures 21 A and 21 B (A=$[\alpha_0]/[\alpha]$), where $[\alpha_0]$ is the initial specific rotation and $[\alpha_t]$ is the specific rotation at time t.

The slopes of the first order plots (Figure 21 A and Figure 21 B) correspond to the rates of racemization. The average rate of racemization of methyl-2-α-naphthyl-3-nitrobenzoate (**51a**) in the presence of KF/18-crown-6 is $9.0 \pm 0.1 \times 10^{-4}$ h^{-1} and the average rate of thermal racemization is 5.3×10^{-4} h^{-1}. The racemization is 1.7 times faster in the presence of fluoride ion.

Figure 21 A. First-order Plots for the Racemization of Methyl-2-α-naphthyl-3-nitrobenzoate (51a) at 83° C, Run 1.

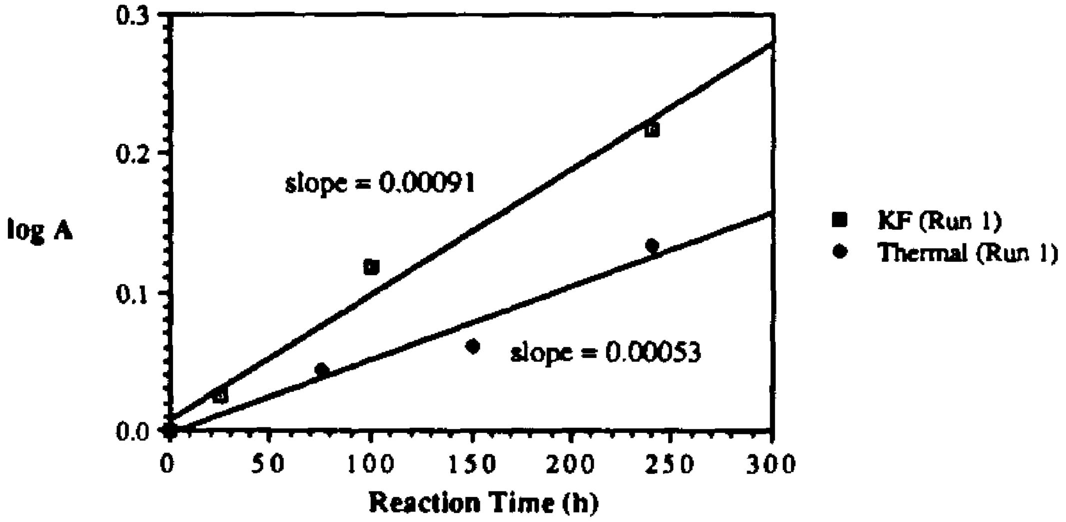
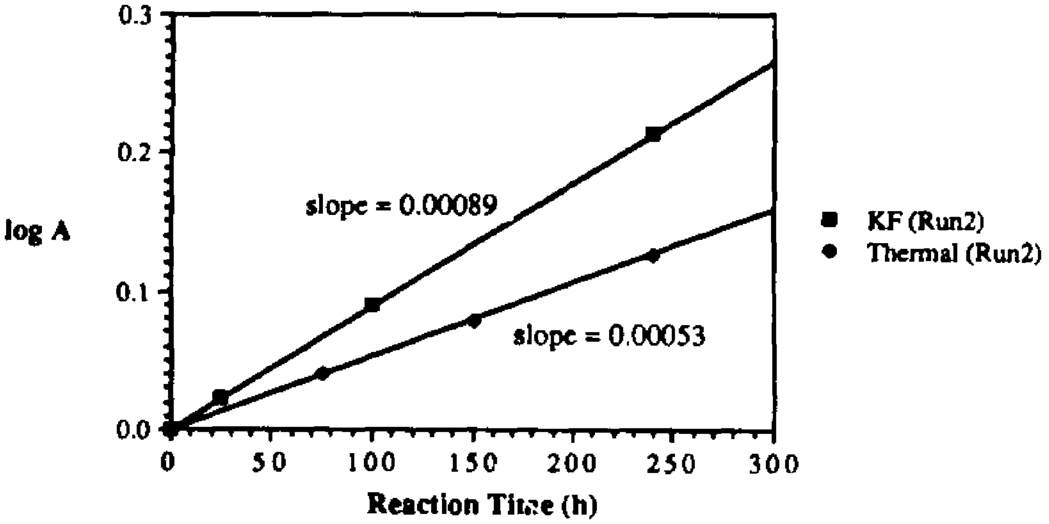


Figure 21 B. First-order Plots for the Racemization of Methyl-2-α-naphthyl-3-nitrobenzoate (51a) at 83° C, Run 2.



This suggests that the F^- causes the racemization of methyl-2-α-naphthyl-3-nitrobenzoate (**51a**) via reversible addition. The intermediate Meisenheimer complex (σ-complex) formed by the addition of the fluoride ion to methyl-2-α-naphthyl-3-nitrobenzoate (**51a**) must have a lower rotation energy barrier than the barrier to thermal rotation of the neutral molecule. Loss of the fluoride ion from the intermediate σ-complex (reversibility) would lead to racemized biaryl **51a**.

4.3 Racemization of Methyl-2-α-naphthyl-3-nitrobenzoate (51a) in the Presence of Excess KF and 0.16M 18-Crown-6 in Acetonitrile at 100°±0.1°C (Sealed Tubes).

To standardize the concentration of KF in each racemization tube, it was decided to run the reaction with excess KF. The reaction of optically active methyl-2-α-naphthyl-3-nitrobenzoate (**51a**) with excess KF in 0.16 M acetonitrile solution of 18-crown-6 at 100° ± 0.1°C under nitrogen resulted in the recovery of partially racemized biaryl **51a**. The reaction was carried out in sealed tubes degassed by the freeze pump thaw process. Table XXV shows the percentage racemization as a function of reaction time for one experiment.

Table XXV. Percentage Racemization* of Methyl-2-α-naphthyl-3-nitrobenzoate (51a) in the Presence of Excess KF in 0.16 M 18-Crown-6 solution in CH_3CN at 100°±0.1°C

Reaction Time (h)	% Racemization	log $[\alpha_0]/[\alpha]$	Average log $[\alpha_0]/[\alpha]$
0			
20	22.5%	0.111	0.1133
	22.9%	0.113	
	23.4%	0.116	
70	66.7%	0.477	0.4410
	60.9%	0.408	
	63.6%	0.438	
121	75.7%	0.614	0.6060
	75.3%	0.608	
	72.9%	0.567	
	76.8%	0.634	
140	83.0%	0.770	0.723
	78.9%	0.676	
	79.6%	0.690	
	80.6%	0.711	
	83.0%	0.770	

* each entry represents a separate tube.

In the absence of KF, methyl-2-α-naphthyl-3-nitrobenzoate (51a) was observed to thermally racemized in acetonitrile solution with and without 0.16 M 18-crown-6 at 100°C. The thermal racemization of biaryl 51 a was not effected by the presence of 18-crown-6. The extent of thermal racemization was less than the racemization observed with KF present. Table XXVI shows the thermal racemization of methyl-2-α-naphthyl-3-nitrobenzoate (51a) in acetonitrile as a function of reaction time for one experiment.

Table XXVI. Thermal Racemization of Methyl-2-α-naphthyl-3-nitromethylbenzoate (51a) in CH_3CN at 100°±0.1°C

Reaction Time (h)	% Racemization	log $[\alpha_0]/[\alpha]$
0	0	0
24	19.4%	0.094
48	36.1%	0.194
72	44.9%	0.259
96	54.0%	0.337
120	63.1%	0.434
145	68.7%	0.504

First order plots of log $[\alpha_0]/[\alpha]$ versus reaction time for the racemization of methyl-2-α-naphthyl-3-nitrobenzoate (**51a**) at 100°C with and without KF in 0.16 M 18-crown-6 solution in acetonitrile are shown in Figure 22 ($A=[\alpha_0]/[\alpha]$), where $[\alpha_0]$ is the initial specific rotation and $[\alpha_t]$ is the specific rotation at time t.

The slopes of the first order plots (Figure 22) correspond to the rate of racemization. The rate of racemization of methyl-2-α-naphthyl-3-nitrobenzoate (**51a**) in the presence of excess KF in 18-crown-6 solution of acetonitrile is 5.1×10^{-3} h^{-1} and the rate of thermal racemization in acetonitrile is 3.5×10^{-3} h^{-1}.

Figure 22. First-order Plots for the Racemization of Methyl-2-α-naphthyl-3-nitrobenzoate (51a) at 100° C.

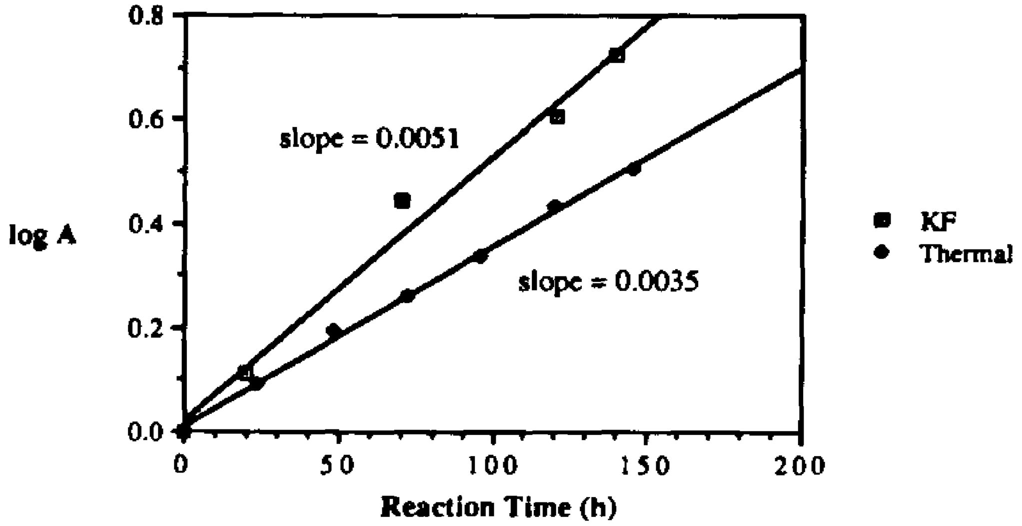


Table XXVII summarizes the slopes obtained from the plots of log $[\alpha_0]/[\alpha]$ versus reaction time for different runs, each done in duplicate.

Table XXVII. Slopes of log $[\alpha_0]/[\alpha]$ Versus Reaction Time For the Racemization of Methyl-2-α-naphthyl-3-nitrobenzoate (51a) in CH_3CN at 100°±0.1°.

Thermal Run		Excess KF	
Without 18-Crown-6	0.16 M 18-Crown-6	0.16 M 18-Crown-6	0.026 M 18-Crown-6
0.0033 0.0036 0.0033 0.0032 0.0035	0.0033 0.0032 0.0032	0.0043 0.0047 0.0051 0.0040 0.0040	0.0030 0.0040
Average			
0.0034 ±0.0001	0.0032 ±0.00004	0.0045 ±0.0003	0.0035 ±0.0005

From the average slopes, the racemization of the mononitro compound (51a) is 1.4 times faster in the presence of KF in 0.16 M 18-crown-6 in acetonitrile than the thermal racemization observed in 0.16 M 18-crown-6.

Experimental Section

General.

Sealed tube reactions were degassed by the freeze pump thaw process as follows: A doughnut shaped manifold with ten stopcocks, each connected to a TS 10/30 outer joint was connected to a vacuum pump, an open end manometer, a closed end manometer and an oxygen free source of nitrogen (ultra pure, Union Carbide-Linde Division, Danbury, CT 06817) with a drying tube and an oxygen scrubber. The reaction solutions were transferred to 3X10 cm heavy wall tubes, each with a TS 10/30 inner joint which attached to the outer joints of the manifold. The samples were frozen in a liquid nitrogen or dry ice/acetone bath, and the system was evacuated for 10-15 min after a minimum pressure was obtained. The stopcocks to the vacuum pump were closed, and the samples are allowed to melt and warm to room temperature. Mild boiling was seen during the thawing process. After the thawing was complete, the samples were frozen again and the vacuum was reapplied (by opening the stopcocks). After pumping for a few minutes, oxygen free nitrogen was introduced until a pressure equivalent to atmospheric pressure was obtained in the system. Vacuum was applied again for 10-15 min to evacuate the system, the stopcocks to the samples were closed and the thawing process was repeated. Generally 3 freeze pump thaw cycles were performed. Finally the system was frozen and evacuated again, nitrogen was introduced to a pressure of 100 torr and the tubes were sealed while the samples were frozen. The sealed tubes were heated in a thermo-regulated Haake NBS constant temperature circulator filled with silicone oil (Dow Corning, 210 H fluid).

Column chromatography was performed using silica gel (Davisil 60, Aldrich Chemical Company, Milwaukee, WI 53233) as the adsorbent. Preparative TLC was performed on 2000 μ silica gel plates (Analtech, Newark, Delaware 19711). Phenylazotriphenylmethane (PAT) (Custom Chemical Labs Inc., 2127 Research Drive #10, Livermore CA 94550) was purified by column chromatography using a 4 : 1 mixture of hexanes-benzene as the eluting solvent to give a yellow solid (mp 107°-108°C, decomp., lit.[75b] 107°-108° C). PAT was stored in an amber bottle to avoid decomposition. Diphenylmercury (Alfa Products, Danvers, MA 01923), benzoyl peroxide (Aldrich Chemical Company, Milwuakee WI 53233), dibenzylmercury (Alfa Products, Danvers, MA 01923), thiophenol (Aldrich Chemical Company, Milwuakee, WI 53233) and dicyclohexylphosphine (Aldrich Chemical Company,Milwuakee,WI 53233) were used without further purification. Bromobenzene (Aldrich, Chemical Company, Milwaukee,WI 53233) was purified by extracting 4X with conc. sulfuric acid followed by water until the washings were neutral to litmus. The bromobenzene was dried over anhyd. $MgSO_4$, filtered and distilled under reduced pressure. Acetonitrile was distilled over calcium hydride followed by another distillation over phosphorus pentoxide. Reagent grade nitrobenzene was fractionally distilled under reduced pressure discarding the first 20% of the distillate. KF (Alfa products, Danvers, MA 01923) was dried in a vacuum oven at 180° C for 3-4 h at 2 torr and stored in a desiccator. An ethereal solution of diazomethane was generated from DIAZALD™ (*N*-methyl-*N*-nitroso-*p*-tolunesulfonamide, Aldrich Chemical Company, Milwuakee,WI 53233) by the method described in Aldrich Technical Bulletin No. AL-113.

Melting points were measured on a Thomas Hoover Unimelt apparatus (mp < 300°) or Mel-Temp apparatus (mp > 300°) and are uncorrected. Optical rotations were measured on a Perkin-Elmer 141 polarimeter in a 1 decimeter microcell with a water jacket. The cell temperature was maintained at 25±0.1° C by a Forma-Scientific circulating bath. Infrared spectra were recorded on a Perkin-Elmer 247 grating spectrophotometer. NMR spectra were recorded on Varian EM-360, Bruker NR/200 or Bruker NR/300 spectrophotometers. Mass spectra were taken at the Rockefellar University, 1230 York Avenue, New York, NY 10021.

1. Purification of (±)2,2'-Dicyano-9,9'-bianthryl.

Crude 2,2'-dicyano-9,9'-bianthryl (prepared by Dr. Chen Shek Yu)[106] which contained 2,2'-dichloro-9,9'-bianthryl and 2-chloro-2'-cyano-9,9'-bianthryl was purified by column chromatography. Ten grams of the crude sample was dissolved in 75 mL of hot $CHCl_3$ and filtered. The solution was cooled to room temperature and chromatographed on a column containing ~500 g of silica gel packed as a slurry in 1:1 benzene-chloroform. The column was eluted by the same solvent mixture. The progress of the chromatography was monitored by analytical TLC (silica gel, 1:1 benzene-chloroform). The first two bands eluted, which showed green fluorescence under UV light on a TLC plate were 2,2'-dichloro-9,9'-bianthryl and 2-chloro-2'-cyano-9,9'-bianthryl, respectively. The third band (R_f 0.45), which appeared blue under UV light, was 2,2'-dicyano-9,9'-bianthryl. The fractions containing the dicyano compound were combined and the solvent was evaporated to obtain 5.16 g of the yellow solid: mp 346°-349°C (lit. 342°-344°C).[38a]

2. Hydrolysis of (±)2,2'-Dicyano-9,9'-bianthryl.

In a 1-L round bottom flask equipped with a reflux condenser and a magnetic stirrer were placed 5.16 g (0.0128 mol) of 2,2'-dicyano-9,9'-bianthryl, 75 g of NaOH, 200 mL of water and 600 mL of ethanol. The reaction mixture was refluxed (silicone-oil bath) with rigorous stirring for 20 h. The reaction mixture was cooled in an ice bath and acidified with conc. HCl to precipitate (±)-2,2'-dicarboxy-9,9'-bianthryl. The yellow solid was extracted in 2 : 1 THFdiethylether. The organic layer was washed 3X with water, followed by saturated NaCl and dried over anhyd. $MgSO_4$. The solution was filtered by suction and the solvent evaporated to yield 5.55 g (98%) of the diacid: mp 419°-421°C (lit[38a] 417°-420°C); IR (KBr) 3600-2400 (s, COOH), 1680 (s, COOH).

3. Preparation of Quinidine Hydrate from Quinidine Sulfate.

Quinidine sulfate (20 g, 0.048 mol, Aldrich Chemical Co., Milwuakee, WI 53233) was stirred using a magnetic stirrer with 200 mL of NH_4OH and 200 mL of water for 20 min. The resulting suspension was transferred into a separatory funnel and extracted with $CHCl_3$. The $CHCl_3$ layer was washed 3X with water, dried over anhyd. $MgSO_4$, filtered and evaporated to give 17.8 g of quinidine hydrate.

4. Resolution of (±)-2,2'-Dicarboxy-9,9'-bianthryl.

A suspension of 5.5 g (0.0125 mol) of (±) 2,2'-dicarboxy-9,9'-bianthryl in 400 mL of acetone was placed in a 500 mL liquid-liquid continuous extraction assembly. The side arm of the extraction assembly was connected to a 1-L round bottom flask containing 2 eq of quinidine hydrate (9.27 g, 0.025 mol) in 800 mL of acetone and a magnetic stirrer. The flask was heated to reflux (heating mantle) with stirring for 20 h until all the acid has been extracted into the flask (no yellow color or blue fluorescence was observed in the extraction assembly). The flask was cooled to room temperature and the mixture was allowed to crystalize slowly to give yellow crystals.

The yellow crystals were isolated by suction filtration, washed with acetone and air dried to yield 4.87 g of a dextrorotatory quinidine salt; mp 235°-236°C; $[\alpha]_D$=+48.1°(*c* 0.3; $CHCl_3$).

The mother liquor was concentrated to 300 mL and on cooling no crystals were formed. The mother liquor was evaporated to dryness (rotary evaporator) to yield a yellow solid. The solid was dissolved in 10% NaOH and extracted with $CHCl_3$ (3X) to remove the quinidine hydrate. The NaOH layer was cooled to 0 °C and acidified with conc. HCl to precipitate (+) 2,2'-dicarboxy-9,9'-bianthryl. The yellow solid was extracted into THF-ether (2:1). The organic layer was washed with water (3X) followed by sat. NaCl and dried over anhyd. $MgSO_4$. The solution was filtered by suction and the solvent was evaporated to yield 2.42 g of (+) 2,2'-dicarboxy-9,9'-bianthryl; $[\alpha]_D$=+62.5°(*c* 0.3, acetone).

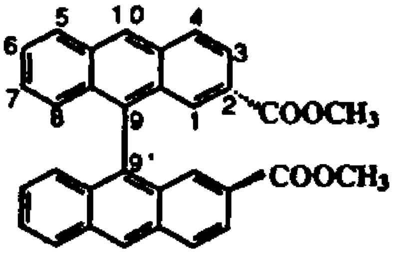
The dextrorotatory salt was hydrolysed similarly to yield 2.3 g of (-) 2,2'-dicarboxy-9,9'-bianthryl; $[\alpha]_D$= -100.3°(*c* 0.3, acetone).

5. Preparation of Diazomethane. Esterification of 2,2'-Dicarboxy-9,9'-bianthryl.

Ethanol (25 mL) was added to a solution of 5 g of KOH in 8 mL of water in a 100 mL distilling flask fitted with a dropping funnel. The condenser was connected to two receiving flasks in series, the second flask containing 20 mL of anhyd. ether. Both receivers were cooled to 0 °C in an ice bath. The distilling flask was heated in an oil bath to 65 °C and a solution of 21.5 g of Diazald™(*N*-methyl-*N*-nitroso-*p*-tolunesulfonamide; Aldrich Chemical Company, Milwaukee, WI 53233) in 200 mL of anhyd. ether was added through the dropping funnel. The rate of addition was approximately equal to the rate of distillation. When the addition was complete, another 50 mL of ether was slowly added till the distillate was colorless.

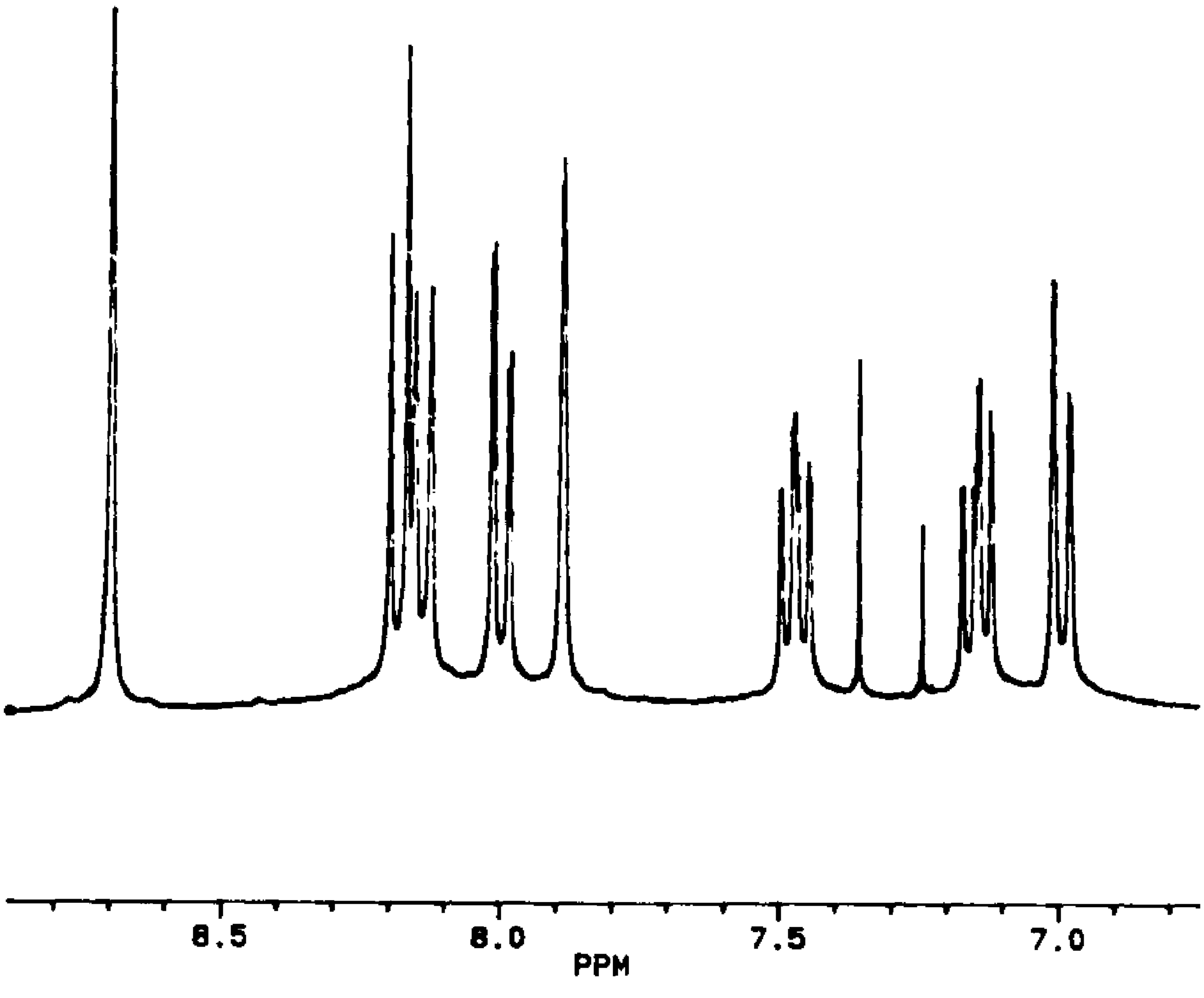
A solution of 2.3 g of (-) 2,2'-dicarboxy-9,9'-bianthryl (5.2 mmol); $[\alpha]_D$=-100.3° (c 0.3, acetone); in THF-ether (2:1) was cooled to 0 °C in a round bottom flask containing a magnetic stirrer and the ethereal solution of diazomethane was added dropwise with stirring until bubbles no longer appeared. The solution had a greenish-yellow color due to a slight excess of CH_2N_2. The excess CH_2N_2 was destroyed with ~1ml of acetic acid. The ether was evaporated, and the crude ester was purified by column chromatography on 50 g of silica gel. The column was eluted with $CHCl_3$. A yellow band was collected, while a red band remained at the origin. The solution was evaporated to yield 2.38 g (97.3%) of (-) 2,2'-dicarbomethoxy-9,9'-bianthryl (**1**); mp 232°-233 °C, $[\alpha]_D$= -120.4°, $[\alpha]_{546}$ = 172.4° (*c* 0.3, $CHCl_3$).

The peaks in the ^1H NMR spectrum of bianthryl **1** was assigned from Homo-nuclear decoupling experiments and a ^1H-^1H COSY spectrum. The ^1H spectrum of bianthryl **1** (aromatic region) is shown in Figure 23. Proton H10 (δ 8.68, s) is easily identified on the basis of its low-field chemical shift due to edge-deshielding. Trivial assignments can be made based on spectral splitting patterns: H3, H4, H5, and H8 are expected to be doublets, whereas H6 and H7 are expected to be triplets (doublet of doublets) and H1 should be a singlet.



1

Figure 23. ^{1}H NMR Spectrum (Aromatic Region) of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1)



Homo-nuclear Decoupling.

(i) Irradiating the doublet at δ 8.15 (H4), resulted in the doublet at δ 7.97 (H3) to collapse to a singlet.

(ii) Irradiating the doublet at δ 8.11 (H5 or H8), resulted in collapse of the triplet at δ 7.45 (H6 or H7) to a doublet.

(iii) Irradiating the doublet at δ 7.97 (H3), resulted in the doublet at δ 8.15 (H4) to collapse to a singlet.

(iv) Irradiating the triplet at δ 7.45 (H6 or H7), resulted in the doublet at δ 8.11 (H5 or H8) to collapse to a singlet and the triplet at δ 7.12 (H6 or H7) to a doublet.

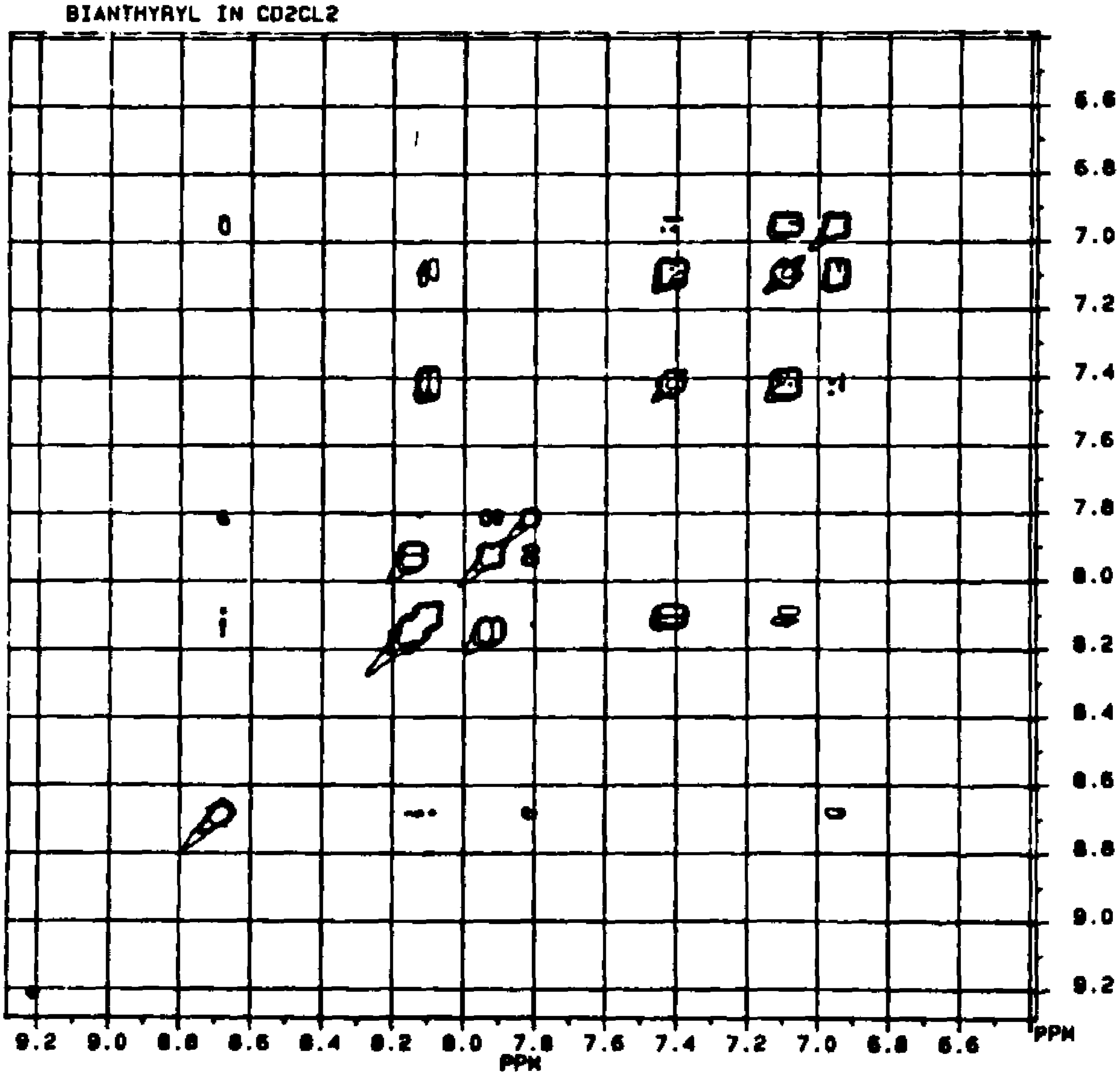
(v) Irradiating the triplet at δ 7.12 (H6 or H7), resulted in the triplet at δ 7.45 (H6 or H7) to collapse to a doublet and the doublet at δ 6.98 (H5 orH8) to a singlet.

