CHEN, CHING HONG

RADICAL CATALYZED RACEMIZATION OF OPTICALLY ACTIVE 2,2'-DICARBOMETHOXY-9,9'-BIANTHRYL

City University of New York PH.D. 1980

RADICAL CATALYZED RACEMIZATION OF OPTICALLY ACTIVE 2,2'-DICARBOMETHOXY-9,9'-BIANTHRYL

By

Ching Hong Chen

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.

1980

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.

May 29, 1980
Date

Leonard H. Schwartz
Chairman of Examining Committee

June 5, 1980
Date

David C. Locke
Executive Officer

Herbert Meislich

Norman L Holman

Robert A. O'Leary
Supervisory Committee

The City University of New York

ABSTRACT

Radical Catalyzed Racemization of Optically Active 2,2'-Dicarbomethoxy-9,9'-bianthryl.

by

Ching Hong Chen

Mentor: Professor Leonard H. Schwartz

The racemization of optically active 2,2'-dicarbomethoxy-9,9'-bianthryl (Ia), in several media, has been studied. It was discovered that the racemization of Ia in the presence of oxygen or diphenyl disulfide or dibenzyl mercury or tert- butyl peroxide occurs more easily than in the absence of these substances. In the presence of oxygen, the rotation of a solution of Ia lost 87 % of its original value on heating at 148.8 ± 0.1° C for two hours. The starting material was recovered in 41 % yield from the heated material. This chemically unchanged Ia was 62 % racemized. In the presence of diphenyl disulfide, racemization occurred to the extent of 45 % after 96 hours heating at 197.0 ± 0.1° C. The chemically unchanged starting material was recovered in 78 % yield. It was 45 % racemized. In the presence of dibenzyl mercury, the degree of racemization was found to be 70 % after heating at 187.0 ± 0.1° C for two hours.

Eighty percent of the starting material was recovered. It was 72 % racemized. In the presence of tert- butyl peroxide, the degree of racemization was found to be 82.5 % after heating at 124.7 ± 0.1° C for 2.5 hours. Twenty five percent of the starting material was recovered. It was 41 % racemized.

In all the above systems, it was demonstrated that radicals initiated by these substances were the species which catalyzed the racemization of Ia. These include radicals derived from triglyme by autoxidation, radicals derived from hydrogen abstraction of triglyme by phenylthiyl radicals, benzyl radicals derived from the thermolysis of dibenzyl mercury and radicals derived from hydrogen abstraction of dimethyl suberate by oxygen-containing radicals (derived from tert-butyl peroxide) or by benzyl radicals.

It is postulated that the addition of a radical to Ia results in the formation of a 1,4-cyclohexadienyl radical complex (σ - complex). The boat conformation of this radical complex permits the two benzo-benzo interactions, during the rotation of the central bond (C_9-$C_{9'}$), to occur consecutively instead of simultaneously. The

rotational barrier is thus reduced. Therefore, racemization of the radical complex of Ia can occur more rapidly than in the case of Ia.

The recovery of chemically unchanged racemized Ia demonstrates that the addition of a radical to the aromatic ring of Ia is reversible. It is suggested that the observation of racemization of optically active biaryls would be a useful tool in a study of the reversibility of the first step of homolytic aromatic substitution reactions.

DEDICATION

To my wife,

Julie

ACKNOWLEDGEMENTS

I wish to express my respect and gratitude to the members of my thesis supervisory committee: Professors Norman L. Goldman, Herbert Meislich, Robert A. Odum and Leonard H. Schwartz. Their criticisms and suggestions have been invaluable during my years of graduate research.

I am grateful to my mentor, Professor Leonard H. Schwartz, for his guidance, patience and inspiration. I especially wish to thank him for the immeasurable amount of time he spent with me in the development of this dissertation.

I am thankful to my parents for their love and support.

I wish to acknowledge with thanks the following persons: Mr. Hugo M. Schimatz, my glassblowing instructor and friend, who prepared many special pieces of apparatus for me over the years; Misters Migel Mieles and Ramsey Pal for running mass spectra during the course of my work; Mrs Clara Silver for typing this dissertation.

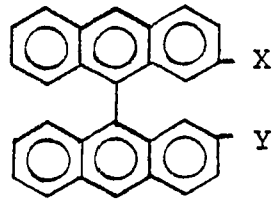
Finally I wish to express my gratitude to the Department of Chemistry, City College and to the PSC-BHE award program for the financial support.

TABLE OF CONTENTS

INTRODUCTION

I. Racemization of Optically Active 9,9'-Bianthryl.

The purpose of this research project is to investigate the possibility of radical-catalyzed racemization of optically active 9,9'-bianthryls, e.g., Ia.



Ia, X = Y = $COOCH_3$

Ib, X = Y = COOH

Ic, X = Y = C≡N

Id, X = Cl, Y = C≡N

Atropisomerism in biaryls has been recognized for some time.[1] It was first demonstrated in 1922 by Christie and Kenner, by their successful resolution of 6,6'-dinitrodiphenic acid.[2] Since then, numerous substituted biphenyls,[4] binaphthyls,[4,5] and bianthryls[6,7,8] have been obtained in optically active form.

Steric hindrance is believed to be the major factor responsible for restricted rotation in biphenyls. Thus, it is the "bulkiness" of the ortho substituents which mainly determines the energy barrier to rotation. This is evidenced by the fact that the order of interference of ortho substituents, as determined by racemization studies, is I > Br >> CH_3 > Cl > NO_2 > CO_2H >> OCH_3 > F, which roughly parallels their van der Waals radii.[3]

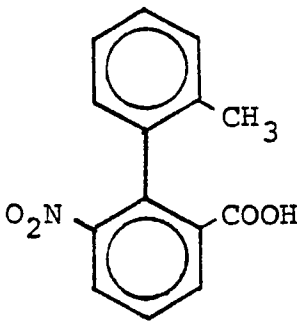
With the binaphthyls and bianthryls, benzo-benzo interactions and the interactions of the 2,2'-substituents (or hydrogens) are the major contributors to the rotational barrier.[4d,7]

The determination of rotational barriers, from both the theoretical[9] and experimental approaches,[10,11 17,18] has been an active area of interest in organic chemistry. The knowledge obtained from such studies has contributed importantly to advances in modern structural organic chemistry.

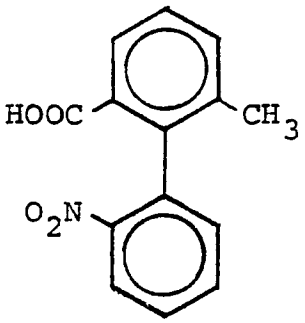
The measurement of the rate of racemization of optically active biaryls has been a standard method for the determination of the rotational barriers of these compounds.

In general, the relative magnitudes of the rotational barriers in a series of biphenyls can be predicted from consideration of the van der Waals radii of the ortho substituents. However, exceptions do exist.

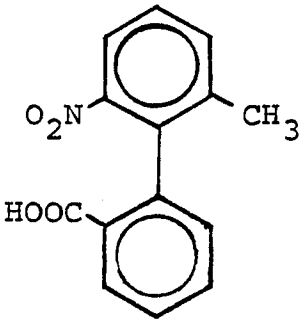
The order of optical stabilities of II, III, and IV would be predicted to be II > III ≈ IV on steric grounds alone. However, the optical stabilities were found to be IV > III > II.[12]



II

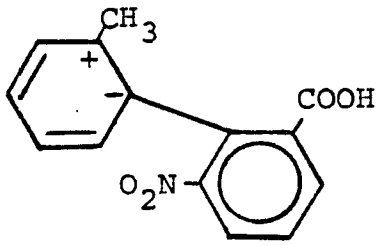


III



IV

Baddely[13] has proposed that out of plane bending about the 1,1'-bond would facilitate racemization. The ease of this bending should depend on the availability of electrons to stabilize structures such as V. The bent

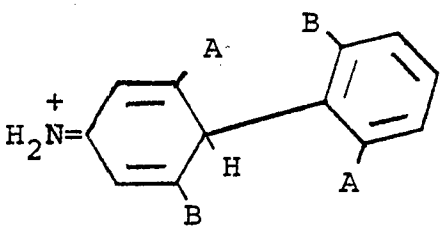


V

structure would have more sp^3 character at C-1, and would be favored by a high electron density. It should be noted that the electron densities in the upper rings of compounds II, III, and IV parallel the rates of racemization.

Crawford and Smyth[14] have shown that racemization of optically active biphenyl is facilitated by an electrophilic attack of H^+ on C-1, e.g., VI. Here, one of the

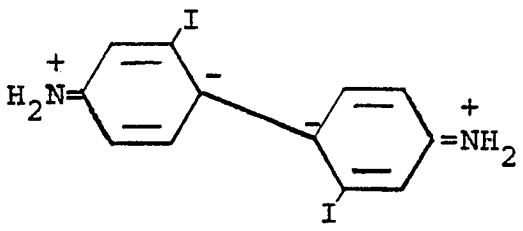
C-1 atoms obtains complete sp^3 character. Activating substituents in the ortho and para positions, such as



VI

the amino group, would assist racemization, whereas deactivating substituents, such as carboxyl, would oppose racemization.

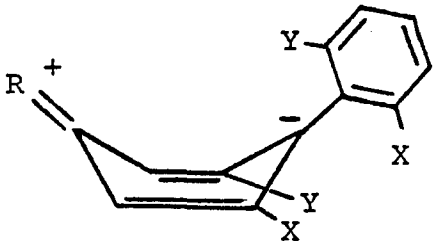
Harris[11a] refined these ideas by suggesting that the transition state to racemization of biphenyls might not be planar as previously assumed. The 1,1'-bond could be bent,e.g., with 4,4'-diamino-2,2'-iodobiphenyl, the transition state was suggested to resemble VII.



VII

According to this proposal, racemization would occur by two consecutive ortho-ortho interactions, rather than by two simultaneous interactions. Therefore, the energy of racemization would be reduced.

Harris' postulate may be restated in the following way. In the presence of certain substituents in the 4,4'-positions, optically active biphenyls are capable of forming a 1,4-cyclohexadiene structure (VIII), which exists in a boat conformation. The interference between the two sets



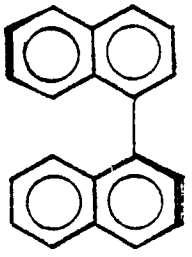
VIII

of ortho substituents (X and Y) during the rotational process would be greatly reduced by the formation of VIII.

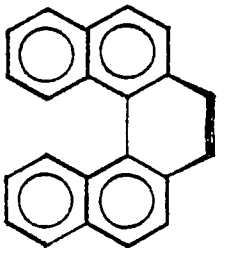
The boat-shaped conformation of the 1,4-cyclohexadiene system has been recognized for a number of years.[15] The formation of VIII would be facilitated by an electron-releasing group at C-4 and would be opposed by an electron-withdrawing group at the same position.[11a] Electrophilic attack at C-1 by a species such as H^+ would aid in the formation of a 1,4-cyclohexadiene structure, and this would increase the ease of racemization.[14]

Harris and coworkers demonstrated this polar effect in a study of a series of 4,4'-substituted 1,1'- binaphthyls. Electron withdrawing groups increased the energy of racemization while electron donating groups decreased it.[10c]

The addition of an electron to a 1,1'-binaphthyl decreases the rotational barrier considerably.[16,18] Ito and Hatano[16] reported that the radical anions of 1,1'-binaphthyl (IX) and 9,10-dihydro-3,4,5,6-dibenzophenanthrene (X) racemized more rapidly than the corresponding neutral compounds without cleavage of the 1,1'-bond.



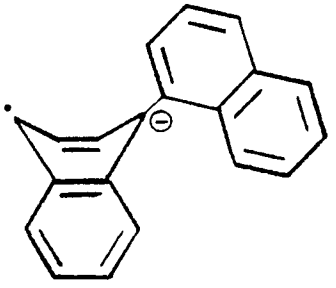
IX



X

In the biphenyl system, a similar effect of the addition of an electron was observed. The rotational barrier of 9,10-dihydrophenanthrene was estimated to be ≤ 9 Kcal/mole from a nmr measurement by Oki and coworkers.[17] The corresponding radical anion was shown by an esr study to have a rotational barrier of 6.1 Kcal/mole.[18] The difference in the rotational barriers was interpreted[16] as due to the addition of an electron. However, the

mode of action leading to a reduced rotational barrier in the anion was not explained. It is conceivable that the resulting radical anion could exist in a boat conformation, such as XI.

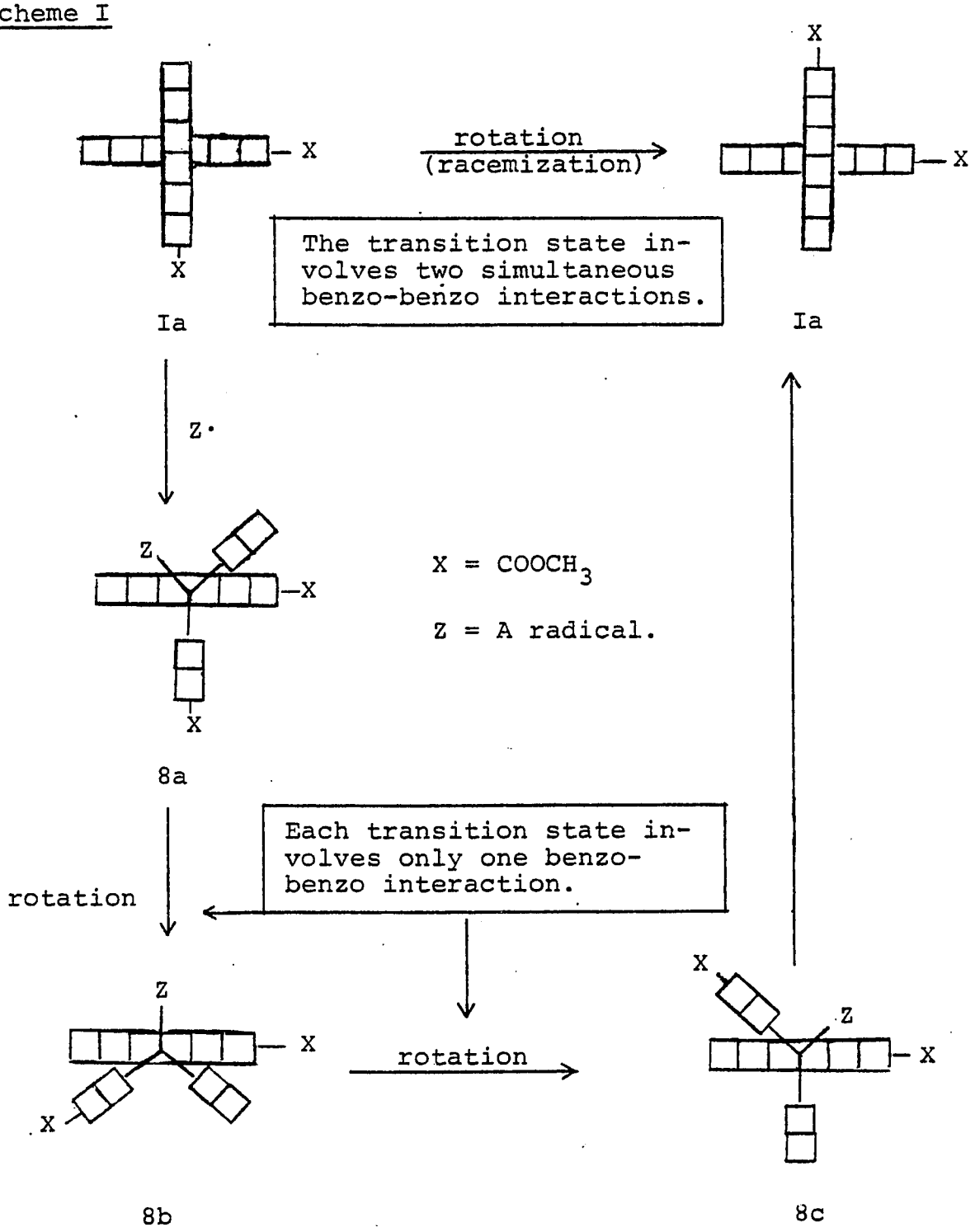


XI

The simultaneous steric interactions which lead to the large rotational barriers in 1,1-binaphthyls would occur consecutively in a species such as XI, thus leading to a lower rotational barrier.

Koukotas[7], in 1968, reported that optically active Ia partially racemized when heated at 220°C, in the presence of oxygen, for two hr.. No racemization occurred in similar experiments under a nitrogen atmosphere. This was attributed to the reversible addition of oxygen to Ia. This process would result in a change in hybridization at C-9 from sp^2 to sp^3. A change in hybridization at C-9 from sp^2 to sp^3 should reduce the rotational barrier, because the number of simultaneous interaction between benzo groups would be decreased from two to one, as shown in Scheme I.