(vi) Irradiating the doublet at δ 6.98 (H5 or H8), resulted in the triplet at δ 7.13 (H6 or H7) to collapse to a doublet.

H5 is expected to be less shielded than H8 and therefore the doublet at δ 8.11 is assigned to H5 and the doublet at δ 6.98 to H8. Correspondingly, the triplet at δ 7.45 is assigned to H6 and the triplet at δ 7.12 is assigned to H7

Based on the homo-nuclear decoupling results, all the aromatic protons of bianthryl (1) were assigned. These assignments were confirmed from the ^1H-^1H COSY spectrum (Figure 24).

Figure 24. ^1H-^1H COSY Spectrum of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1). Aromatic Region.



The assignments of the hydrogen-bearing carbons was made from heteronuclear COSY spectrum (Figure 25).

Figure 25. Heteronuclear COSY Spectrum (Aromatic Region) of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1).

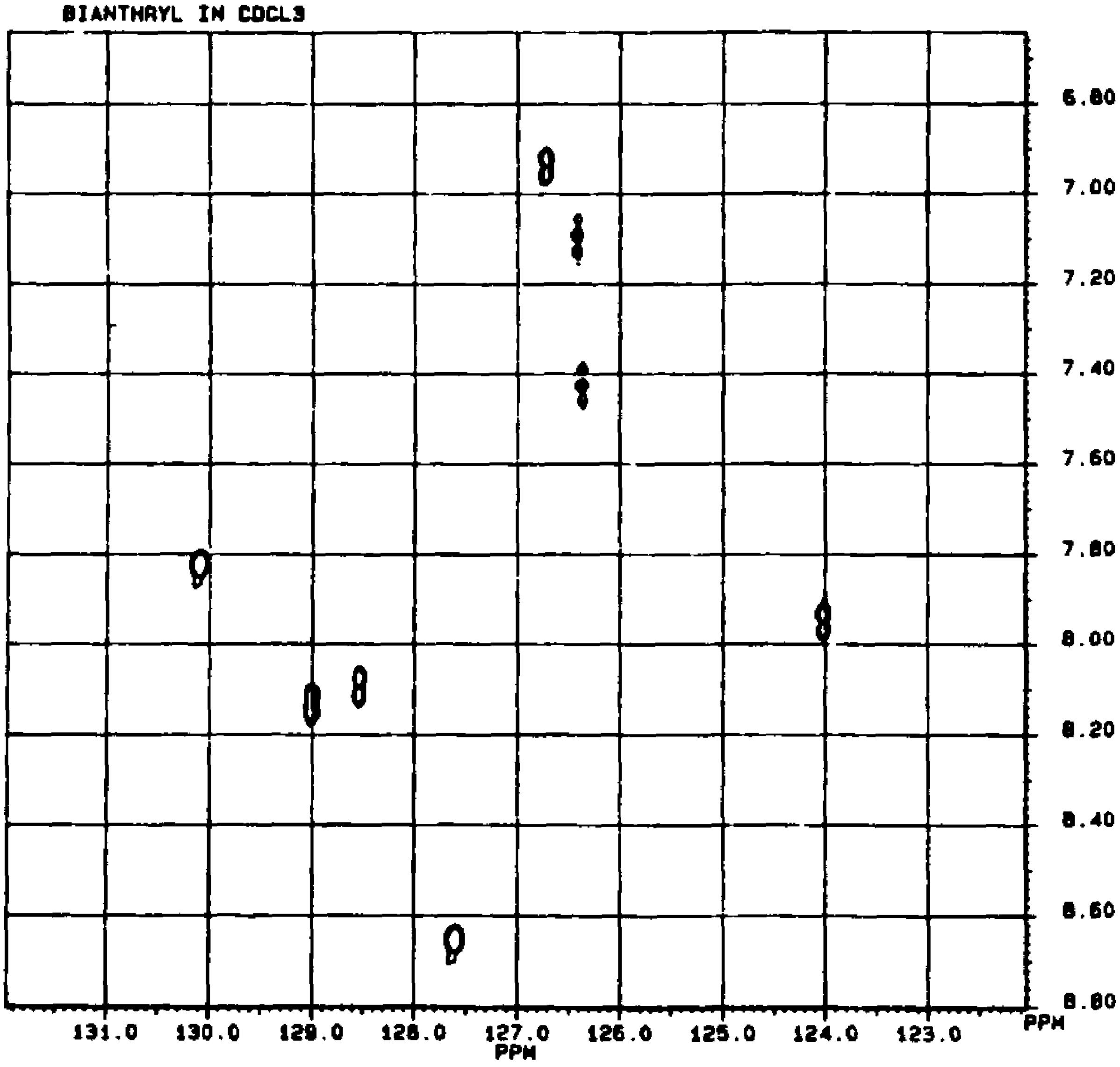


Figure 26. ^{13}C NMR Spectrum (Aromatic Region) of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1).

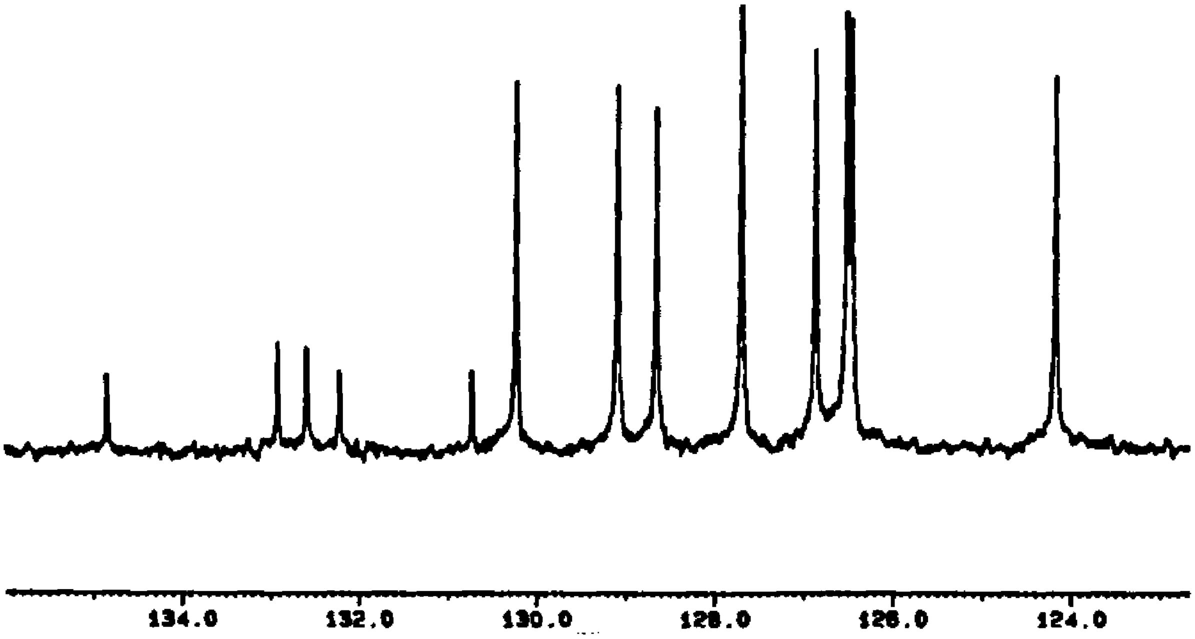


Table XXVIII summarizes the ^{1}H and ^{13}C NMR (300 MHz, $CDCl_3$) chemical shifts.

Table XXVIII. ^{1}H and ^{13}C NMR Chemical Shifts for 2,2'-Dicarbomethoxy-9,9'-bianthryl (1)

	δ ^{1}H	δ ^{13}C
C-1	7.885 (s)	130.214
C-3	7.960, 7.990 (d)	124.138
C-4	8.170, 8.140 (d)	129.094
C-5	8.130, 8.100 (d)	128.643
C-6	7.470, 7.450, 7.420 (t)	126.460
C-7	7.150, 7.120, 7.100 (d of d)	126.507
C-8	6.998, 6.968 (d)	126.842
C-10	8.675 (s)	127.697
CH_3	3.665 (s)	51.858
C=O		166.880

6. Racemization of Optically Active 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the Presence of Phenylazotriphenylmethane (PAT) at 50°±0.1°C in Bromobenzene.

Reaction solutions were prepared volumetrically from stock solutions of optically active bianthryl **1** and PAT in bromobenzene (unless otherwise noted). To measure an appreciable observed rotation of the bianthryl **1**, the concentration required was approximately 0.3 g/100 mL (0.0064 M). A bianthryl **1** stock solution was prepared in bromobenzene with 2X the concentration needed, i.e., 0.6 g/100 mL (0.0128 M). In reactions where the [bianthryl **1**] is a constant, the [bianthryl **1**] in the reaction solution was 0.0064 M. A PAT stock solution corresponding to 10 equivalents of PAT per equivalent of bianthryl in solution was prepared by dissolving 1.1095 g of PAT in 25 mL of bromobenzene (0.128 M). To prepare solutions of different ratios of bianthryl **1** : PAT, the stock solutions were mixed corresponding to the ratios desired. For example, to prepare 10 mL of bianthryl **1** : PAT = 1:10 reaction solution, 5 mL of 0.0128 M bianthryl **1** stock solution was added to 5 mL of 0.128 M PAT stock solution in a 10 mL volumetric flask. To prepare 10 mL bianthryl **1** : PAT = 1:5 reaction solution, 5 mL of bianthryl **1** stock solution was added to 2.5 mL of PAT stock solution and bromobenzene was added to make up the volume to 10 mL.

(i) Bianthryl 1 : PAT = 1 : 15

In a 10 mL volumetric flask, 5 mL of 0.0128 M (+)-bianthryl 1 stock solution (0.030 g, 0.064 mmol) was added to 15 eq of PAT (0.3328 g, 0.957 mmol) and diluted to 10 mL with bromobenzene. The initial rotation of the reaction solution was determined and 1 mL samples were transferred to each of the 10 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (100 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 50°±0.1°C. To duplicate results, pairs of tubes were removed periodically and the optical rotation of the solutions were determined. The results are summarized in Tables XXIX A.

The reaction was repeated and the results for run 2 are summarized in Table XXIX B.

Table XXIX A. Percent Racemization for the Reaction of Bianthryl 1 : PAT=1 : 15 in Bromobenzene at 50°C (Run 1).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	+0.448°			+0.622°		
0.25	+0.429°	4.3%	0.0188	+0.595°	4.3%	0.0192
	+0.429°	4.3%	0.0188	+0.595°	4.3%	0.0192
0.50	+0.417°	6.9%	0.0311	+0.579°	6.9%	0.0311
	+0.417°	6.9%	0.0311	+0.579°	6.9%	0.0311
1.00	+0.402°	10.3%	0.0481	+0.558°	10.3%	0.0472
	+0.402°	10.3%	0.0481	+0.558°	10.3%	0.0472
2.00	+0.381°	14.9%	0.0704	+0.529°	14.9%	0.0704
	+0.381°	14.9%	0.0704	+0.529°	14.9%	0.0704
3.00	+0.371°	17.2%	0.0820	+0.515°	17.2%	0.0820
	+0.371°	17.2%	0.0820	+0.515°	17.2%	0.0820

Table XXIX B. Percent Racemization for the Reaction of Bianthryl 1 : PAT=1 : 15 in Bromobenzene at 50°C (Run 2).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	+0.448°			+0.622°		
0.25	+0.428°	4.5%	0.020	+0.594°	4.5%	0.020
	+0.428°	4.5%	0.020	+0.594°	4.5%	0.020
0.50	+0.417°	6.9%	0.0311	+0.579°	6.9%	0.0311
	+0.417°	6.9%	0.0311	+0.579°	6.9%	0.0311

(ii) Bianthryl 1 : PAT=1 : 10

In a 10 mL volumetric flask, 5 mL of 0.0128 M bianthryl 1 stock solution (0.030 g, 0.064 mmol) was added to 5 mL of 0.128 M PAT stock solution (0.223 g, 0.640 mmol). The initial rotation of the reaction solution was determined, and 1 mL samples were transferred to each of the 10 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (100 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 50° ± 0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table XXX A.

The reaction was repeated and the results for run 2 are summarized in Table XXX B.

Table XXX A. Percent Racemization for the Reaction of Bianthryl 1 : PAT = 1 : 10 in Bromobenzene at 50°C (Run 1).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	+0.459°			+0.644°		
0.50	+0.434°	5.4%	0.0240	+0.608°	5.6%	0.0250
	+0.433°	5.7%	0.0250	+0.607°	5.7%	0.0257
1.00	+0.420°	8.5%	0.0386	+0.589°	8.5%	0.0388
	+0.420°	8.5%	0.0386	+0.589°	8.5%	0.0388
2.00	+0.398°	13.3%	0.0619	+0.558°	13.4%	0.0622
	+0.399°	13.1%	0.0608	+0.559°	13.2%	0.0615
4.00	+0.379°	17.4%	0.0832	+0.532°	17.4%	0.0830
	+0.379°	17.4%	0.0832	+0.532°	17.4%	0.0830
5.00	+0.378°	17.6%	0.0843	+0.531°	17.5%	0.0838
	+0.379°	17.4%	0.0832	+0.532°	17.4%	0.0830

Table XXX B. Percent Racemization for the Reaction of Bianthryl 1 : PAT = 1 : 10 in Bromobenzene at 50°C (Run 2).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	+0.448°			+0.622°		
0.25	+0.433°	3.4%	0.0148	+0.601°	3.4%	0.0149
	+0.433°	3.4%	0.0148	+0.601°	3.4%	0.0149
0.50	+0.424°	5.4%	0.0240	+0.588°	5.5%	0.0244
	+0.424°	5.4%	0.0240	+0.588°	5.5%	0.0244

(iii) Bianthryl 1 : PAT = 1 : 7.5

In a 10 mL volumetric flask, 5 mL of 0.0128 M bianthryl 1 stock solution (0.030 g, 0.064 mmol) was added to 3.75 mL of 0.128 M PAT stock solution (0.167 g, 0.480 mmol). Bromobenzene was added to make up the volume to 10 mL. The initial rotation of the reaction solution was determined, and 1 mL samples were transferred to each of the 10 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum. The tubes were placed in a Haake constant temperature bath pre-heated to 50°±0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table XXXI A.

The reaction was repeated and the results for run 2 are summarized in Table XXXI B.

Table XXXI A. Percent Racemization for the Reaction of Bianthryl 1 : PAT = 1 : 7.5 in Bromobenzene at 50°C (Run 1).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	+0.448°			+0.622		
0.25	+0.438°	2.2%	0.0098	+0.607°	2.4%	0.0106
	+0.438°	2.2%	0.0098	+0.607°	2.4%	0.0106
0.50	+0.430°	4.0%	0.0178	+0.597°	4.0%	0.0178
	+0.430°	4.0%	0.0178	+0.597°	4.0%	0.0178
1.00	+0.418°	6.7%	0.0301	+0.581°	6.6%	0.0296
	+0.418°	6.7%	0.0301	+0.581°	6.6%	0.0296
2.00	+0.404°	10.0%	0.0460	+0.559°	10.1%	0.0464
	+0.403°	10.0%	0.0460	+0.559°	10.1%	0.0464
3.00	+0.395°	11.8%	0.0550	+0.548°	11.9%	0.0550
	+0.395°	11.8%	0.0550	+0.548%	11.9%	0.0550

Table XXXI B. Percent Racemization for the Reaction of Bianthryl 1 : PAT = 1 : 7.5 in Bromobenzene at 50°C (Run 2).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	+0.448°			+0.622°		
0.25	+0.437°	2.5%	0.0108	+0.606°	2.6%	0.011
	+0.437°	2.5%	0.0108	+0.606°	2.6%	0.011
0.50	+0.430°	4.0%	0.0178	+0.597°	4.0%	0.0178
	+0.430°	4.0%	0.0178	+0.597°	4.0%	0.0178

(iv) Bianthryl 1 : PAT = 1 : 5

In a 10 mL volumetric flask, 5 mL of 0.0128 M bianthryl 1 stock solution (0.030 g, 0.064 mmol) was added to 2.5 mL of 0.128 M PAT stock solution (0.1114 g, 0.320 mmol). Bromobenzene was added to make up the volume to 10 mL. The initial rotation of the reaction solution was determined, and 1 mL samples were transferred to each of the 10 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (100 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 50°±0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table XXXII A.

The reaction was repeated and the results for run 2 are summarized in Table XXXII B.

Table XXXII A. Percent Racemization for the Reaction of Bianthryl 1 : PAT = 1 : 5 in Bromobenzene at 50°C (Run 1).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	+0.448°			+0.620°		
0.50	+0.435°	2.9%	0.0128	+0.602°	2.9%	0.0128
	+0.435°	3.1%	0.0135	+0.601°	3.1%	0.0135
1.00	+0.424°	5.4%	0.0240	+0.587°	5.3%	0.0240
	0.424°	5.4%	0.0240	+0.587°	5.3%	0.0240
2.00	+0.410°	8.5%	0.0385	+0.568°	8.4%	0.0380
	+0.411°	8.3%	0.0374	+0.568°	8.4%	0.0380
3.00	+0.405°	9.6%	0.0440	+0.560°	9.6%	0.0440
	+0.405°	9.6%	0.0440	+0.560°	9.6%	0.0440
5.00	+0.405°	9.6%	0.0440	+0.560°	9.6%	0.0440
	+0.405°	9.6%	0.0440	+0.560°	9.6%	0.0440

Table XXXII B. Percent Racemization for the Reaction of Bianthryl 1 : PAT = 1 : 5 in Bromobenzene at 50°C (Run 2).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	+0.448°			+0.622°		
0.25	+0.441°	1.6%	0.007	+0.612°	1.6%	0.007
	+0.441°	1.6%	0.007	+0.612°	1.6%	0.007
0.50	+0.435°	2.9%	0.0128	+0.604°	2.9%	0.0128
	+0.435°	2.9%	0.0128	+0.604°	2.9%	0.0128

(v) Bianthryl 1 : PAT = 2 : 10

Ten mL of 0.0128 M bianthryl 1 stock solution (0.060 g, 0.128 mmol) was added to 0.223 g, (0.640 mmol) of PAT. The initial rotation of the reaction solution was determined, and ~1 mL samples were transferred to each of the 8 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (100 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 50°±0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table XXXIII A.

The reaction was repeated and the results for run 2 are summarized in Table XXXIII B.

Table XXXIII A. Percent Racemization for the Reaction of Bianthryl 1 : PAT = 2 : 10 in Bromobenzene at 50°C (Run 1).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	+0.881°			+1.232°		
0.25	+0.856° +0.856°	2.8% 2.8%	0.0125 0.0125	+1.197° +1.197°	2.8% 2.8%	0.0125 0.0125
0.50	+0.843° +0.843°	4.3% 4.3%	0.0190 0.0190	+1.179° +1.179°	4.3% 4.3%	0.0190 0.0190
0.75	+0.830° +0.830°	5.8% 5.8%	0.0260 0.0260	+1.161° +1.160°	5.8% 5.8%	0.0260 0.0262
1.00	+0.820° +0.820°	6.9% 6.9%	0.0310 0.0310	+1.147° +1.147°	6.9% 6.9%	0.0310 0.0310

Table XXXIII B. Percent Racemization for the Reaction of Bianthryl 1 : PAT = 2 : 10 in Bromobenzene at 50°C (Run 2).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	+0.880°			+1.231°		
0.25	+0.853°	3.1%	0.0135	+1.192°	3.2%	0.0140
	0.853°	3.1%	0.0135	1.192°	3.2%	0.0140
0.50	+0.842°	4.3%	0.0192	+1.178°	4.3%	0.0191
	0.842°	4.3%	0.0192	1.178°	4.3%	0.0191

(vi) Bianthryl 1 : PAT = 1.5 : 10.

In a 10 mL volumetric flask, 7.5 mL of 0.0128 M bianthryl 1 stock solution (0.045 g, 0.096 mmol) was added to 0.223 g (0.640 mmol) of PAT and diluted with bromobenzene to 10 mL. The initial rotation of the reaction solution was determined, and ~1 mL samples were transferred to each of the 8 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (100 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 50°±0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table XXXIV A.

The reaction was repeated and the results for run 2 are summarized in Table XXXIV B.

Table XXXIV A. Percent Racemization for the Reaction of Bianthryl 1 : PAT = 1.5 : 10 in Bromobenzene at 50°C (Run 1).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	+0.682°			+0.951°		
0.25	+0.662°	2.9%	0.0129	+0.923°	2.9%	0.0130
	+0.662°	2.9%	0.0129	+0.923°	2.9%	0.0130
0.50	+0.648°	4.9%	0.0220	+0.904°	4.9%	0.0220
	+0.648°	4.9%	0.0220	+0.904°	4.9%	0.0220
0.75	+0.636°	6.7%	0.0303	+0.887°	6.7%	0.0303
	+0.636°	6.7%	0.0303	+0.887°	6.7%	0.0303
1.00	+0.628°	7.9%	0.0360	+0.876°	7.9%	0.0360
	+0.628°	7.9%	0.0360	+0.876°	7.9%	0.0360

Table XXXIV B. Percent Racemization for the Reaction of Bianthryl 1 : PAT = 1.5 : 10 in Bromobenzene at 50°C (Run 2).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	+0.680°			+0.951°		
0.25	+0.659°	3.1%	0.0136	+0.923°	2.9%	0.0130
	0.659°	3.1%	0.0136	0.923°	2.9%	0.0130
0.50	+0.647°	4.9%	0.0216	+0.904°	4.9%	0.0220
	0.647°	4.9%	0.0216	+0.904°	4.9%	0.0220

7. Effect of Phenylthiol on the Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the Presence of PAT in Bromobenzene at 50° ± 0.1°C.

The reaction mixture containing the molar ratio of bianthryl **1** : PAT : PhSH = 1 : 10 : 20 was prepared as follows. Five mL of 0.0128 M bianthryl **1** stock solution (0.030 g, 0.064 mmol) and 5 mL of 0.128 M PAT stock solution (0.223 g, 0.640 mmol) were added to 0.1405 g (1.280 mmol) of PhSH. The initial rotation of the reaction solution was determined, and ~2 mL samples of the above solution transferred to each of four racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (100 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 50°±0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table XXXV.

Table XXXV. Percent Racemization for the Reaction of Bianthryl 1 : PAT : PhSH = 1 : 10 : 20 in Bromobenzene at 50°C.

Time	λ/589 nm		λ/546 nm	
(h)	α_{589}	% Rac	α_{546}	% Rac
0	+0.435°		+0.610°	
1.0	+0.435°	0	+0.610°	0
2.0	+0.435°	0	+0.610°	0
4.0	+0.435°	0	+0.610°	0
6.0	+0.435°	0	+0.610°	0

8. Effect of Dicyclohexylphosphine (DCHP) on the Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the Presence of PAT in Bromobenzene at 50°±0.1°C.

A reaction mixture containing the molar ratio of bianthryl **1** : PAT : DCHP = 1 : 10 : 20 was prepared as follows. Five mL of 0.0128

M bianthryl 1 stock solution (0.030 g, 0.064 mmol) and 5 mL of 0.128 M PAT stock solution (0.223 g, 0.640 mmol) were added to 0.2529 g (1.280 mmol) of dicyclohexylphosphine under a nitrogen atmosphere. The initial rotation of the reaction solution was determined, and ~2 mL samples of the above solution were transferred, under nitrogen using a syringe, to each of four racemization tubes with a side arm for a septum inlet. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (100 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 50°±0.1°C. To duplicate results, pairs of tubes were removed periodically and the optical rotations of the solutions were determined. The results are summarized in Table XXXVI.

Table XXXVI. Percent Racemization for the Reaction of Bianthryl 1 : PAT : DCHP = 1 : 10 : 20 in Bromobenzene at 50°C.

Time	λ/589 nm		λ/546 nm	
(h)	α_{589}	% Rac	α_{546}	% Rac
0	+0.354°		+0.496°	
1.0	+0.345°	2.5%	+0.484°	2.4%
5.0	+0.333°	5.9%	+0.466°	6.0%
20.0	+0.318°	10.2%	+0.444°	10.5%

9. Effect of Triphenylmethane on the Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the Presence of PAT in Bromobenzene at 50°±0.1°C.

A reaction mixture containing the molar ratio of bianthryl **1** : PAT : Ph_3CH = 1 : 10 : 10 was prepared as follows. Five mL of 0.0128 M bianthryl **1** stock solution (0.030 g, 0.064 mmol) and 5 mL of 0.128 M PAT stock solution (0.223 g, 0.640 mmol) were added to 0.1556 g (0.640 mmol) of Ph_3CH (Aldrich Chemical Company, Milwuakee, WI 53233). The initial rotation of the reaction solution was determined, and ~2 mL samples of the above solution were transferred to each of four racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (100 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 50°±0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table XXXVII.

Table XXXVII. Percent Racemization for the Reaction of Bianthryl 1 : PAT : Ph_3CH = 1 : 10 : 10 in Bromobenzene at 50°C.

Time	λ/589 nm		λ/546 nm	
(h)	α_{589}	% Rac	α_{546}	% Rac
0	+0.442°		+0.612°	
1.0	+0.409°	7.5%	+0.567°	7.4%
3.0	+0.399°	9.7%	+0.549°	10.3%
5.0	+0.383°	13.8%	+0.527°	13.9%
20.0	+0.379°	14.3%	+0.525°	16.7%

10. Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the Presence of Trityl Radical ($Ph_3C\cdot$) in Bromobenzene at 160° and 50°C.

The trityl radical has been generated by the reaction of tritylchloride (Ph_3CCl) and Hg^0 in bromobenzene at room temperature.[107a] A 70% yield was reported.

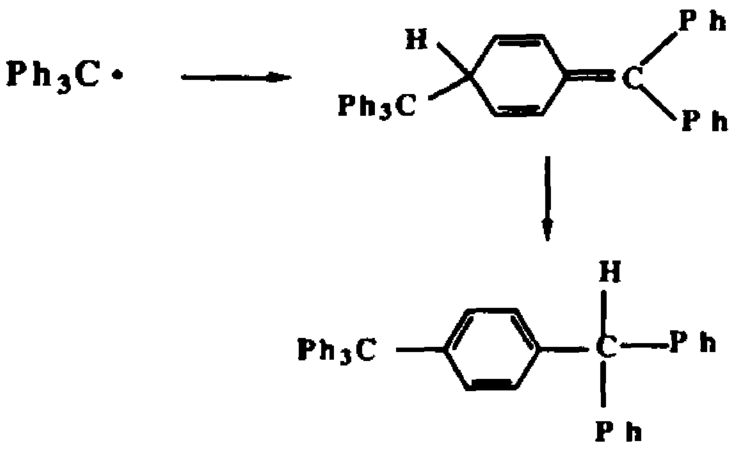
$$Ph_3C\text{-}Cl + Hg^0 \longrightarrow Ph_3C\cdot$$

Tritylchloride (Aldrich Chemical Company, Milwuakee, WI 53233) was purified by column chromatography on silica gel with chloroform as the eluting solvent. The trityl radical is very air sensitive and reacts rapidly with oxygen to form the peroxide. To avoid this reaction, all operations were carried out under a nitrogen atmosphere.

$$Ph_3C\bullet \xrightarrow{O_2} Ph_3C\text{-}O\text{-}O\text{-}CPh_3$$

A special reaction flask was designed for this experiment.
It consists of two round bottom flasks 'A' and 'B' connected to each other on the side by a coarse sintered glass frit. Flask 'A' has a TS 14/20 outer joint and a septum inlet. Flask 'B' has a septum inlet and a vacuum stopcock with a luer lock to connect a syringe needle. Tritylchloride (1.2664 g, 4.543 mmol) and 5 eq of Hg^0 (4.554 g, 0.0227 mol) were placed in flask 'A' with 15 mL of bromobenzene and a magnetic stirrer. This flask was then fitted with a 3-way vacuum stopcock connected to a nitrogen balloon and a vacuum pump. The system was evacuated with the vacuum pump and flushed with nitrogen from the balloon several times till both flasks were under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 24 h. The reaction flask was tilted to filter the radical solution through the frit into flask 'B'. Flask 'A' was then rinsed with 10 mL of bromobenzene (introduced by a syringe). Assuming a 70% yield,[107a] flask 'B' contained 3.20 mmol of trityl radical in 25 mL bromobenzene. Twenty-five mL of 0.0128 M bianthryl **1** stock solution (0.150 g, 0.320 mmol, $[\alpha]_{589} = -147.3°$) was syringed into flask 'B'. This solution represents a molar ratio of bianthryl **1** : $Ph_3C\bullet$ = 1 : 10.

Five racemization tubes with side arms for a septum inlet were evacuated on the manifold and flushed with nitrogen. The reaction mixture from flask 'B' was transferred into the tubes via the vacuum stopcock connected to a luer lock and a syringe needle. The volume in each tube was approximately 10±5 mL. The tubes were degassed by the freeze pump thaw process and sealed under a nitrogen pressure of ~200 torr. Four tubes were heated at 160° in a Haake constant temperature bath. Tubes were removed after 6 h and 25 h (2 tubes each aliquot). The other tube was heated at 50°±2°C in an oil bath for 25 h. Rotations of the reaction solutions could not be measured as they were dark yellow. Each aliquot was worked up to recover bianthryl **1** as follows. Bromobenzene was distilled (30°C, 1 torr) and the residue was purified by column chromatography (Silica gel/benzene). Three fractions were collected. Analytical TLC (silica gel, 1:1 chloroform-benzene) showed two spots for fraction 1 with R_f 0.88 and 0.74. Fractions 2 and 3 consisted of one spot with R_f's of 0.56 and 0.27, respectively. Fraction 1 was identified as the dimer[107b,c] of $Ph_3C\bullet$ (**53**): ^1H NMR ($CDCl_3$) δ 5.54 (s), δ 7.27-7.09 (m). Fraction 2 was recovered bianthryl **1**, and fraction 3 was not identified.



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Amounts recovered are summarized in Table XXXVIII. Percentage racemization of recovered bianthryl (fraction 2) is summarized in Table XXXIX.

Table XXXVIII. Recovery From The Reaction of Bianthryl 1 with $Ph_3C\cdot$ at 160° and 50° in Bromobenzene

		Fraction 1	Fraction 2	Fraction 3
160°	6 h	0.1353 g	0.0480 g	
	25 h	0.1974 g	0.0714 g	
50°	25 h	0.0922 g	0.0320 g	
Total recovery		0.4249 g (77%)	0.1514 g(100%)	0.0069 g

Table XXXIX. Percent Racemization of Bianthryl 1 in the Presence of $Ph_3C\cdot$ in Bromobenzene at 160° and 50°C.

Time	λ/589 nm		λ/546 nm	
(h)	$[\alpha]_{589}$	% Rac	$[\alpha]_{546}$	% Rac
160° 0.0	-147.3°		-211.8°	
6.0	-137.2°	6.9%	-196.9°	7.0%
25.0	-136.3°	7.5%	-195.7°	7.6%
50° 25.0	-145.7°	1.1%	-208.5°	1.6%

11. Recovery and Identification of Products From the Reaction of Bianthryl 1 : PAT = 1 : 10 in Bromobenzene at 50°C.

In a 25 mL volumetric flask, 12.5 mL of 0.0128 M bianthryl **1** stock solution (0.075 g, 0.159 mmol, $[\alpha]_D$=+130.3°) was added to 12.5 mL of 0.128 M PAT stock solution (0.5596 g, 1.60 mmol). The rotation of the reaction solution was determined (α_0=+0.459°). The solution was transferred to a large racemization tube, degassed by the freeze pump thaw process and sealed under a nitrogen pressure of 100 torr. The tube was heated at 50°±0.1°C in a Haake constant temperature bath for 25 h. The reaction solution was 17.5% racemized (α_D=+0.378°). Bromobenzene was distilled (35°, 1 torr), and the residue was purified by column chromatography (silica gel, 1:1 benzene-chloroform) to get two fractions. The one with a higher R_f value was biphenyl (0.4134 g, 84% yield), and the other with R_f 0.45 contained bianthryl **1** along with substitution products. The fraction containing bianthryl 1 was purified twice by preparative TLC (silica gel, benzene, 3 developments) to get 0.0212 g (28.8% recovery) of bianthryl **1** (NMR spectrum identical with a pure sample), $[\alpha]_D$=+102° (21.5% racemized), 0.0408 g (45.4% yield) of 2,2'-dicarbomethoxy-10-phenyl-9,9'-bianthryl (**38**), $[\alpha]_D$=+88.2° and 0.0117 g (11.8% yield) of 2,2'-dicarbomethoxy-10,10'-diphenyl-9,9'-bianthryl (**39**), $[\alpha]_D$=+67.9°.

2,2'-Dicarbomethoxy-10-phenyl-9,9'-bianthryl (**38**): High Resolution MS (EI$^+$), M$^+$ found : 546.18311, calculated for $C_{38}H_{26}O_4$:

546.18310. ^1H NMR (300 MHz, $CDCl_3$): δ 3.64 (OCH_3, s), δ 3.72 (OCH_3, s), δ 8.84 (H10', s), δ 8.22 (H4', d), δ 8.18 (H5', d), δ 8.01 (H3', d), δ 7.97 (H1', s), δ 7.88-7.84 (H1, H3, H4 overlapping s, d, d), δ 7.82 (H5, d) δ 7.70-7.60 (phenyl, m) δ 7.50 (H6', t), δ 7.36 (H6, t), δ 7.19 (H7', t), δ 7.12 (H7. t), δ 7.05 (H8', d), δ 7.00 (H8, d).

2,2'-Dicarbomethoxy-10,10'-diphenyl-9,9'-bianthryl (**39**): High Resolution MS (EI^+), M^+ found : 622.2144, calculated for $C_{44}H_{30}O_4$: 622.2144. ^1H NMR (300 MHz, $CDCl_3$): δ 3.71 (OCH_3, s), δ 8.01 (H1,s), δ 7.88-7.85 (H3, H4, overlapping m), δ 7.83 (H5, d), δ 7.72-7.60 (phenyl, m), δ 7.38 (H6, t), δ 7.17 (H7, t), δ 7.10 (H8, d).

Two methoxy peaks at δ 3.64 and 3.72 in the ^1H NMR spectrum of **38** indicates that the anthracene rings are not equivalent and is consistent with the mono-substituted product whereas only one methoxy peak δ 3.71 for **39** indicates that the two anthracene rings are symmetrically substituted.

Homo-nuclear decoupling experiment for 2,2'-dicarbomethoxy-10-phenyl-9,9'-bianthryl (38).

(i) Irradiation of the doublet at δ 8.22 (H4'), resulted in the collapse of the doublet at δ 8.01 (H3') to a singlet.

(ii) Irradiation of the doublet at δ 8.18 (H5'), resulted in the collapse of the triplet at δ 7.50 (H6') to a doublet.

(iii) Irradiation of the doublet at δ 8.01 (H3'), resulted in the collapse of the doublet at δ 8.22 (H4') to singlet.

(iv) Irradiation of the triplet at δ 7.50 (H6'), resulted in the collapse of the doublet at δ 8.18 (H5') to a singlet and the triplet at δ 7.19 (H7') to a doublet.

(v) Irradiation of the triplet at δ 7.19 (H7'), resulted in the collapse of the triplet at δ 7.50 (H6') to a doublet and the doublet at δ 7.05 (H8') to a singlet.

(vi) Irradiation of the doublet at δ 7.05 (H8'), resulted in the collapse of the triplet at δ 7.19 (H7') to a doublet.

(vii) Irradiation of the doublet at δ 7.82 (H5) resulted in the collapse of the triplet at δ 7.36 (H6) to a doublet.

(viii) Irradiation of the triplet at δ 7.36 (H6), resulted in the collapse of the doublet at δ 7.82 (H5) to a singlet and the triplet at δ 7.12 (H7) to a doublet.

(ix) Irradiation of the triplet at δ 7.12 (H7) resulted in the collapse of the triplet at δ 7.36 (H6) to a doublet and the doublet at δ 7.00 (H8) to a singlet.

(x) Irradiation of the multiplet at δ 7.70-7.60 (phenyl substituent) did not result in any change to the rest of the spectrum.

Homo-nuclear decoupling experiment for 2,2'-dicarbomethoxy-10,10'-diphenyl-9,9'-bianthryl (39).

(i) Irradiation of the doublet at δ 7.83 (H5), resulted in the collapse of the triplet at δ 7.38 (H6) to a doublet.

(ii) Irradiation of the triplet at δ 7.38 (H6), resulted in the collapse of the doublet at δ 7.83 (H5) to a singlet and the triplet at δ 7.17 (H7) to a doublet.

(iii) Irradiation of the triplet at δ 7.17 (H7), resulted in the collapse of the triplet at δ 7.38 (H6) to a doublet and the doublet at δ 7.10 (H8) to a singlet.

(iv) Irradiation of the doublet at δ 7.10 (H8), resulted in the collapse of the triplet at δ 7.17 (H7) to a doublet.

(v) Irradiation of the multiplet at δ 7.72-7.60 (phenyl substituent) did not result in any change to the rest of the spectrum.

(vi) Irradiation of the multiplet at δ 7.88-7.85 (H4, H3), resulted in the collapse of the doublet at δ 7.83 (H5) to a singlet.

Figures 27 and 28 show the aromatic region of the ^{1}H and ^{13}C NMR spectra of 2,2'-dicarbomethoxy-10-phenyl-9,9'-bianthryl (**38**) (top trace) and 2,2'-dicarbomethoxy-10,10'-diphenyl-9,9'-bianthryl (**39**) (bottom trace).

Figure 27. Aromatic Region of the ^{1}H NMR Spectra of 2,2'-Dicarbomethoxy-10-phenyl-9,9'-bianthryl (38) (top trace) and 2,2'-Dicarbomethoxy-10,10'-diphenyl-9,9'-bianthryl (39) (bottom trace).

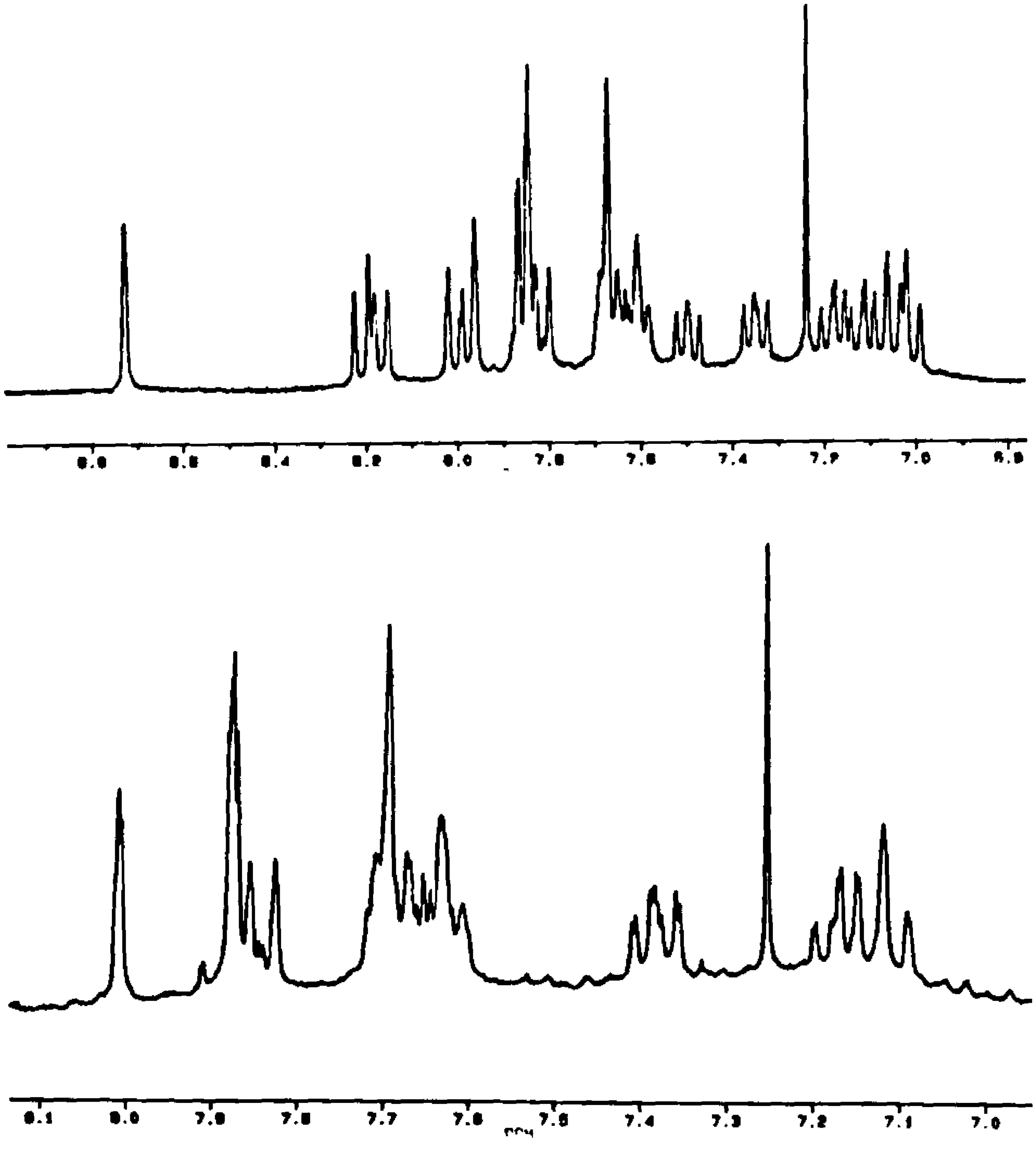
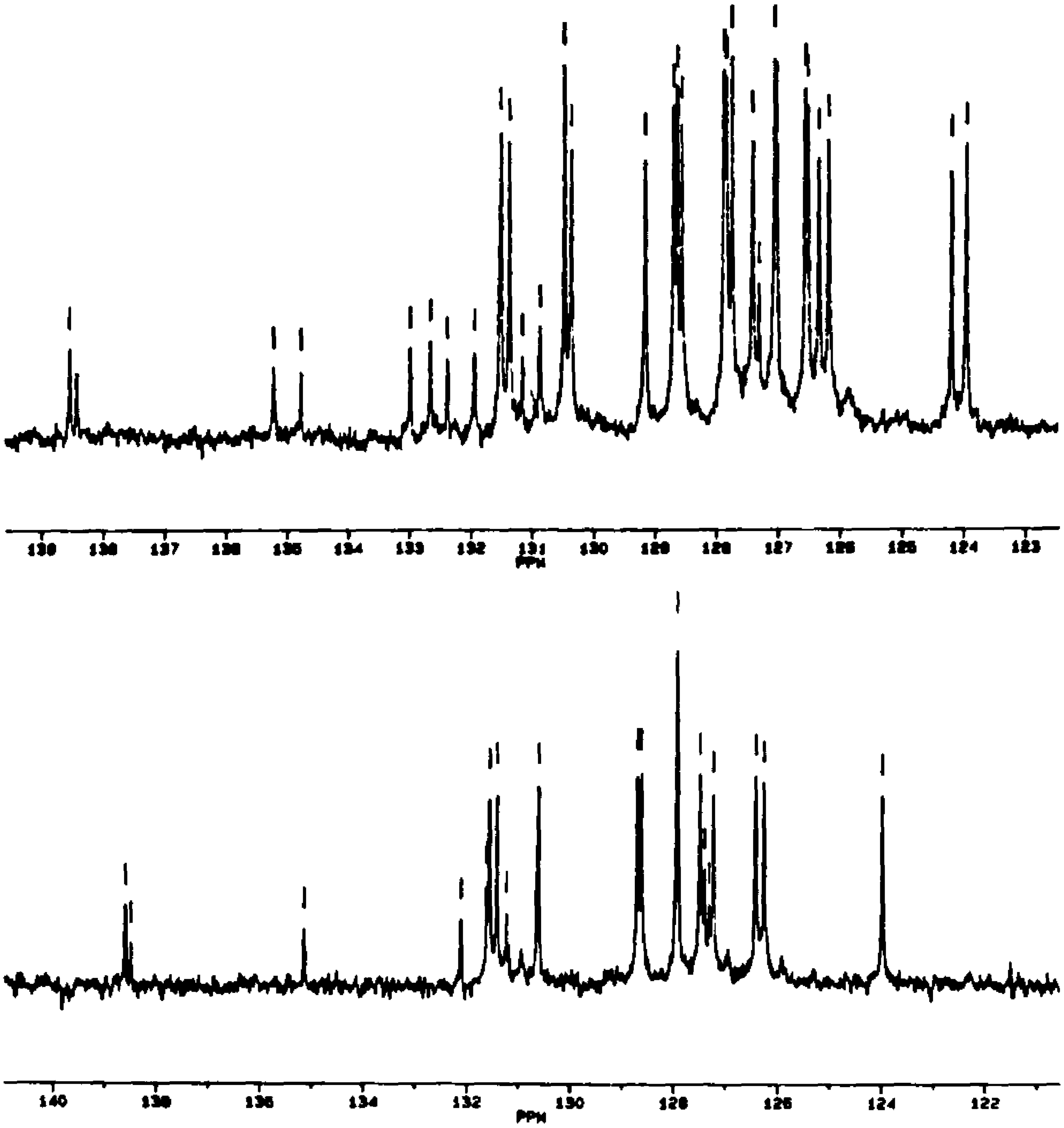


Figure 28. Aromatic Region of the ^{13}C NMR Spectra of 2,2'-Dicarbomethoxy-10-phenyl-9,9'-bianthryl (38) (top trace) and 2,2'-Dicarbomethoxy-10,10'-diphenyl-9,9'-bianthryl (39) (bottom trace).



12. Rate of Decomposition of PAT in bromobenzene at 50°C.

The decomposition of 0.0064 M phenylazotriphenylmethane (PAT) in bromobenzene at 50° was monitored via the absorbance of the azo-linkage (-N=N-) which has an absorbance maximum at 418 nm ($\varepsilon \sim 115$). A solution of PAT (0.0064 M) was prepared in a 50 mL volumetric flask by dissolving 0.11095 g (0.3133 mmol) of PAT in bromobenzene. Approximately 3.5 mL of the above solution was transferred to each racemization tube. The solution was degassed by the freeze pump thaw process and sealed under a nitrogen pressure of 100 torr. The tubes were heated in a Haake constant temperature bath at 50±0.1°C. The tubes were removed periodically and their absorbance was measured at 418 nm (HP 8452A UV-Vis spectrophotometer). Table XL summarizes the absorbance measured as a function of time.

Table XL. Absorbance as a Function of Reaction Time for the Decomposition of PAT in Bromobenzene at 50°C.

Reaction Time (h)	λ/418 nm	
	A	log A_0/A
0.00	0.7389	0.0000
0.50	0.6338	0.0666
0.75	0.5480	0.1298
1.00	0.5065	0.1640
1.25	0.4866	0.1814
1.50	0.4381	0.2269
1.75	0.4115	0.2542
2.00	0.3675	0.3034
2.50	0.2920	0.4032
3.00	0.2461	0.4775
3.50	0.2097	0.5471
4.00	0.1718	0.6334

13. Racemization of Optically Active 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the Presence of Benzoyl Peroxide at 80°±0.1°C in Bromobenzene

Reaction solutions were prepared volumetrically from stock solutions of optically active bianthryl **1** and benzoyl peroxide in bromobenzene. A bianthryl **1** stock solution (0.0128 M) was prepared in bromobenzene by dissolving 0.60 g (1.28 mmol) of bianthryl in 100 mL of solution. In reactions where the [bianthryl **1**] was a constant, the bianthryl **1** concentration in the reaction solution was 0.0064 M. A benzoyl peroxide stock solution, corresponding to 10 equivalents of benzoyl peroxide per equivalent of bianthryl in solution, was prepared by dissolving 0.7722 g (3.20 mmol) of $(PhCOO)_2$ in 25 mL of bromobenzene (0.128 M). To prepare solutions of different ratios of bianthryl **1** : $(PhCOO)_2$, the stock solutions were mixed corresponding to the ratios desired.

(i). Bianthryl 1 : $(PhCOO)_2$ = 1 : 10

In a 25 mL volumetric flask, 12.5 mL of 0.0128 M bianthryl **1** stock solution (0.075 g, 0.159 mmol) was added to 12.5 mL of 0.128 M $(PhCOO)_2$ stock solution (0.3876 g, 1.60 mmol). The initial rotation of the reaction solution was determined, and ~1.5 mL samples of the above solution were transferred to each of 15 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (100 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 80°±0.1°C. To duplicate results, pairs of tubes were removed periodically and the optical rotations of the solutions were determined. The results are summarized in Table XLI A. The reaction was duplicated and the results of run 2 are summarized in Table XLI B

Table XLI A. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCOO)_2$ = 1 : 10 in Bromobenzene at 80°C. (Run 1)

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	+0.459°			+0.641°		
1.0	+0.422°	8.1%	0.0365	+0.589°	8.1%	0.0367
	+0.422°	8.1%	0.0365	+0.589°	8.1%	0.0367
2.0	+0.396°	13.7%	0.0641	+0.552°	13.9%	0.0649
	+0.396°	13.7%	0.0641	+0.552°	13.9%	0.0649
3.0	+0.381°	17.0%	0.0809	+0.531°	17.2%	0.0818
	+0.380°	17.2%	0.0820	+0.531°	17.2%	0.0818
4.0	+0.367°	20.0%	0.0971	+0.508°	20.7%	0.1009
	+0.367°	20.0%	0.0971	+0.508°	20.7%	0.1009
5.0	+0.358°	22.0%	0.1080	+0.499°	22.2%	0.1090
	+0.359°	21.8%	0.1070	+0.500°	22.0%	0.0180
6.0	+0.355°	22.7%	0.1120	+0.496°	22.6%	0.1110
	+0.355°	22.7%	0.1120	+0.496°	22.6%	0.1110
12.0	+0.351°	23.5%	0.1170	+0.490°	23.6%	0.1170
	+0.351°	23.5%	0.1170	+0.490°	23.6%	0.1170

Table XLI B. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCOO)_2$ = 1 : 10 in Bromobenzene at 80°C (Run 2).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	+0.460°			+0.642°		
1.0	+0.423°	8.0%	0.0364	+0.591°	7.9%	0.0359
	+0.422°	8.3%	0.0374	+0.590°	8.1%	0.0367
2.0	+0.397°	13.7%	0.0640	+0.554°	13.7%	0.0640
	+0.397°	13.7%	0.0640	+0.554°	13.7%	0.0640
3.0	+0.381°	17.2%	0.0818	+0.532°	17.1%	0.0816
	+0.381°	17.2%	0.0818	+0.531°	17.3%	0.0824
4.0	+0.367°	20.2%	0.0981	+0.512°	20.2%	0.0983
	+0.367°	20.2%	0.0981	+0.512°	20.2%	0.0983
5.0	+0.358°	22.2%	0.1089	+0.499°	22.3%	0.1094
	+0.358°	22.2%	0.1089	+0.499°	22.3%	0.1094
6.0	+0.355°	22.8%	0.1125	+0.495°	22.9%	0.1129
	+0.355°	22.8%	0.1125	+0.495°	22.9%	0.1129
12.0	+0.350°	23.9%	0.1187	+0.488°	24.0%	0.1191
	+0.350°	23.9%	0.1187	+0.488°	24.0%	0.1191

(ii). Bianthryl 1 : $(PhCOO)_2$ = 1 : 5

In a 25 mL volumetric flask, 12.5 mL of 0.0128 M bianthryl 1 stock solution (0.075 g, 0.159 mmol) was added to 6.25 mL of 0.128 M $(PhCOO)_2$ stock solution (0.194 g, 0.80 mmol), and bromobenzene was added to make up the volume to 25 mL. The initial rotation of the reaction solution was determined and ~1.5 mL samples of the above solution were transferred to each of 15 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (100 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 80°±0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table XLII A. The reaction was repeated and the results for run 2 are summarized in Table XLII B.

Table XLII A. Percent Racemization for the Reaction of Bianthryl 1 : (PhCOO)$_2$ = 1 : 5 in Bromobenzene at 80° C (Run 1).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	+0.459°			+0.641°		
1.0	+0.440°	4.1%	0.0184	+0.614°	4.2%	0.0186
	+0.440°	4.1%	0.0184	+0.615°	4.1%	0.0180
2.0	+0.423°	7.8%	0.0350	+0.590°	7.9%	0.0360
	+0.423°	7.8%	0.0350	+0.590°	7.9%	0.0360
3.0	+0.414%	9.8%	0.0450	+0.578°	9.8%	0.0450
	+0.413°	10.0%	0.0460	+0.577°	9.9%	0.0460
4.0	+0.406°	11.5%	0.0530	+0.568°	11.4%	0.0530
	+0.406°	11.5%	0.0530	+0.567°	11.5%	0.0530
5.0	+0.401°	12.6%	0.0580	+0.560°	12.6%	0.0586
	+0.402°	12.4%	0.0580	+0.561°	12.5%	0.0580
6.0	+0.397°	13.5%	0.0620	+0.555°	13.4%	0.0626
	+0.398°	13.3%	0.0620	+0.556°	13.3%	0.0620
12.0	+0.391°	14.8%	0.0696	+0.546°	14.8%	0.0696
	+0.392°	14.6%	0.0690	+0.547°	14.7%	0.0690

Table XLII B. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCOO)_2$ = 1 : 5 in Bromobenzene at 80° C (Run 2).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	+0.459°			+0.641°		
1.0	+0.439°	4.4%	0.0193	+0.613°	4.4%	0.0194
	+0.439°	4.4%	0.0193	+0.613°	4.4%	0.0194
2.0	+0.422°	8.1%	0.0365	+0.589°	8.1%	0.0367
	+0.423°	7.8%	0.0355	+0.589°	8.1%	0.0367
3.0	+0.413%	10.0%	0.0459	+0.577°	10.0%	0.0457
	+0.413°	10.0%	0.04599	+0.577°	10.0%	0.0457
4.0	+0.406°	11.5%	0.0533	+0.567°	11.5%	0.0533
	+0.406°	11.5%	0.0533	+0.567°	11.5%	0.0533
5.0	+0.401°	12.6%	0.0587	+0.560°	12.6%	0.0587
	+0.401°	12.6%	0.0587	+0.560°	12.6%	0.0587
6.0	+0.398°	13.3%	0.0619	+0.556°	13.3%	0.0618
	+0.398°	13.3%	0.0619	+0.556°	13.3%	0.0618
12.0	+0.392°	14.6%	0.0685	+0.547°	14.7%	0.0689
	+0.392°	14.6%	0.0685	+0.547°	14.7%	0.0689

(iii). Bianthryl 1 : $(PhCOO)_2$ = 1 : 1

In a 10 mL volumetric flask, 5 mL of 0.0128 M bianthryl 1 stock solution (0.030 g, 0.064 mmol) was added to 0.5 mL of 0.128 M $(PhCOO)_2$ stock solution (0.0155 g, 0.064 mmol). The initial rotation of the reaction solution was determined and ~1 mL samples of the above solution were transferred to each of 8 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (100 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 80°±0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table XLIII A.

The reaction was repeated and the results for run 2 are summarized in Table XLIII B.

Table XLIII A. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCOO)_2$ = 1 : 1 in Bromobenzene at 80° C (Run 1).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	+0.464°			+0.646°		
1.0	+0.460°	0.9%	0.0037	+0.640°	0.9%	0.0037
	+0.460°	0.9%	0.0037	0.640°	0.9%	0.0037
5.0	+0.448°	3.4%	0.0152	+0.624°	3.4%	0.0150
	+0.448°	3.4%	0.0152	+0.624°	3.4%	0.0150
15.0	+0.443°	4.5%	0.0201	+0.618°	4.3%	0.0192
	+0.443°	4.5%	0.0201	+0.618°	4.3%	0.0192
24.0	+0.443°	4.5%	0.0201	+0.618°	4.3%	0.0192
	+0.443°	4.5%	0.0201	+0.618°	4.3%	0.0192

Table XLIII B. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCOO)_2$ = 1 : 1 in Bromobenzene at 80° C (Run 2).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	+0.459°			+0.641°		
1.0	+0.455° +0.455°	0.9% 0.9%	0.0038 0.0038	+0.635° +0.635°	0.94% 0.94%	0.0041 0.0041
2.0	+0.452° +0.452°	1.5% 1.5%	0.0067 0.0067	+0.631° +0.631°	1.6% 1.6%	0.0068 0.0068
3.0	+0.449° +0.449°	2.2% 2.2%	0.0096 0.0096	+0.627° +0.627°	2.2% 2.2%	0.0096 0.0096
5.0	+0.443° +0.443°	3.5% 3.5%	0.0154 0.0154	+0.619° +0.619°	3.4% 3.4%	0.0152 0.0152
6.0	+0.441° +0.441°	3.9% 3.9%	0.0173 0.0173	+0.616° +0.616°	3.9% 3.9%	0.0173 0.0173
15.0	+0.438° +0.438°	4.6% 4.6%	0.0203 0.0203	+0.612° +0.612°	4.5% 4.5%	0.0201 0.0201
24.0	+0.438° +0.438°	4.6% 4.6%	0.0203 0.0203	+0.612° +0.612°	4.5% 4.5%	0.0201 0.0201

14. Effect of Phenylthiol on the Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the Presence of Benzoyl Peroxide in Bromobenzene at 80°±0.1°C.

The reaction mixture containing the molar ratio of bianthryl **1** : $(PhCOO)_2$: PhSH = 1 : 10 : 20 was prepared as follows. Five mL of 0.0128 M bianthryl **1** stock solution (0.030 g, 0.064 mmol) and 5 mL of 0.128 M $(PhCOO)_2$ stock solution (0.155 g, 0.640 mmol) were added to 0.1405 g (1.280 mmol) of PhSH. The initial rotation of the reaction solution was determined and ~2 mL samples of the above solution were transferred to each of 5 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (100 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 80°±0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table XLIV.

Table XLIV. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCOO)_2$: PhSH = 1 : 10 : 20 in Bromobenzene at 80°C.