Scheme I

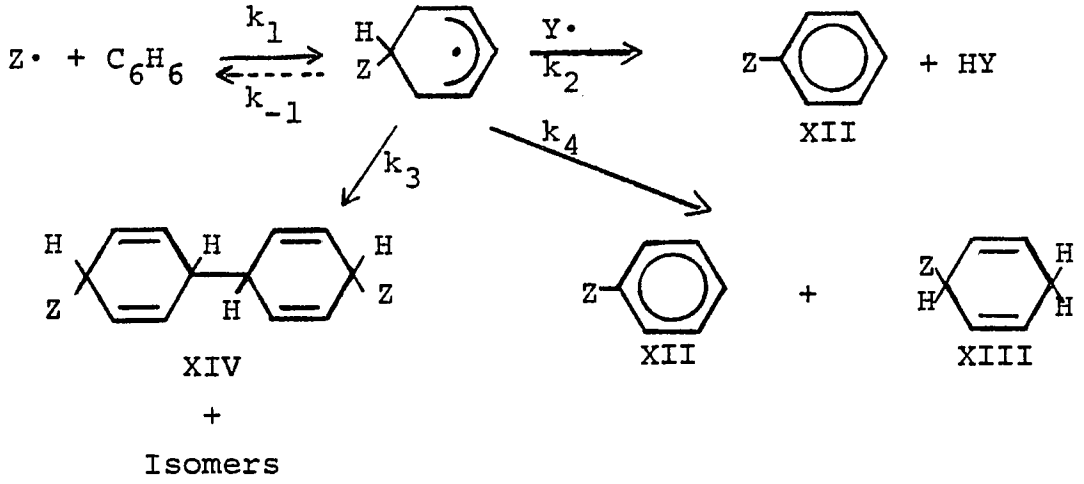

X
rotation
(racemization)
X
X
X
The transition state involves two simultaneous benzo-benzo interactions.
Ia
Ia
Z·
Z
X
X
X = COOCH3
Z = A radical.
8a
Each transition state involves only one benzo-benzo interaction.
rotation
Z
X
X
rotation
X
Z
X
8b
8c

Koukotas' explanation is based on the assumption that oxygen participates directly in the racemization. It was also noted that other species, derived from the attack of oxygen on the solvent, might be responsible for the ease of racemization. A search for the actual role of oxygen in the racemization of Ia is one of the subjects of this dissertation. On the basis of our work, we believe that the reversible addition of a radical to one of the anthracene rings of Ia converts this ring into a cyclohexadienyl-type radical, which exists in a boat conformation. Such an intermediate would be expected to racemize more easily than 2,2'-dicarbomethoxy-9,9-bianthryl (Ia).

II. Reversibility of Radical Attack on Aromatic Substrates.

The question of reversibility of radical attack on aromatic substrates in homolytic substitution reactions has been the subject of numerous reports during the past 25 years.[31] A general mechanism which fits much of the data is shown in Scheme II. From some aromatic substrates, cyclohexadienyl compounds (XIII) and/or dimers (XIV) or products derived from dimers have been isolated, while from others, only the simple substitution products, XII, have been obtained.[28] Intermediate cyclohexadienyl radicals (σ complexes) have been observed directly.[19,20,21] Three general approaches have been used to study the possibility of reversibility in the formation of the σ complex.

Scheme II Homolytic Aromatic Substitution Reaction Mechanism.

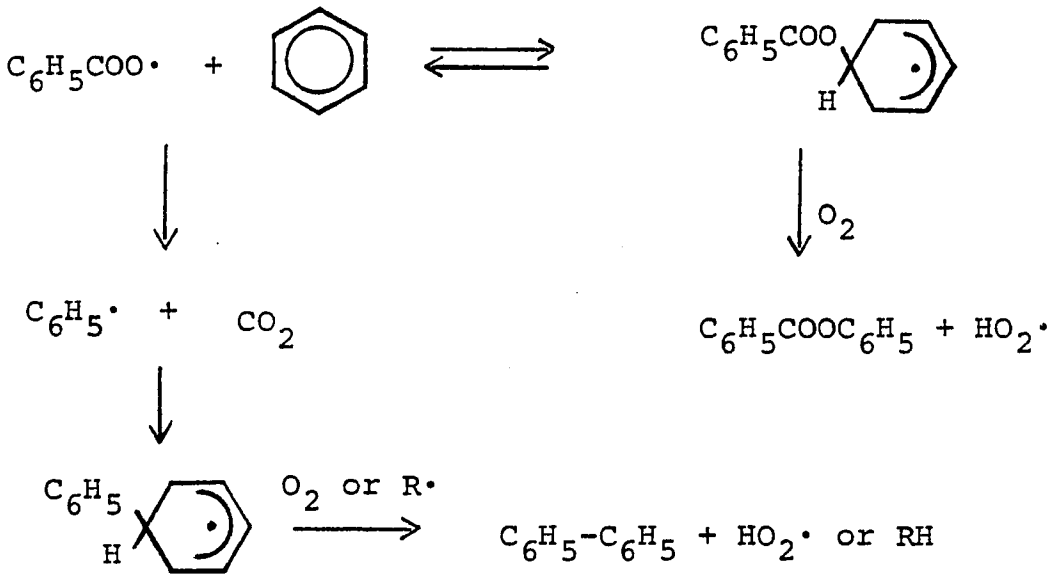


(1) Isotope Effects -- Typically, the reaction of a radical Z·, with an equimolar mixture of C_6H_6 and C_6D_6, or another such pair of aromatic substrates, is studied. The substitution products C_6H_5Z and C_6D_5Z are determined quantitatively, and the isotope effect is reported as the ratio of C_6H_5Z to C_6D_5Z. With a reaction such as an electrophilic substitution reaction, the observance of such an isotope effect would allow one to conclude that the first step, the formation of the σ complex, is reversible. However, in the present case, if an isotope effect is found, additional information is needed before a definite conclusion concerning the reversibility of step 1 can be made. This is so because there are added complexities in homolytic aromatic substitution reactions that one does not find in electrophilic aromatic substitution reactions. As an example, consider the possibility that the σ complex (Scheme II) is formed irreversibly and is competitively oxidized to substitution products (XII) on the one hand (step 2 and/or 4) and transformed to dimer (XIV) on the other hand (step 3). Steps 2 and 4 could exhibit appreciable isotope effects while step 3 would not. Thus an irreversibly formed σ complex would lead to the formation of a greater amount of C_6H_5Z than C_6D_5Z. The dimers would, therefore, be enriched in deuterated species.

Since more C_6H_5Z is formed than C_6D_5Z, an isotope effect would be reported. The additional information that is necessary before conclusions can be drawn concerning the reversibility of step 1 would be an accurate material balance (which is not always possible in radical reactions). This would establish whether competing pathways are present which can partition the σ complex with isotope discrimination. Alternatively, one could isolate and compare their ratio to their starting ratio. If unchanged, step 1 would be concluded to be irreversible. To obtain either type of additional data may involve considerable experimental difficulties. There are relatively few demonstrations in the literature, using isotope effects, of reversibility in the intermolecular formation of such σ complexes.[22,23,24] In a number of cases an observed isotope effect has been shown not to be due to the reversible formation of the σ complex.[25,26] In any event, isotope effect evidence must be treated with caution.[27,28] A small isotope effect could mean reversibility or could be due to a second order phenomenon such as a change in hybridization at the reacting carbon.

(2) Addition of a Trapping Agent — In this method, a reagent that can divert the σ complex, thus preventing reversibility, is added. As an example consider the reaction between benzoyl peroxide and benzene.[22] In the absence of oxygen, the major product is biphenyl. Phenyl benzoate is obtained in 13% yield. Most if not all, of this latter compound arises from a cage combination of $C_6H_5COO\cdot$ and $C_6H_5\cdot$. In the presence of oxygen, 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 $C_6H_5COO\cdot$ to benzene (see Scheme III).

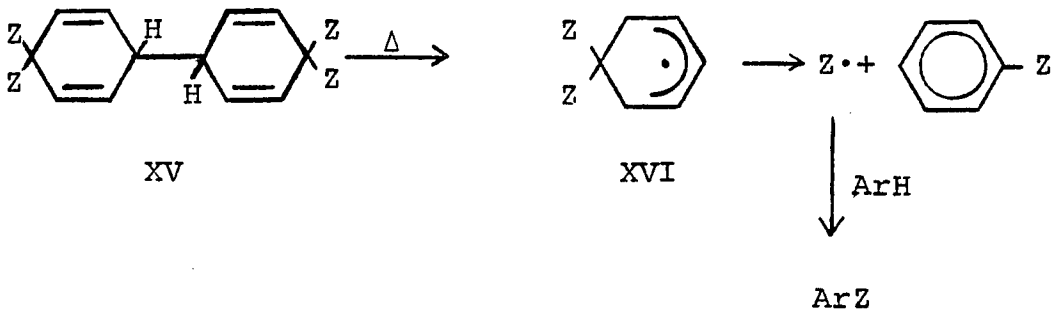
Scheme III



With oxygen, the σ complex formed from the addition of $C_6H_5COO\cdot$ is trapped as phenyl benzoate. In the absence of oxygen, the loss of H· from this σ complex is relatively slow, and both the reversal of the first step and the irreversible decomposition of $C_6H_5COO\cdot$ to $C_6H_5\cdot$ compete favorably with phenyl benzoate formation. Similar studies have been carried out with other oxidizing agents.[29] Using such an approach, it must be assumed that the added oxidizing agent does not alter the nature of the attacking radical on the reaction pathway. This assumption is difficult to verify.

(3) Decomposition of Cylcohexadienyl Radicals Formed from Paths Other than Addition of a Radical to an aromatic.[30,31] — This approach is illustrated in Scheme IV.

Scheme IV



The isolation of ArZ would indicate that the cyclohexadienyl radical XVI decomposes to Z. This is the reverse of the addition step to form a σ complex. It should be noted, however, that the temperatures necessary to convert XV to XVI are generally much higher than those employed for the corresponding aromatic substitution reactions. A negative result, i.e., failure to observe ArZ, therefore has much more significance than a positive result. In the latter case, one can still not be certain of the situation at lower temperatures.

As mentioned earlier, Koukotas[7] discovered that optically active 2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) racemizes, in the presence of oxygen, at a lower temperature than in the absence of oxygen. The present work has reinvestigated this reaction. It has been found that the catalysis results from a radical in solution, derived from the attack of oxygen on the solvent (see pp. 21-35).

The reaction of a radical, Z·, with optically active Ia might be a useful method for probing the reversibility of radical attack on this aromatic substrate. The observance of a reduced optical rotation of Ia, after exposure to the radical in question, would allow the conclusion that the first step, the formation of the σ complex (Scheme I, p. 8), is reversible. The obvious

advantage of this method is its simplicity and certainty. All that is necessary is to be able to reisolate the starting material and to measure its optical rotation.

The same method can be employed to study other kinds of biaryls, as long as these compounds possess optical activity which is due to restricted rotation about the central bond.

RESULTS AND DISCUSSION

Background

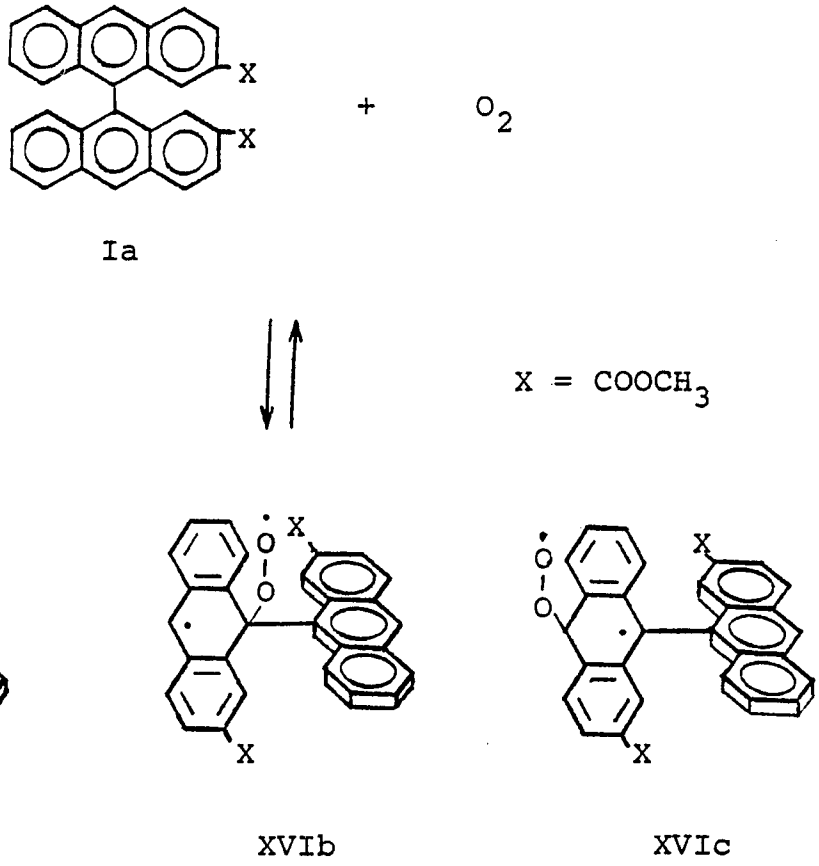
The oxygen catalyzed racemization of optically active 2,2'-dicarbomethoxy-9,9'-bianthryl(Ia) was first reported in 1968.[7,8] Koukotas found that optically active Ia partially racemized when heated at 220°C in triglyme in the presence of oxygen, for two hr.[7,8] No racemization occurred in similar experiments under a nitrogen atmosphere. The recovered, partially racemized, material was shown to be chemically unchanged, within the limits of nmr spectroscopy. It thus appeared that oxygen might be acting as a catalyst in the racemization of Ia.

The 9,9'-bianthryl system differs from biphenyl and binaphthyl systems in that its 9,10-positions are much more reactive. Oxygen could possibly interact reversibly with the 9,10-positions of a 9,9'-bianthryl changing the hybridization of the pivotal carbon and therefore reducing the barrier to racemization.

Scheme V, p. 18, represents the pathway postulated by Koukotas for this catalysis. Intermediate XVIa could be formed by the attachment of a singlet oxygen molecule ($^1\Delta_g$) to the 9,10 positions of 2,2'-dicarbomethoxy-9,9'-bianthryl (Ia). Similarly, the attack of triplet oxygen ($^3\Sigma_g^+$) on Ia could form XVIb and/or XVIc.

With adducts XVIa and XVIb, the C-9 position of the oxygenated ring has been converted from sp^2 hybridization to sp^3 hybridization. With adduct XVIc, although C-9 is

Scheme V

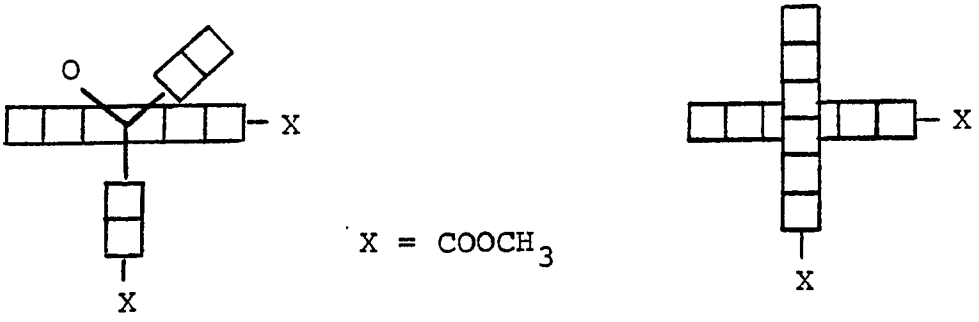


Ia

XVIa XVIb XVIc

not necessarily sp^3 hybridized, it was argued that the angles could be more easily distorted from 120° towards 109° than in the case of Ia. A change in hybridization, from sp^2 to sp^3 should reduce the rotational barrier (increase the ease of racemization) because the number of simultaneous interactions between benzo groups will be decreased from two to one, as shown in Figure I (see also Scheme I, p. 8).

Figure I



One benzo-benzo interaction at a time upon rotation leading to racemization

Two simultaneous benzo-benzo interactions upon rotation leading to racemization

It had been assumed in proposing Scheme V, p.18, that oxygen participates directly in the racemization of optically active 2,2'-dicarbomethoxy-9,9'-bianthryl (Ia). The interaction between oxygen and Ia results in the rehybridization of the C-9 position, and reduces the rotational barrier of the C_9-$C_{9'}$ bond. This path is, by no means, the only one that can be envisioned. Alternatively, a species which is produced by the presence of oxygen may be acting in a role similar to that shown for oxygen in Scheme V, p. 18.

Statement of the Problem

The objectives of the work reported in this dissertation are: (1) To determine the actual role of oxygen in the catalysis of the racemization of optically active 2,2'-dicarbomethoxy-9,9'-bianthryl (Ia). (2) To elucidate the mechanism by which optically active 2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) racemizes in the presence of some reactive species. (3) To investigate the reversibility of homolytic aromatic substitution reactions through the observation of the racemization of optically active compounds.

I. Racemization of Optically Active 2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of Oxygen.

A. Racemization of (+)2,2'-Dicarbomethoxy-9,9-bianthryl (Ia) in the Absence of Oxygen. Freeze-Pump-Thaw Procedure.

The earlier work by Koukotas[7,8] established that the racemization of 2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) was catalyzed by oxygen.

It was first necessary to confirm the results of Koukotas,[7,8] which indicated that in the absence of oxygen little racemization (4%) occurred. In the earlier experiments, samples were prepared by bubbling through gaseous nitrogen and sealing the tubes under nitrogen. In order to prepare oxygen-free samples, an improved degassing method was used. The degassing was done in the apparatus shown in Figure VI , p. 99.. The detailed procedure is described on page 98..

The initial attempts to repeat the racemization of Ia in the absence of oxygen showed the extent of racemization to be as high as 39 percent instead of 4 percent as reported by Koukotas.[7] Since all samples had been thoroughly degassed by the Freeze-Pump-Thaw procedure, p. 98 , and helium ($O_2 \leq 1$ PPM, Matheson, East Rutherford, N.J.) had been introduced as an atmosphere before sealing the tubes, the presence of a significant amount of oxygen

in the samples is considered to be very unlikely. An examination of the molecular structure of triglyme, the solvent, suggested a reason for the discrepancy between our results and those of Koukotas.

Triglyme, 1,2-bis-(methoxyethoxy)ethane (XVII), is a polyether. All the carbon-hydrogen bonds are activated by

$$CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3$$

XVII

the presence of the adjacent oxygen atoms. It is known that ethers are very prone to form hydroperoxides.[49a,c] The degradation of these hydroperoxides could lead to radicals.[49b,c] It is conceivable that the discrepancy between the present results and those of Koukotas could very well be due to the presence of peroxides in the samples.