Time	λ/589 nm		λ/546 nm	
(h)	α_{589}	% Rac	α_{546}	% Rac
0	+0.435°		+0.610°	
1.0	+0.435°	0	+0.610°	0
2.0	+0.435°	0	+0.610°	0
4.0	+0.435°	0	+0.610°	0
6.0	+0.435°	0	+0.610°	0
12.0	+0.435°	0	+0.610°	0

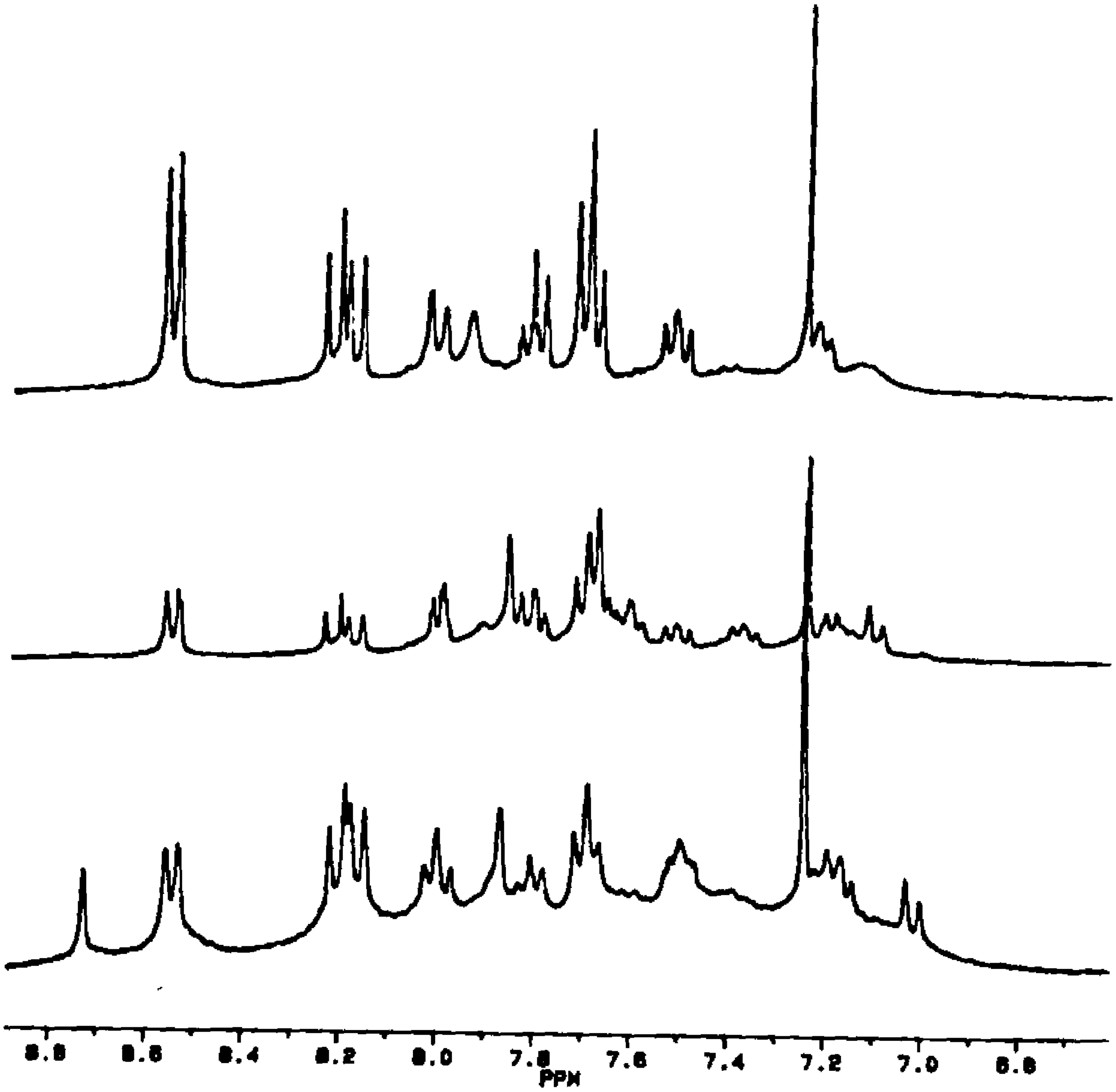
15. Recovery and Investigation of Products from the Reaction of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) with Benzoyl Peroxide at 80°C in Bromobenzene.

(i). Bianthryl 1 : $(PhCOO)_2$=1 : 10. Reaction Time 20 h.

Ten mL of 0.0128 M bianthryl 1 stock solution (0.060 g, 0.128 mmol, $[\alpha]_D$ = -152°) was added to 10 mL of 0.128 M $(PhCOO)_2$ solution (0.310 g, 1.28 mmol). The initial rotation of the reaction solution was measured (α_D = -0.508°), and the solution was transferred to a racemization tube. The solution was degassed by the freeze pump thaw process and sealed under a nitrogen pressure of 10 torr. The tube was heated in a Haake constant temperature bath at 80°±0.1°C for 20 h. After 20 h the reaction solution was 30.7% racemized (α_D=-0.352°). Bromobenzene was distilled off (35° C, 1 mm Hg) and the residue was chromatographed by column chromatography (silica gel) using benzene as the eluent till traces of bromobenzene and diphenyl were eluted. The eluent was then changed to benzene-chloroform (2 : 1) until a yellow band was collected. The yellow band was further purified by preparative TLC (silica gel, 1000 μ , benzene, 3 developments) to collect 3 fractions which were each again chromatographed by preparative TLC (silica gel,1000 μ , benzene, 3 developments). Fraction 1, which had the lowest R_f value, was identified as 2,2'-dicarbomethoxy-10,10'-dibenzoyl-9,9'-bianthryl (**41**), (0.0181 g, 20.0% yield): ^{1}H NMR ($CDCl_3$) δ 3.69 (s), δ 7.23-8.57 (m). Fraction 2, which had the intermediate R_f value of the three fractions, was identified as 2,2'-dicarbomethoxy-10-benzoyl-9,9'-bianthryl (**40**), (0.0079 g, 10.5% yield):^{1}H NMR ($CDCl_3$) δ 3.70 (s), δ 3.66 (s), δ 8.74-7.04 (m). Fraction 3 which had the highest Rf value was identified as 2,2'-dicarbomethoxy-10-benzoyl-10'-phenyl-9,9'-bianthryl (**42**), (0.0139 g, 16.4%):^{1}H NMR ($CDCl_3$) δ.3.72 (s), δ 3.68 (s), δ 8.59-7.13 (m).

Figure 29 shows the aromatic region of the ^{1}H NMR spectra of **40** (top trace), **41** (bottom trace) and **42** (middle trace).

Figure 29. Aromatic Region of the ^{1}H NMR Spectra of 2,2'-Dicarbomethoxy-10,10'-dibenzoyl-9,9'-bianthryl (41) (top trace), 2,2'-Dicarbomethoxy-10-benzoyl-9,9'-bianthryl (40) (bottom trace) and 2,2'-Dicarbomethoxy-10-benzoyl-10'-phenyl-9,9'-bianthryl (42) (middle trace)



Homo-nuclear decoupling of 2,2'-dicarbomethoxy-10,10'-dibenzoyl-9,9'-bianthryl (41).

(i) Irradiation of the doublet at δ 8.56 (ortho H of the benzoyloxy substituent), resulted in the collapse of the triplet at δ 7.70 (meta H of the benzoyloxy substituent) to a doublet.

(ii) Irradiation of the doublet at δ 8.23 (H4), resulted in the collapse of the doublet at δ 8.01 (H3) to a singlet.

(iii) Irradiation of the doublet at δ 8.18 (H5), resulted in the collapse of the triplet at δ 7.55 (H6) to a doublet.

(iv) Irradiation of the triplet at δ 7.82 (para H of the benzoyloxy substituent), resulted in the collapse of the triplet at δ 7.70 (meta H of the benzoyloxy substituent) to a doublet.

(v) Irradiation of the triplet at δ 7.55 (H6), resulted in the collapse of the doublet at δ 7.23 (H7) to a singlet and the doublet at δ 8.18 (H5) to a singlet.

(vi) Irradiation of the doublet at δ 7.23 (H7), resulted in the collapse of the triplet at δ 7.56 (H6) to a doublet.

Homo-nuclear decoupling of 2,2'-dicarbomethoxy-10-benzoyl-9,9'-bianthryl (40).

(i) Irradiation of the doublet at δ 8.56 (ortho H of the benzoyloxy substituent), resulted in the collapse of the triplet at δ 7.70 (meta H of the benzoyloxy substituent) to a doublet.

(ii) Irradiation of the doublet at δ 8.22 (H4, H4'), resulted in the collapse of the triplet (two overlapping doublets) at δ 8.01 (H3, H3') to two singlets.

(iii) Irradiation of the doublet at δ 8.18 (H5, H5'), resulted in the collapse of the multiplet (two overlapping triplets) at δ 7.51 (H6, H6') to two doublets.

(iv) Irradiation of the triplet at δ 7.82 (para H of the benzoyloxy substituent), resulted in the collapse of the triplet at δ 7.70 (meta H of the benzoyloxy substituent) to a doublet.

(v) Irradiation of the multiplet (two overlapping triplets) at δ 7.51 (H6, H6'), resulted in the collapse of the two overlapping triplets at δ 7.23 (H7, H7') to two doublets and the doublet at δ 8.18 (H5, H5') to a singlet.

(vi) Irradiation of the two overlapping triplets at δ 7.23 (H7, H7'), resulted in the collapse of the multiplet at δ 7.51 (H6, H6') to a doublet and the doublet at δ 7.04 (H8, H8') to a singlet.

(vii) Irradiation of the singlets at δ 8.74 (H10') and 7.88 (H1, H1') did not affect the rest of the spectrum.

Homo-nuclear decoupling of 2,2'-dicarbomethoxy-10-benzoyl-10'-phenyl-9,9'-bianthryl (42).

(i) Irradiation of the doublet at δ 8.57 (ortho H of the benzoyloxy substituent), resulted in the collapse of the triplet at δ 7.70 (meta H of the benzoyloxy substituent) to a doublet.

(ii) Irradiation of the doublet at δ 8.22 (H4, or H4'), resulted in the collapse of the doublet at δ 8.03 (H3 or H3') to a singlet.

(iii) Irradiation of the doublet at δ 8.19 (H5 or H5'), resulted in the collapse of the triplet at δ 7.53 (H6 or H6') to a doublet.

(iv) Irradiation of the doublet at δ 8.03 (H3 or H3'), resulted in the collapse of the doublet at δ 8.24 (H4 or H4') to a singlet.

(v) Irradiation of the triplet (two overlapping doublets) at δ 7.82 (H5 or H5'), resulted in the collapse of the triplet at δ 7.39 (H6 or H6') to a doublet.

(vi) Irradiation of the multiplet between δ 7.74-7.60 (the phenyl substituent and the meta and para H's of the benzoyloxy substituent), resulted in the collapse of the doublet at δ 8.57 (ortho H's of the benzoyloxy substituent) to a singlet.

(vii) Irradiation of the triplet at δ 7.53 (H6 or H6') resulted in the collapse of the doublet at δ 8.19 (H5 or H5') to a singlet and the triplet at δ 7.19 (H7 or H7') to a doublet.

(viii) Irradiation of the triplet at δ 7.39 (H6 or H6') resulted in the collapse of the triplet (two doublets) at δ 7.82 (H5 ar H5') to a singlet and the triplet at δ 7.19 (H7 or H7') to a doublet.

(ix) Irradiation of the triplet at δ 7.19 (H7 and H7') resulted in the collapse of the triplets at δ 7.53 (H6 or H6') and 7.39 (H6 or H6') to two doublets and the doublet at δ 7.12 (H8 and H8') to a singlet.

(x) Irradiating the doublet at δ 7.12 (H8 and H8') resulted in the triplet at δ 7.19 (H7 and H7') to collapse to a doublet.

Figure 30. ^1H-^1H COSY Spectrum of 2,2'-Dicarbomethoxy-10-benzoyl-9,9'-bianthryl (40). Aromatic Region.

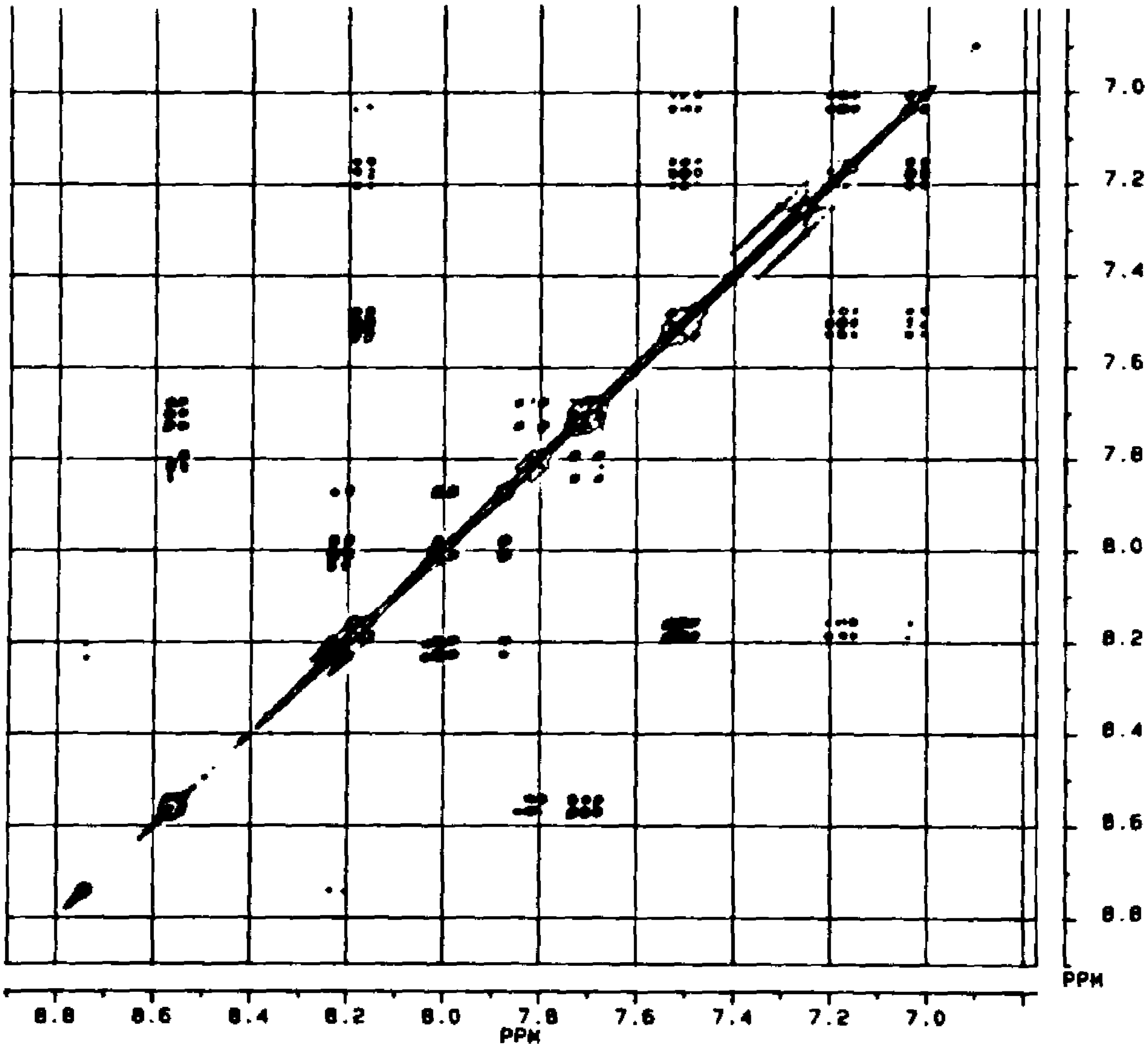


Figure 31. $^1H-^1H$ Spectrum of 2,2'-Dicarbomethoxy-10,10'-dibenzoyl-9,9'-bianthryl (41). Aromatic Region.

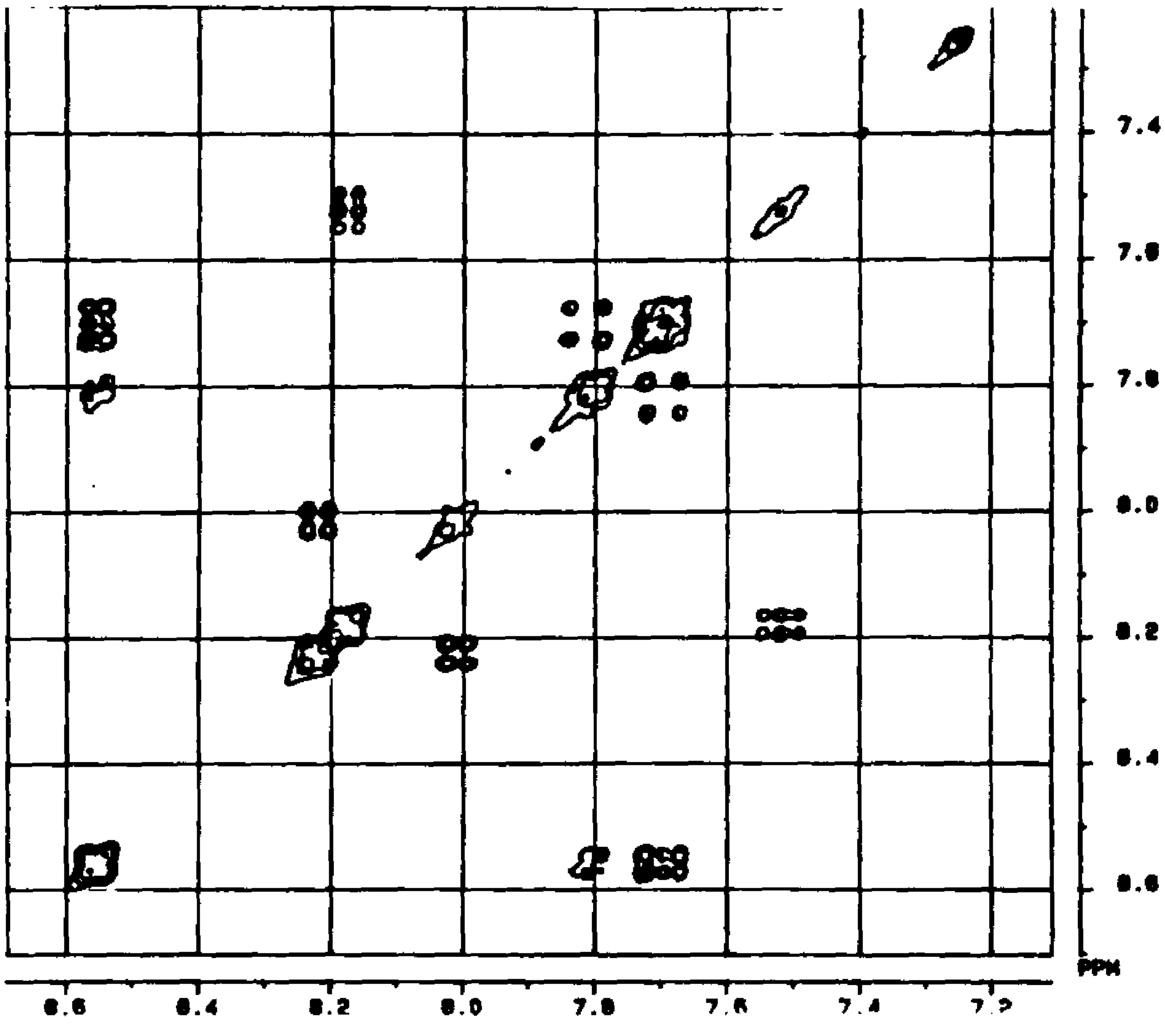


Figure 32. ^1H-^1H Spectrum of 2,2'-Dicarbomethoxy-10-benzoyl-10'-phenyl-9,9'-bianthryl (42). Aromatic Region.

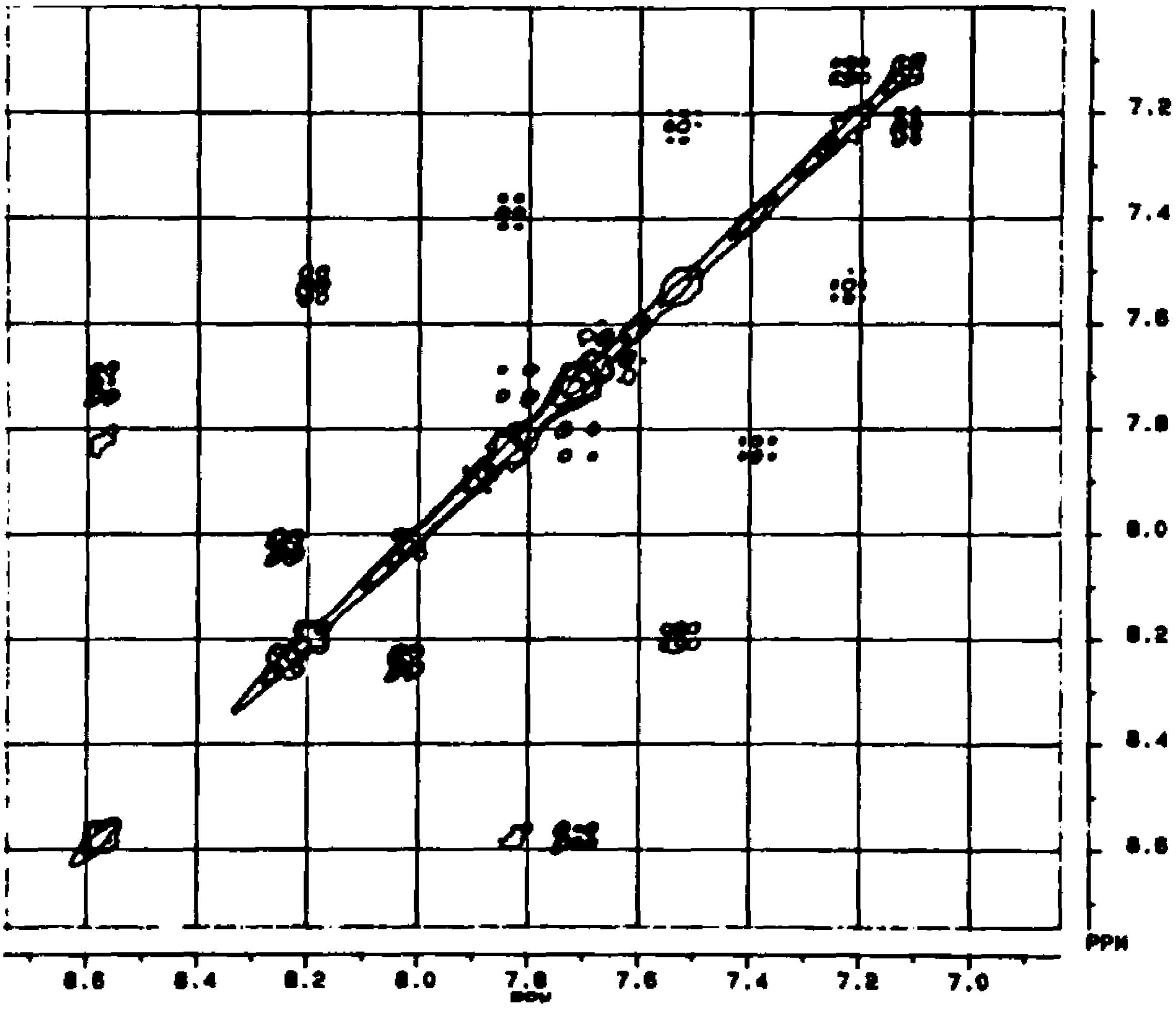
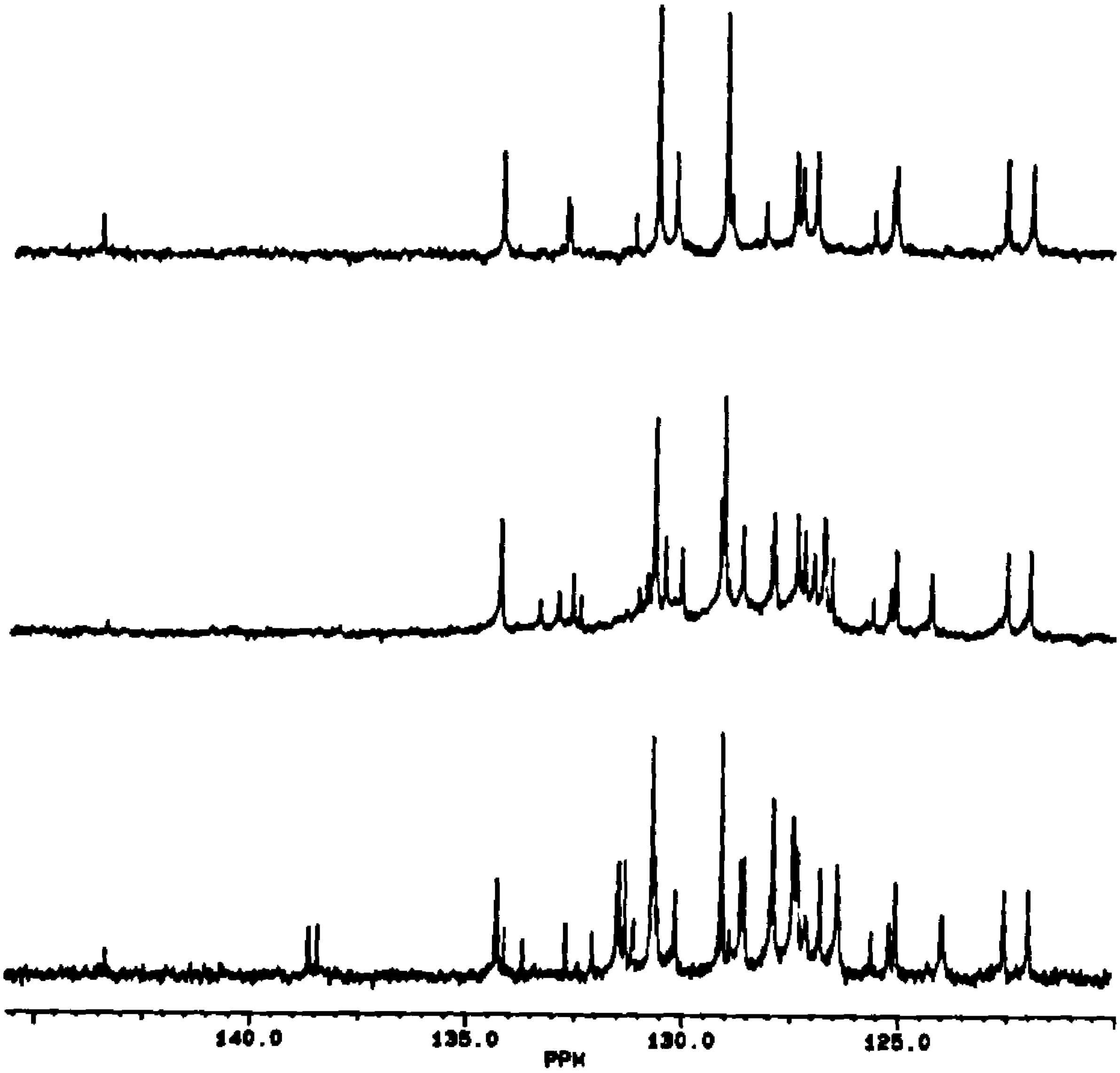


Figure 33. Aromatic Region of the ^{13}C NMR Spectra of 2,2'-Dicarbomethoxy-10,10'-dibenzoyl-9,9'-bianthryl (41) (top trace), 2,2'-Dicarbomethoxy-10-benzoyl-9,9'-bianthryl (40) (bottom trace) and 2,2'-Dicarbomethoxy-10-benzoyl-10'-phenyl-9,9'-bianthryl (42) (middle trace)



(ii). Bianthryl 1 : $(PhCOO)_2$ = 1 : 5. Reaction Time 3 h.

Ten mL of 0.0128 M bianthryl 1 stock solution (0.060 g, 0.128 mmol, $[\alpha]_{589}$ = -151.1°, $[\alpha]_{546}$ = 216.95°) was added to 5 mL of 0.128 M $(PhCOO)_2$ solution (0.1550 g, 0.640 mmol) and 5 mL of bromobenzene. The initial rotation of the reaction solution was measured (α_{589}=-0.511°, α_{546}=-0.712°), and the solution was transferred to a racemization tube. The solution was degassed by the freeze pump thaw process and sealed under a nitrogen pressure of 10 torr. The tube was heated in a Haake constant temperature bath at 80°±0.1°C for 3 h. After 3 h the reaction solution was 11% racemized (α_D=-0.450°, α_{589}=-0.632°). Bromobenzene was distilled off (35° C, 1 mm Hg) and the residue was chromatographed by column chromatography (silica gel) using benzene as the eluent until traces of bromobenzene and diphenyl were eluted. The eluent was changed to benzene-chloroform (2 : 1) until a yellow band was collected. The yellow band was further purified by preparative TLC (silica gel, 1000 µ, benzene, 3 developments). Two fractions were obtained; fraction 1, with a higher R_f value, was recovered bianthryl 1 (NMR spectrum identical with a pure sample, 0.0267 g, 44.5% recovery), $[\alpha]_{589}$ = -131.7° (12.8% racemized), $[\alpha]_{546}$ = 189.7° (12.6% racemized). Fraction 2 was identified as 2'2'-dicarbomethoxy-10-benzoyl-9,9'-bianthryl (**40**), (0.01135 g, 17.9% yield).

16. Racemization of Optically Active 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the Presence of Diphenylmercury at 200°±0.1°C in Bromobenzene

Reaction solutions were prepared volumetrically from stock solutions of optically active bianthryl **1** and diphenylmercury in bromobenzene. A bianthryl **1** stock solution (0.0128 M) was prepared in bromobenzene by dissolving 0.60 g (1.28 mmol) of bianthryl in 100 mL of solution. In reactions where the [Bianthryl **1**] is a constant, the bianthryl **1** concentration in the reaction solution was 0.0064 M. The diphenylmercury stock solution corresponded to 10 equivalents of diphenylmercury per equivalent of bianthryl **1** in solution and was prepared by dissolving 0.5625 g (1.59 mmol) of Ph_2Hg in 25 mL of bromobenzene (0.064 M). To prepare solutions of different ratios of bianthryl **1** : Ph_2Hg, the stock solutions were mixed corresponding to the ratios desired.

Bianthryl **1** : Ph_2Hg = 1 : 5 solution was prepared as follows: 30 mL of 0.0128 M bianthryl **1** stock solution (0.180 g, 0.3825 mmol, $[\alpha]_{589}$ = +92.0°, $[\alpha]_{546}$ = 130.0°) was added to 30 mL of 0.064 M diphenylmercury stock solution (0.6808 g, 1.920 mmol). Ten mL of the above solution were transferred to 6 racemization tubes. The tubes were degassed by freeze pump thaw process and sealed under a nitrogen pressure of 100 torr. The tubes were placed in a Haake constant temperature oil bath pre-heated to 200°±0.2°C. Tubes were removed periodically and worked up to recover partially racemized bianthryl as follows: Bromobenzene was distilled (35°C, 1 torr), and the residue was chromatographed by column chromatography (silica gel, $CHCl_3$) to collect the yellow band containing the bianthryl 1. The yellow band was further purified by preparative TLC (silica gel, 1000 μ, 1:1 benzene-chloroform) to recover the bianthryl 1 (NMR spectrum identical with a pure sample). Total recovery of the bianthryl 1 was 0.1337 g, (74.3%). Rotations of the recovered bianthryl 1 were measured and are summarized in Table XLV.

Table XLV. Percent Racemization For The Reaction of Bianthryl 1 : Ph_2Hg = 1 : 5 in Bromobenzene at 200°±0.2°C

Time (h)	λ/589 nm			λ/546 nm		
	$[\alpha]_{589}$	% Rac	$\log\alpha_0/\alpha$	$[\alpha]_{546}$	% Rac	$\log\alpha_0/\alpha$
0	+92.0°			+130.0°		
48	+69.7°	24.2%	0.120	+98.6°	24.2%	0.120
75	+60.0°	34.8%	0.186	+84.7°	34.8%	0.186
95	+57.8°	37.2%	0.202	+81.6°	37.2%	0.202
121	+51.5°	44.0%	0.252	+72.8°	44.0%	0.252
140	+40.3°	56.2%	0.358	+57.0°	56.1%	0.358
160	+36.0°	60.9%	0.407	+50.9°	60.8%	0.407

17. Racemization of Optically Active 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the Presence of Diphenylmercury at 180°±0.1°C in Bromobenzene

A bianthryl **1** : Ph_2Hg = 1 : 5 solution was prepared as follows: 20 mL of 0.0128 M bianthryl **1** stock solution (0.120 g, 0.2550 mmol, $[\alpha]_{589} = -152.0°$, $[\alpha]_{546} = -218.6°$) was added to 20 mL of 0.064 M diphenylmercury stock solution (0.4521 g, 1.278 mmol). Ten mL samples of the above solution was transferred to four racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under a nitrogen pressure of 100 torr. The tubes were placed in a Haake constant temperature bath pre-heated to 180°±0.1°C. Tubes were removed periodically and worked up to recover partially racemized bianthryl as follows: Bromobenzene was distilled (35°C, 1 torr), and the residue was purified by column chromatography (silica gel, $CHCl_3$) to collect the yellow band containing bianthryl **1**. The yellow band was further purified by preparative TLC (silica gel, 1000 μ, 1:1 benzene-chloroform) to recover bianthryl **1** (NMR spectrum identical with a pure sample). Total recovery of bianthryl was 0.0895 g, (74.6%). Rotations of recovered bianthryl **1** were measured and are summarized in Table XLVI.

Table XLVI. Percent Racemization For The Reaction of Bianthryl 1 : Ph_2Hg = 1 : 5 in Bromobenzene at 180°±0.1°C

Time (h)	λ/589 nm			λ/546 nm		
	$[\alpha]_{589}$	% Rac	$\log\alpha_0/\alpha$	$[\alpha]_{546}$	% Rac	$\log\alpha_0/\alpha$
0	-152.0°			-218.6°		
100	-107.1°	29.5%	0.152	-154.0°	29.6%	0.152
140	-93.1°	38.8%	0.213	-133.9°	38.7%	0.213
200	-75.5°	50.1%	0.302	-109.1°	50.1%	0.302
240	-67.1°	55.8%	0.355	-96.5°	55.8%	0.355

18. Effect of Phenylthiol on the Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the Presence of Ph_2Hg at 180° in Bromobenzene.

A bianthryl 1 : Ph_2Hg : PhSH = 1 : 5 : 10 solution was prepared as follows: 5 mL of 0.0128 M bianthryl 1 stock solution (0.030 g, 0.064 mmol, $[\alpha]_{589}$ = -152.0°, $[\alpha]_{546}$ = -218.6°) and 5 mL of 0.064 M diphenylmercury stock solution (0.1135 g, 0.320 mmol) were added to 0.0701 g (0.64 mmol) of PhSH. The above solution was transferred to a racemization tube. The tube was degassed by the freeze pump thaw process and sealed under a nitrogen pressure of 100 torr.

The tube was placed in a Haake constant temperature bath preheated to 180° ± 0.1°C for 140 h. The reaction solution was worked up to recover partially racemized bianthryl **1** as follows: bromobenzene was distilled (35°C, 1 torr), and the residue was chromatographed by column chromatography (silica gel, $CHCl_3$) to collect the yellow band containing bianthryl **1**. The yellow band was further purified by preparative TLC (silica gel, 1000 μ, 1 : 1 benzene-chloroform) to recover the bianthryl **1** (NMR spectrum identical with a pure sample). The recovery of bianthryl **1** was 0.0274 g, (91.3%). Rotation of the recovered bianthryl **1** was measured, $[\alpha]_{589}$ = -142.5° (6.3% racemized), $[\alpha]_{546}$ = -204.3° (6.5% racemized).

19. Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the Presence of Phenylthiol in Bromobenzene at 180°C.

Bianthryl **1** : PhSH = 1 : 10 was prepared as follows: In a 10 mL volumetric flask, 5 mL of 0.0128 M bianthryl **1** stock solution (0.030 g, 0.064 mmol, $[\alpha]_{589}$ = -152.0°, $[\alpha]_{546}$ = -218.6°) was added to 0.0701 g (0.64 mmol) of PhSH and bromobenzene was added to make up the volume to 10 mL. The initial rotation of the reaction solution was determined (α_{589} = -0.499°, α_{546} = -0.706°), and the solution was transferred to a racemization tube. The tube was degassed by the freeze pump thaw process and sealed under a nitrogen pressure of 100 torr. The tube was heated at 180°C in a Haake constant temperature bath for 140 h. After 140 h the rotation of the reaction solution was measured, α_{589} = -0.474°(5.0% racemized), α_{546} = -0.671°(4.95% racemized).

20. Racemization of Optically Active 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the Presence of Dibenzylmercury at 160°±0.1°C in Bromobenzene

Reaction solutions were prepared volumetrically from stock solutions of optically active bianthryl **1** and dibenzylmercury in bromobenzene. The bianthryl **1** stock solution (0.0128 M) was prepared in bromobenzene by dissolving 0.600 g (1.28 mmol) of bianthryl **1** in 100 mL of solution. In reactions where the [Bianthryl **1**] is a constant, the bianthryl **1** concentration in the reaction solution was 0.0064 M. Dibenzylmercury stock solution corresponds to 10 equivalents of dibenzylmercury per equivalent of bianthryl in solution and was prepared by dissolving 1.213 g (3.20 mmol) of $(PhCH_2)_2Hg$ in 25 mL of bromobenzene (0.128 M). To prepare 0.0064 M $(PhCH_2)_2Hg$, 0.50 mL of 0.128 M $(PhCH_2)_2Hg$ stock solution was diluted to 10 mL with bromobenzene.

(i) Percent Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) as a function of $[(PhCH_2)_2Hg]$ at 160°C. Reaction Time 40 h.

To prepare 10 mL of the reaction solutions with different ratios of bianthryl **1** : $(PhCH_2)_2Hg$, 5 mL of 0.0128 M bianthryl stock solution was added to the volumes of $(PhCH_2)_2Hg$ stock solution shown in Table XLVII. Bromobenzene was added to make up the total volume to 10 mL where necessary.

Table XLVII. Preparation of Reaction Solutions With Different Ratios of Bianthryl 1 : $(PhCH_2)_2Hg$.

Bianthryl 1 : $(PhCH_2)_2Hg$	Volume of $(PhCH_2)_2Hg$ stock solution added to 5 mL of 0.0128 M Bianthryl solution.
1 : 10.0	5.0 mL of 0.128M $(PhCH_2)_2Hg$
1 : 5.0	2.5 mL of 0.128 M $(PhCH_2)_2Hg$
1 : 1.0	0.50 mL of 0.128 M $(PhCH_2)_2Hg$
1 : 0.50	5.0 mL of 0.0064 M $(PhCH_2)_2Hg$
1 : 0.33	3.33 mL of 0.0064 M $(PhCH_2)_2Hg$
1 : 0.25	2.5 mL of 0.0064 $(PhCH_2)_2Hg$
1 : 0.20	2.0 mL of 0.0064 $(PhCH_2)_2Hg$
1 : 0.10	1.0 mL of 0.0064 $(PhCH_2)_2Hg$
1 : 0.060	0.68 mL of 0.0064 $(PhCH_2)_2Hg$
1 : 0.050	0.50 mL of 0.0064 M $(PhCH_2)_2Hg$
1 : 0.030	0.33 mL of 0.0064 M $(PhCH_2)_2Hg$

The solutions of different ratios of bianthryl **1** : $(PhCH_2)_2Hg$ were transferred to racemization tubes (2 tubes per ratio to duplicate results). The tubes were degassed by the freeze pump thaw process and sealed under a nitrogen pressure of 100 torr. The tubes were heated for 40 h at 160° ± 0.1°C in a constant temperature Haake bath. The tubes were removed after 40 h and the rotations of the reaction solutions were measured. The results are summarized in Table XLVIII.

Table XLVIII. Percent Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) as a function of [$(PhCH_2)_2Hg$]. at 160°C. Reaction Time 40 h.

Bianthryl: $(PhCH_2)_2Hg$	α_{589}	% Rac	α_{546}	% Rac
1 : 0	-0.508° -0.508°	0 0	-0.712° -0.712°	0 0
1 : 10.0	-0.115° -0.116°	77.4% 77.2%	-0.164° -0.166°	77.0% 76.7%
1 : 5.0	-0.178° -0.178°	64.9% 64.9%	-0.253° -0.253°	64.7% 64.7%
1 : 0.50	-0.349° -0.349°	31.3% 31.3%	-0.484° -0.485°	32.0% 31.8%
1 : 0.33	-0.373° -0.372°	26.6% 26.8%	-0.520° -0.518°	26.9% 27.2%
1 : 0.25	-0.391° -0.390°	23.0% 23.2%	-0.545° -0.544°	23.6% 23.5%
1 : 0.20	-0.416° -0.416°	18.1% 18.1%	-0.582° -0.581°	18.3% 18.4%
1 : 0.10	-0.445° -0.445°	12.4% 12.4%	-0.624° -0.626°	12.4% 12.1%
1 : 0.060	-0.460° -0.460	9.4% 9.4%	-0.644° -0.644°	9.5% 9.5%
1 : 0.050	-0.473° -0.474°	6.9% 6.7%	-0.662° -0.663°	7.0% 6.9%
1 : 0.030	-0.486° -0.490°	4.3% 3.5%	-0.678° -0.682°	4.8% 4.2%

(ii) Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 5

In a 25 mL volumetric flask, 12.5 mL of 0.0128 M bianthryl 1 stock solution (0.075 g, 0.159 mmol) was added to 6.25 mL of 0.128 M dibenzylmercury stock solution (0.303 g, 0.797 mmol), and bromobenzene was added to make up the volume to 25 mL. The initial rotation of the reaction solution was determined, and ~2 mL samples of the above solution were transferred to each of 12 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (10 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 160° ± 0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table XLIX.

Table XLIX. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 5 in Bromobenzene at 160°C.

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	-0.508°			-0.712°		
1.0	-0.258°	49.2%	0.294	-0.364°	48.9%	0.291
	-0.259°	49.0%	0.293	-0.366°	48.6%	0.289
2.0	-0.211°	58.5%	0.382	-0.302°	57.6%	0.372
	-0.211°	58.5%	0.382	-0.302°	57.6%	0.372
2.5	-0.206°	59.4%	0.392	-0.292°	59.0%	0.387
	-0.204°	59.8%	0.396	-0.291°	59.1%	0.389
3.0	-0.195°	61.6%	0.416	-0.275°	61.4%	0.413
	-0.197°	61.2%	0.411	-0.276°	61.2%	0.411
3.5	-0.185°	63.6%	0.439	-0.261°	63.3%	0.436
	-0.184°	63.8%	0.441	-0.262°	63.2%	0.434
24.0	-0.173°	65.9%	0.468	-0.265°	65.6%	0.463
	-0.173°	65.9%	0.468	-0.264°	65.4%	0.462

To determine the initial rate the reaction was repeated, and samples were taken at shorter reaction times. In a 10 mL volumetric flask, 5 mL of 0.0128 M bianthryl 1 stock solution (0.030 g, 0.064 mmol) was added to 2.5 mL of 0.128 M dibenzylmercury stock solution (0.1218 g, 0.320 mmol) and bromobenzene was added to make up the volume to 10 mL. The initial rotation of the reaction solution was determined, and ~1 mL samples of the above solution were transferred to each of 10 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (10 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 160°±0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table L A (run 1).

The reaction was repeated. The results for run 2 are summarized in Table L B.

Table L A. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 5 in Bromobenzene at 160°C (Run 1).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	α_0-α	α_{546}	% Rac	α_0-α
0	-0.513°			-0.718°		
0.25	-0.404°	21.2%	0.109	-0.566°	21.2%	0.152
	-0.405°	21.1%	0.108	-0.567°	21.0%	0.152
0.50	-0.338°	34.1%	0.175	-0.466°	35.1%	0.252
	-0.337°	34.3%	0.176	-0.466°	35.1%	0.252
0.75	-0.297°	42.1%	0.216	-0.417°	41.9%	0.301
	-0.297°	42.1%	0.216	-0.417°	41.9%	0.301
1.00	-0.277°	46.0%	0.236	-0.386°	46.2%	0.332
	-0.276°	46.2%	0.237	-0.385°	46.4%	0.333
1.25	-0.249°	51.5%	0.264	-0.347°	51.7%	0.371
	0.250°	51.3%	0.263	-0.348°	51.7%	0.370

Table L B. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 5 in Bromobenzene at 160°C (Run 2).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	α_0-α	α_{546}	% Rac	α_0-α
0	-0.512°			-0.718°		
0.25	-0.404°	21.1%	0.108	-0.566°	21.2%	0.152
	-0.404°	21.1%	0.108	-0.566°	21.2%	0.152
0.50	-0.338°	34.0%	0.174	-0.474°	34.0%	0.244
	-0.338°	34.0%	0.174	-0.474°	34.0%	0.244
0.75	-0.296°	42.2%	0.216	-0.415°	42.2%	0.303
	-0.296°	42.2%	0.216	-0.415°	42.2%	0.303
1.00	-0.276°	46.1%	0.236	-0.387°	46.1%	0.331
	-0.276°	46.1%	0.236	-0.387°	46.1%	0.331
1.25	-0.249°	51.4%	0.263	-0.350°	51.3%	0.368
	0.249°	51.4%	0.263	-0.349°	51.4%	0.369

(iii) Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 1

In a 25 mL volumetric flask, 12.5 mL of 0.0128 M bianthryl 1 stock solution (0.075 g, 0.159 mmol) was added to 1.25 mL of 0.128 M dibenzylmercury stock solution (0.0605 g, 0.159 mmol) and bromobenzene was added to make up the volume to 25 mL. The initial rotation of the reaction solution was determined, and ~2 mL samples of the above solution were transferred to each of 12 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (10 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 160°±0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotation of the solutions were determined. The results are summarized in Table LI

Table LI Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 1 in Bromobenzene at 160°C.

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	-0.508°			-0.712°		
2.0	-0.351°	30.9%	0.161	-0.491°	31.0%	0.161
	-0.350°	31.1%	0.162	-0.490°	31.1%	0.162
3.0	-0.329°	35.2%	0.189	-0.459°	35.5%	0.191
	-0.328	35.4%	0.190	-0.459°	35.5%	0.191
3.5	-0.321°	36.8%	0.199	-0.448°	37.1%	0.201
	-0.321°	36.8%	0.199	-0.449°	36.9%	0.200
5.0	-0.308°	39.4%	0.217	-0.431°	39.5%	0.218
	-0.310°	39.0%	0.216	-0.433°	39.2%	0.216
10.0	-0.302°	40.6%	0.226	-0.427°	40.0%	0.222
	-0.302°	40.6%	0.226	-0.427°	40.0%	0.222
24.0	-0.300°	40.9%	0.229	-0.421°	40.9%	0.228
	-0.302°	40.6%	0.226	-0.422°	40.7%	0.227

To determine the initial rate the reaction was repeated, and samples were taken at shorter reaction times. In a 25 mL volumetric flask, 12.5 mL of 0.0128 M bianthryl 1 stock solution (0.075 g, 0.159 mmol) was added to 1.25 mL of 0.128 M dibenzylmercury stock solution (0.0605 g, 0.159 mmol), and bromobenzene was added to make up the volume to 25 mL. The initial rotation of the reaction solution was determined, and ~1 mL samples of the above solution were transferred to each of 16 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (10 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 160°±0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table LII A (run 1). The reaction was repeated and the results for run 2 are summarized in Table LII B.

Table LII A. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 1 in Bromobenzene at 160°C (Run1).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	α_0-α	α_{546}	% Rac	α_0-α
0	-0.514°			-0.718°		
0.25	-0.464°	9.7%	0.050	-0.649°	9.6%	0.069
	-0.464°	9.7%	0.050	-0.649°	9.6%	0.069
0.50	-0.438°	14.8%	0.076	-0.612°	14.8%	0.106
	-0.438°	14.8%	0.076	-0.612°	14.8%	0.106
0.75	-0.414°	19.5%	0.100	-0.578°	19.5%	0.140
	-0.412°	19.8%	0.102	-0.576°	19.8%	0.142
1.00	-0.395°	23.2%	0.119	-0.552°	23.1%	0.196
	-0.395°	23.2%	0.119	-0.552°	23.1%	0.196
1.25	-0.378°	26.5%	0.136	-0.529°	26.3%	0.189
	-0.379°	26.3%	0.135	-0.528°	26.5%	0.190
1.50	-0.368°	28.4%	0.146	-0.514°	28.4%	0.204
	-0.368°	28.4%	0.146	-0.514°	28.4%	0.204
1.75	-0.359°	30.2%	0.155	-0.502°	30.1%	0.216
	-0.360°	29.9%	0.154	-0.502°	30.1%	0.216
2.00	-0.354°	31.1%	0.160	-0.494°	31.2%	0.224
	-0.354°	31.1%	0.160	-0.494°	31.2%	0.224

Table LII B. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 1 in Bromobenzene at 160°C (Run 2).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	α_0-α	α_{546}	% Rac	α_0-α
0	-0.512°			-0.718°		
0.25	-0.464° -0.464°	9.2% 9.2%	0.048 0.048	-0.651° -0.651°	9.3% 9.3%	0.067 0.067
0.50	-0.443° -0.443°	13.5% 13.5%	0.069 0.069	-0.621° -0.621°	13.5% 13.5%	0.097 0.097
0.75	-0.423° -0.423°	17.4% 17.4%	0.089 0.089	-0.593° -0.593°	17.4% 17.4%	0.125 0.125
1.00	-0.404° -0.404°	21.1% 21.1%	0.108 0.108	-0.562° -0.562°	21.7% 21.7%	0.156 0.156

(iv) Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 0.20

In a 25 mL volumetric flask, 12.5 mL of 0.0128 M bianthryl 1 stock solution (0.075 g, 0.159 mmol) was added to 5.0 mL of 0.0064 M dibenzylmercury stock solution (0.01210 g, 0.0318 mmol), and bromobenzene was added to make up the volume to 25 ml. The initial rotation of the reaction solution was determined, and ~2 mL samples of the above solution were transferred to each of 12 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (10 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 160°±0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table LIII.

Table LIII. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 0.20 in Bromobenzene at 160°C.

	λ/589 nm			λ/546 nm		
Time (h)	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	-0.508°			-0.712°		
1.0	-0.437°	13.9%	0.065	-0.613°	13.9%	0.065
	-0.438°	13.8%	0.064	-0.613°	13.9%	0.065
3.0	-0.426°	16.1%	0.076	-0.598°	16.0%	0.076
	-0.426°	16.1%	0.076	-0.598°	16.0%	0.076
6.0	-0.416°	18.1%	0.087	-0.582°	18.3%	0.087
	-0.417°	17.9%	0.086	-0.582°	18.3%	0.087
10.0	-0.416°	18.1%	0.087	-0.582°	18.3%	0.087
	-0.417°	17.9%	0.086	-0.582°	18.3%	0.087
12.0	-0.416°	18.1%	0.087	-0.582°	18.3%	0.087
	0.415°	18.3%	0.088	-0.582°	18.3%	0.087
24.0	-0.416°	18.1%	0.087	-0.582°	18.3%	0.087
	-0.416°	18.1%	0.087	-0.582°	18.3%	0.087

To determine the initial rate the reaction was repeated and samples were taken at shorter reaction times. In a 10 mL volumetric flask, 5.0 mL of 0.0128 M bianthryl 1 stock solution (0.030 g, 0.064 mmol) was added to 2.0 mL of 0.0064 M dibenzylmercury stock solution (0.0049 g, 0.0128 mmol), and bromobenzene was added to make up the volume to 10 mL. The initial rotation of the reaction solution was determined, and ~1 mL samples of the above solution were transferred to each of 10 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (10 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 160°±0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table LIV A (run 1). The reaction was repeated and the results for run 2 are summarized in Table LIV B.

Table LIV A. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 0.20 in Bromobenzene at 160°C (Run 1).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	-0.506°			-0.710°		
0.25	-0.491°	3.0%	0.0131	-0.689°	3.0%	0.0130
	-0.491°	3.0%	0.0131	-0.689°	3.0%	0.0130
0.50	-0.477°	5.7%	0.0256	-0.669°	5.8%	0.0258
	-0.477°	5.9%	0.0255	-0.668°	5.9%	0.0265
0.75	-0.463°	8.5%	0.0386	-0.649°	8.6%	0.0390
	-0.463°	8.5%	0.0386	-0.649°	8.6%	0.0390
1.00	-0.449°	11.3%	0.0519	-0.630°	11.3%	0.0520
	-0.449°	11.3%	0.0519	-0.630°	11.3%	0.0520
1.25	-0.435°	14.0%	0.0656	-0.611°	13.9%	0.0652
	-0.436°	13.8%	0.0646	-0.611°	13.9%	0.0652

Table LIV B. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 0.20 in Bromobenzene at 160°C (Run 2).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\alpha_0 - \alpha$	α_{546}	% Rac	$\alpha_0 - \alpha$
0	-0.506°			-0.710°		
0.25	-0.490°	3.2%	0.016	-0.688°	3.1%	0.022
	-0.490°	3.2%	0.016	-0.688°	3.1%	0.022
0.50	-0.476°	5.9%	0.030	-0.668°	5.9%	0.042
	-0.476°	5.9%	0.030	-0.668°	5.9%	0.042
0.75	-0.462°	8.7%	0.044	-0.648°	8.7%	0.062
	-0.462°	8.7%	0.044	-0.648°	8.7%	0.062
1.00	-0.448°	11.5%	0.058	-0.629°	11.4%	0.081
	-0.448°	11.5%	0.058	-0.629°	11.4%	0.081
1.25	-0.435°	14.0%	0.071	-0.610°	14.1%	0.100
	-0.435°	14.0%	0.071	-0.610°	14.1%	0.100

(v) Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 0.40.

In a 10 mL volumetric flask, 5 mL of 0.0128 M bianthryl 1 stock solution (0.030 g, 0.064 mmol) was added to 4.0 mL of 0.0064 M dibenzylmercury stock solution (0.0097 g, 0.0256 mmol), and bromobenzene was added to make up the volume to 10 mL. The initial rotation of the reaction solution was determined, and ~1 mL samples of the above solution were transferred to each of 10 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (10 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 160°±0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table LV A (run 1).

The reaction was repeated and the results for run 2 are summarized in Table LV B.

Table LV A. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 0.40 in Bromobenzene at 160°C (Run 1).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	-0.506°			-0.710°		
0.25	-0.477° -0.477°	5.7% 5.7%	0.0256 0.0256	-0.669° -0.669°	5.8% 5.8%	0.0258 0.0258
0.50	-0.457° -0.457°	9.7% 9.7%	0.0442 0.0442	-0.642° -0.642°	9.6% 9.6%	0.0440 0.0440
0.75	-0.439° -0.439°	13.2% 13.2%	0.0617 0.0617	-0.617° -0.617°	13.1% 13.1%	0.0610 0.0610
1.00	-0.424° -0.425°	16.2% 16.0%	0.0768 0.0758	-0.596° -0.596°	16.1% 16.1%	0.0760 0.0760
1.25	-0.417° -0.417°	17.6% 17.6%	0.0840 0.0840	-0.585° -0.585°	17.6% 17.6%	0.0841 0.0841

Table LV B. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 0.40 in Bromobenzene at 160°C (Run 2).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\alpha_0 - \alpha$	α_{546}	% Rac	$\alpha_0 - \alpha$
0	-0.506°			-0.710°		
0.25	-0.476°	5.9%	0.030	-0.668°	5.9%	0.042
	-0.476°	5.9%	0.030	-0.668°	5.9%	0.042
0.50	-0.456°	9.9%	0.050	-0.640°	9.9%	0.070
	-0.456°	9.9%	0.050	-0.640°	9.9%	0.070
0.75	-0.439°	13.2%	0.067	-0.616°	13.2%	0.094
	-0.439°	13.2%	0.067	-0.616°	13.2%	0.094
1.00	-0.424°	16.2%	0.082	-0.595°	16.2%	0.115
	-0.424°	16.2%	0.082	-0.595°	16.2%	0.115
1.25	-0.417°	17.6%	0.089	-0.585°	17.6%	0.125
	-0.417°	17.6%	0.089	-0.585°	17.6%	0.125

(vi) Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 0.133.

In a 10 mL volumetric flask, 5.0 mL of 0.0128 M bianthryl 1 stock solution (0.030 g, 0.064 mmol) was added to 1.33 mL of 0.0064 M dibenzylmercury stock solution (0.0033 g, 0.0085 mmol), and bromobenzene was added to make up the volume to 10 mL. The initial rotation of the reaction solution was determined, and ~1 mL samples of the above solution is transferred to each of 8 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (10 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 160°±0.1°C. To duplicate results, pairs of tubes were removed periodically and the optical rotations of the solutions were determined. The results are summarized in Table LVI A (run 1). The reaction was repeated and the results for run 2 are summarized in Table LVI B.

Table LVI A. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 0.133 in Bromobenzene at 160°C (Run 1).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	-0.506°			-0.711°		
0.25	-0.497°	1.8%	0.0078	-0.699°	1.7%	0.0074
	-0.497°	1.8%	0.0078	-0.699°	1.7%	0.0074
0.50	-0.489°	3.4%	0.0148	-0.687°	3.4%	0.0149
	-0.489°	3.4%	0.0148	-0.687°	3.4%	0.0149
0.75	-0.480°	5.1%	0.0229	-0.675°	5.1%	0.0226
	-0.480°	5.1%	0.0229	-0.675°	5.1%	0.0226
1.00	-0.472°	6.7%	0.0302	-0.663°	6.8%	0.0760
	-0.472°	6.7%	0.0302	-0.663°	6.8%	0.0760

Table LVI B. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 0.133 in Bromobenzene at 160°C (Run 2).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\alpha_0 - \alpha$	α_{546}	% Rac	$\alpha_0 - \alpha$
0	-0.506°			-0.710°		
0.25	-0.496° -0.496°	1.97% 1.97%	0.010 0.010	-0.696° -0.696°	1.97% 1.97%	0.014 0.014
0.50	-0.488° -0.488°	3.6% 3.6%	0.018 0.018	-0.684° -0.684°	3.7% 3.7%	0.026 0.026
0.75	-0.479° -0.479°	5.3% 5.3%	0.027 0.027	-0.672° -0.672°	5.4% 5.4%	0.038 0.038
1.00	-0.472° -0.472°	6.7% 6.7%	0.034 0.034	-0.662° -0.662°	6.8% 6.8%	0.048 0.048
1.25	-0.464° -0.464°	8.3% 8.3%	0.042 0.042	-0.651° -0.651°	8.3% 8.3%	0.059 0.059

(vii) Bianthryl 1 : $(PhCH_2)_2Hg$ = 2 : 1.

Ten mL of 0.0128 M bianthryl 1 stock solution (0.060 g, 0.128 mmol) was added to 0.02426 g (0.064 mmol) of dibenzylmercury. The initial rotation of the reaction solution was determined, and ~1 mL samples of the above solution were transferred to each of 10 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (10 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 160° ± 0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table LVII A (run 1).

The reaction was repeated and the results for run 2 are summarized in Table LVII B.