In our early experiments, the triglyme used as the solvent was purified by distillation from $LiAlH_4$ (p. 95). It was then stored in a tightly closed bottle for several days before the preparation of the samples. Before the samples were prepared, a test with $Fe(CNS)_2$, produced a red color, which confirmed the presence of hydroperoxide.

This result indicates that storage of the purified triglyme, over alumina, under a nitrogen atmosphere in a tightly closed bottle is not effective in preventing the triglyme from undergoing autoxidation, under the influence of air. An experiment was conducted with the samples

being prepared immediately after the purification of triglyme, p. 101. The average racemization of several runs was only 2.0%, after 3 hr. heating at 148.8 ± 0.1°C.

The results from these experiments clearly indicate that hydroperoxides derived from triglyme participate in the racemization of (+)2,2'-dicarbomethoxy-9,9'-bianthryl (Ia). Another experiment aimed to test the relationship between the concentration of peroxides and the degree of racemization was performed. The concentration of hydroperoxides in each sample was controlled by varying the time of exposure of triglyme to air. Table V, p. 104, shows that the longer the exposure to air, the higher the degree of racemization.

It is known that radicals can arise from the thermal decomposition of hydroperoxides at elevated temperatures.[49b,c] The species which directly catalyze the racemization of (+)2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) could very well be radicals derived from the hydroperoxides. A racemization experiment, p. 105, in the presence of 2,6-di-tert-butyl-p-cresol, a radical scavenger, was performed. The results, p. 106 shows that the presence of 2,6-di-tert-butyl-p-cresol effectively inhibits the racemization of Ia.

It thus appears that in the absence of oxygen, the racemization of Ia can be catalyzed by radicals derived from hydroperoxides which originate from triglyme.

B. Racemization of (+)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of Oxygen Using Triglyme as the Solvent.

It had been confirmed that there was no racemization of Ia, in the absence of oxygen using triglyme, free from hydroperoxides, as the solvent, p. 23. It had also been discovered that racemization of Ia in the absence of oxygen was catalyzed by the radicals derived from hydroperoxides of triglyme, p. 23.

Koukotas reported[7] that Ia partially racemized in 2 hr. at 220°C in the presence of oxygen, using triglyme as the solvent. The actual role of oxygen was not investigated at that time. On one hand, oxygen could be interacting with Ia directly at the $C_9$and C_{10} positions (see p. 18). The resulting oxygenated intermediates would exhibit reduced rotational barriers at the C_9-C_9, bonds and thus racemize more rapidly than Ia. These intermediates would subsequently decompose to form chemically unchanged, yet racemized, 2,2'-dicarbomethoxy-9,9'-bianthryl (Ia). On the other hand, oxygen could be participating in the autoxidation of triglyme (Scheme VI).

Scheme VI Autoxidation of Triglyme (TH).[48]

$$\text{Initiation} \begin{cases} \text{Initiation} \rightarrow 2\ \text{In}\cdot \\ \text{In}\cdot + \text{TH} \rightarrow \text{T}\cdot + \text{InH} \end{cases}$$

$$\text{Propogation} \begin{cases} \text{T}\cdot + \text{O}_2 \rightarrow \text{TOO}\cdot \\ \text{TOO}\cdot + \text{TH} \rightarrow \text{T}\cdot + \text{TOOH} \end{cases}$$

$$\text{Termination} \begin{cases} \text{TOO}\cdot + \text{TOO}\cdot \rightarrow \text{O}_2 + \text{TOOT} \\ \text{TOO}\cdot + \text{T}\cdot \rightarrow \text{TOOT} \\ \text{T}\cdot + \text{T}\cdot \rightarrow \text{T - T} \end{cases}$$

It is conceivable that radical T· could react in a homolytic aromatic substitution type reaction with (+)2,2'-dicarbomethoxy-9,9'-bianthryl (BH). The resulting intermediate TBH· would have a reduced rotational barrier at the C_9-$C_{9'}$ bond and would racemize more easily than (+)2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) (see pp. 32-35).

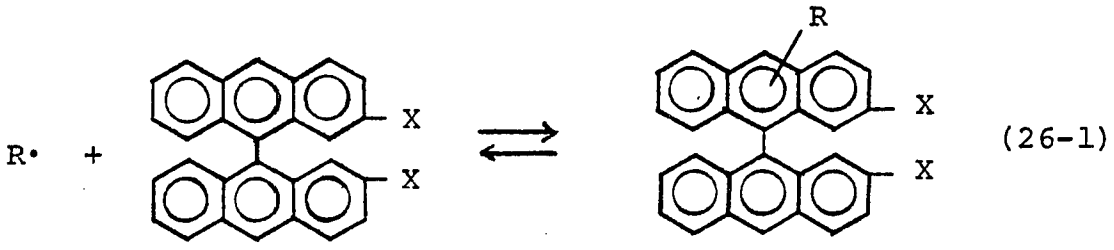
The racemization of (+)2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) in the presence of oxygen (Table IV, p. 96) occurred to the extent of 87% after two hr. of heating at 148.8 ± 0.1°C. When the racemization was conducted in the presence of oxygen and 2,6-di-tert-butyl-p-cresol, essentially no racemization was observed (p. 102) after heating for 4.5 hr. at 148.8 ± 0.1°C.

C. S. Foote[32] reported that the reactions involving singlet oxygen could not be quenched by a free radical

inhibitor, e.g., 2,6-di-tert-butylphenol. The results from our experiments indicate racemization is catalyzed by a species which is radical in nature, and not singlet oxygen. The principal function of oxygen in the racemization seems to be in the formation of triglyme hydroperoxides, Scheme VI, p. 25.

C. Recovery and Investigation of the Products of the Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia).

A sample, containing 0.3 g. of Ia in 60 ml. of triglyme with oxygen as the atmosphere, was heated at 148.8 ± 0.1°C for 2.5 hr. (p. 107). Separation of the components of the racemized material, by prep. tlc, resulted in a recovery of 40.6% of the starting material. This chemically unchanged 2,2'-dicarbomethoxy-9,9'-bianthryl (Ia)[33] showed 62.4% racemization. This finding suggests that the attack of a radical on Ia is a reversible process (eq. 26-1).



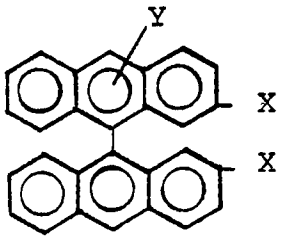
(26-1)

Ia

X = $COOCH_3$

The reversibility will be discussed on pp. 33-35.

Three substitution products, XVIIIa, XVIIIb, XVIIIc were also isolated.

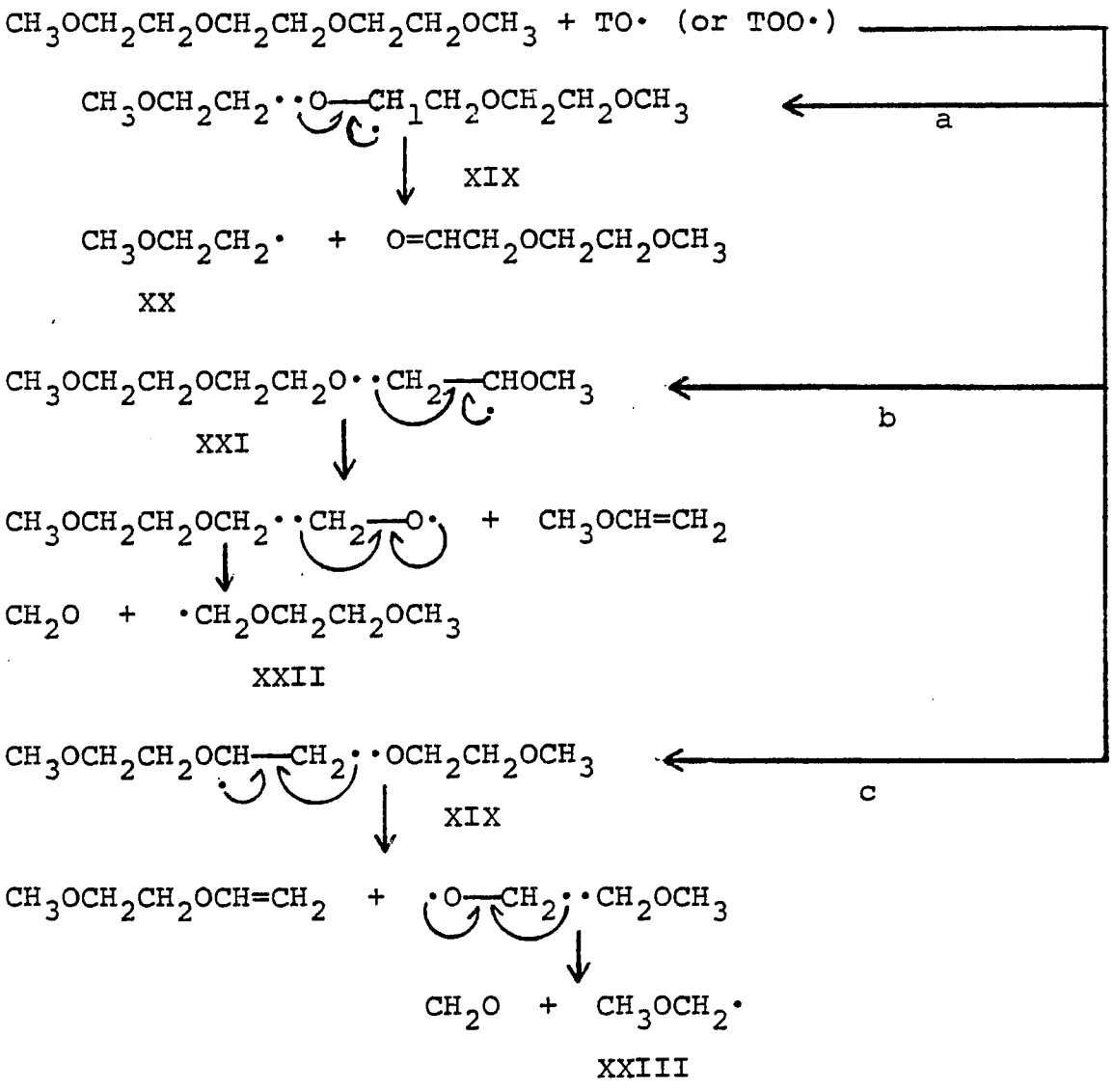


XVIIIa; X = $COOCH_3$, Y = CH_2OCH_3

XVIIIb; X = $COOCH_3$, Y = $CH_2OCH_2CH_2OCH_3$

XVIIIc; X = $COOCH_3$ Y = $CH_2CH_2OCH_3$

Scheme VII Formation of Radicals from Triglyme.[34]



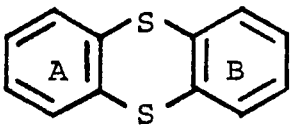
Radicals XIX and XXI can arise by hydrogen abstraction[34] from triglyme by radical TO·(or TOO·) as shown in Scheme VII, p. 27. Disintegration of XIX by route a[34] gives radical XX (F.W. = 59), and by route c yields XXIII (F.W. = 45). Disintegration by path b gives radical XXII (F.W. = 89). XX, XXII, and XXIII appear to be the major radicals participating in the homolytic aromatic substitution reaction with 2,2'-dicarbomethoxy-9,9'-bianthryl(Ia) during the racemization process.

A close examination of the mass spectra of XVIIIa, XVIIIb and XVIIIc reveals that a peak at m/e = 483 (M.W. of Ia = 470) exists in these three spectra. This information is consistent with the structures assigned for XX, XXII and XXIII, which indicates these three radicals are carbon radicals not alkoxy radicals.

Our present evidence does not allow us to ascertain to which position the substituent is attached in XVIIIa, XVIIIb and XVIIIc (p. 27). The broad peaks observed in the nmr and ir spectra of XVIIIa, XVIIIb, and XVIIIc imply that there are positional isomers present in each case.

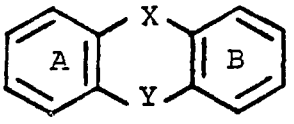
D. Mechanism

In 1932, E. Bergman and M. Tschudrowsky[35] found that thianthren (XXIV) had a considerable dipole moment (1.7 esu;



XXIV

solvent benzene) and suggested that the central ring was folded about the line joining the two sulphur atoms. Since then various authors[36] have reported the folded conformation in molecules of type XXV, with X and Y



XXVa, X = Y = CH_2

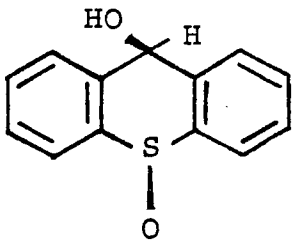
XXVb, X = Y = O

varying among C, O, S, and As. The general case may be stated as follows:[37] In a molecule of type XXV, the atoms X and Y will, under all conditions, lie in the planes containing rings A and B. These planes may be inclined to one another at an angle ψ or they may be one and the same when the molecule is planar (as in the case of XXVb). The two factors controlling the magnitude of ψ are: (i) the preferred, i.e., natural valency angles of X and Y, and (ii) the atomic radii of X and Y.

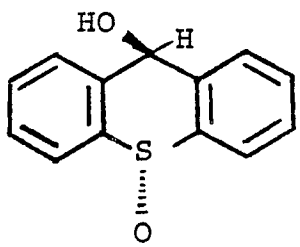
In 1954, Ferrier and Iball[38] reported, from an x-ray study that 9,10-dihydroanthracene (XXVa) exists in a folded conformation. The two halves of the molecule are inclined to each other at an angle of approximately 145°.

Ternay, Jr. and coworkers reported[39] the x-ray study of the stereoisometric thioxanthen-9-ol-10-oxides

(XXVIα and XXVIβ). The dihedral angle between the planes



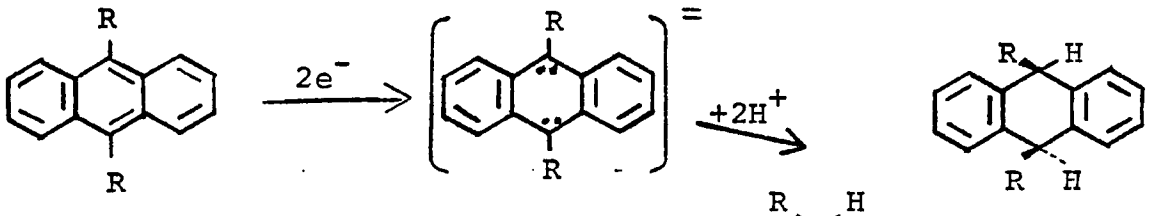
XXVIα



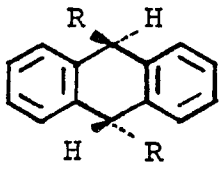
XXVIβ

of the benzene rings was reported to be 132.4°.

Harvey and coworkers[40] in a study of metal-ammonia reductions of 9,10-dialkyl anthracenes (XXVII), suggested

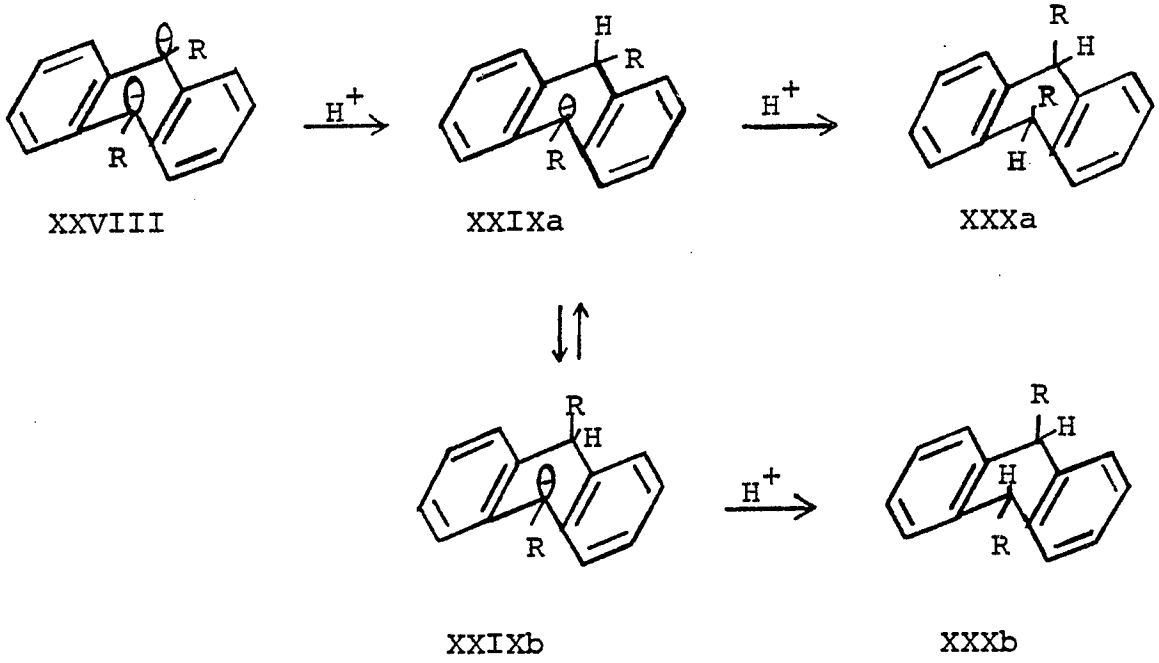


XXVII XXVIII XXXa



XXXb

a flattened boat conformation for the intermediate dianions (XXVIII) (or radical anions) in order to account for the observed unequal proportions of the <u>cis</u> and <u>trans</u> 9,10-dialkyl-9,10-dihydroanthracenes (XXXa and XXXb) obtained. Thus, lithium-ammonia reduction of 9,10-dimethylanthracene (XXVII) yielded the <u>cis</u>- and trans-9,10-dimethyl-9,10-dihydroanthracenes (XXXa and XXXb, R = CH_3), in approximately

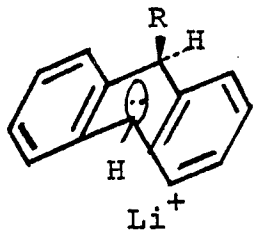


XXVIII XXIXa XXXa

XXIXb XXXb

equal proportions. On the other hand, reduction of 9,10-diethyl, dibenzyl-, di-t-butyl- and 9-ethyl-10-methyl-anthracene proceeded with a high degree of stereospecificity to furnish the trans isomers in 90-95% yields. The latter results were attributed to the greater bulk of the substituents which favored the sterically less encumbered trans conformers, XXIXb.

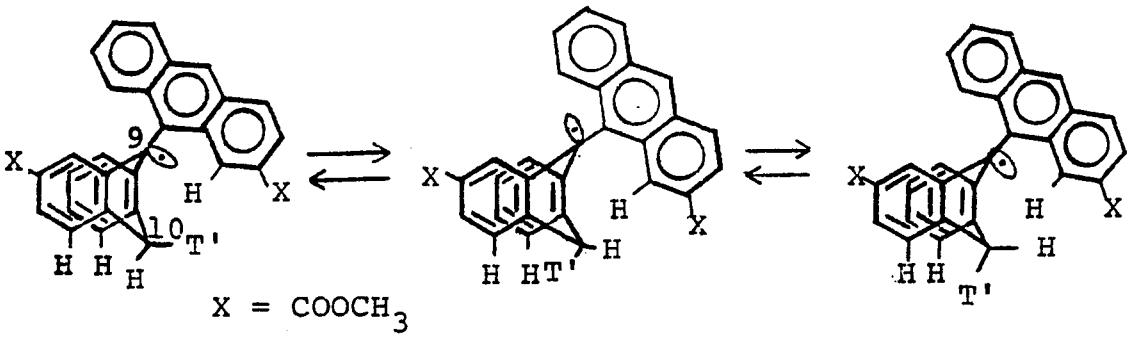
A number of authors[41] have also reported a flattened boat conformation for 9-alkyl-10-lithio-9,10-dihydro-anthracenes (XXXI), the intermediate in the alkylation of



XXXI

9-alkyl-9,10-dihydroanthracenes. The favored orientation of bulky groups such as 9-ethyl, 9-isopropyl and 9-tert-butyl is essentially 100% quasiaxial.[41a]

A radical analog of XXIXb, XXXII, can arise when a radical, T'·, attacks 2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) at the C-10 position. (The attack at the other positions will be discussed shortly.)



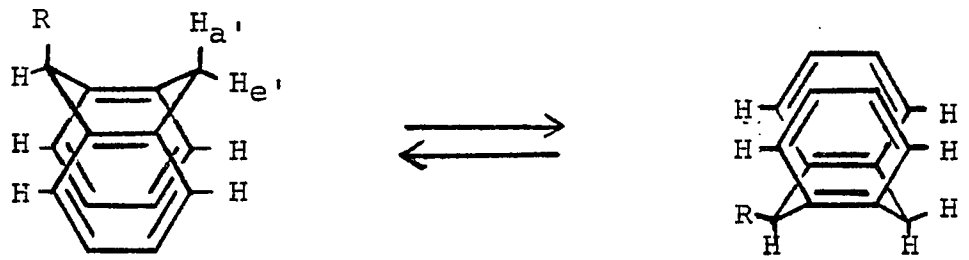
XXXIIa XXXIIb XXXIIc

It seems reasonable to assume that radical T'· approaches perpendicularly to one of the two anthracene planes of Ia which results in the formation of XXXIIa. The boat conformation XXXIIa may be converted into conformation XXXIIb by reverse folding about the 9,10-axis, with consequent interconversion of quasiaxial (a') and quasiequatorial (e') bonds. XXXIIb can be converted into XXXIIc by inversion at C-9, which releases the severe non-bonded interaction between the C-10 and C-1' hydrogens and also

stabilizes the unpaired electron by delocalization into the aromatic rings. The quasiequatorial (e') groups are subjected to greater non-bonded interactions, with the peri-hydrogens, than the corresponding a' groups in this system.[41b] The preferred conformation should therefore be XXXIIa.

The formation of XXXII should reduce the rotational barrier (increase the ease of racemization) because the number of simultaneous interactions between benzo groups will be decreased from two to one, as can be seen from Figure I, p. 19 (with 0 being T').

The fate of radical intermediate XXXII depends on the susceptibility of its C-10 hydrogen towards abstraction by another radical. On one hand, XXXII could give up the C-10 hydrogen to form an addition product if the C-10 hydrogen could be reached by another radical. On the other hand, XXXII could dissociate to give racemized 2,2'-dicarbomethoxy- 9,9'-bianthryl (Ia) and T'· if the C-10 hydrogen could not be reached by another radical, due to steric hindrance.[46] The "boat-boat" interconversion between XXXIIIa' and XXXIIIe' (R = H) is reported to be rapid down to -27°C.[36b,43] The presence of a C-9 substituent can bias this equilibrium to favor one of the two forms.[44] Earlier chemical studies[36b,43] and recent nmr studies[41,45] all clearly



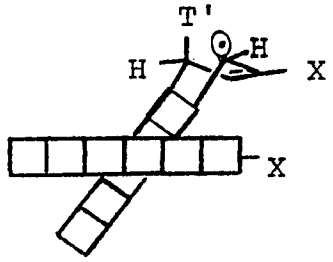
XXXIIIa' XXXIIIe'

point to an overwhelming preference for XXXIIIa' (R = t-Butyl, Ethyl, isopropyl).

In our present system, XXXIIa and XXXIIc (through XXXIIb) (p. 32) are considered to be in equilibrium. Some of XXXIIa may lose T' before converting to XXXIIb. The C-10 hydrogen in XXXIIa would be sterically hindered and difficult to abstract, whereas in XXXIIc it would be more open and could be removed more easily by another radical to form an addition product. Racemized 2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) might, therefore, arise predominantly from XXXIIa while the addition products XVIII, p. 27, might arise predominantly from XXXIIc.

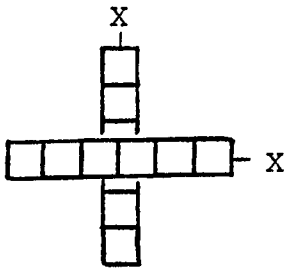
The attack of radical T'• at positions other than C-10 should also lead to reduced rotational barriers. The resulting radicals would no longer have the two end rings in one plane. The number of simultaneous interactions between benzo groups would thus be decreased from two to one, as shown in Figure II, p. 35, for addition to C-4.

Figure II



One interaction at a time upon rotation leading to racemization

$X = COOCH_3$



Two simultaneous benzo-benzo interactions upon rotation leading to racemization

It has been shown by Dickerman and coworkers[47] that the relative reactivities of the three positions in anthracene towards homolytic phenylation are C-9:C-1:C-2 = 59:4:1 Accordingly, one may consider that the C-10 and C-10' positions in 2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) are the two positions most susceptible toward radical attack. The majority of the radicals present in the solution during the racemization reaction would attack these two positions preferentially. This attack need not lead to the

preferential formation of 10-substituted products because it is counterbalanced by the difficulty of removing the sterically hindered quasiequatorial C-10 hydrogen. The present results, provided by a study of the recovered addition products, p. 108, do not permit a conclusion about the positions of free radical attack on 2,2'-dicarbomethoxy-9,9'-bianthryl (Ia). Nor are the positions occupied by the substituents Y in the addition products XVIIIa, XVIIIb, and XVIIIc, p. 27 established. This matter is discussed on p. 63.

Scheme VIII, p. 37, represents the proposed mechanism for the racemization of optically active 2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) in the presence of oxygen using triglyme as the solvent.

Reaction 1 to 4 and 7 to 9 describe the autoxidation of the solvent, triglyme. There is general agreement[49,52,54,57] that initiation can be achieved by the thermolysis of catalytic amounts of hydroperoxides present in solution[49,54] (eq. 36-1), or by spontaneous initiation[52] (eq. 36-2).

$$TOOH \rightarrow TO\cdot + HO\cdot \qquad (36\text{-}1)$$

$$TH + O_2 \rightarrow T\cdot + HOO\cdot \qquad (36\text{-}2)$$

Scheme VIII Mechanism for the Racemization of (-)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia).

Abbreviations

TH - Triglyme

BH - (-)2,2'-Dicarbomethoxy-9,9'-bianthryl

R· - A radical (T·, T'· or In·)

In· - A radical (TOO·, TO·, or HO·) from the initiator (TOOH).

N - Non-radical compound.

1. Initiator → 2 In· (TOO·)
2. TOO· + TH → T· + TOOH
3. $T\cdot + O_2 \rightarrow TOO\cdot$
4. T· → T'· + N
5. R· + BH ⇄ R-BH ·
6. R-BH · + R·→ R-B + RH
7. $2TOO\cdot \rightarrow O_2 + TOOT$
8. TOO·+ R· → TOOR
9. 2R· → R-R

The resulting alkoxy, hydroxyl and peroxy radicals can undergo hydrogen abstraction with triglyme (TH) as the hydrogen donor (reaction 2).[34,50,85] Normally, reaction 3 in Scheme VIII is very fast, and the only important

termination reaction is that involving two TOO• radicals (reaction 7) when the oxygen pressure is higher than 100 mm..[50,51a] Radical fragmentation[34,54b] (reaction 5) can readily happen to T• (see Scheme VII, p. 27). The driving force for this process arises, at least in part, from the stability of the resultant non-radical products (N).[34]

Reaction 5 and 6 describe the homolytic aromatic substitution of 2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) by R•. R• can be any one of T•, T'•, TOO•, TO• and HO•. Only T'• has been found to form the substitution products (p. 27). It is the reversibility of reaction 5 which accounts for the recovered, racemized starting material. The explanation for the ease of racemization in the radical intermediate T'-BH• appears on pp. 32-35.

II. Racemization of Optically Active 2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of Diphenyl Disulfide Using Triglyme as the Solvent.

The discovery of the radical catalyzed racemization of optically active 2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) suggests that the addition step in the homolytic aromatic substitution of the 9,9'-bianthryl (Ia) system can be reversible. The observation of the racemization of Ia, if expanded to include other radicals and other biaryl systems could potentially become a method for illustrating the reversibility of the addition step in homolytic aromatic substitution reactions.

It has been known for some time that the S-S bonds in organic disulfides are cleaved homolytically by heat or light into thiyl radicals.[57,63,70] Addition of thiyl radicals to aromatic systems are rare and occur only in special circumstances.[62,66b] The failure to obtain addition can be ascribed to the unfavorable energetics involved in disrupting an aromatic system.

From the fact that no substitution or addition products are obtained, one can not really say whether thiyl radicals attack the aromatic ring or not. Addition could occur, but the rate of elimination compared to hydrogen abstraction may be so high that addition products are not obtained.

Matsuda and coworkers reported[63] that diphenyl disulfide decomposes to form phenylthiyl radicals at 196°C with a decomposition rate of 4.7×10^{-7} sec^{-1}. No substitution product derived from phenylthiyl radical and the solvent (tetralin) was discovered.

To ascertain whether phenylthiyl radical does, in fact, attack an aromatic ring without leading to products (completely reversible addition), it was feasible to study the racemization of Ia in the presence of diphenyl disulfide at a temperature of about 196°C.

A. Racemization of (-)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of Diphenyl Disulfide.

Racemization of a solution consisting of Ia (0.03 g., 6.4×10^{-5} mole) and diphenyl disulfide (0.07 g., 3.2×10^{-3} mole) in 10 ml. of triglyme, showed 34% and 45% racemization, after heating at 196.6°C for 48 hr and 96 hr periods, respectively (p. 109).

An interesting feature of this reaction is the lack of dependency of the degree of racemization on the concentration of diphenyl disulfide. Thus, contrary to what was expected, variation of the concentration of diphenyl disulfide from $\frac{\text{PhSSPh}}{\text{bianthryl}} = \frac{1}{16}$ to $\frac{\text{PhSSPh}}{\text{bianthryl}} = 5$ did not change the degree of racemization significantly (Table I, p. 41).

This result implies that phenylthiyl radicals do not directly catalyze the racemization of Ia. If this is the case, then which species is responsible for the catalysis?

Table I

Sample	PhSSPh (mole x 10^6)	$\frac{\text{PhSSPh}}{\text{bianthryl}}$	Racemization (%)[a]
1	320	5.0	35
2	260	4.1	35
3	190	3.0	39
4	130	2.0	40
5	64	1.0	40
6	32	0.50	41
7	16	0.25	39
8	8	0.13	36
9	4	0.063	40
10	0	0	7.6

a. After 48 hr. heating at 197 ± 1°C. See p. 111.

Hydrogen abstraction by thiyl radicals from organic substrates has been reported by a number of authors (eq. 42-1).[65,66,67,68,69]

$$RS\cdot + TH \rightarrow RSH + T\cdot \qquad (42\text{-}1)$$

Here, RS· may come from the thermolysis or photolysis of a disulfide (eq. 42-2).[63,70]

$$RSSR \xrightarrow[\text{or } h\nu]{\Delta} 2RS\cdot \qquad (42\text{-}2)$$

Radical T·, thus formed, could react with 2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) in a homolytic aromatic substitution reaction similar to that of reaction 5, Scheme VIII, p. 37.

In order to explain why the degree of racemization is not sensitive to a change in the concentration of diphenyl disulfide, Scheme IX is proposed.

Scheme IX

1. $PhSSPh \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2PhS\cdot$

2. $PhS\cdot + TH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} PhSH + T\cdot$

3. $T\cdot + BH \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} TBH\cdot$

4. $TBH\cdot + R\cdot(T\cdot \text{or } PhS\cdot) \xrightarrow{k_4} TB + RH$

5. $PhS\cdot + T\cdot \xrightarrow{k_5} PhS\text{-}T$

6. $T\cdot + T\cdot \xrightarrow{k_6} T\text{-}T$

Initially, the samples with the greater concentrations of PhSSPh would tend to have greater concentrations of PhS·. This would result in an increase in the concentrations of PhSH and T·, according to eq. 2 (p. 42), which would lead to an increased rate of racemization. However, as the reaction proceeds the concentration of T· will tend to decrease because of two factors: (1) The reaction with PhS· to yield PhST. T· can be terminated in two ways (eq. 5 and 6, Scheme IX). Of these two possibilities, only reaction 5 seems to be important since T-T has not been found, whereas a significant amount of PhST was found to be present together with the racemized material. (p. 49). (2) The reversal of step 2, because of the increasing concentration of PhSH. k_{-2} is expected to be approximately 10^3 times k_2.[69] The effects of the reversal in eq. 2, p. 42, has been tested by conducting the racemization in the presence of both benzenethiol (PhSH) and diphenyl disulfide (PhSSPh). The results (Table VIII, p. 113) show that racemization is retarded by the presence of PhSH. The greater the amount of PhSH, the less the racemization. Since T· is lost during the reaction, while the concentration of PhSH is continuously increasing, the concentration of T· should eventually decrease significantly.

Thus, it may be postulated that at high initial concentrations of PhSSPh, the initial racemization rate is relatively high but it slows down rapidly due to the two factors above. At lower initial concentrations of PhSSPh, the initial racemization rate will be lower, but it will slow down more slowly. This results in a cancellation of effects as far as the degree of racemization within a fixed period of time is concerned. The net result is only a minor variation in the degree of racemization with the concentration of PhSSPh.

Inconsistencies have been observed in the results of the reference sample in our various experiments. These reference samples, prepared without added diphenyl disulfide, have shown varying degrees of racemization, ranging from 7.5% to 63%, for a heating period of 48 hr. at 197°C (p. 114). The samples with added diphenyl disulfide consistently have shown 34 ± 1% racemization under the same reaction conditions.

Based on the results obtained in triglyme alone, p. 23, it can be concluded that the racemization observed in the reference samples is caused by the presence of residual hydroperoxides in the solvent.

Hawkins and Santer have reported that diphenyl disulfide (0.1% in concentration) inhibited the autoxidation of polyolefins.[71] This was attributed to the ability of the disulfide to decompose hydroperoxides into non-radical products (eq. 45-1). The resulting sulfoxide was reported to be an even better radical scavenger than

$$ROOH + PhSSPh \rightarrow PhS(=O)SPh + ROH \qquad (45\text{-}1)$$

diphenyl disulfide.

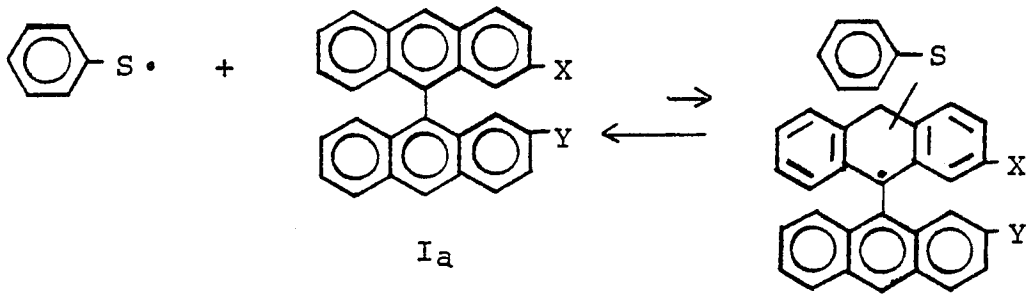
In the present work, the concentration of triglyme in each sample was 5.5 mole/l. and that of diphenyl disulfide was 3.2×10^{-2} mole/l.. Even if the concentration of triglyme hydroperoxide were assumed to be as high as 10% (an unreasonably high figure since the triglyme used was purified), the ratio of diphenyl disulfide to hydroperoxide would still be higher than in Hawkins' work. probably cnly a small portion of this disulfide is necessary to decompose the hydroperoxides present in the sample, and thus quench the reaction initiated by hydroperoxides. Therefore, the 34% racemization can be considered as essentially due to catalysis initiated by phenylthiyl radicals.