Table LVII A. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 2 : 1 in Bromobenzene at 160°C (Run 1).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	-1.018°			-1.428°		
0.25	-0.931° -0.931°	8.5% 8.5%	0.0388 0.0388	-1.308° -1.308°	8.4% 8.4%	0.0381 0.0381
0.50	-0.859° -0.860°	15.6% 15.5%	0.0737 0.0732	-1.210° -1.208°	15.3% 15.4%	0.0719 0.0727
0.75	-0.816° -0.816°	19.8% 19.8%	0.0961 0.0961	-1.146° -1.146°	19.7% 19.7%	0.0955 0.0955
1.00	-0.781° -0.781°	23.3% 23.3%	0.1151 0.1151	-1.095° -1.095°	23.3% 23.3%	0.1153 0.1153
1.25	-0.756° -0.756°	25.5% 25.5%	0.129 0.129	-1.064° -1.064°	25.5% 25.5%	0.128 0.128

Table LVII B. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 2 : 1 in Bromobenzene at 160°C (Run 2).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\alpha_0 - \alpha$	α_{546}	% Rac	$\alpha_0 - \alpha$
0	-1.021°			-1.430°		
0.25	-0.935°	8.4%	0.086	-1.310°	8.4%	0.120
	-0.935°	8.4%	0.086	-1.310°	8.4%	0.120
0.50	-0.864°	15.4%	0.157	-1.209°	15.5%	0.221
	-0.864°	15.4%	0.157	-1.209°	15.5%	0.221
0.75	-0.819°	19.8%	0.202	-1.145°	19.9%	0.285
	-0.818°	19.9%	0.203	-1.144°	20.0%	0.286
1.00	-0.761°	25.5%	0.260	-1.064°	25.6%	0.366
	-0.760°	25.6%	0.261	-1.063°	25.7%	0.367

(viii) Bianthryl 1: $(PhCH_2)_2Hg$ = 1.5 : 1.

In a 10 mL volumetric flask, 7.5 mL of 0.0128 M bianthryl **1** stock solution (0.0452 g, 0.096 mmol) was added to 0.5 mL of 0.128 M dibenzylmercury stock solution (0.0244 g, 0.064 mmol), and bromobenzene was added to make up the volume to 10 mL. The initial rotation of the reaction solution was determined, and ~1 mL samples of the above solution were transferred to each of 10 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (10 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 160° ± 0.1°C. To duplicate results, pairs of tubes were removed periodically and the optical rotations of the solutions were determined. The results are summarized in Table LVIII A (run 1).

The reaction was repeated and the results for run 2 are summarized in Table LVIII B.

Table LVIII A. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 1.5 : 1 in Bromobenzene at 160°C (Run 1).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	-0.768°			-1.073°		
0.25	-0.714°	7.0%	0.0317	-0.999°	6.9%	0.0310
	-0.715°	6.9%	0.0311	-0.999°	6.9%	0.0310
0.50	-0.670°	12.8%	0.0593	-0.936°	12.8%	0.0593
	-0.670°	12.8%	0.0593	-0.936°	12.8%	0.0593
0.75	-0.636°	17.2%	0.0820	-0.889°	17.2%	0.0817
	-0.635°	17.3%	0.0826	-0.888°	17.2%	0.0822
1.00	-0.610°	20.6%	0.1000	-0.850°	20.7%	0.101
	-0.611°	20.4%	0.0993	-0.850°	20.7%	0.101
1.25	-0.582°	24.2%	0.1204	-0.814°	24.1%	0.1199
	-0.582°	24.2%	0.1204	-0.814°	24.1%	0.1199

Table LVIII B. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 1.5 : 1 in Bromobenzene at 160°C (Run 2).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\alpha_0 - \alpha$	α_{546}	% Rac	$\alpha_0 - \alpha$
0	-0.769°			-1.074°		
0.25	-0.716°	6.9%	0.053	-0.999°	7.0%	0.075
	-0.716°	6.9%	0.053	-0.999°	7.0%	0.075
0.50	-0.671°	12.7%	0.098	-0.938°	12.7%	0.136
	-0.671°	12.87%	0.098	-0.937°	12.8%	0.137
0.75	-0.636°	17.3%	0.133	-0.887°	17.4%	0.187
	-0.635°	17.4%	0.133	-0.887°	17.4%	0.187
1.00	-0.611°	20.5%	0.158	-0.853°	20.6%	0.221
	-0.611°	20.5%	0.158	-0.853°	20.76%	0.221

(ix) Bianthryl 1 : $(PhCH_2)_2Hg$ = 0.75 : 1.

In a 10 mL volumetric flask, 3.75 mL of 0.0128 M bianthryl 1 stock solution (0.0225 g, 0.048 mmol) was added to 0.5 mL of 0.128 M dibenzylmercury stock solution (0.0244 g, 0.064 mmol), and bromobenzene was added to make up the volume to 10 mL. The initial rotation of the reaction solution was determined, and ~1 mL samples of the above solution were transferred to each of 10 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (10 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 160°±0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table LIX A.

The reaction was repeated and the results for run 2 are summarized in Table LIX B.

Table LIX A. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 0.75 : 1 in Bromobenzene at 160°C (Run 1).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	-0.388°			-0.541°		
0.25	-0.355° -0.354°	8.5% 8.7%	0.0386 0.0398	-0.494° -0.494°	8.7% 8.7%	0.0395 0.0395
0.50	-0.329° -0.330	15.2% 15.0%	0.0716 0.0703	-0.459° -0.460°	15.2% 15.0%	0.0714 0.0704
0.75	-0.311° -0.312°	19.8% 19.6%	0.0961 0.0947	-0.435° -0.435°	19.6% 19.6%	0.0947 0.0947
1.00	-0.295° -0.295°	24.0% 24.0%	0.1190 0.1190	-0.411° -0.411°	24.0% 24.0%	0.1194 0.1194
1.25	-0.285° -0.284°	26.5% 26.8%	0.1339 0.1355	-0.398° -0.389°	26.4% 26.6%	0.1333 0.1344

Table LIX B. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 0.75 : 1 in Bromobenzene at 160°C (Run 2).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\alpha_0 - \alpha$	α_{546}	% Rac	$\alpha_0 - \alpha$
0	-0.388°			-0.541°		
0.25	-0.355°	8.5%	0.033	-0.495°	8.5%	0.046
	-0.355°	8.5%	0.033	-0.495°	8.5%	0.046
0.50	-0.330°	14.9%	0.058	-0.461°	14.8%	0.080
	-0.331	14.8%	0.057	-0.461°	14.8%	0.080
0.75	-0.311°	19.8%	0.077	-0.434°	19.8%	0.107
	-0.311°	19.8%	0.077	-0.434°	19.8%	0.107
1.00	-0.284°	26.8%	0.104	-0.396°	26.8%	0.145
	-0.284°	26.8%	0.104	-0.396°	26.8%	0.145

(x) Bianthryl 1 : $(PhCH_2)_2Hg$ = 0.5 : 1.

In a 10 mL volumetric flask, 2.5 mL of 0.0128 M bianthryl 1 stock solution (0.0150 g, 0.032 mmol) was added to 0.5 mL of 0.128 M dibenzylmercury stock solution (0.0244 g, 0.064 mmol), and bromobenzene was added to make up the volume to 10 mL. The initial rotation of the reaction solution was determined, and ~1 mL samples of the above solution were transferred to each of 10 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (10 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 160°±0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotation of the solutions were determined. The results are summarized in Table LX A (run 1).

The reaction was repeated and the results for run 2 are summarized in Table LX B.

Table LX A. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 0.5 : 1 in Bromobenzene at 160°C (Run 1).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	-0.258°			-0.363°		
0.25	-0.233°	9.7%	0.0443	-0.327°	9.9%	0.0454
	-0.232°	10.1%	0.0461	-0.326°	10.2%	0.0467
0.50	-0.217°	15.9%	0.0752	-0.305°	16.0%	0.0757
	-0.217°	15.9%	0.0752	-0.305°	16.0%	0.0757
0.75	-0.202°	21.7%	0.1063	-0.284°	21.8%	0.1066
	-0.202°	21.7%	0.1063	-0.284°	21.8%	0.0166
1.00	-0.193°	25.2%	0.1260	-0.272°	25.1%	0.1250
	-0.194°	24.8%	0.1240	-0.272°	25.1%	0.1250
1.25	-0.187°	27.5%	0.1398	-0.263°	27.5%	0.1399
	-0.187°	27.5%	0.1398	-0.263°	27.5%	0.1399

Table LX B. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 0.5 : 1 in Bromobenzene at 160°C (Run 2).

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\alpha_0 - \alpha$	α_{546}	% Rac	$\alpha_0 - \alpha$
0	-0.257°			-0.361°		
0.25	-0.233°	9.3%	0.024	-0.327°	9.4%	0.034
	-0.233°	9.3%	0.024	-0.327°	9.4%	0.034
0.50	-0.216°	15.9%	0.041	-0.305°	15.5%	0.056
	-0.217°	15.7%	0.040	-0.304°	15.8%	0.057
0.75	-0.201°	21.8%	0.056	-0.282°	21.9%	0.079
	-0.202°	21.7%	0.057	-0.283°	21.6%	0.078
1.00	-0.186°	27.6%	0.071	-0.261°	27.7%	0.100
	-0.186°	27.6%	0.071	-0.261°	27.7%	0.100

(xi) Bianthryl 1 : $(PhCH_2)_2Hg$ = 2 : 5.

Ten mL of 0.0128 M bianthryl 1 stock solution (0.060 g, 0.128 mmol) was added to 0.1213 (0.32 mmol) of dibenzylmercury. The initial rotation of the reaction solution was determined, and ~1 mL samples of the above solution were transferred to each of 10 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (10 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 160° ± 0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table LXI.

Table LXI. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 2 : 5 in Bromobenzene at 160°C.

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	α_0-α	α_{546}	% Rac	α_0-α
0	-1.018°			-1.424°		
0.25	-0.837°	17.8%	0.181	-1.170°	17.8%	0.254
	-0.836°	17.9%	0.181	-1.169°	17.9%	0.255
0.50	-0.717°	29.6%	0.301	-1.002°	29.6%	0.422
	-0.717°	29.6%	0.301	-1.002°	29.6%	0.422
0.75	-0.639°	37.2%	0.379	-0.897°	37.0%	0.527
	-0.637°	37.4%	0.381	-0.897°	37.0%	0.527
1.00	-0.581°	42.9%	0.437	-0.819°	42.5%	0.605
	-0.582°	42.8%	0.436	-0.819°	42.5%	0.605
1.25	-0.538°	47.2%	0.480	-0.760°	46.7%	0.664
	-0.539°	47.1%	0.479	-0.750°	46.7%	0.665

(xii) Bianthryl 1 : $(PhCH_2)_2Hg$ = 1.5 : 5.

In a 10 mL volumetric flask, 7.5 mL of 0.0128 M bianthryl 1 stock solution (0.045 g, 0.0956 mmol) was added to 2.5 mL of 0.128 M (0.1218 g, 0.32 mmol) of dibenzylmercury stock solution. The initial rotation of the reaction solution was determined, and ~1 mL samples of the above solution were transferred to each of 10 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (10 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 160°±0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table LXII.

Table LXII. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 1.5 : 5 in Bromobenzene at 160°C.

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	α_0-α	α_{546}	% Rac	α_0-α
0	-0.768°			-1.073°		
0.25	-0.618°	19.5%	0.150	-0.865°	19.4%	0.208
	-0.617°	19.7%	0.151	-0.864°	19.5%	0.209
0.50	-0.524°	31.8%	0.244	-0.736°	31.4%	0.337
	-0.525°	31.8%	0.243	-0.735°	31.5%	0.338
0.75	-0.453°	41.0%	0.315	-0.637°	40.6%	0.436
	-0.454°	10.9%	0.314	-0.636°	40.7%	0.436
1.00	-0.413°	46.2%	0.355	-0.580°	45.9%	0.493
	-0.413°	46.2%	0.355	-0.580°	45.9%	0.493
1.25	-0.392°	48.9%	0.376	-0.552°	48.6%	0.521
	-0.392°	48.8%	0.375	-0.552°	48.6%	0.521

(xiii) Bianthryl 1 : $(PhCH_2)_2Hg$ = 0.75 : 5.

In a 10 mL volumetric flask, 3.75 mL of 0.0128 M bianthryl 1 stock solution (0.0225 g, 0.0480 mmol) was added to 2.5 mL of 0.128 M (0.1218 g, 0.32 mmol) of dibenzylmercury stock solution. Bromobenzene was added to make up the volume to 10 mL. The initial rotation of the reaction solution was determined, and ~1 mL samples of the above solution were transferred to each of 10 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (10 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 160° ± 0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table LXIII.

Table LXIII. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 0.75 : 5 in Bromobenzene at 160°C.

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	α_0-α	α_{546}	% Rac	α_0-α
0	-0.402°			-0.560°		
0.25	-0.321°	20.1%	0.081	-0.448°	20.0%	0.112
	-0.322°	19.9%	0.080	-0.449°	19.8%	0.111
0.50	-0.254°	36.8%	0.148	-0.356°	36.4%	0.258
	-0.255°	36.6%	0.147	-0.357°	36.3%	0.257
0.75	-0.216°	46.3%	0.186	-0.302°-	46.1%	0.258
	-0.217°	46.0%	0.185	0.303°	45.9%	0.257
1.00	-0.207°	48.5%	0.195	-0.290°	48.2%	0.270
	-0.207°	48.5%	0.195	-0.290°	48.2%	0.270
1.25	-0.144°	64.2%	0.258	-0.204°	63.6%	0.356
	-0.145°	64.9%	0.257	-0.203°	63.8%	0.357

(xiv) Bianthryl 1 : $(PhCH_2)_2Hg$ = 0.5 : 5.

In a 10 mL volumetric flask, 2.5 mL of 0.0128 M bianthryl 1 stock solution (0.015 g, 0.0320 mmol) was added to 2.5 mL of 0.128 M (0.1218 g, 0.320 mmol) of dibenzylmercury stock solution. Bromobenzene was added to make up the volume to 10 mL. The initial rotation of the reaction solution was determined, and ~1 mL samples of the above solution were transferred to each of 10 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (10 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 160° ± 0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table LXIV.

Table LXIV. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 0.5 : 5 in Bromobenzene at 160°C.

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	α_0-α	α_{546}	% Rac	α_0-α
0	-0.256°			-0.360°		
0.25	-0.194°	24.2%	0.062	-0.275°	23.6%	0.085
	-0.195°	23.8%	0.061	-0.276°	23.4%	0.084
0.50	-0.158°	38.3%	0.098	-0.222°	38.3%	0.138
	-0.158°	38.3%	0.098	-0.222°	38.3%	0.138
0.75	-0.134°	47.7%	0.122	-0.188°	47.8%	0.172
	-0.133°	48.0%	0.123	-0.187°	48.1%	0.173
1.00	-0.121°	52.7%	0.135	-0.171°	52.5%	0.189
	-0.120°	53.1%	0.136	-0.170°	52.8%	0.190
1.25	-0.110°	57.0%	0.146	-0.156°	56.7%	0.204
	-0.111°	56.6%	0.145	-0.157°	56.4%	0.203

(xv) Recovery of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) from the Reaction with 10 equivalents of $(PhCH_2)_2Hg$ in Bromobenzene at 160°

In a 25 mL volumetric flask, 12.5 mL of 0.0128 M bianthryl 1 stock solution (0.075 g, 0.159 mmol, $[\alpha]_{589}$ = -151.1°) was added to

12.5 mL of 0.128 M dibenzylmercury stock solution (0.605 g, 1.59 mmol). The initial rotation of the reaction solution was measured (α_{589} = -0.506°), and the solution was transferred to a racemization tube and degassed by the freeze pump thaw process. The tube was sealed under a nitrogen pressure of 100 torr. The tube was heated at 160°±0.1°C in a Haake constant temperature bath. After 10 h the tube was removed, and the rotation of the reaction solution was determined (α_{589} = -0.132°, 73.9% racemized). The solution was filtered to recover 0.3185 g (99.5% recovery) of Hg^0. Bromobenzene was distilled (35°C, 1 torr), and the residue was chromatographed on a column (silica gel/benzene) to recover 0.2046 g (70.7%) of bibenzyl and a yellow band containing the bianthryl **1**. The yellow band was purified by preparative TLC (silica gel, 1000 μ, 1:1 benzene-hexanes, 3 developments) to recover 0.0286 g (38.1% recovery) of racemized bianthryl **1**, $[\alpha]_{589}$ = -42.0° (72.2% racemized).along with 0.0106 g and 0.0096 g of unidentified products.

(xvi).Effect of Phenylthiol on the Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the Presence of $(PhCH_2)_2Hg$ at 160° in Bromobenzene

A solution containing bianthryl **1** : $(PhCH_2)_2Hg$: PhSH = 1 : 5 : 10 was prepared as follows: In a 10 mL volumetric flask, 5 mL of 0.0128 M bianthryl 1 stock solution (0.030 g, 0.064 mmol) and 2.5 mL of 0.128 M dibenzylmercury stock solution (0.1218 g, 0.320 mmol) was added to 0.0703 g (0.640 mmol) of phenyl thiol.

Bromobenzene was added to make up the volume to 10 mL. The initial rotation of the reaction solution was measured, and the solution was transferred to 4 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under a nitrogen pressure of 100 torr. The tubes were placed in a Haake constant temperature bath pre-heated to 160° ± 0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the reaction solution were determined. The results are summarized in Table LXV.

Table LXV. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$: PhSH = 1 : 5 : 10 in Bromobenzene at 160°C.

Time	λ/589 nm		λ/546 nm	
(h)	α_{589}	% Rac	α_{546}	% Rac
0	-0.498°		-0.698°	
2	-0.498° -0.498°	0 0	-0.698° -0.698°	0 0
24	-0.498° -0.498°	0 0	-0.698° -0.698°	0 0

(xvii). Effect of Dicyclohexylphosphine (DCHP) on the Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the Presence of $(PhCH_2)_2Hg$ at 160° in Bromobenzene

A solution containing bianthryl 1 : $(PhCH_2)_2Hg$: DCHP = 1 : 5 : 20 was prepared as follows: In a 10 mL volumetric flask, 5 mL of 0.0128 M bianthryl 1 stock solution (0.030 g, 0.064 mmol) and 2.5 mL of 0.128 M dibenzylmercury stock solution (0.1218 g, 0.320 mmol) was added to 0.254 g (1.28 mmol) of DCHP. Bromobenzene was added to make up the volume to 10 mL. The initial rotation of the reaction solution was measured, and the solution was transferred under nitrogen, using a syringe to 4 racemization tubes which contained a side arm for a septum inlet. The tubes were degassed by the freeze pump thaw process and sealed under a nitrogen pressure of 100 torr. The tubes were placed in a Haake constant temperature bath pre-heated to 160° ± 0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the reaction solution were determined. The results are summarized in Table LXVI.

Table LXVI. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$: DCHP = 1 : 5 : 20 in Bromobenzene at 160°C.

Time	λ/589 nm		λ/546 nm	
(h)	α_{589}	% Rac	α_{546}	% Rac
0	-0.434°		-0.608°	
1	-0.428°	1.4%	-0.601°	1.2%
	-0.428°	1.4%	-0.610°	1.2%
15	-0.428°	1.4%	-0.601°	1.2%
	-0.428°	1.4%	-0.601°	1.2%

(xviii).Effect of Oxygen on the Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the Presence of $(PhCH_2)_2Hg$ at 160° in Bromobenzene

A solution containing bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 5 was prepared as follows: in a 10 mL volumetric flask, 5 mL of 0.0128 M bianthryl 1 stock solution (0.030 g, 0.064 mmol, $[\alpha]_{589}$=-153.4°) was added to 2.5 mL of 0.128 M dibenzylmercury stock solution (0.1218 g, 0.320 mmol), and bromobenzene was added to make up the volume to 10 mL. The initial rotation of the reaction solution was measured, and the solution was transferred to a racemization tube. The tube was degassed by the freeze pump thaw process and flushed with oxygen. The tube was sealed under an oxygen pressure corresponding to atmospheric pressure. The tube was heated in a

Haake constant temperature bath at 160° ± 0.1°C. After 12 h, the reaction solution was dark, and its rotation could not be measured. The reaction solution was worked up to recover the bianthryl 1 as follows: bromobenzene was distilled (35°C, 1 torr), and the residue was purified by preparative TLC (silica gel, 1:1 benzene-chloroform) to recover 0.0182 g (60.7% recovery) of partially racemized bianthryl 1. The specific rotations were calculated and are summarized in Table LXVII.

Table LXVII. Effect of Oxygen on the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 5 in Bromobenzene at 160°C.

Time	λ/589 nm		λ/546 nm	
(h)	$[\alpha]_{589}$	% Rac	$[\alpha]_{546}$	% Rac
0	-153.4°		-220.7°	
12	-56.9°	62.9%	-83.4°	62.2%

(xix).Effect of Triphenylmethane on the Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the Presence of $(PhCH_2)_2Hg$ at 160° in Bromobenzene

A solution containing bianthryl 1 : $(PhCH_2)_2Hg$: Ph_3CH = 1 : 5 : 20 was prepared as follows: 10 mL of 0.0128 M bianthryl 1 stock solution (0.060 g, 0.128 mmol, $[\alpha]_{589}$=-153.4°) and 5 mL of 0.128 M dibenzylmercury stock solution (0.2436 g, 0.640 mmol) were added to 0.6198 g (2.55 mmol) of Ph_3CH. Bromobenzene was added to make up the volume to 20 mL. The initial rotation of the reaction solution was measured, and 10 mL of the solution was transferred to two racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under a nitrogen pressure of 100 torr. The tubes were heated in a Haake constant temperature at 160°±0.1°C. Tubes were removed after 1 and 15 h. The reaction solution was dark, and its rotation could not be measured. The reaction solution was worked up to recover bianthryl **1** as follows: bromobenzene was distilled (35°C, 1 torr), and the residue was purified by column chromatography (silica gel, chloroform) followed by preparative TLC (silica gel, 1:1 benzene-chloroform) to recover partially racemized bianthryl **1** (0.0221 g, 73.7% recovery after 1 h of heating and 0.0229 g, 76.3% recovery after 15 h of heating). The specific rotations were calculated and are summarized in Table LXVIII.

Table LXVIII. Effect of Triphenylmethane on the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 5 in Bromobenzene at 160°C.

Time	λ/589 nm		λ/546 nm	
(h)	$[\alpha]_{589}$	% Rac	$[\alpha]_{546}$	% Rac
0	-153.4°		-220.7°	
1	-97.9°	32.2%	-140.9°	32.2%
15	-97.8°	32.2%	-140.8°	32.2%

21. Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the presence of Dibenzylmercury at 130°±0.1°C in Bromobenzene.

(i). Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 5.

In a 50 mL volumetric flask, 25 mL of 0.0128 M bianthryl 1 stock solution (0.150 g, 0.320 mmol) was added to 12.5 mL of 0.128 M dibenzylmercury stock solution (0.606 g, 1.594 mmol), and bromobenzene was added to make up the volume to 50 mL. The initial rotation of the reaction solution was determined, and ~1 mL samples of the above solution were transferred to 26 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under a nitrogen pressure of 100 torr. The tubes were heated in a Haake constant temperature bath at 130°±0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solution were determined. The results are summarized in Table LXIX.

Table LXIX. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 5 in Bromobenzene at 130°C.

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	-0.509°			-0.711°		
1	-0.464°	8.8%	0.0402	-0.650°	8.6%	0.0390
	-0.464°	8.8%	0.0402	-0.650°	8.6%	0.0390
2	-0.433°	14.9%	0.0702	-0.606°	14.8%	0.0698
	-0.433°	14.9%	0.0702	-0.606°	14.8%	0.0698
3	-0.408°	19.8%	0.0960	-0.570°	19.8%	0.0960
	-0.407°	20.0%	0.0970	-0.569°	19.9%	0.0970
5	-0.355°	30.3%	0.156	-0.500°	29.7%	0.153
	-0.355°	30.3%	0.156	-0.499°	29.8%	0.154
7	-0.311°	38.9%	0.214	-0.439°	38.3%	0.209
	-0.312°	38.7%	0.213	-0.439°	38.3%	0.209
10	-0.258°	49.3%	0.295	-0.361°	49.2%	0.294
	-0.259°	49.1%	0.293	-0.360°	49.4%	0.294
13	-0.228°	55.2%	0.349	-0.325°	54.3%	0.340
	-0.288°	55.2%	0.349	-0.325°	54.3%	0.340
16	-0.197°	61.3%	0.412	-0.282°	60.3%	0.402
	-0.197°	61.3%	0.412	-0.280°	60.6%	0.402
19.5	-0.162°	68.2%	0.497	-0.233°	67.2%	0.485
	-0.162°	68.2%	0.497	-0.233°	67.2%	0.485
26.0	-0.120°	76.4%	0.628	-0.173°	75.7%	0.614
	-0.120°	76.4%	0.628	-0.173°	75.7%	0.614
33.0	-0.120°	76.4%	0.628	-0.171°	75.9%	0.619
	-0.120°	76.4%	0.628	-0.171°	75.9%	0.619
55.0	-0.092°	81.9%	0.743	-0.132°	81.4%	0.731
	-0.092°	81.9%	0.743	-0.132°	81.4%	0.731
75.0	-0.085°	83.3%	0.777	-0.120°	83.1%	0.773
	-0.086°	83.1%	0.772	-0.119°	83.3%	0.776

(ii). Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 1.

In a 50 mL volumetric flask, 25 mL of 0.0128 M bianthryl 1 stock solution (0.150 g, 0.320 mmol) was added to 2.5 mL of 0.128 M dibenzylmercury stock solution (0.122 g, 0.320 mmol), and bromobenzene was added to make up the volume to 50 mL. The initial rotation of the reaction solution was determined, and ~1 mL samples of the above solution were transferred to 26 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under a nitrogen pressure of 100 torr. The tubes were heated in a Haake constant temperature bath at 130°±0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solution were determined. The results are summarized in Table LXX.

Table LXX. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 1 in Bromobenzene at 130°C.

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	-0.512°			-0.715°		
1	-0.499°	2.5%	0.011	-0.698°	2.3%	0.011
	-0.500°	2.3%	0.010	-0.697°	2.5%	0.011
2	-0.482°	5.9%	0.026	-0.679°	5.0%	0.022
	-0.482°	5.9%	0.026	-0.679°	5.0%	0.022
3	-0.474°	7.4%	0.034	-0.661°	7.6%	0.034
	-0.474°	7.4%	0.034	-0.661°	7.6%	0.034
5	-0.450°	12.1%	0.056	-0.633°	11.5%	0.053
	-0.450°	12.1%	0.056	-0.633°	11.5%	0.053
7	-0.428°	16.4%	0.078	-0.599°	16.2%	0.077
	-0.429°	16.2%	0.078	-0.598°	16.4%	0.078
10	-0.403°	21.3%	0.104	-0.566°	20.8%	0.101
	-0.401°	21.6%	0.106	-0.565°	21.0%	0.102
13	-0.379°	26.0%	0.131	-0.530°	25.9%	0.130
	-0.379°	26.0%	0.131	-0.530°	25.9%	0.130
16	-0.363°	29.1%	0.149	-0.507°	29.1%	0.149
	-0.362°	29.3%	0.151	-0.507°	28.8%	0.148
23	-0.314°	38.7%	0.212	-0.437°	38.9%	0.214
	-0.314°	38.7%	0.212	-0.437°	38.9%	0.214
30	-0.281°	45.1%	0.261	-0.391°	45.3%	0.262
	-0.281°	45.1%	0.261	-0.391°	45.3%	0.262
35	-0.264°	48.4%	0.288	-0.373°	47.8%	0.283
	-0.263°	48.6%	0.289	-0.373°	47.8%	0.283
55.0	-0.224°	56.3%	0.359	-0.321°	55.1%	0.348
	-0.225°	56.1%	0.357	-0.318°	55.5%	0.352
75.0	-0.208°	59.4%	0.391	-0.291°	59.3%	0.390
	-0.208°	59.4%	0.391	-0.291°	59.3%	0.390

(iii). Bianthryl **1** : $(PhCH_2)_2Hg$ = 1 : 0.20.

In a 50 mL volumetric flask, 25 mL of 0.0128 M bianthryl **1** stock solution (0.150 g, 0.320 mmol) was added to 10 mL of 0.0064 M dibenzylmercury stock solution (0.0244 g, 0.064 mmol), and bromobenzene was added to make up the volume to 50 mL. The initial rotation of the reaction solution was determined, and ~1 mL samples of the above solution were transferred to 26 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under a nitrogen pressure of 100 torr. The tubes were heated in a Haake constant temperature bath at 130°±0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solution were determined. The results are summarized in Table LXXI.

Table LXXI. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 0.20 in Bromobenzene at 130°C.

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	-0.510°			-0.712°		
1.0	-0.506°	0.78%	0.003	-0.706°	0.84%	0.004
	-0.506°	0.78%	0.003	-0.706°	0.84%	0.004
2.0	-0.501°	1.7%	0.008	-0.702°	1.4%	0.006
	-0.501°	1.7%	0.008	-0.702°	1.4%	0.006
5.0	-0.491°	3.7%	0.016	-0.686°	3.7%	0.016
	-0.491°	3.7%	0.016	-0.686°	3.7%	0.016
8.0	-0.479°	6.1%	0.027	-0.669°	6.0%	0.027
	-0.479°	6.1%	0.027	-0.669°	6.0%	0.027
10.0	-0.469°	8.0%	0.036	-0.654°	8.1%	0.037
	-0.469°	8.0%	0.036	-0.654°	8.1%	0.037
15.0	-0.454°	11.0%	0.051	-0.633°	11.1%	0.051
	-0.454°	11.0%	0.051	-0.633°	11.1%	0.051
20.5	-0.435°	14.7%	0.069	-0.609°	14.5%	0.068
	-0.435°	14.7%	0.069	-0.609°	14.5%	0.068
25.0	-0.423°	17.1%	0.081	-0.590°	17.1%	0.082
	-0.423°	17.1%	0.081	-0.590°	17.1%	0.082
30.0	-0.410°	19.6%	0.095	-0.572°	19.7%	0.095
	-0.410°	19.6%	0.095	-0.572°	19.7%	0.095
35.0	-0.399°	21.8%	0.107	-0.557°	21.8%	0.107
	-0.399°	21.8%	0.107	-0.557°	21.8%	0.107
50.5	-0.369°	27.6%	0.141	-0.515°	27.7%	0.141
	-0.369°	27.6%	0.141	-0.515°	27.7%	0.141
59.0	-0.358°	29.8%	0.154	-0.499°	29.9%	0.154
	-0.358°	29.8%	0.154	-0.499°	29.9%	0.154
83.0	-0.342°	32.9%	0.174	-0.476°	33.1%	0.175
	-0.342°	32.9%	0.174	-0.476°	33.1%	0.175

22. Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the presence of Dibenzylmercury at 100°±0.1°C in Bromobenzene.