No racemization of 2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) was observed when the reaction was conducted in a solvent which did not contain easily abstractable hydrogens (pp. 120-122). Two possible explanations could be envisioned for the failure to observe racemization in aromatic solvents such as diphenyl ether (p. 121) and dimethyl phthalate (p. 122). First, it might be due to the competition for thiyl radical by the aromatic solvent. The enormous amount of aromatic solvent would act as a scavenger for the thiyl radical. Second, it might be due to the lack of a chain transfer agent, i.e., an abstractable hydrogen atom, in these systems. If the first possibility is correct, the substitution product of the aromatic solvent by the phenylthiyl group would have formed. If the second possibility is correct it is a further indication that phenylthiyl radicals do not directly catalyze the racemization of Ia. The results at hand, presently, do not permit a conclusion about this matter.

Thus, the general case for the present system can be stated as follows: (i) In order to obtain racemization of Ia in the presence of diphenyl disulfide, a solvent containing abstractable hydrogens is necessary. (ii) Phenylthiyl radical itself does not catalyze the racemization of Ia.

Phenylthiyl radical can react, in solution, in two different ways. First, it can attack aromatic substrates and subsequently, although rarely, lead to the formation of a substitution product.[62,66b] Second, it can abstract a hydrogen from the solvent.

The attack of phenylthiyl radical on Ia (eq. 47-1) could result in the formation of a radical complex XXXV. The newly formed C-S bond may be so weak that the



(47-1)

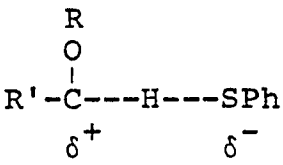
Ia

XXXV

X=Y = $COOCH_3$

elimination rate of PhS· from XXXV is very high and the racemization of XXXV does not have a chance to occur.

The bond dissociation energy of a C-H bond in triglyme is estimated to be less than 88 Kcal/mole (the C-H bond dissociation energy in $CH_3\underset{H}{\underset{|}{C}}HOH$ was reported to be $\leq$88 Kcal/mole[72b]). The bond dissociation energy of the S-H bond in benzenethiol was reported to be 82 Kcal/mole.[72a] Hydrogen abstraction from triglyme by thiyl radical is thus not an appreciable endothermic process. This hydrogen abstraction is also aided by a favorable polar situation (48-1).[66c]



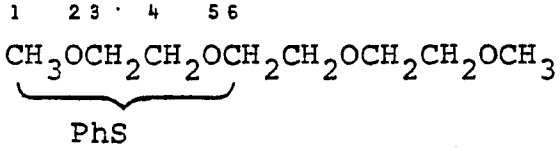
(48-1)

B. Recovery and Investigation of the Products of the Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (I_a)

A sample containing 0.2 g of I_a and 0.35 g. of diphenyl disulfide was heated at 196.6 ± 0.1°C for 96 hr. (p.116). The racemized material (43.4% racemization) was separated into four fractions by column chromatography. The first fraction consisted of diphenyl disulfide (p.117) in 37% recovery.

The second fraction was chemically unchanged Ia, in 78% recovery. It was 43.9% racemized.

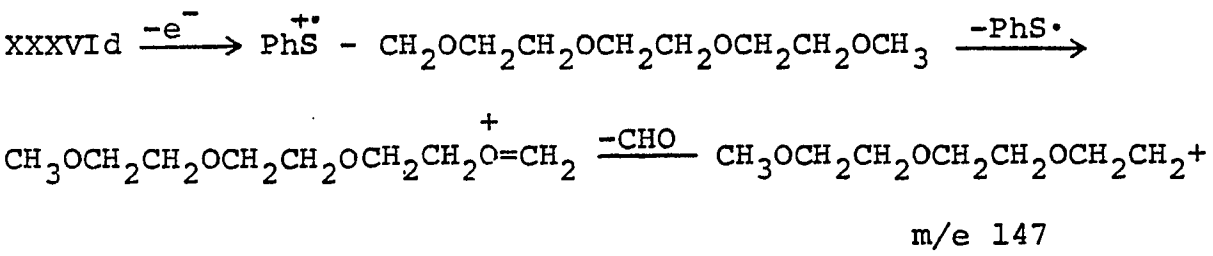
The third fraction was a substitution product of the phenylthiyl group on triglyme, perhaps a mixture (p. 117) of positional isomers (XXXVIa-c).



Compounds	PhS- at
XXXVIa,	C-3
XXXVIb,	C-4
XXXVIc,	C-6
XXXVId,	C-1

XXXVId would be expected to show a fragment peak at m/e 147 (Scheme X) in its mass spectrum.[73]

Scheme X



This peak is absent. Intense peaks at m/e 103 (98%), m/e 59 (100%) and m/e 15 (77%) are present.

Calculation of the recovery of these substitution products shows that 70% of the phenylthiyl radicals reacted with T· (eq. 5, Scheme IX, p. 42). It is postulated that when a diphenyl disulfide decomposes to form two PhS· radicals, before these radicals can move away from each other, one of them abstracts a hydrogen atom from triglyme to form T·, and the other terminates the T· right away. This makes the reaction rate of the termination step (eq. 5), Scheme IX) extraordinarily high and explains the high yield of XXXVI that is observed.

The fourth fraction was a mixture of homolytic aromatic substitution products of Ia by T·. Because of the complexity of the nmr spectrum, detailed information could not be obtained.

C. Mechanism.

Scheme IX, steps 1-5, p. 42, is proposed as the pathway for the racemization of (+)2,2'-dicarbomethoxy-9,9'-bianthryl(Ia) in the presence of diphenyl disulfide, where TH and T· are triglyme and its derived radical, respectively. A thiyl radical formed from step 1 abstracts hydrogen from triglyme (step 2). The triglyme radical (T·) thus formed can behave in several ways. In step 3, T· attacks Ia (BH) to form the radical complex TBH·. Racemization of TBH· requires less energy than the racemization of Ia due to a

reduced rotational barrier, as discussed on pp. 32-36. TBH• can then give up T• (reverse of reaction 3) to form racemized Ia, or it can give up H (step 4, hydrogen abstraction by T• or PhS•) to form a substitution product.

The reverse reaction of step 3 accounts for the observed chemically unchanged racemized Ia (p. 42). The recovery of this material is high (78%). This suggests that the C-10 hydrogen in the radical complex TBH• (see p. 32, XXXII) is highly hindered. Neither PhS• nor T• is able to remove the C-10 hydrogen, and so TBH• preferentially dissociates. A small amount of substitution products were, however, formed. Further discussion on this matter appears on p. 74 and p. 78.

III. Racemization of Optically Active 2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of Dibenzyl Mercury Using Dimethyl Suberate as the Solvent.

In the systems already presented, the isolation of aromatic substitution products demonstrated the existence of carbon radicals (see p. 28), which arose by hydrogen abstraction from the solvent by other radicals.

A major difficulty inherent in these systems is the existence of more than one kind of radical during the racemization reaction. This makes the interpretation of the catalytic effect of a specific radical on the racemization of Ia less conclusive. For instance, in the racemization of Ia, in the presence of oxygen there are four different kinds of radicals (T·, TO·, TOO·, and HO·) possibly present in solution. Although no substitution products derived from TO·, TOO· and HO· were obtained, the attack of these radicals on Ia cannot be ruled out. They may indeed add to the aromatic system, but the rate of radical elimination compared to hydrogen abstraction may be high so that addition products are not obtained. It is possible that the recovered, chemically unchanged Ia, may arise from the attack of these radicals, whereas carbon radicals attack Ia irreversibly to form the addition products (XVIIIa, XVIIIb, XVIIIc, p. 27).

The literature contains conflicting reports concerning the reversibility of addition of a carbon radical to an aromatic ring.[30a, 72,75] There is general agreement that the addition is irreversible at low temperatures, however, it may become reversible at higher temperatures.[54] In order to investigate the possibility of reversible addition of carbon radicals to Ia, the racemization in the presence of $Hg(PhCH_2)_2$ was studied.

Dimethyl suberate was chosen as the solvent in order to remove the possibility of oxygen-radical catalysis as would be the case with triglyme as the solvent.

A. Racemization of (+)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of Dibenzyl Mercury Using Dimethyl Suberate as the Solvent.

The generation of benzyl radicals by the thermal decomposition of dibenzyl mercury was first reported by Razuvaev and Koton in 1931.[52] $(PhCH_2)_2Hg$ was decomposed into Hg and $(PhCH_2)_2$ with and without the presence of a hydrogen donor. It was suggested that benzyl radicals were intermediates in the pyrolysis. Since then, many authors have utilized dibenzyl mercury as the source of benzyl radicals. In 1963, R. A. Jackson[56] reported the reaction of benzyl radicals with substituted toluenes. Scheme XI was proposed to account for the observed results. It was

Scheme XI

$Hg(CH_2Ph)_2 \rightarrow Hg + 2PhCH_2\cdot$ (1)

$2PhCH_2\cdot \rightarrow PhCH_2CH_2Ph$ (2)

$PhCH_2\cdot + CH_3C_6H_4Cl \rightarrow PhCH_3 + \cdot CH_2C_6H_4Cl$ (3)

$PhCH_2\cdot + \cdot CH_2C_6H_4Cl \rightarrow PhCH_2CH_2C_6H_4Cl$ (4)

$2 \cdot CH_2C_6H_4Cl \rightarrow ClC_6H_4CH_2CH_2C_6H_4Cl$ (5)

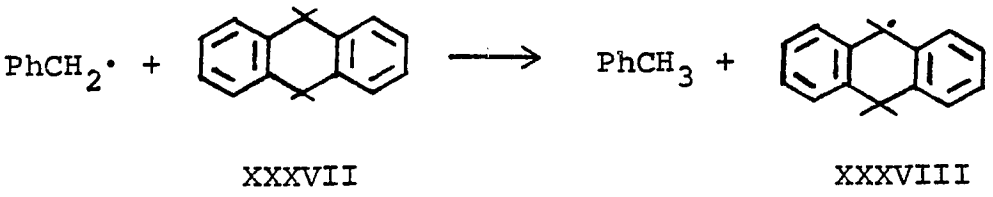
suggested that reaction 3, Scheme XI, takes place to a considerable extent giving rise to 4-chlorobenzyl radicals which subsequently dimerize or react with benzyl radicals to give the chlorinated bibenzyls observed. In 1964, K. C. Bass[59] reported the hydrogen abstraction from 9,10-dihydroanthracene (XXXVII, Scheme XII) by benzyl radicals generated by the thermal decomposition of dibenzyl mercury. Scheme XII was proposed to account for the formation of 9,9',10,10'-tetrahydro-9,9'-bianthryl (XXXIX).

In 1965, Bass and Nababsing[53] reported the reaction of benzyl radicals, from dibenzyl mercury, with anthracene. In addition to other disproportionation and substitution products, they were able to isolate 9-benzyl anthracene (XXXXI). Scheme XIII, p. 56, was proposed to account for the formation of these observed products. In an earlier study, Beckwith and Waters[60] did not find XXXXI in the reaction of anthracene with benzyl radicals derived from the hydrogen

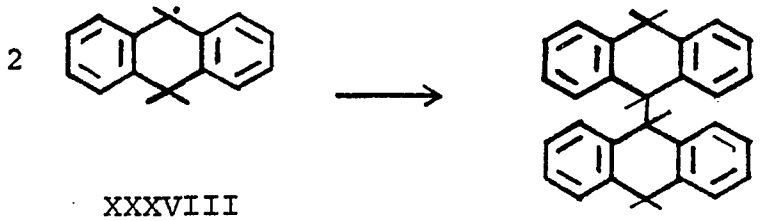
Scheme XII

$$(PhCH_2)_2Hg \rightarrow 2PhCH_2\cdot + Hg$$

$$2PhCH_2\cdot \rightarrow (PhCH_2)_2$$

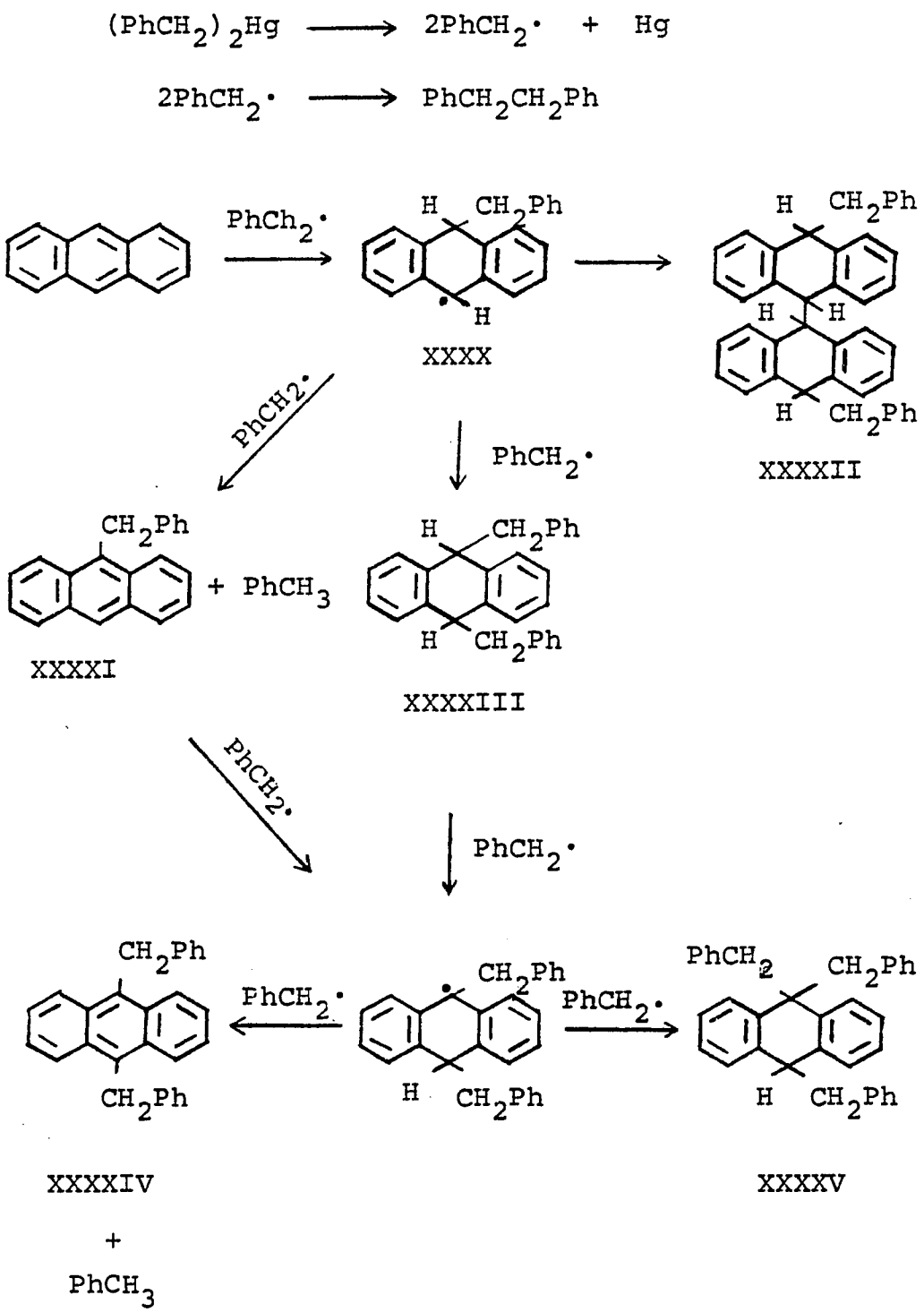


XXXVII XXXVIII



XXXVIII XXXIX

Scheme XIII


(PhCH2)2Hg → 2PhCH2· + Hg
2PhCH2· → PhCH2CH2Ph
PhCh2·
H CH2Ph
H
XXXX
H CH2Ph
H H
H CH2Ph
XXXXII
PhCH2·
PhCH2·
CH2Ph
+ PhCH3
XXXXI
H CH2Ph
H CH2Ph
XXXXIII
PhCH2·
PhCH2·
CH2Ph
CH2Ph
PhCH2·
CH2Ph
H CH2Ph
PhCH2·
PhCH2 CH2Ph
H CH2Ph
XXXXIV
+
PhCH3
XXXXV

abstraction of toluene by tert-butoxyl radicals. However, XXXX, XXXXII, XXXXIII, XXXXIV and XXXXV were isolated, in agreement with those found by Bass and Nababsing.

It has been pointed out[86a,87] that thermolysis of organomercury compounds at elevated temp. can happen in a single stage

$$R_2Hg \rightarrow 2R\cdot + Hg$$

or, less often, in two stages

$$R_2Hg \rightarrow RHg\cdot + R\cdot$$

$$RHg\cdot \rightarrow R\cdot + Hg$$

The actual route of decomposition may depend on the reaction temperature.[88] The two-stage decomposition occurs more readily under UV irradiation.[86b]

From the above results we see that a benzyl radical, formed from the pyrolysis of dibenzyl mercury, can behave in two ways in solution. First, when feasible, it can abstract a hydrogen. Second, it can undergo a homolytic aromatic substitution reaction. In the reaction of anthracene with benzyl radicals, radical complex XXXX, p.56, was suggested to be an intermediate leading to the formation of the observed products.

The racemization of (+)2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) in the presence of dibenzyl mercury proceeded

to the extent of 66% on heating at 186.8 ± 0.1°C for two hr. (p. 123). It appears that dibenzyl mercury decomposes rapidly at 186.8°C. The percent racemization reached as high as 50% after only 10 min. of heating.

To ascertain that the racemization was caused by benzyl radicals, derived from dibenzyl mercury, and not by mercury, another experiment was conducted.

A sample containing (+)2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) (0.03 g., 6.4×10^{-5} mole) and mercury (0.06 g., 3×10^{-4} mole) in 10 ml. of dimethyl suberate, was heated at 187 ± 0.1°C for 2 hr. No racemization occurred. A control sample (without added mercury) also showed no racemization. It thus appears that benzyl radical is the species which is involved in the racemization.

In our study of the racemization of (-)2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) in the presence of diphenyl disulfide, it was discovered (Table I, p. 41) that the degree of racemization did not change significantly with changes in the concentrations of diphenyl disulfide. This was attributed to the ineffectiveness of phenylthiyl radicals in catalyzing the racemization of (-)2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) in triglyme as the solvent. The observed racemization of Ia was considered to be due to the catalysis by carbon radicals of triglyme, generated by the hydrogen abstraction of phenylthiyl radicals.[53,64]

An experiment designed to test the effect of the concentration of dibenzyl mercury was conducted. Table II shows that the degree of racemization was dependent on the concentration of dibenzyl mercury.

Table II

Sample	Dibenzyl Mercury(mole)	Dibenzyl Mercury bianthryl	Racemization(%)[a]
1	6.4×10^{-4}	10	75
2	3.2×10^{-4}	5.0	69
3	1.9×10^{-4}	3.0	66
4	6.4×10^{-5}	1.0	54
5	3.2×10^{-5}	0.50	43

a. After heating at 186.3 ± 0.1°C for 2 hr. See p. 127.

It thus appears that the benzyl radical, unlike the phenylthiyl radical, directly participates in the racemization of Ia. On the other hand, benzyl radical could abstract a hydrogen from dimethyl suberate (DMS-H), 59-1, and the

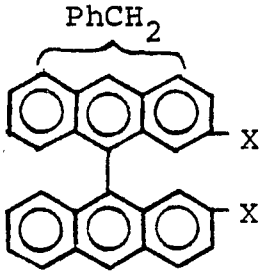
$$PhCH_2\cdot + DMS\text{-}H \rightarrow DMS\cdot + PhCH_3 \qquad (59\text{-}1)$$

resulting DMS· could be the species which causes the racemization of Ia. Since substitution products from the attack of $PhCH_2\cdot$ and DMS· were isolated (p. 60), it appears as if both $PhCH_2\cdot$ and DMS· directly participate in the racemization.

B. Investigation of the Products of the Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia).

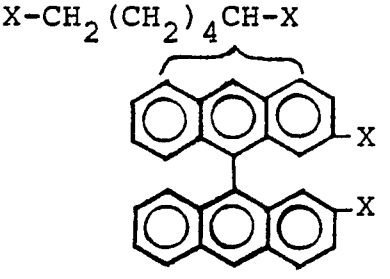
A sample containing 0.4 g. (3.2×10^{-4} mole) of Ia and 1.22 g. (1.6×10^{-3} mole) of dibenzyl mercury in 50 ml. of dimethyl suberate was heated at 187 ± 0.1°C for 2 hr. (70% racemization). Preparative tlc resulted in the recovery of 80% of the starting material. It was 72% racemized.

Two substitution products, XXXXVI and XXXXVII were also isolated.



XXXXVI

X = $COOCH_3$



XXXXVII

Compound XXXXVI was obtained in 2% yield and was found to be optically inactive. Its mass spectrum shows a molecular ion at m/e 560.

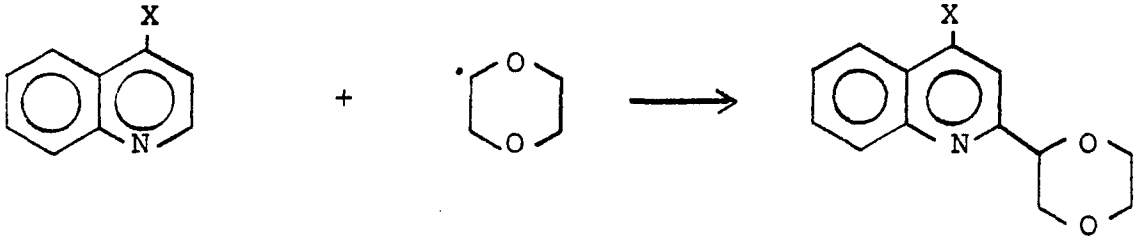
S. C. Dickerman and coworkers[47] reported that the relative reactivities of the three positions of anthracene in homolytic phenylation were C-9:C-1:C-2 = 59:4:1. Since benzyl radical is expected to be more stable than phenyl radical, it would be expected that benzyl radical would be more selective than phenyl radical in an homolytic aromatic substitution reaction.[74]

Of the eight possible positions of attachment for the benzyl substituent in XXXXVI, p. 60, positions 4, 5 and 10 are considerd more likely than the other positions, based on the relative reactivities reported by Dickerman et al.[47] and the geometry (steric hindrance) of the molecule. The 10-position should be the most reactive. The nmr spectrum of XXXXVI suggests that the major substitution is not at C-10. At the original C-10 hydrogen absorption position in the nmr spectrum of XXXXVI two equal intensity peaks appear, indicating two different hydrogens at the C-10 and C-10' positions. If the position of attachment of the benzyl substituent was at C-10, only one peak at the original C-10 hydrogen absorption region would be present. One of the two observed peaks is at the original C-10 hydrogen absorption position (δ 8.66), the other is 12 Hz up-field at δ 8.54.

XXXXVI could be considered as a mixture of three positional isomers, such as 4-benzyl and 10-benzyl or 5-benzyl and 10 benzyl. In light of the equal heights of

the two peaks appearing at the original C-10 hydrogen absorption region, this possibility is considered to be unlikely. For if it were so, the peak at δ 8.66 would be higher than the peak at δ 8.54.

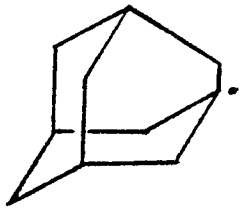
In 1971, W. Buratti and coworkers[77a] demonstrated a substituent effect on the position of substitution in the homolytic dioxanylation of 4-substituted quinolines (XXXXVIII).



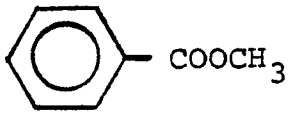
XXXXVIII

When X = $CO_2C_2H_5$, $\frac{K_X}{K_H}$ was reported to be 7.1. No substitution products resulting from the attack of dioxanyl radical at the other positions were found.

In 1975 L. Testoferri and coworkers[61,81] reported that the reactions between the 1-adamantyl radical, XXXXIX, and methyl benzoate, L, was 11 times faster than the reactions between XXXXIX and benzene.



XXXXIX



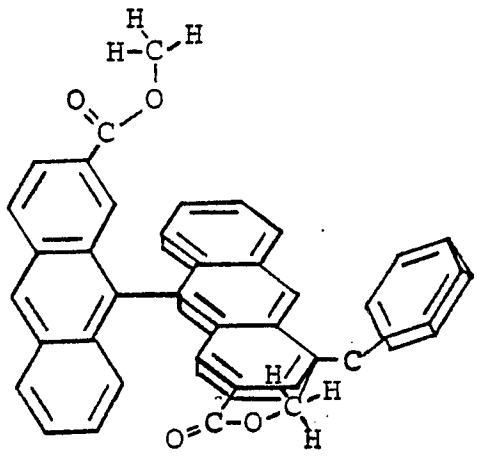
L

In both of the above cases, the rate increase caused by the presence of the ester group was attributed to the nucleophilic character of the incipient carbon radicals.[78]

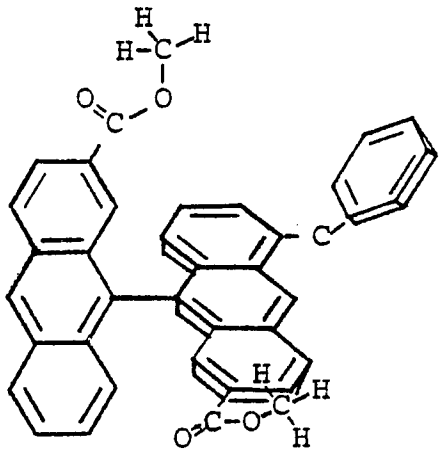
The nmr data of XXXXVI, p. 60, also suggests that the carbomethoxy group has a large effect on the orientation of the benzyl group in the homolytic benzylation of 2,2'-dicarbomethoxy-9,9'-bianthryl(Ia). There are two $-OCH_3$ peaks, indicating that the environments of the two carbomethoxy groups are not equal. One of these peaks is at the original position, δ 3.70, the other is 22 Hz up-field at 3.48. (See f, p. 130).

A benzyl group at C-5 (LII) would have a much smaller shielding effect on the methoxy hydrogens of the same

anthracyl ring than would a benzyl group at C-4 (LI). An estimate of the distance between the center of



LI



LII

the benzene ring of the benzyl group and the methoxy hydrogens reveals that in LI the distance is in the range of 2.7 to 3.2 units. A unit is defined, by Johnson and Bovey[83] as being equal to the C-C distance in benzene (approximately 1.4 Å). The methoxy hydrogens in such a case would be moved up-field by 0.2 to 0.5 ppm.[83] In LII the distance is more than four units, out of the effective shielding range. This assumes that the two anthracene planes are positioned approximately 90° to each other.[94] The methoxy hydrogens on the other anthracene ring are out of the effective shielding range of the benzyl group, in both LI and LII.

Radical attack at C-3 is expected to be unlikely for the following reasons. First, C-3 is reported to be the least reactive site in the homolytic aromatic phenylation of anthracene.[47] Although C-3 is ortho to the carbomethoxy group, the presence of this group is expected to increase the reactivity at C-1, not at C-3, due to the destabilization by the disruption of aromaticity in the latter case. Second, steric hindrance may impede the incoming benzyl radical from attacking this position. Also, an examination of a Drieding model shows that the C-10 hydrogen would not be in the effective shielding range of the benzene ring of the benzyl group at the C-3 position. In order to determine the actual position of benzyl substitution in XXXXVI, p. 60, an attempt was made to study the ^{13}C nmr spectrum of XXXXVI. Unfortunately, this approach was not successful. A suitable solvent could not be found.

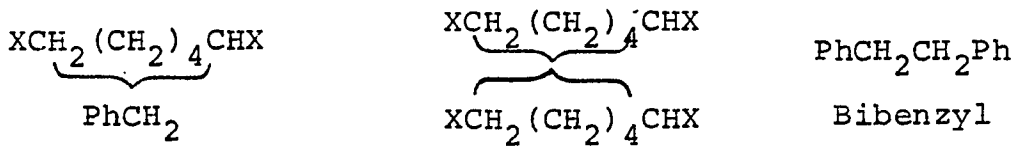
From the above arguments we tentatively conclude that the benzyl group exists at C-4 or C-5.

Compound XXXXVII, p. 60, was also found to be optically inactive. It was obtained in 14% yield. Its mass spectrum shows a molecular ion at m/e 670. Its nmr spectrum, like compound XXXXVI, also shows two peaks of equal height near the original C-10 hydrogen absorption position. The difference in chemical shifts of these peaks

is 4 Hz, smaller than in the case of compound XXXXVI. Three peaks due to the carbomethoxy groups are overlapped, an indication of nonequivalent carbomethoxy groups (h, p. 130).

Based on the same reasoning as described for XXXXVI (pp. 61-65), XXXXVII might have its substituent attached to C-4 or C-5.

In addition to the solvent, dimethyl suberate, LIII, LIV, bibenzyl and toluene were also isolated (pp. 129-131).



LIII LIV

X = CO_2CH_3

Toluene apparently comes from the hydrogen abstraction of dimethyl suberate by benzyl radical. LIII, LIV and bibenzyl are the products of radical termination reactions.

Hydrogen abstraction from solvent is known to be one of the most frequently encountered reactions of free radicals.[34] There are several examples which illustrate that C-H bonds adjacent to carboxyl or ester groups are activated towards nucleophilic radical attack. Methyl radical, for instance, abstracts hydrogen from the C-H bond adjacent to the ester groups of dimethyl benzyl malonate.[84]

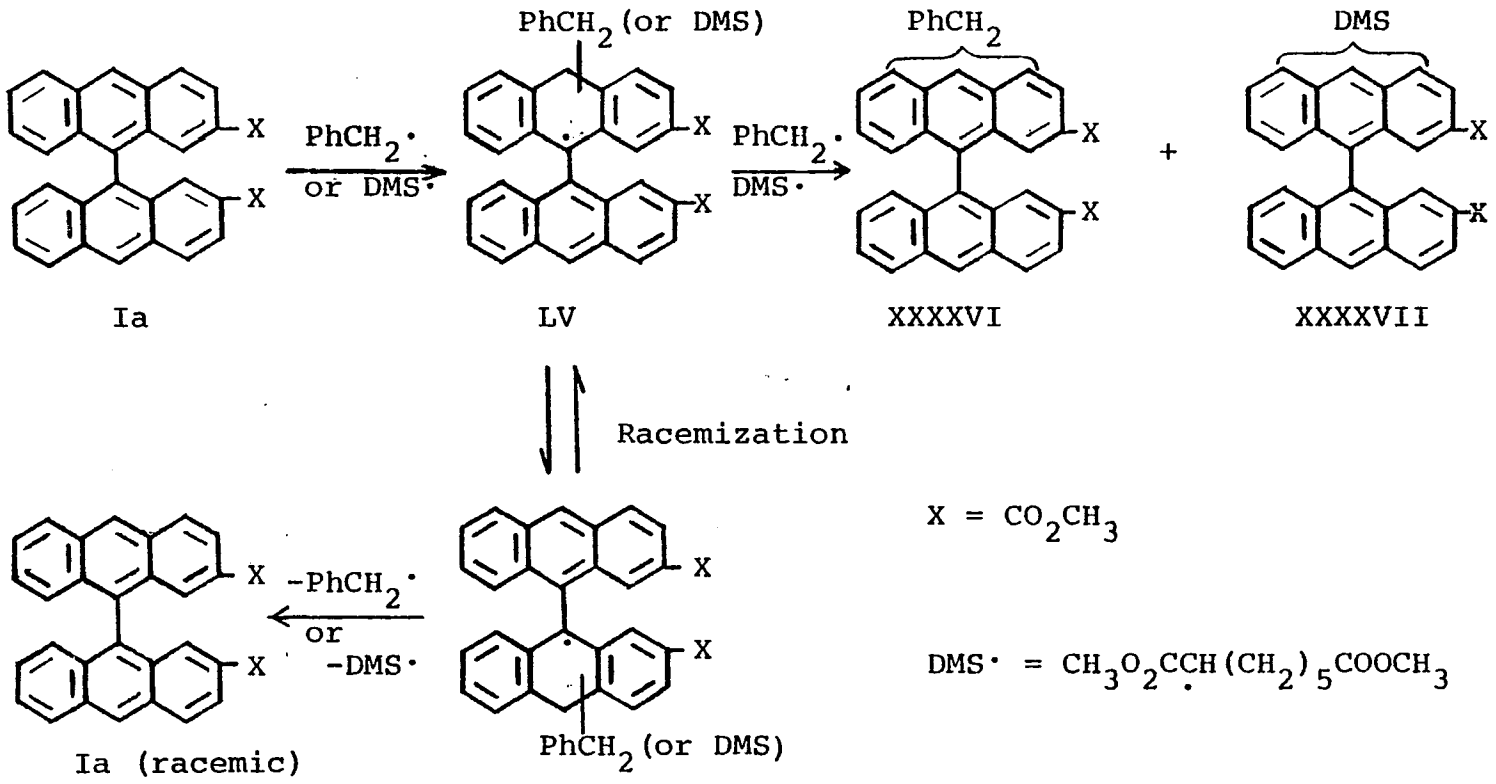
Some electrophilic radicals also exhibit similar behavior. For example, in the reaction between tert-butoxy radicals and propionic acid, abstraction of the α-hydrogen is sixteen times more rapid than abstraction of the β-hydrogens.[85] In the reaction between tert-butoxy radicals and ethyl butyrate, attack on the α position occurs more than ten times faster than attack at β position. The position of attachment in LIII and LIV is probably at the α positions. This does not mean to completely exclude the possibility of other positions of attachment. There are reports that β abstraction may exceed α abstraction.[82] The other isomers might have been present in low concentrations.

C. Mechanism.

The racemization of (+)2,2'-dicarbomethoxy-9,9-bianthryl (Ia) in the presence of dibenzyl mercury is suggested to follow the same type of pathway as described in Scheme XIII, p. 56. The formation of radical complex LV, p. 68, is indirectly indicated by the measurement of the optical rotation of Ia before and after the reaction and by the isolation of the addition products XXXXVI and XXXXVII, Scheme XIV, p. 68.

Ia was recovered in 80% yield. It was extensively racemized (72%). Compound XXXXVI was obtained in 2% yield and compound XXXXVII was obtained in 14% yield.