The reaction solution with a molar ratio of bianthryl **1** : $(PhCH_2)_2Hg$ = 1 : 5 was prepared as follows. In a 10 mL volumetric flask, 5 mL of 0.0128 M bianthryl **1** stock solution (0.030 g, 0.064 mmol) was added to 2.5 mL of 0.128 M dibenzylmercury stock solution (0.1218 g, 0.320 mmol), and bromobenzene was added to make up the volume to 10 mL. The initial rotation of the reaction solution was determined, and ~2 mL samples of the above solution were transferred to each of 4 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (100 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 100°±0.1°C. Tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table LXXII.

Table LXXII. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 5 in Bromobenzene at 100°C.

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	-0.509°			-0.711°		
30	-0.401°	21.2%	0.104	-0.556°	21.8%	0.155
75	-0.322°	36.7%	0.199	-0.455°	36.0%	0.197
200	-0.176°	65.8%	0.466	-0.255°	64.1%	0.456
410	-0.091°	82.1%	0.747	-0.131°	82.0%	0.741

23. Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the presence of Dibenzylmercury at 50°±0.1°C in Bromobenzene.

The reaction solution, with a molar ratio of bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 5 was prepared as follows. In a 10 mL volumetric flask, 5 mL of 0.0128 M bianthryl 1 stock solution (0.030 g, 0.064 mmol) was added to 2.5 mL of 0.128 M dibenzylmercury stock solution (0.1218 g, 0.320 mmol), and bromobenzene was added to make up the volume to 10 mL. The initial rotation of the reaction solution was determined, and ~2 mL samples of the above solution were transferred to each of 4 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum

(100 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 50° ± 0.1°C. Tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table LXXIII.

Table LXXIII. Percent Racemization for the Reaction of Bianthryl 1 : $(PhCH_2)_2Hg$ = 1 : 5 in Bromobenzene at 50°C.

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	-0.507°			-0.711°		
288	-0.335°	33.9%	0.178	-0.474°	33.3%	0.176
435	-0.308°	39.3%	0.216	-0.431°	39.4%	0.217
620	-0.304°	40.0%	0.222	-0.432	39.2%	0.216
820	-0.290°	42.8%	0.243	-0.505°	41.8%	0.235

24. Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the presence of Diethylmercury at 50°±0.1°C in Bromobenzene.

The reaction solution, with a molar ratio of bianthryl 1 : $(CH_3CH_2)_2Hg$ = 1 : 5 was prepared as follows. In a 10 mL volumetric flask, 5 mL of 0.0128 M bianthryl 1 stock solution (0.030 g, 0.064 mmol) was added to 2.5 mL of 0.128 M diethylmercury stock solution (0.0735 g, 0.320 mmol), and bromobenzene was added to make up the volume to 10 mL. The initial rotation of the reaction solution was determined, and ~2 mL samples of the above solution were transferred to each of 4 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (100 torr). The tubes were placed in a Haake constant temperature bath pre-heated to 50° ± 0.1°C. Tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table LXXIV.

Table LXXIV. Percent Racemization for the Reaction of Bianthryl 1 : $(CH_3CH_2)_2Hg$ = 1 : 5 in Bromobenzene at 50°C.

Time	λ/589 nm		λ/546 nm	
(h)	α_{589}	% Rac	α_{546}	% Rac
0	+0.395°		+0.546°	
288	+0.387°	2.0%	+0.536°	1.8%
435	+0.387°	2.0%	+0.536°	1.8%
620	+0.381°	3.5%	+0.527°	3.5%
820	+0.364°	7.8%	+0.507°	7.1%

25. Thermal Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) at 50°±0.1°C in Bromobenzene.

In a 10 mL volumetric flask, 5 mL of 0.0128 M bianthryl 1 stock solution (0.030 g, 0.064 mmol) was diluted to 10 mL with bromobenzene. The initial rotation of the reaction solution was determined, and ~2 mL samples of the above solution were transferred to each of 3 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under vacuum (100 torr). The tubes were placed in a Haake constant temperature bath preheated to 50° ± 0.1°C. Tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table LXXV.

Table LXXV. Thermal Racemization of Bianthryl 1 in Bromobenzene at 50°C.

Time	λ/589 nm		λ/546 nm	
(h)	α_{589}	% Rac	α_{546}	% Rac
0	-0.507°		-0.711°	
435	-0.507°	0	-0.711°	0
620	-0.507°	0	-0.711°	0
1272	-0.507°	0	-0.711°	0

26. Preparation of Bis(*m*-fluorobenzyl)mercury.

Magnesium metal (1.414 g, 0.0582 mol) was placed in a 500 mL 3-neck flask fitted with a reflux condenser and a pressure equalizing addition funnel. The flask was evacuated and flushed with nitrogen using a 3-way stop-cock connected to a vacuum pump and a nitrogen balloon. *m*-Fluorobenzylbromide (10 g, 6.5 mL, 0.0529 mol) was dissolved in 50 mL anhyd. ether and stored in the addition funnel. One mL of this solution was added to the 3-neck flask and the resulting mixture was stirred with a magnetic stirrer till the reaction mixture turned cloudy. After the reaction had started, the remainder of the *m*-fluorobenzylbromide solution was added dropwise at such a rate that the reaction mixture refluxed by itself (addition time ~45 min). After the addition was complete, the reaction mixture was refluxed with stirring for 0.5 h. A solution of $HgCl_2$ (7.1812 g, 0.0265 mol) in 100 mL ether was added dropwise and the reaction mixture was refluxed for 5 h. after the addition was completed. The reaction mixture was poured into 300 mL of 10% NH_4Cl solution and extracted with ether (3X 200 mL). The ether layer was washed with water followed by saturated NaCl solution and dried over anhydrous $MgSO_4$. The solution was filtered, and the solvent was evaporated to give 7.65 g of the crude product (mp 89°-93°C). The crude bis(*m*-fluorobenzyl)mercury was crystallized from hexanes to give 6.92 g (62.5%) of white crystals (mp 101°-102°C, lit.[90] 99°-101°C). The crystals were stored in an amber bottle in the dark. Bis(*m*-fluorobenzyl)mercury undergoes decomposition (turns brown) in the presence of light.

27. Racemization of Optically Active 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the Presence of Bis(*m*-fluorobenzyl)mercury at 160°±0.1°C in Bromobenzene.

0.128 M solution of bis(*m*-fluorobenzyl)mercury was prepared by dissolving 2.669 g (6.40 mmol) in 50 mL of bromobenzene. The reaction mixture, with a molar ratio of bianthryl **1** : (m-F-$C_6H_4CH_2)_2Hg$ = 1 : 5 was prepared in a 25 mL volumetric flask by adding 12.5 mL of 0.0128 M bianthryl **1** stock solution (0.075 g, 0.159 mmol) to 6.25 mL of 0.128 M (m-F-$C_6H_4CH_2)_2Hg$ stock solution (0.3349 g, 0.8 mmol). Bromobenzene was added to make up the volume to 25 mL. The initial rotation of the reaction solution were determined, and ~1 mL samples of the above solution were transferred to 25 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under a nitrogen pressure of 100 torr. The tubes were heated in a Haake constant temperature bath at 160° ± 0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table LXXVI.

Table LXXVI. Percent Racemization for the Reaction of Bianthryl 1 : $(m\text{-F-}C_6H_4CH_2)_2Hg$ = 1 : 5 in Bromobenzene at 160°C.

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	-0.498°			-0.696°		
0.5	-0.385% -0.385%	22.7% 22.7%	0.112 0.112	-0.536° -0.536°	22.9% 22.9%	0.113 0.113
1.0	-0.304° -0.304°	38.9% 38.9%	0.214 0.214	-0.426° -0.426°	38.3% 38.8%	0.213 0.213
1.5	-0.257° -0.257°	48.4% 48.4%	0.287 0.287	-0.359° -0.359°	48.4% 48.4%	0.287 0.287
2.0	-0.213° -0.213°	57.2% 57.2%	0.369 0.369	-0.298° -0.298°	57.2% 57.2%	0.368 0.368
3.0	-0.167° -0.167°	66.5% 66.5%	0.475 0.475	-0.234° -0.234°	66.4% 66.4%	0.473 0.473
4.0	-0.138° -0.138°	72.3% 72.3%	0.557 0.557	-0.195° -0.195°	72.0% 72.0%	0.553 0.553
5.0	-0.120° -0.120°	75.9% 75.9%	0.618 0.618	-0.169° -0.169°	75.7% 75.7%	0.615 0.515
6.0	-0.112° -0.112°	77.5% 77.5%	0.648 0.648	-0.156° -0.156°	77.6% 77.6%	0.649 0.649
7.0	-0.109° -0.109°	78.1% 78.1%	0.660 0.660	-0.153° -0.153°	78.0% 78.0%	0.658 0.658
8.0	-0.104° -0.104°	79.1% 79.1%	0.680 0.680	-0.145° -0.145°	79.2% 79.2%	0.681 0.681
10.0	-0.096° -0.096°	80.7% 80.7%	0.715 0.715	-0.134° -0.134°	80.7% 80.7%	0.716 0.716
12.0	-0.094° -0.094°	81.1% 81.1%	0.724 0.724	-0.131° -0.131°	81.2% 81.2%	0.725 0.725
24.0	-0.091° -0.091	81.7% 81.7%	0.738 0.738	-0.129° -0.129°	81.5% 81.5%	0.732 0.732
48.0	-0.092° -0.092°	81.5% 81.5%	0.733 0.733	-0.129° -0.129°	81.5% 81.5%	0.732 0.732

28. Racemization of Optically Active 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the Presence of Bis(*m*-fluorobenzyl)mercury at 130°±0.1°C in Bromobenzene.

(i) Bianthryl 1 : $(m\text{-F-}C_6H_4CH_2)_2Hg$ = 1 : 5

The reaction mixture with a molar ratio of bianthryl 1 : $(m\text{-F-}C_6H_4CH_2)_2Hg$ = 1 : 5 was prepared in a 25 mL volumetric flask by adding 12.5 mL of 0.0128 M bianthryl 1 stock solution (0.075 g, 0.159 mmol) to 6.25 mL of 0.128 M $(m\text{-F-}C_6H_4CH_2)_2Hg$ stock solution (0.3349 g, 0.8 mmol). Bromobenzene was added to make up the volume to 25 mL. The initial rotation of the reaction solution was determined, and ~1 mL samples of the above solution were transferred to 25 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under a nitrogen pressure of 100 torr. The tubes were heated in a Haake constant temperature bath at 130° ± 0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table LXXVII.

Table LXXVII. Percent Racemization for the Reaction of Bianthryl 1 : (m-F-$C_6H_4CH_2)_2Hg$ = 1 : 5 in Bromobenzene at 130°C.

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	-0.508°			-0.712°		
1.0	-0.490°	3.3%	0.016	-0.688°	3.4%	0.015
	-0.490°	3.3%	0.016	-0.688°	3.4%	0.015
3.0	-0.455°	10.4%	0.048	-0.639°	10.3%	0.047
	-0.455°	10.4%	0.048	-0.639°	10.3%	0.047
5.0	-0.420°	17.3%	0.083	-0.589°	17.3%	0.083
	-0.420°	17.3%	0.083	-0.589°	17.3%	0.083
7.0	-0.387°	23.8%	0.118	-0.542°	23.9%	0.118
	-0.388°	23.6%	0.117	-0.543°	23.7%	0.118
10.0	-0.356°	29.9%	0.154	-0.494°	30.6%	0.159
	-0.355°	30.1%	0.155	-0.496°	30.3%	0.158
15.0	-0.302°	40.6%	0.226	-0.423°	40.6%	0.226
	-0.302°	40.6%	0.226	-0.423°	40.6%	0.226
20.0	-0.252°	50.4%	0.304	-0.357°	49.9%	0.300
	-0.252°	50.4%	0.304	-0.357°	49.9%	0.300
25.0	-0.219°	56.9%	0.365	-0.310°	56.5%	0.361
	-0.219°	56.9%	0.365	-0.310°	56.5%	0.361
30.0	-0.182°	64.2%	0.446	-0.256°	64.0%	0.444
	-0.182°	64.2%	0.446	-0.256°	64.0%	0.444
45.0	-0.128°	74.8°	0.599	-0.181°	74.6%	0.595
	-0.127°	75.0%	0.602	-0.181°	74.6%	0.595
70.0	-0.077°	84.8%	0.818	-0.110°	84.6%	0.811
	-0.077°	84.8%	0.818	-0.110°	84.6%	0.811

(ii) Bianthryl 1 : $(m\text{-F-}C_6H_4CH_2)_2Hg$ = 1 : 1

The reaction mixture with a molar ratio of bianthryl **1** : $(m\text{-F-}C_6H_4CH_2)_2Hg$ = 1 : 1 was prepared in a 25 mL volumetric flask by adding 12.5 mL of 0.0128 M bianthryl 1 stock solution (0.075 g, 0.159 mmol) to 1.25 mL of 0.128 M $(m\text{-F-}C_6H_4CH_2)_2Hg$ stock solution (0.0670 g, 0.160 mmol). Bromobenzene was added to make up the volume to 25 mL. The initial rotation of the reaction solution was determined, and ~1 mL samples of the above solution were transferred to 25 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under a nitrogen pressure of 100 torr. The tubes were heated in a Haake constant temperature bath at 130°±0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the solutions were determined. The results are summarized in Table LXXVIII.

Table LXXVIII. Percent Racemization for the Reaction of Bianthryl 1 : (m-F-$C_6H_4CH_2)_2Hg$ = 1 : 1 in Bromobenzene at 130°C.

Time (h)	λ/589 nm			λ/546 nm		
	α_{589}	% Rac	$\log\alpha_0/\alpha$	α_{546}	% Rac	$\log\alpha_0/\alpha$
0	-0.507°			-0.711°		
2.0	-0.499°	1.6%	0.007	-0.700°	1.6%	0.007
	-0.499°	1.6%	0.007	-0.700°	1.6%	0.007
4.0	-0.484°	4.5%	0.020	-0.680°	4.4%	0.019
	-0.484°	4.5%	0.020	-0.680°	4.4%	0.019
6.0	-0.469°	7.5%	0.034	-0.657°	7.5%	0.034
	-0.469°	7.5%	0.034	-0.657°	7.5%	0.034
10.0	-0.449°	11.4%	0.053	-0.629°	11.5%	0.053
	-0.449°	11.4%	0.053	-0.629°	11.5%	0.053
15.0	-0.409°	19.3%	0.093	-0.574°	19.3%	0.093
	-0.409°	19.3%	0.093	-0.574°	19.3%	0.093
21.0	-0.383°	24.5%	0.122	-0.534°	24.7%	0.124
	-0.383°	24.5%	0.122	-0.534°	24.7%	0.124
25.0	-0.364°	28.2%	0.144	-0.510°	28.3%	0.144
	-0.364°	28.2%	0.144	-0.510°	28.3%	0.144
35.0	-0.319°	37.1%	0.201	-0.449°	36.8%	0.200
	-0.320°	37.2%	0.200	-0.450°	36.8%	0.200
55.0	-0.256°	49.5%	0.297	-0.360°	49.4%	0.296
	-0.255°	49.7%	0.297	-0.359°	49.5%	0.297
76.0	-0.211°	58.4%	0.381	-0.296°	58.4%	0.381
	-0.211	58.4%	0.381	-0.296°	58.4%	0.381
104.0	-0.175°	65.5%	0.462	-0.245°	65.5%	0.463
	-0.175°	65.5%	0.462	-0.245°	65.5%	0.463

29. Effect of Phenylthiol on the Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (1) in the Presence of $(m\text{-F-}C_6H_4CH_2)_2Hg$ at 160° in Bromobenzene

A solution containing bianthryl **1** : $(m\text{-F-}C_6H_4CH_2)_2Hg$: PhSH = 1 : 5 : 10 was prepared as follows: In a 10 mL volumetric flask, 5 mL of 0.0128 M bianthryl **1** stock solution (0.030 g, 0.064 mmol) and 2.5 mL of 0.128 M $(m\text{-F-}C_6H_4CH_2)_2Hg$ stock solution (0.134 g, 0.320 mmol) was added to 0.0703 g (0.640 mmol) of phenyl thiol. Bromobenzene was added to make up the volume to 10 mL. The initial rotation of the reaction solution was measured, and the solution was transferred to 4 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under a nitrogen pressure of 100 torr. The tubes were placed in a Haake constant temperature bath pre-heated to 160° ± 0.1°C. To duplicate results, pairs of tubes were removed periodically, and the optical rotations of the reaction solution were determined. The results are summarized in Table LXXIX.

Table LXXIX. Percent Racemization for the Reaction of Bianthryl 1 : $(m\text{-F-C}_6H_4CH_2)_2Hg$: PhSH = 1 : 5 : 10 in Bromobenzene at 160°C.

Time	λ/589 nm		λ/546 nm	
(h)	α_{589}	% Rac	α_{546}	% Rac
0	-0.498°		-0.698°	
2	-0.498°	0	-0.698°	0
	-0.498°	0	-0.698°	0
24	-0.498°	0	-0.698°	0
	-0.498°	0	-0.698°	0

30. Preparation of Anhydro-2-hydromercuri-3-nitrobenzoic Acid.[108] To a warm solution of 20 g (0.50 mol) of NaOH in 200 mL of water was added 52.75 g (0.250 mol) of 3-nitrophthalic acid (99%, Aldrich Chemical Company, Milwaukee, Wisconsin 53233). A small amount of insoluble material was removed by vacuum filtration. A solution of 87.64 g (0.275 mol) of $Hg(OAc)_2$ was prepared in 20 mL acetic acid and 200 mL of water. Heating was required to dissolve the $Hg(OAc)_2$. Impurities were filtered off by hot vacuum filtration. The two hot solutions were poured into a 1-L round bottom flask fitted with a reflux condenser and a magnetic stirrer. The flask was immersed in an oil bath and the temperature was raised to 170°C over a period of 1 h. The reaction mixture was stirred at 170°C for 90 h. The evolution of CO_2 was monitored by a tube leading from the top of the condenser into a test-tube containing a solution of $BaCl_2$ in NaOH. After 90 h, evolution of CO_2 had ceased, and the reaction mixture was cooled to room temperature and filtered by suction. The product was washed with 50 mL of water followed by 50 mL of ethanol and allowed to air-dry under aspirator suction for 2 h to yield 80.7 g of a cream colored solid (89% yield).

31. Preparation of 2-Bromo-3-nitrobenzoic Acid. To a hot solution of 17 g NaOH in 500 mL water in a 1-L three neck flask was added crude anhydro-2-hydromercuri-3-nitrobenzoic acid (80.7 g, 0.222 mol) with stirring (magnetic stirrer). The flask was fitted with a reflux condenser and an addition funnel. The stirred reaction mixture was heated to reflux in an oil bath, and 30 mL of conc. HCl was added slowly through the addition funnel. Heating was discontinued, and 12 mL of glacial acetic acid was added dropwise through the addition funnel. A thick white precipitate formed. A solution of bromine was prepared by adding 34 g (0.33 mol) of NaBr and 20 mL of Br_2 in 50 mL of water. The bromine solution was added rapidly with continuous stirring. The white precipitate dissolved (if not, more bromine solution was added). The reaction solution was refluxed for 10 min, cooled and made alkaline by adding solid NaOH. At this point, $HgBr_2$ precipitated as a black paste. The solution was filtered with suction, and the filtrate was acidified with conc. HCl to precipitate 2-bromo-3-nitrobenzoic acid. The acid was extracted into 1:1 diethyl ether-ethylmethylether (3 X 200 mL).

The organic layer was washed with water followed by saturated NaCl and dried over anhyd. $MgSO_4$. The solution was filtered and the solvent was evaporated to give 41.9 g (79.9% based on 3-nitrophthalic acid) of 2-bromo-3-nitrobenzoic acid: mp 183-184°C. (lit.[109] 185°-187° C)

32. **Preparation of Methyl-2-Bromo-3-nitrobenzoate.** An ethereal solution of diazomethane was added dropwise to a stirred solution of 45 g (0.184 mol) of 2-bromo-3-nitrobenzoic acid in THF until the addition no longer resulted in the evolution of N_2 gas. Excess diazomethane was destroyed by adding several drops of acetic acid. The solvent was evaporated on a rotary evaporator to give 44.19 g (92.4%) of the crude ester. The crude ester was recrystalized from 400 mL of methanol to yield 29.46 g of crystals: mp 78-79°C (lit.[114] 81° C). The mother liquor was evaporated to 300 mL to yield an additional 12.36 g of the product: mp 78-79°C (lit.[114] 81° C). Total yield 87.5% : ^1H NMR(acetone d-6) δ 3.8 (s), δ 7.2-7.8 (m).

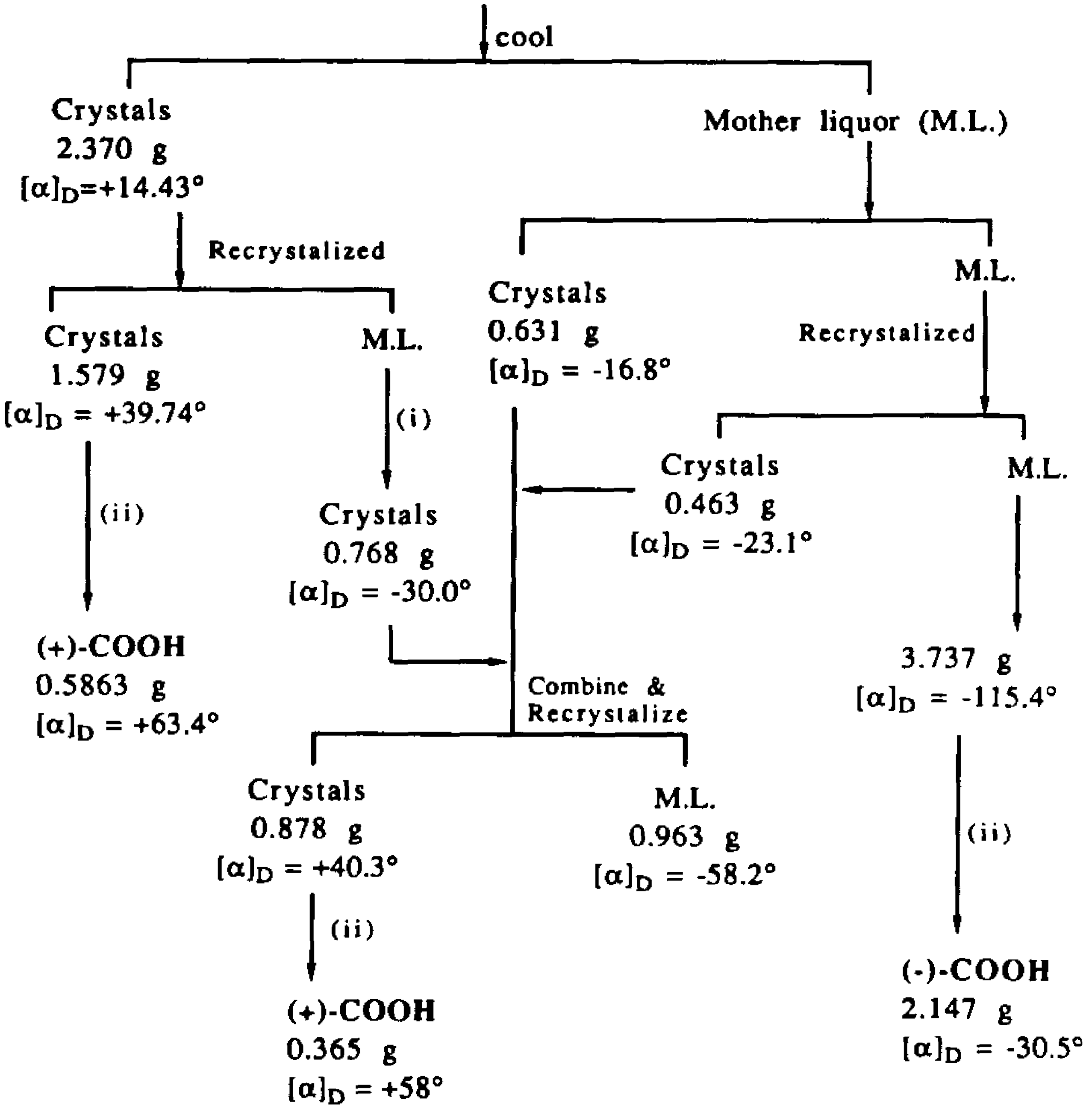
33. **Preparation of (±)-Methyl-2-α-naphthyl-3-nitrobenzoate (51a).** In a 100 mL 3-neck flask fitted with a reflux condenser, magnetic stirrer and a pressure equalizing addition funnel, was added 8.72 mL of α-naphthyl iodide (15.2 g, 59.7 mmol), 6.319 g of activated Cu powder[110] and 10 mL of nitrobenzene. A solution of 5.1723 g (19.9 mmol) of methyl-2-bromo-3-nitrobenzoate in 40 mL nitrobenzene was placed in the addition funnel. The top of the reflux condenser was connected via a 3-way stopcock to a vacuum pump and a nitrogen balloon. The flask was evacuate (oil pump) and flushed with nitrogen several times. The flask was

heated in an oil bath to reflux (bp of $PhNO_2$ is 210°C) with stirring and the solution of methyl-2-bromo-3-nitrobenzoate was added dropwise from the addition funnel over a period of 3 h. After the addition was complete, the reaction mixture was refluxed for an additional 1.5 h. The reaction flask was cooled to room temperature and filtered by suction to remove the Cu. The Cu was washed with acetone till the washings were clear (500-600 mL). Acetone was evaporated on a rotary evaporator, and the resulting solution was fractionally distilled under reduced pressure to remove $PhNO_2$ (bp 65°-70°C, 2.5 torr) and α-naphthyl iodide (bp 110°-115°C, 2.5 torr). The residue was purified by column chromatography (silica gel, 1:1 chloroform-hexanes) to give 3.95 g (64.8% yield based on methyl-2-bromo-3-nitrobenzoate) of product (**51 a**). The product was recrystalized 3 times from MeOH to a constant mp of 102°-102.5°C : ^1H NMR ($CDCl_3$) δ 3.3 (s), δ 8.16-7.29 (m); MS (EI^+) exact mass found 307.0853, calculated 307.08449.

34. Hydrolysis of (±)-Methyl-2-α-naphthyl-3-nitrobenzoate (51a). In a 100 mL round bottom flask, 2.264 g (7.4 mmol) of (±)-methyl-2-α-naphthyl-3-nitrobenzoate (**51a**) was mixed with 12.5 mL of water, 60 mL of acetic acid and 25 mL of H_2SO_4. The resulting mixture was refluxed for 5 h. The reaction mixture was cooled and extracted into ether. The ether layer was extracted with saturated Na_2CO_3 (3 X 25 mL). The basic layer was acidified with HCl and extracted with ether. The ether solution was washed with water, followed by saturated NaCl and dried over anhyd. $MgSO_4$. The solution was filtered, and the solvent was evaporated to yield 1.844 g of (±)-2-α-naphthyl-3-nitrobenzoic acid (**51 b**), mp 171-172°C; ^{1}H NMR (acetone-d6) δ 8.0-6.5 (m) .

35. Resolution of 2-α-Naphthyl-3-nitrobenzoic Acid (51b). A hot solution of 3.9332 g (0.0134 mol) of (±)-2-α-naphthyl-3-benzoic acid (**51b**) in 40 mL of acetone was added to a hot solution of 3.048 g of (-) quinine (0.700 equiv, 0.009 mol) in 100 mL of acetone. The mixture was treated according to Scheme XIII.

Scheme XIII. Resolution of 2-α-Naphthyl-3-nitrobenzoic Acid



(i). Evaporate.

(ii). The crystals were dissolved in 10% NaOH and quinine was extracted (3 X) with ether. The basic layer was acidified with HCl and the acid was extracted with ether.

36. Esterification of (+)-2-α-Naphthyl-3-nitrobenzoic Acid (51b). An ethereal solution of diazomethane was added dropwise with stirring to a solution of 0.586 g of (+)-2-α-naphthyl-3-nitrobenzoic acid (2.0 mmol, $[\alpha]_D$ = +63.4°) in ether until nitrogen evolution ceased The excess diazomethane was destroyed by the addition of acetic acid. The solvent was evaporated to yield 0.585 g of (+)-methyl-2-α-naphthyl-3-nitrobenzoate (**51a**) (95.2%): $[\alpha]_D$ = +93.9°; mp 79.5-80.5°C; NMR identical to the racemic sample.

The mp of optically active (+)-methyl-2-α-naphthyl-3-nitrobenzoate (**51a**) is less than that of the racemic sample (Table LXXX).

Table LXXX. Melting Points of Methyl-2-α-naphthyl-3-nitrobenzoate (51a)

51a	Melting Point
Racemic	102-102.5°C
$[\alpha]_D$ = +93.9°	79.5-80.5°C
$[\alpha]_D$ = -39.1°	74-101°C

Therefore, racemic methyl-2-α-naphthyl-3-nitrobenzoate (**51a**) is expected to be less soluble than the optically active form. This turned out to be the case. Partially resolved methyl-2-α-naphthyl-3-nitrobenzoate was optically enriched by recrystallization from methanol. (-)-Methyl-2-α-naphthyl-3-nitrobenzoate (**51a**) (2.289 g, $[\alpha]_D$ = -39.1°) was recrystallized from 75 mL of methanol to obtain

0.751 g of crystals, $[\alpha]_D = 0$ (mp 101-102°C). The mother liquor was evaporated to obtain 1.440 g of optically enriched methyl-2-α-naphthyl-3-nitrobenzoate (**51a**), $[\alpha]_D = -63.5°$ (mp 86.5°-88° C).