Scheme XIV


PhCH2 (or DMS)
PhCH2
DMS
X
PhCH2·
or DMS·
PhCH2·
DMS·
+
Ia
LV
XXXXVI
XXXXVII
Racemization
-PhCH2·
or
-DMS·
Ia (racemic)
PhCH2 (or DMS)
X = CO2CH3
DMS· = CH3O2CCH(CH2)5COOCH3

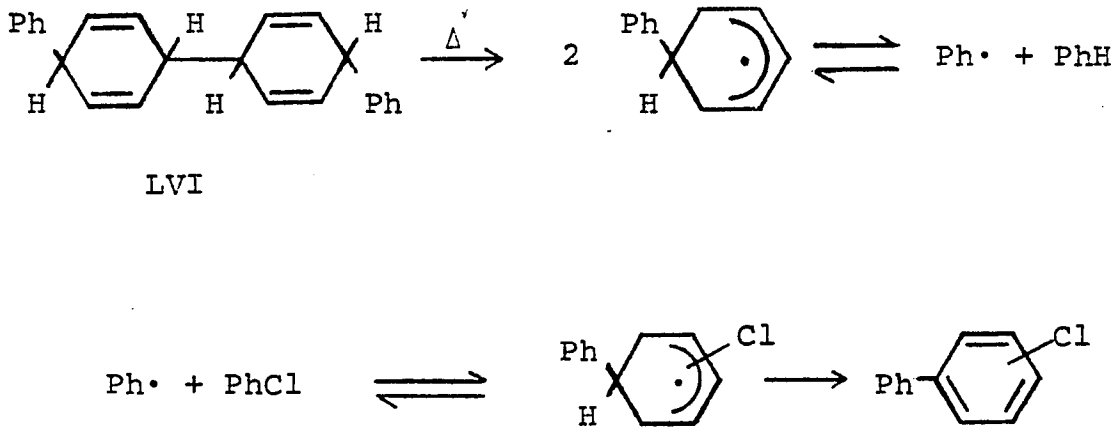
These findings suggest the formation of radical complex LV, and indicate that the attack of carbon radicals (benzyl or DMS.) on the poly-aromatic ring of Ia is reversible.

The discovery of the reversible homolytic alkylation in the present study is consistent with the results from the previous systems already described.

As mentioned in the introduction, p. 10 , the reversibility of radical attack on an aromatic ring has been a controversial subject in the literature. The failure to observe a large isotope effect has been interpreted as indicating that the formation of arylcyclohexadienyl radicals is an irreversible process.[22,25] At higher temperatures the process does seem to be reversible. Perkins demonstrated that phenylcyclohexadienyl radicals, generated by the thermolysis of 1,1',4,4'-tetrahydro-quaterphenyl (LVI),undergo fragmentation to give phenyl radicals.[30a] This was indicated by the formation of chloro-biphenyls when the reaction was carried out in chloro-benzene as solvent (Scheme XV).

A further indication of the reversibility of the addition step is that isotope effects have been observed in the phenylation of chloro and nitrobenzenes, which is greatest for the formation of ortho-substituted products.[23]

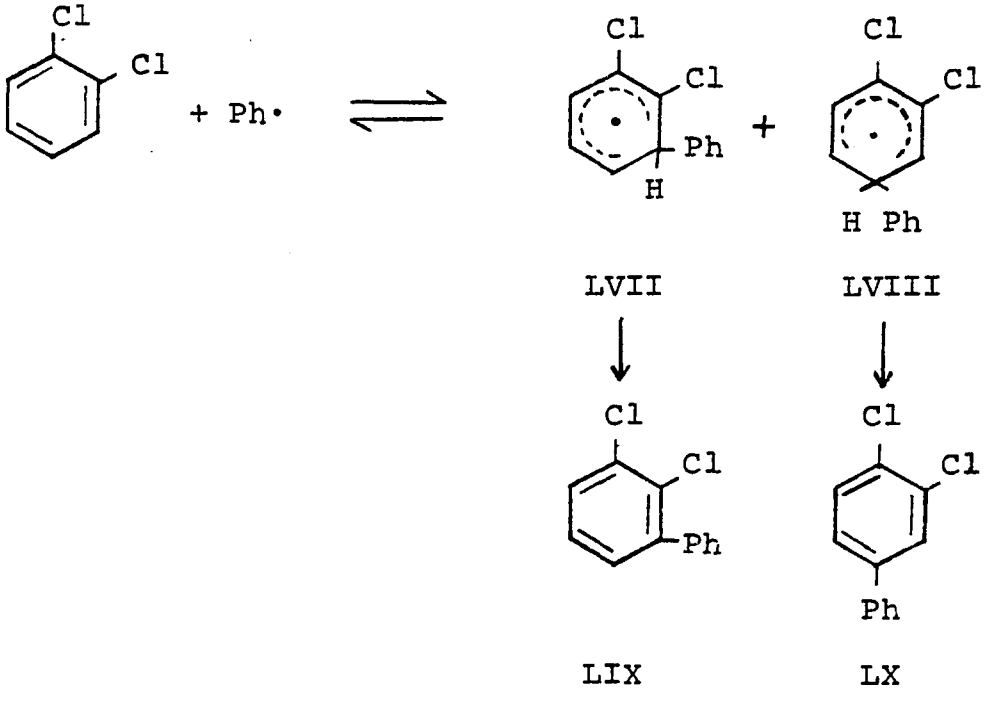
Scheme XV

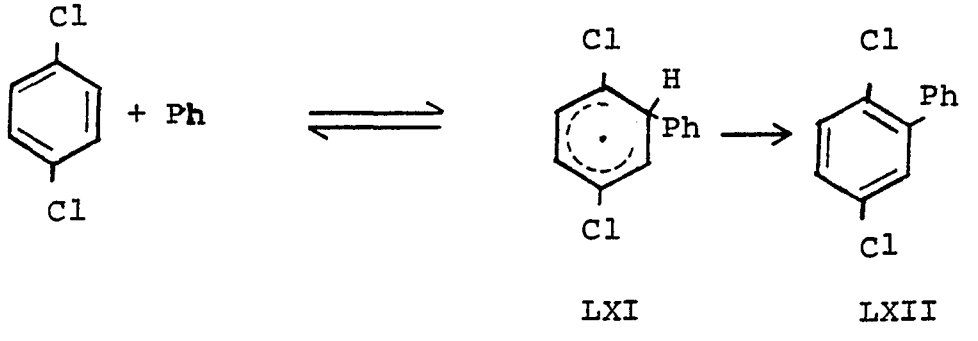


Phenylcyclohexadienyl radicals with substituents in the 2-position would be expected to undergo dissociation more readily than the isomeric radicals with substituents in the 3- and 4-positions because of steric effects. Nonhebel and Henriquez[29d] have presented evidence for the reversibility of the addition of phenyl radicals to benzenoid compounds from a study of the phenylation of o-dichlorobenzene and p-dichlorobenzene. Addition of phenyl radicals to o-dichlorobenzene affords two isomeric phenyldichlorocyclohexadienyl radicals, LVII and LVIII, which lead to 2,3- and 3,4-dichlorobiphenyls (LIX and LX), respectively

(Scheme XVI). The ratio of LIX/LX was found to increase with the addition of copper (II) salts (oxidants) as had been expected on steric grounds, since LVII would be more easily dissociated. The presence of copper (II) salts would convert more LVII to LIX (see p. 72).

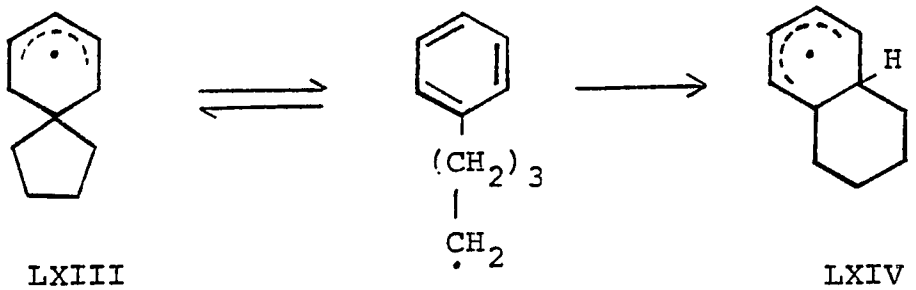
Scheme XVI





This assumes that the presence of Cu^{+2} does not alter the activation energies for the phenylation of each of the isomeric positions. Addition of copper (II) benzoate to the reaction mixture of the phenylation of p-di-substituted benzenes (against benzene as the reference compound) resulted in an increase in the relative rate at each of the temperatures employed. This was interpreted in terms of the reversible formation of radical LXI. LXI should be more prone to undergo dissociation than the unsubstituted phenylcyclohexadienyl radical, because of steric effects. Copper (II) salts affect the efficient oxidation of cyclohexadienyl radical prior to their dissociation, disproportionation or dimerization.

The addition of the $\cdot CF_3$ radical was reported to be irreversible at 65°C, however at 150°C (or higher temp.) it was reversible.[95] The $\cdot CF_2Cl$ radical showed the same behavior as $\cdot CF_3$.[96] Julia[97] has shown that ring closure of 4-phenylbutyl radicals to LXIII, which accompanies cyclization to LXIV, is reversible.[98]



LXIII LXIV

Scheme XVII is proposed as the mechanism for the racemization of (+) 2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) in the presence of dibenzyl mercury.

Scheme XVII Mechanism for the Racemization of Optically Active 2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of Dibenzyl Mercury.

Abbreviations:

$(PhCH_2)_2Hg$ - Dibenzyl Mercury

BH - 2,2'-Dicarbomethoxy-9,9'-bianthryl

HDMS - Dimethyl Suberate

R· - $PhCH_2$· or DMS·

1. $(PhCH_2)_2Hg \rightarrow 2\ PhCH_2\cdot + Hg$
2. $PhCH_2\cdot + HDMS \rightarrow PhCH_3 + DMS\cdot$
3. $PhCH_2\cdot + BH \rightleftarrows (PhCH_2\text{-}BH)\cdot$
4. $(PhCH_2\text{-}BH)\cdot + R\cdot \rightarrow PhCH_2\text{-}B + RH$
5. $DMS\cdot + BH \rightleftarrows (DMS\text{-}BH)\cdot$
6. $(DMS\text{-}BH)\cdot + R\cdot \rightarrow DMS\text{-}B + RH$
7. $2\ DMS\cdot \rightarrow DMS\text{-}DMS$
8. $PhCH_2\cdot + DMS \rightarrow PhCH_2\text{-}DMS$
9. $2\ PhCH_2\cdot \rightarrow PhCH_2CH_2Ph$

Step 1 in Scheme XVII, p. 73, may partially follow the two-stage pathway, as described previously on p. 57. It is conceivable that the resulting $PhCH_2Hg\cdot$ radical could also catalyze the racemization of Ia. However $PhCH_2Hg\cdot$ decomposes very rapidly at room temp.[88] The bond dissociation energy for R-Hg· is less than 6 Kcal/mole.[88,89,90,91] No substitution products resulted from the attack of $PhCH_2Hg\cdot$ on Ia was found.

Step 2 is the familiar hydrogen abstraction from the solvent (dimethyl suberate) by benzyl radicals.

Racemization of Ia occurs after the formation of $(PhCH_2\text{-}BH)\cdot$ and $(DMS\text{-}BH)\cdot$. The explanation for the ease of racemization of these two complexes has been presented on pp. 32-36.

It is interesting to note that C-10 substituted XXXXVI and XXXXVII (p.60) were not found in the racemized material. Based on the reactivities of the various positions of anthracene (p. 61), one might have expected that the major products would be C-10 substituted XXXXVI and XXXXVII, not the C-4 or C-5 substitution products which were obtained. This result can be explained by the difficulty of hydrogen abstraction (steps 4 and 6 of Scheme XVII, p. 73) from the C-10 substituted radicals complexes $(PhCH_2\text{-}BH)\cdot$ and $(DMS\text{-}BH)\cdot$. The C-10 hydrogen of LV (p. 68) is highly hindered by the neighboring peri hydrogens (see page 32 for a similar situation with XXXII). Hydrogen

abstraction from this position would thus be very difficult. Therefore, LV would dissociate back to R• and Ia. The converted and then inverted conformation, analogous to XXXIIc (p. 32), has the C-10 hydrogen in a quasi-axial position. A Drieding model of XXXIIc shows that this hydrogen is hindered by the anthryl group. Moreover, the quasiequatorial R group (T' of p. 32) may be pushed away from the ideal equatorial position in order to minimize the repulsions from the peri hydrogens.[42] This movement will force the quasiaxial hydrogen to bend closer towards the anthryl group, making it even more difficult to abstract by another radical. The attack at C-10 by R• may thus result in total reversibility regardless of which conformation the resulting radical complex assumes. It thus appears that much of the recovered (80%), chemically unchanged, highly racemized (72%), 2,2'-dicabomethoxy-9,9'-bianthryl (Ia) had undergone an attack at C-10 by a radical.

IV. Racemization of Optically Active 2,2'-Dicarbomethoxy-9,9'-bianthryl(Ia) in the Presence of tert-Butyl Peroxide Using Dimethyl Suberate as the Solvent.

In order to assess the generality of the radical catalyzed racemization of Ia, other radical systems were investigated.

The homolytic aromatic substitution by alkoxy radicals has not been reported.[55] Alkoxy radicals, however, can initiate other kinds of radicals by hydrogen abstraction from the solvent.[51c, 85,92,93]

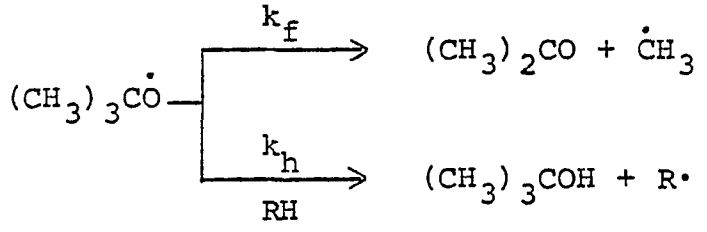
Chronologically, tert-butyl peroxide was studied before dibenzyl mercury (p. 52). The results reveal some interesting points which deserve comment.

A. Racemization of (+)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of tert-Butyl Peroxide.

In a typical experiment a sample which contained Ia (0.03 g., 6.4×10^{-5} mole) and tert-butyl peroxide (0.16 g., 1.1×10^{-3} mole) in 10 ml.of dimethyl suberate (p. 133) showed 82.5% racemization after being heated at 124.7 ± 0.1°C for 161 min. A control sample (without added tert-butyl peroxide) showed no racemization under the same conditions.

Twenty-five percent of the starting material was recovered from a racemized sample (p. 136). This chemically unchanged Ia was 40.6% racemized. The rest of the products

were shown to arise from a homolytic aromatic substitution reaction by dimethyl suberate radicals, derived from hydrogen abstraction by radicals present in the solution. It is known that, in addition to hydrogen abstraction, a tert-butoxy radical can fragment to form a methyl radical and acetone.[58] In the present system, RH is dimethyl



suberate and R· is its radical; k_f/k_h in cyclohexane as solvent was reported to be 0.021.[58] Beckwith[85] reported that decomposition of di-tert-butyl peroxide in butyric acid yields 24% acetone and 60% tert-butanol. It is conceivable that both tert-butoxy and methyl radicals in our system abstract hydrogen from dimethyl suberate to form dimethyl suberate radicals (DMS·). It is possible that all three radicals (tert-butoxy, methyl, DMS·) participate in the homolytic aromatic substitution with I a. However, only substitution products of dimethyl suberate radical was found to be present.

The 75% yield of substitution products was higher than those found in the other systems studied. One possible explanation is that the C-10 hydrogen in the radical intermediate XXXII, p. 32 can be easily removed by alkoxy radicals in the present system. The tert-butoxy radical is inherently smaller than a carbon radical (it only has one substituent bonded to the odd electron-containing atom, while a carbon radical has three substituents) and is better able to abstract the hindered C-10 hydrogen.

As mentioned previously (p. 33), whether or not the C-10 hydrogen can be removed, determines the reversibility of the addition of a radical to bianthryl Ia. In the present system, for the reason outlined in the preceding paragraph, the C-10 hydrogens are more easily removed by tert-butoxy radicals. Therefore, a greater amount of addition products are observed.

Table III., p. 79, summarizes the results from the four systems previously described. It is noteworthy that in systems I and IV, the yield of substitution products are higher than with the systems II and III. Both of the former systems contain oxygen radicals. The results from our investigations point to a trend in the reactions involving oxygen radicals. Hydrogen abstraction becomes

Table III

System	Solvent	Radical Initiator	Radicals Present in the Solution	Heating Temp. (Time)	Degree of Racemization (%)[c]	Recovery of Starting Material (% Racemization)	Yield of Substitution Products (%) (% Racemization)[d]
I	Triglyme	Triglyme Hydroperoxide	TO·, TOO·, T·, HO·, T'·[a]	148.8°C (2.5 hr)	85	41% (62)	46% (95)
II	Triglyme	PhSSPh	PhS·, T·	197°C (96 hr)	45	78% (45)	≈16% (74)
III	Dimethyl Suberate	Dibenzyl Mercury	$PhCH_2$·, DMS·[b]	187°C (2 hr)	70	80% (72)	16% (100)
IV	Dimethyl Suberate	t-Butyl Peroxide	$(CH_3)_3CO$·, CH_3·, DMS·	125°C (3 hr)	64	25% (42)	≈75% (91)

[a] T stands for triglyme.

[b] DMS· stands for dimethyl suberate radicals.

[c] Of the original solution after heating.

[d] Based on the assumption that the original specific rotation was the same as that of the starting material (Ia).

a prominent reaction in contrast to the addition of oxygen radicals to aromatic substrates. The strength of the bond formed by addition of an oxygen radical to the aromatic substrate (e.g. Ia) may be so weak that if a σ complex is formed, its lifetime is relatively short. Bond rotation does not occur in this short-lived radical intermediate. The rapid dissociation (reverse reaction) of this intermediate would yield a chemically and optically unchanged I a as well as the original oxygen radical.

B. Mechanism

Scheme XVIII Mechanism for the Racemization of (+)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of tert-Butyl Peroxide.

Abbreviations

t-BuO· - tert-Butoxy Radical

HDMS - Dimethyl Suberate

BH - 2,2'-Dicarbomethoxy-9,9'-bianthryl

R· - DMS· or t-BuO·

1. tert-Butyl Peroxide $\xrightarrow[k_1]{\Delta}$ 2t-BuO·

2. t-BuO· + HDMS $\xrightarrow{k_2}$ t-BuOH + DMS·

3. DMS· + BH $\underset{k_4}{\overset{k_3}{\rightleftharpoons}}$ DMS-BH·

4. DMS-BH· + R· $\xrightarrow{k_4}$ DMS-B + RH

5. 2DMS· $\xrightarrow{k_5}$ DMS-DMS

6. t-BuO· + DMS· $\xrightarrow{k_6}$ t-BuO -DMS

Scheme XVIII, p. 80, is proposed as the pathway for the racemization of (+) 2,2'-dicarbomethoxy-9,9'-bianthryl (Ia), in the presence of tert-butyl peroxide. The addition of a tert-butoxy radical to bianthryl (Ia) is ignored, because the resulting substitution products have not been found in the products of the racemization of Ia.