37 Reaction of (+)-Methyl-2-α-naphthyl-3-nitrobenzoate (51a) with KF/18-Crown-6 in Refluxing Acetonitrile (83°).

In a 100 mL 3-neck flask was placed 0.0997 g of (+)-methyl-2-α-naphthyl-3-nitrobenzoate (**51a**) (0.325 mmol, $[\alpha]_D = +93.9°$) and 0.0377 g of KF (0.649 mmol). The flask was fitted with a reflux condenser, 3-way stopcock, a septum inlet and a magnetic stirrer. The flask was evacuated using an oil pump and the 3-way stopcock and flushed with nitrogen (balloon) several times. A solution of 0.237 g of 18-crown-6 (0.974 mmol) in 45 mL of acetonitrile was added to the reaction flask via a syringe. The reaction mixture was heated to reflux in an oil bath with stirring. Aliquots of 15 mL each were syringed out after 25 h, 100 h and 240 h. Each aliquot was dissolved in 50 mL chloroform and extracted with water. The chloroform layer was dried over anhydrous $MgSO_4$, filtered and evaporated. The residue was chromatographed on a column (silica gel, chloroform) to remove 18-crown-6 and recover partially racemized methyl-2-α-naphthyl-3-nitrobenzoate (**51a**) (0.030 g after 25 h, 0.030 g after 100 h and 0.0224 g after 240 h). Total recovery was 0.0884 g (88.7%). The specific rotations of the recovered methyl-2-α-naphthyl-3-nitrobenzoate (**51a**) were measured in chloroform and are shown in Table LXXXI A (run 1).

The reaction was repeated and the results for run 2 are summarized in Table LXXXI B.

Table LXXXI A. Percentage Racemization of Methyl-2-α-naphthyl-3-nitrobenzoate (51a) in The Presence of KF/18-Crown-6 in Refluxing Acetonitrile (Run 1).

Time (h)	λ/589 nm			λ/546 nm		
	$[\alpha]_{589}$	% Rac	log α_0/α	$[\alpha]_{546}$	% Rac	log α_0/α
0	+93.9°			+116.6°		
25	+88.9°	5.3%	0.024	+110.3°	5.4%	0.024
100	+71.7°	23.6%	0.117	+88.2°	24.5%	0.121
240	+57.4°	38.9%	0.214	+70.3°	39.7%	0.220

Table LXXXI B. Percentage Racemization of Methyl-2-α-naphthyl-3-nitrobenzoate (51a) in The Presence of KF/18-Crown-6 in Refluxing Acetonitrile (Run 2).

Time (h)	λ/589 nm			λ/546 nm		
	$[\alpha]_{589}$	% Rac	log α_0/α	$[\alpha]_{546}$	% Rac	log α_0/α
0	+63.9°			+79.9°		
25	+60.6°	5.2%	0.023	+75.7°	5.3%	0.024
100	+52.1°	18.5%	0.089	+65.1°	18.5%	0.089
240	+39.0°	38.9%	0.214	+48.8%	38.9%	0.214

38 Thermal Racemization of (+)-Methyl-2-α-naphthyl-3-nitrobenzoate (51a) in Refluxing Acetonitrile.

In a 100 mL 3-neck fitted with a reflux condenser, a 3-way stopcock, and a magnetic stirrer was placed 0.115 g of (+)-methyl-2-α-naphthyl-3-nitrobenzoate (0.374 mmol, $[\alpha]_D$ = +93.9°). The flask was evacuated (oil pump) and flushed with nitrogen (balloon) using a 3-way stop cock several times. Dry acetonitrile (45 mL) was introduced in the flask using a syringe and the flask was heated to reflux with stirring in an oil bath. Aliquots of 15 mL each were syringed out after 75 h, 150 h and 240 h. The solvent was evaporated, and the residue dried under vacuum to recover (0.0331 g after 75 h, 0.0373 g after 150 h and 0.0362 g after 240 h) partially racemized **51a**. Total recovery 0.1066 g (92.3%). The specific rotations were measured and are summarized in Table LXXXII A (run 1). The reaction was repeated and the results from run 2 are summarized in Table LXXXII B.

Table LXXXII A. Thermal Racemization of Methyl-2-α-naphthyl-3-nitrobenzoate (51a) in Refluxing Acetonitrile (Run 1).

Time	λ/589 nm			λ/546 nm		
(h)	$[\alpha]_{589}$	% Rac	log α_0/α	$[\alpha]_{546}$	% Rac	log α_0/α
0	+93.9°			+116.6°		
75	+84.9°	9.5%	0.044	+105.4°	9.6%	0.043
150	+81.5°	13.2%	0.062	+100.5°	13.8%	0.065
240	+69.2°	26.3%	0.133	+85.8%	26.4%	0.133

Table LXXXII B. Thermal Racemization of Methyl-2-α-naphthyl-3-nitrobenzoate (51a) in Refluxing Acetonitrile (Run 2).

Time	λ/589 nm			λ/546 nm		
(h)	$[\alpha]_{589}$	% Rac	log α_0/α	$[\alpha]_{546}$	% Rac	log α_0/α
0	+93.9°			+116.6°		
75	+85.6°	8.8%	0.040	+106.3°	8.8%	0.040
150	+78.3°	16.6%	0.079	+97.2°	16.6%	0.079
240	+70.1°	25.3%	0.127	+87.0°	25.4%	0.127

39. Racemization of (+)-Methyl-2-α-naphthyl-3-nitrobenzoate (51a) in the Presence of Excess KF/0.16 M 18-Crown-6 in Acetonitrile at 100°C.

A solution of 0.54 g (1.76 mmol) of (+)-methyl-2-α-naphthyl-3-nitrobenzoate (**51a**) was prepared in 270 mL of 0.16 M 18-crown-6 (11.4195 g, 0.0432 mol, in acetonitrile). The above solution (15 mL each tube) was transferred to 18 racemization tubes, each containing ~0.1 g (2.38 mmol) of KF. The tubes were degassed by the freeze pump thaw process and sealed under a nitrogen pressure of 100 torr. The tubes were heated at 100°±0.1° in a Haake constant temperature bath. Tubes were removed periodically and worked up to recover partially racemized **51a** as follows: acetonitrile was evaporated, and the residue was dissolved in 25 mL chloroform and washed with water. The chloroform layer was dried over anhyd. $MgSO_4$, filtered and evaporated. The residue obtained was chromatographed on a column (silica gel, chloroform) to remove 18-crown-6 and recover partially racemized **51a** (0.501 g, 92.8% recovery). The specific rotations were measured and are summarized in Table LXXXIII. Each entry in the Table represents a different tube.

Table LXXXIII. Percentage Racemization of Methyl-2-α-naphthyl-3-nitrobenzoate (51a) in the Presence of Excess KF/0.16 M 18-Crown-6 in Acetonitrile at 100°C

Time (h)	$[\alpha]_D$	% Rac.	log $[\alpha]_0/[\alpha]$	avg. log $[\alpha]_0/[\alpha]$
0	+61.2°			
20	+47.4°	22.5%	0.111	
	+47.2°	22.9%	0.113	
	+46.9°	23.4%	0.116	0.113
70	+20.4°	66.7%	0.477	
	+23.9°	60.9%	0.408	
	+22.3°	63.6%	0.438	0.441
121	+14.9°	75.7%	0.614	
	+15.1°	75.3%	0.608	
	+16.6°	72.9%	0.567	
	+14.2°	76.8%	0.634	0.606
140	+10.4°	83.0%	0.770	
	+12.9°	78.9%	0.676	
	+12.5°	79.6%	0.690	
	+11.9°	80.6%	0.711	
	+10.4°	83.0%	0.770	0.723

40. Thermal Racemization of Methyl-2-α-naphthyl-3-nitrobenzoate (51a) in Acetonitrile at 100°±0.1°C.

A solution of 0.1925 g of methyl-2-α-naphthyl-3-nitrobenzoate (**51a**) was prepared in 60 mL of acetonitrile. Ten mL samples of this solution were transferred to 6 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under a nitrogen pressure of 100 torr. The tubes were heated at 100°±0.1°C in a Haake constant temperature bath. Tubes were removed periodically, and the solvent was evaporated to recover partially racemized **51a**. Total recovery was 99.8%. The specific rotations were measured and are summarized in Table LXXXIV.

Table LXXXIV. Thermal Racemization of Methyl-2-α-naphthyl-3-nitrobenzoate (51a) in Acetonitrile at 100°±0.1°C.

Time (h)	$[\alpha]_D$	% Rac	log $[\alpha]_0/[\alpha]$
0	-63.5°		
24	-51.2°	19.4%	0.094
48	-40.6°	36.1%	0.194
72	-35.0°	44.9%	0.259
96	-29.2°	54.0%	0.337
120	-23.4°	63.1%	0.434
145	-19.9°	68.7%	0.504

41. Thermal Racemization of Methyl-2-α-naphthyl-3-nitrobenzoate (51a) in 0.16 M 18-Crown-6 in Acetonitrile at 100°±0.1°C.

A solution of 0.120 g of methyl-2-α-naphthyl-3-nitrobenzoate (51a) ($[\alpha]_D$ = -106.9°) was prepared in 40 mL of 0.16 M 18- crown-6 (1.69 g, 6.4 mmol) in acetonitrile. Ten mL samples of this solution were transferred to 4 racemization tubes. The tubes were degassed by the freeze pump thaw process and sealed under a nitrogen pressure of

100 torr. The tubes were heated at 100°±0.1°C in a Haake constant temperature bath. Tubes were removed periodically, and the solvent was evaporated. The residue was chromatographed on a column (silica gel, chloroform) to remove 18-crown-6 and recover partially racemized **51a**. The specific rotation was measured and is summarized in Table LXXXV.

Table LXXXV. Thermal Racemization of Methyl-2-α-naphthyl-3-nitrobenzoate (51a) in 0.16 M 18-Crown-6 in Acetonitrile at 100°±0.1°C.

Time (h)	$[\alpha]_D$	% Rac	$\log [\alpha]_0/[\alpha]$
0	-106.9°		
20	-91.9°	14.0%	0.066
70	-64.0°	40.1%	0.223
120	-43.0°	59.8%	0.396
144	-35.4°	66.9%	0.479

References

1 For a listing of relatively stable Meisenheimer Complexes and their stability, see: (a) Strauss, M. J. *Chem. Rev.* **1970**, *70*, 667.(b) Terrier, F. *Chem. Rev.* **1982**, *82*, 77. (c) Artamkina, G. A.; Egorov, M. P.; Beletskaya, I. P. *Chem. Rev.* **1982**, *82*, 427.

2 For leading references see: Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Haper Row: New York, Second Ed. 1981.

3 Berliner, E. In *Progress in Organic Chemistry*; Cohen, S. G.; Streitweiser, A. Jr.; Trafts, R. W., Eds.; Interscience: New York, 1964, Vol 2, p253.

4 Bolton, R.; Williams, G. H.; *Chem. Soc. Rev.* **1986**, *15*, 261-289.

5 Perkins, J. M. In *Free Radicals*; Kochi, J. C. Ed.; Wiley-Interscience: New York, 1972; Vol II, Chapter 16.

6 Nonhebel, D. C.; Teddar, J. M.; Walton, J. C. In Radicals; Cambridge: New York, 1979.

7 (a) Convery, R. J.; Price, C. C. *J. Am. Chem. Soc.* **1958**, *80*, 4101. (b) Shih, C.; Hey, D. H.; Williams, G. H. *J. Chem. Soc.* **1959**, 1871. (c) Eliel, E. L.; Meyerson, S.; Welvart, Z.; Wilen, S. H. *J. Am. Chem. Soc.* **1960**, *82*, 2936. (d) Atkinson, D. J.; Perkins, M. J.; Ward, P. *J. Chem. Soc. C*, **1971**, 3240. (e) Dickerman, S. C.; Feigenbaum, W. M.; Fryd, M.; Milstein, N.; Vermount, G. B.; Zimmerman, I.; McOmie, J. F. *J. Am. Chem. Soc.* **1973**, *95*, 4624.

8 (a) Kaboyashi, M.; Minato, H.; Kobori, N. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2738. (b) Kamigata, N,; Minato, H.; Kabayashi, M. *ibid.* **1972**, *45*, 2042. (c) Henriquez, R.; Nonhebel, D.C. *Tetrahedron Lett.* **1975**, 3855 and 3857.

9 Minisci, F.; Vismara, E.; Fontana, F.; Morini, G.; Serrawalla, M.; Giordana, C. *J. Org. Chem.* **1987**, *52*, 730-736.

10 Sakurai, H.; Hosomi, A. *J. Am. Chem. Soc* **1971**, *93*, 1709.

11 Denny, D. B.; Klemchuk, P. P. *J. Am. Chem. Soc* **1958**, *80*, 3289.

12 Salteil, J.; Curtis, H. C. *J. Am. Chem. Soc* **1971**, *93*, 2056.

13 Kabayashi, M.; Usui, M.; Minato, H. *Chem. Lett.* **1976**, 121.

14 For leading references see: (a) Digregorio, S.; Yim, M. B.; Wood, D. E. *J. Am. Chem. Soc* **1973**, *95*, 8455. (b) Kurz, M.; Kovacia, P.; Bose, A. K.; Kugajevsky, I. *ibid.* **1968**, *90*, 1818. (c) *Organic Peroxides*; Swern, D., Ed., Wiley-Interscience, New York, Vol. II 1971. (d) see 8c.

15 For a brief discussion, see ref 5, p 256.

16 For example, see: (a) Farenhorst, E.; Kooyman, E. C. *Recl. Trav. Chim. Pays-Bas* **1962**, *81*, 816. (b) Beckwith, A. L. J.; Leydon, R. J. *Aust. J. Chem.* **1968**, *21*, 817.

17 Kuhn, R. In *Molekulare Asymmetric in Stereochemie;* Freudenberg, H., Ed., Franz Deutike: Leipzig-Wien, 1933, pp 803-824.

18 Christie, G. H.; Kenner, J. *J. Chem. Soc.* **1922**, *121*, 616.

19 (a) Adams, R.; Yuan, H. C. *Chem. Rev.* **1933**, *12*, 261. (b) Grundy, J. In *Stereochemistry*; Butterworths: Washington, D.C., 1964, Chapter 8. (c) Harris, M. M. *In Progress in Stereochemistry*; Klyne, W. de La Mare, P. B. D., Eds.; Butterwoths: Washington, D.C., 1958, Vol.2 Chapter 6. (d) Harris M. M.; Hall, D. M. *J. Chem. Soc.* **1960**, 490.

20. Eliel, E. L. In *Stereochemistry of Carbon Compounds*; McGraw Hill: New York, 1962, Chapter 6.

21 Adams, R.; Finger, G. C. *J. Am. Chem. Soc* **1939**, *61*, 2828.

22 Baddeley, G. *Nature*, **1946**, *157*, 694.

23 Oki, M; Yamamoto, G. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 266.

24 Harris, M. M.; Ling, C. K. *J. Chem. Soc.* **1964**, 1825.

25 Chein, S. L.; Adams, R. *J. Am. Chem. Soc* **1934**, *56*, 1787.

26 (a) Rieger, M.; Westheimer, F. H. *J. Am. Chem. Soc* **1950**, *72*, 19. (b) Westheimer, F. H. *In Calculations of the Magnitudes of Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; Wiley: New York, 1956, Chapter 2.

27 Aoki, M; Nakamura, M.; Oki, M. *Bull. Chem. Soc.* **1982**, *55*, 2512.

28 Yamamoto, G.; Suzuki, M.; Oki, M. *Chem. Lett.* **1980**, 1523

29 (a) Otsuka, S.; Mitsuhashi, T.; Oki, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3663. (b) Otsuka,S.; Yamamoto, G.; Mitsuhashi, T.; Oki, M. *ibid.*, **1980**, *53*, 2095. (c) Yamamoto, G.; Suzuki, M.; Oki, M. *ibid.*, **1983**, *56*, 809. (d) Yamamoto, G.; Suzuki, M.; Oki, M. *ibid.*, **1983**, *56*, 306.

30 Cotler, A. K.; Clemens, L. M. *J. Am. Chem. Soc.* **1965**, *87*, 847.

31 Mulliken, R. S.; Pearson, W. B. In *Molecular Complexes*; Wiley: New York, 1969.

32 Oto, O.; Hatano, M. *Chem. Lett.* **1976**, 39.

33 Hutchins, L. G.; Pincock, R. E. *J. Org. Chem.* **1980**, *45*, 2414.

34 Hutchins, L. G.; Pincock, R. E. *J. Cat.* **1982**, *45*, 295.

35 Hutchins, L. G.; Pincock, R. E. *J. Org. Chem.* **1982**, *47*, 607.

36 Pincock, R. E.; Johnson, W. M.; Haywood-Farmers, J. *Can. J.*

Chem. **1976**, *54*, 548.

37 Crawford, M.; Smyth, I. F. B. *J. Chem. Soc.* **1954**, 3464.

38 (a) Chen, C. H. Ph.D. Thesis, City University of New York, New York, NY. 1980. (b) Aria, P. S.; Chen, C. H.; Henshel, R. F., unpublished results.

39 Schwartz, L. H.; Aria, P. S.; Henshel, R. F. Presented at the 197th National Meeting of the American Chemical Society, Dallas, TX, April 1989; paper ORGN 203.

40 For a review, see: Rabideau, P. W. *Acc. Chem. Res.* **1978**, *11*, 141.

41 (a) Monostori, B. J.; Weber, A. J. *Mol. Spectrosc.* **1964**, *12*, 129. (b) Stidham, H. D. *Spectrochim. Acta.* **1965**, 21. (c) Laane. J.; Baurer, S.H. *J. Mol. Spectrosc.* **1971**, *39*, 340

42 (a) Oberhammer, H.; Baurer, S. H. *J. Am. Chem. Soc.* **1969**, *91*, 10. (b) Saebo, S.; Boggs, J. E. *J. Mol. Struct.* **1981**, *73*, 137. (c) Allinger, N. L. *Adv. Phy. Org. Chem.* **1976**, *13*, 1

43 (a) Paschal, J. W.; Rabideau, P. W. *J. Am. Chem. Soc.* **1974**, *96*, 372. (b) Rabideau, P. W.; Paschal, J. W.; Marshall, J. L. *J. Chem. Soc., Perkin Trans. 2*, **1977**, 842. (c) Grossel, M. C.; Perkins, M. J. *Nouv. J. Chim.* **1979**, *3*, 285.

44 (a) Ferrier, W. G.; Iball, J. *Chem. Ind. (London)*, **1954**, 1236. (b) Sygula, A.; Holak, T. A. *Tetrahedron Lett.* **1983**, *24*, 2893.

45 Dalling, D. K.; Zilm, K. W.; Grant, D. M.; Heeschen, W. A.; Horton, W. J.; Pugmire, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 4817.

46 Smith, W. B.; Shoulder, B. A. *J. Phy. Chem.* **1965**, *69*, 2022.

47 (a) Binkley, J. S.; Whiteside, R. A.; Harihara, P. C.; Seegar,; Pople, J. A. *QCPE*, **1979**, *14*, 368. (b) Binkley, J. S.; Pople, J. A.; Hehra, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

48 (a) Bringham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285. (b) Dewar, M. J. S.; Thiel, W. *ibid.* **1977**, *99*, 4899 and 4907.

49 (a) Boyd, D. B.; Lipkowitz, K. B. *J. Chem. Educ.* **1982**, *56*, 269. (b) Burkert, U.; Allinger, N. L. In *Molecular Mechanics*, American Chemical Society: Washington, DC, ASC Monograph No. 177. (c) For MM1, MMP1 and MM2 refer to emperical forse fields developed by Allinger, N. L. at the University of Georgia. These forse fields are available from the Quantum Chemistry Program Exchange, Dept. of Chem., Indiana University, Bloomington, IN 47405.

50 Lipkowitz, K. B.; Rabideau. P. W.; Raber, D. J.; Hardee, L. E.; Schleyer, P. v. R.; Kos, A. J.; Kahn, R. A. *J. Org. Chem.* **1982**, *47*, 1002.

51 Raber, D. J.; Hardee, L. E.; Rabideau, P. W.; Lipkowitz, *J. Am. Chem. Soc.* **1982**, *104*, 2843.

52 Dalling, D. K.; Zilm, K. W.; Grant, D. M.; Heeschen, W. A.; Horton, W. J.; Pugmire, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 4817.

53 Rabideau, P. W.; Mooney, J. L.; Lipkowitz, K. B. *J. Am. Chem. Soc.* **1986**, *108*, 8130.

54 (a) Brinkman, A. W.; Gordon, M.; Harvey, R. G.; Rabideau, P. W.; Strothers, J. B.; Terney, A. L. *J. Am. Chem. Soc.* **1970**, *92*, 5912. (b) Lapouyade, R.; Labandibar, P. *Tetrahedron Lett.* **1970**, 1589.

55 Daney, M.; Bouas-Laurent, H.; Calas, B.; Giral, L.; Platzer, N. *J. Organomet. Chem.* **1980**, *188*, 277.

56 Rabideau, P. W.; Wetzel, D. M.; Husted, C. A.; Lawrence, J. R. *Tetrahedron Lett.* **1984**, *25*, 31.

57 Sygula, A.; Rabideau, P. W. *J. Org. Chem.* **1987**, *52*, 3521.

58 Roberts, J. D.; Caserio, M. C. In *Modern Organic Chemistry*; W. A. Benjamin: New York, 1967, pp 560-562.

59 (a) Lowe, J. P.; Silverman, B. D. *J. Am. Chem. Soc.* **1981**, *103*, 2852. (b) Lowe, J. P.; Silverman, B. D. *Acc. Chem. Res.* **1984**, *17*, 332.

60 Lowe, J. P. In *Quantum Chemistry*; Academic; New York, 1978, pp 219-220.

61 Dickerman, S. C.; Feigenbaum, W. M.; Fryd, M.; Milstein, N.; Vermount, G. B.; Zimmerman, I.; McOmie, J. F. *J. Am. Chem. Soc.* **1973**, *95*,

62 Balabanov, E. Yn.; Kachurin, O. I.; Velichko, L. I. *Ukr. Khim. Zh.* **1987**, *53*(11), 1178, (Russ.); *Chemical Abstract*, **1987**, *109*, 210298r.

63 (a) Fields, E. K.; Meyerson, S. *J. Org. Chem.* **1967**, *32*. 3114.
(b) Louw, R.; Lucas, H. J. *Recl. Trav. Chim. Pays-Bas*, **1973**, *92*, 55.

64 (a) McBride, J. M.; *J. Am. Chem. Soc.* **1977**, *99*, 6760.
(b) Palm, V.; Hiob, R. *Org. React. (Tartu)*, **1981**, *18*, 152.

65 Kryger, R. G.; Lorand, J. P.; Stevens, N. R.; Herron, N.R. *J. Am. Chem. Soc.* **1977**, *99*, 7589.

66 Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 3609.

67 Louw, R.; Rothuizen, J. W. *Tetrahedron Lett.* **1967**, *39*, 3807.

68 Henriquez, R.; Morgan, A. R.; Mulholland, P.; Nonhebel, D. C.; Smith, G. C. *J. Chem. Soc.* **1974**, 987.

69 Fahr, A.; Stein, S. E. *J. Phys. Chem.* **1988**, *92*, 4951.

70 Fahr,A.; Mallard, W. G.; Stein, S. E. *Proc. 21st Int. Symp. Combust.*, Combust. Inst., Pittsburg, PA, 1987.

71 Arnoud, R.; Douady, J.; Subra, R. *Nouv. J. Chim.* **1981**, *5*, 1981, *Chemical Abstract*, **1981**, *95*, 42111d.

72 For a review, see: Engel, P. S. *Chem. Rev.* **1980**, 99.

73 (a) Porter, N. A.; Marnett, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 4361. (b) Porter, N. A.; Dubay, G. R.; Green, J. G. *ibid.* **1978**, *100*, 920.

74 Pryor, W. A.; Smith, K. J. *J. Am. Chem. Soc.* **1970**, *92*, 5403.

75 (a) Neuman, R. C., Jr.; Lockyer, G. D., Jr.; Amrich, M. J., Jr. *Tetrahedron Lett.* **1972**, 1221. (b) Neuman, R. C., Jr.; Lockyer, G. D., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 3982.

76 (a) Nozaki, K.; Bartlett, P. D. *J. Am. Chem. Soc.* **1946**, *68*, 1686. (b) Barnett, B.; Vaughan, W. E. *J. Phys. Chem.* **1947**, *51*, 926.

77 Bolton, R.; Dailly, B. N. Hirakubo, K.; Lee, K. H.; William, G. H. *J. Chem. Soc., Perkin Trans. 2*, **1981**, 1109.

78 Kurz, M.; Pellegrini, M. E. *J. Org. Chem.* **1970**, *35*, 995.

79 Roitt, I. M.; Waters, W. A. *J. Chem. Soc.* **1952**, 2695.

80 For a recent review, see: Barluenga, J.; Yus, M. *Chem. Rev.* **1988**, *88*, 487.

81 (a) Jackson, R. A. *J. Chem. Soc.* **1963**, 5284. (b) Jackson, R. A.; O'Neill, D. W. *J. Chem. Soc. D*, **1969**, 1210. (c) Jackson, R. A.; O'Neill, D. W. *J. Chem. Soc. Perkin Trans. 2*, **1978**, 509. (d) Agirbas, H.; Jackson, R. A. *J. Chem. Soc. Perkin Trans. 2*, **1983**, 739.

82 (a) Skinner, H. A. *Adv. Orgmet. Chem.* **1964**, *2*, 100. (b) Carter, H. V.; Chappel, E. I.; Warhurst, E. *J. Chem. Soc.* **1956**, 106.

83 O'Brien, J.; Gornick, F. *J. Am. Chem. Soc.* **1955**, *77*, 4757.

84 Hammond, G. S.; Ravve, A.; Modic, F. *Anal. Chem.* **1952**, 1373.

85 Davies, D. I.; Hey, D. H.; William, G. H. *J. Chem. Soc.* **1958**, 1878.

86 Jackson, R. A. *J. Chem. Soc. Chem., Commun.* **1974**, 573.

87 (a) Beckwith, A. L. J.; Waters, W. A. *J. Chem. Soc.* **1957**, 1001. (b) Bass, K. C.; Nabasing, P. *J. Chem. Soc.* **1965**, 4396.

88 Jackson, R. A.; O'Neill, D. W. *J. Chem. Soc., Perkin Trans. 2*, **1978**, 509.

89 Jackson, R. A.; Agirbas, H. *J. Chem. Soc., Perkin Trans. 2*, **1983**, 739.

90 Dincturk, S.; Jackson, R. A.; Townson, M.; Agirbas, H.; Billingham, N. C.; March, G. *J. Chem. Soc., Perkin Trans. 2*, **1981**, 1121.

91 Koukotas, C.; Schwartz, L. H. *J. Chem. Soc., Chem. Commun.* **1969**, 1400.

92 Henshel, R. H. Ph. D. Thesis, The City University of New York, New York, NY, 1990.

93 (a) Bunnett, J. F.; Zahler, R. E. *Chem. Rev.* **1951**, *49*, 273. (b) Bunnett, J. F. *Q. Rev. Chem. Soc.* **1958**, *12*, 1.

94 (a) Miller, J. In *Aromatic Nucleophilic Substitution*, Elsevier, London, 1968. (b) Pietra, F. *Q. Rev. Chem. Soc.* **1969**, *23*, 504.

95 Edwards, J. O.; Pearson, R. G. *J. Am. Chem. Soc.* **1962**, *84*, 16.

96 (a) Smid, J. *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 112. (b) Szwarc, M. In *Ions and Ion Pairs in Organic Reactions*; Wiley: New York, Vol. I and II 1972 and 1974. (c) Gutmann, V. *Chimia*, **1977**, *31*, 1.

97 Vogtle, F.; Weber, E. *Kontakte (Merk)*, **1977**, *1*, 11.

98 Lehn, J. M. *Pure Appl. Chem.* **1980**, *52*, 2303.

99 (a) Gokel, G. W.; Durst, H. D. *Synthesis*, **1976**, 168. (b) Knipe, A. C. *J. Chem. Ed.* **1976**, *53*, 618. (c) Yakobson, G. G.; Akhmatova, N. E. *Synthesis*, **1983**, 169.

100 Clark, J. H. *Chem. Rev.* **1980**, *86*, 429.

101 Liotta, C. L.; Harris, H. P. *J. Am. Chem. Soc.* **1974**, *96*, 2250.

102 (a) Vogtle, F.; Neumann, P. *Chemiker-Ztg.* **1973**, *97*, 600.
(b) Weber, E.; Vogtle, F. *Chem. Expt. Didakt*, **1976**, *2*, 115.

103 Jackson, C. J.; Gazzolo, F. H. *J. Am. Chem. Soc.* **1900**, *23*, 376.

104 Meisenheimer, J. *Justus Liebigs Ann. Chem.* **1902**, *323*, 205.

105 (a) Terrier, F. *Chem. Rev.* **1982**, *82*, 77. (b) Artamkina, G. A.; Egorov, M. P.; Beletskaya, I. P. *Chem. Rev.* **1982**, *82*, 427.

106 Yu, C. S. Ph. D. Thesis, The City University of New York, New York, NY, 1979.

107 (a) Hammond G.S. *J. Org. Chem.*, **1958**, *23*, 98. (b) Lankamp, H.; Nauta, W. Th.; Maclean, C. *Tetrahedron Lett.* **1968**, 249.
(c) McBridge, J. M. *Tetrahedron*, **1974**, 2209.

108 Whitmore, F. C.; Culhane, P. J.; Neher, H. J. *Organic Synthesis*; Wiley: New York, 1932, Coll. Vol. I, pp 56-58.

109 Culhane, P. J. *Organic Synthesis*; Wiley: New York, 1932, Coll. Vol. I, pp125-127.

110 Gibson,;Bailey . *J. Org. Chem.*, **1976**, *41*, 557.