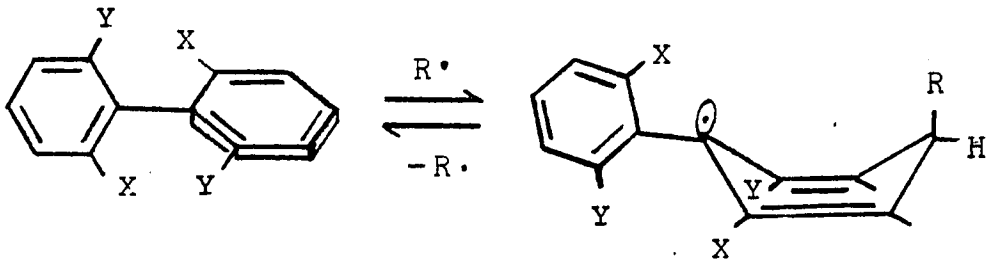
Racemization occurs after the formation of the radical complex DMS-BH• , in step 3, Scheme XVIII. The explanation for the ease of racemization of DMS-BH• appears on pp. 32-35.

The principal functions of the tert-butoxy radical in the present system are two-fold. First, it abstracts a hydrogen from a dimethyl suberate molecule. The resulting dimethyl suberate radical catalyzes the racemization of Ia. Second, it abstracts a C-10 hydrogen from the DMS-BH• complex, resulting in the formation of substitution products.

V. Attempted Racemization of (+)6,6'-Diethyl-2,2'-dicarbomethoxybiphenyl (LXV) in the Presence of Oxygen Using Triglyme as the Solvent.

It is well known that, in addition to bianthryls, biphenyls and binaphthyls can also be made optically active by introducing appropriate groups into the blocking positions.

The discovery of the radical catalyzed racemization of optically active 2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) suggested that other aromatic systems, which owe their optical activity to restricted rotation about the central bond, might also exhibit racemization under the catalysis of radicals. For example, the addition of a radical to the aromatic ring of a biphenyl (LXV) would result in the formation of the radical intermediate LXVI. The boat



LXV LXVI

$X = CO_2CH_3$

$Y = CH_2CH_3$

conformation of LXVI allows the two sets of ortho substituents to pass each other consecutively instead of simultaneously, during the rotation of the central bond, thus reducing the rotational barrier. Therefore, LXVI should be racemized more easily than LXV. The loss of R· from LXVI (reverse reaction) would yield racemized LXV.

The racemization of 6,6'-diethyl-2,2'-dicarbomethoxybiphenyl (LXV, X = CO_2CH_3 and Y = CH_2CH_3) in the presence of oxygen using triglyme as the solvent was studied.

The results of several experiments (p. 142) revealed that there was no racemization of LXV, after heating at 190.0 ± 0.1°C for 3 hr.. Prolonged heating up to 96 hr. still showed no racemization.

After the racemization reaction, the sample could be quantitatively recovered, chemically unchanged. A small amount of impurity from the decomposition of triglyme (p. 143) was present.

Based on the knowledge obtained from the study of the racemization of 2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) in the presence of oxygen (pp. 21-28), one would expect that radicals derived from triglyme should have been formed (by autoxidation). The failure to observe any racemization with LXV (p. 142) in the presence of oxygen may be attributed to the fast dissociation of LXVI (p. 82). The newly formed

bond in LXVI may be so weak that the lifetime of LXVI is relatively short. Bond rotation does not have a chance to occur. Therefore, no racemization was observed.

EXPERIMENTAL SECTION

ANALYSIS

Optical rotations were measured using a Perkin-Elmer 141 polarimeter. Values are reported as the average of three measurements. Melting points were determined using a Thomas-Hoover apparatus, in open capillary tubes, and are corrected; boiling points are uncorrected. Mass spectra were determined using a Varian CH-5 Mass Spectrometer at 70 ev, under direct sample inlet and linear mass scan conditions. Proton magnetic resonance spectra were determined using a Jeol MH-100 spectrometer. Chemical shifts are expressed in ppm (δ) downfield from internal tetramethylsilane ($\delta = 0$). Infrared spectra were taken using either a Beckman IR-20A or a Perkin-Elmer 237 spectrophotometer. Heating of samples was conducted by using a constant temperature circulator, Model NBS, Polyscience-HAAKE Inc., Evanston Ill.. The circulator was filled with silicone oil (Dow Corning, 210 H Fluid). Unless otherwise indicated, silica gel (100-200 mesh, Grace, Baltimore, Md.) was used in column chromatography. Thin layer chromatography analysis were conducted by using precoated silica gel plates (2000μ and/or 250μ , ANALTECH, Newark, Del.). Gas liquid chromatography was performed using either a Varian A 90-P chromatograph

with thermal conductivity detection (column 1) or a HP-5750B Chromatograph with flame ionization detection (column 2).

Column 1 SE-30 (25 %) on 45/60 mesh Chrom. P. in a 1/4" x 15' stainless steel column.

Column 2 SE-30 (10 %) on 60/80 mesh Chrom. W. in a 1/8" x 6' stainless steel column.

I. Preparation of Optically Active 2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia)

A. Preparation of 2,2'-Dicarboxy-9,9'-bianthryl (Ib).

1. Column Chromatography of 2,2'-Dicyano-9,9'-bianthryl (Ic).

Impure 2,2'-dicyano-9,9'-bianthryl (Ic)* (15 g.) was dissolved in a warm solution of 125 ml.$CHCl_3$ and 5 ml. ethanol (95%). This solution (after being cooled to room temp. was chromatographed on 600 g silica gel, packed as a slurry in $CHCl_3$ and benzene (1: 1).

The column was eluted by the same mixture of solvents, $CHCl_3$ and benzene (1:1).

The first band, which showed a green fluorescence under UV light, was 2-chloro-2'-cyano-9,9'-bianthryl (Id).

The second band, which appeared blue under UV light, was 2,2'-dicyano-9,9'-bianthryl (Ic); m.p. 342-344°C; ir (KBr): 3050 (w), 2230 (s, C≡N), 1615 (w), 1510 (w), 1450 (w), 1425 (w), 1405 (w), 1310 (m), 1010 (w), 950 (w), 895 (s), 888 (s), 785 (m), 740 (s).

The third band, which appeared deep blue under UV light, was not identified.

---

*Prepared by Dr. Chen-Shek Yu. It contained 2-chloro-2'-cyano-9,9'-bianthryl.

2. Hyrolysis of 2,2'-Dicyano-9,9'-bianthryl (Ic).

In a 5 l. three-necked flask, equipped with a mechanical stirrer, reflux condenser and a heating mantle, were placed 30 g. (7.42×10^{-2} mole) of 2,2'-dicyano-9,9'-bianthryl (Ic), 942 g. (16.8 mole) of KOH, 3500 ml. of MeOH and 1000 ml. H_2O. The mixture was heated at reflux with stirring for 39 hr.. The cooled mixture was filtered to remove a small amount of insoluble material. The filtrate was acidified with concentrated HCl to give a yellow precipitate which was washed with a large volume of water and recrystallized from acetic acid to yield 21.5 g of 2,2'-dicarboxy-9,9'-bianthryl (Ib); m.p. 417-420°C; mass spectrum m/e (intensity using linear mass scan) 442 (100), 398 (32), 350 (28); ir (KBr) 3600-2400 cm^{-1} (COOH), 1680 cm^{-1} (COOH).

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

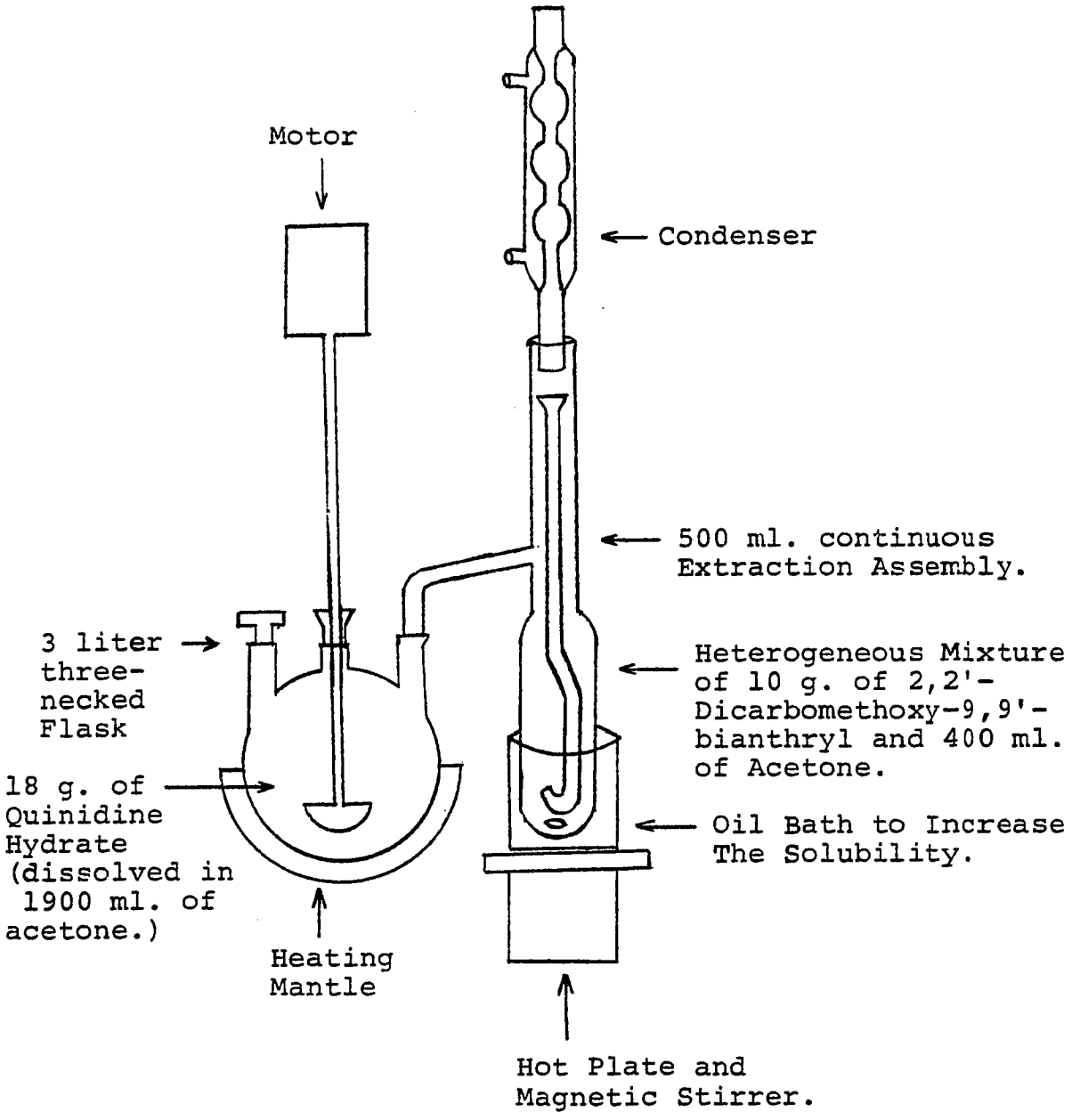
1. Preparation of Quinidine Hydrate from Quinidine Sulfate.

Quinidine hydrate was obtained by treating quinidine sulfate (38 g., 5.1 x 10^{-2} mole) with ammonia (28 %, 500 ml.) and extracting the resulting suspension with ether (2400 ml.). The ether solution was dried over $MgSO_4$, filtered and evaporated to give 28.23 g. of quinidine hydrate.

2. Resolution.

A suspension of 10 g. (2.3 x 10^{-2} mole) (±) 2,2'-dicarboxy-9,9'-bianthryl (Ib), p. 88, in 400 ml. of acetone, was placed in a 500 ml. continuous extraction assembly. The side arm of the extraction assembly was attached to a 3 l. three-necked flask equipped with a mechanical stirrer and a heating mantle (Figure III, p. 90). Into the three-necked flask were placed 18 g. (4.8 x 10^{-2} mole) of quinidine hydrate and 1900 ml. of acetone. This mixture was heated at reflux with stirring until all the (±)2,2'-dicarboxy-9,9'-bianthryl (Ib) had been extracted and had reacted with quinidine hydrate.(The solid Ib was considerably more dense than the liquid phase and remained at the bottom of the extraction vessel.) This took about 24 hr. until no more Ib (yellow color) was left in the extraction assembly. During the extraction period yellow crystals began to precipitate in the three-necked flask. After cooling the precipitated

Figure III Resolution Reaction System.



yellow solid was collected by suction filtration and dried under vacuum at 95-100°C to yield 12.6 g. of quinidine salt; $[\alpha]_{589}^{23°C}$ = +37° (c 0.5, CH_3OH).

The mother liquor was concentrated to 600 ml. which upon cooling deposited a pale yellow sponge-like solid. The mixture was filtered, and the filtrate was evaporated to dryness to yield 9 g. of a yellow solid. This solid was dissolved in 60 ml. of ethanol (95%). The solution was cooled in an ice bath, and 50 ml. of conc. HCl was added over a period of 30 min. with stirring. A yellow solid precipitated. The mixture was stirred for an additional 30 min., 70 ml. of water was added and the precipitated yellow solid was collected by suction filtration. The washing procedure was repeated by suspending the yellow solid in 30 ml. of ethanol (95%) and treating with 25 ml. of conc. HCl. The yellow solid, so obtained, was thoroughly washed with water and dried under vacuum at 95-100°C to yield 2.4 g (+) 2,2'-dicarboxy-9,9'-bianthryl (Ib); $[\alpha]_{589}^{23°C}$ = +100.7 (c 0.3, acetone); m.p. >390°C; ir (KBr) essentially identical to that of racemic 2,2'-dicarboxy-9,9'-bianthryl (Ib).

The dextrorotatory quinidine salt (first crop from the acetone solution) was similarly decomposed, except that it was not completely soluble in 100 ml. of ethanol (95%). To the cooled (ice bath) suspension, 50 ml. of

conc. HCl was slowly added, with stirring. At first a clear yellow solution was obtained, then a yellow solid precipitated. The mixture was stirred for an additional 30 min., 100 ml. of water was added and the yellow precipitated solid was collected by suction filtration. The washing process with HCl was repeated. The yellow solid obtained was washed thoroughly with water and dried under vacuum at 95-100°C to yield 4.15 g (-) 2,2'-dicarboxy-9,9'-bianthryl (Ib); $[\alpha]_{589}^{23°C} = -114.7°$ (c 0.3, acetone); m.p. >390°C; ir (KBr) essentially identically to that of racemic 2,2'-dicarboxy-9,9'-bianthryl (Ib).

C. Esterification of Optically Active 2,2'-Dicarboxy-9,9'-bianthryl (Ib) with Diazomethane.

Ethanol (95%, 25 ml) was added to a solution of potassium hydroxide (5 g) in water (8 ml) in a 100 ml. distilling flask fitted with a Claisen distilling head to which a 250 ml. pressure-equalizing funnel and a water-cooled condenser, set downward for distillation, were connected. The condenser was connected to two (in series) receiving flasks, which were cooled in an ice-salt bath, the second of which contained 50 ml. of ether. The inlet tube of the second receiver dipped below the surface of the ether. The first receiving flask was a 2 l. erlenmeyer flask containing 7.28 g. (1.65×10^{-2} mole) (-)2,2'-dicarboxy-9,9'-bianthryl (Ib), $[\alpha]_{589}^{23°C} = -114.7°$ (c 0.3, acetone), p. 92, 1300 ml. dioxane and a magnetic stirrer.

The flask containing the potassium hydroxide solution was heated in a water bath at 65°C. A solution of 21.6 g. (0.1 mole) of Diazald (N-methyl-N-nitroso-p-toluene-sulfonamide) (Aldrich Chem. Co., Milwaukee, Wisconsin) in 200 ml. of ether, contained in the pressure-equalizing funnel, was added over a period of 2 hr.. The rate of addition was set approximately equal to the rate of distillation. Another 20 ml. of ether was subsequently

slowly added through the addition funnel, and distillation was continued until the distillate was colorless.

Upon the completion of distillation the solution in the first receiving flask became deep yellow due to the large excess of CH_2N_2. The solution was stirred for one additional hr., and then 5 ml. of acetic acid was added. The deep yellow color of the solution changed to pale yellow. The dioxane solution was concentrated to about 100 ml., cooled, and an equal volume of water was added. A yellow solid precipitated which was collected by suction filtration, washed with water and dried under vacuum at 90°C to yield 9.6 g. of a yellow solid. This solid was chromatographed on 200 g of silica gel (60-200 mesh, J.T. Baker Chem. Co., Phillipsburg, N.J.). The column was eluted with $CHCl_3$/Benzene (1:1). A yellow band was collected, while a red band remained at the origin. The solution was evaporated to yield 7.12 g (-)2,2'-dicarbomethoxy-9,9'-bianthryl Ia; m.p. 232-233°C $[\alpha]_{589}^{23°C}$ = -158.6° (c 0.3, $CHCl_3$); nmr ($CDCl_3$), δ 3.62 (s, 6 H, CH_3O), 6.8-8.2 (m, 14 H, aromatic H), 8.63 (s, 2 H, aromatic H at C-10 and C-10'); m.s., m/e (rel. intensity using linear mass scan) 470 (100), 439 (18), 350 (64); ir (KBr), 3050 (w), 2950 (m), 1715 (s, C=O), 1620 (m).

II. Racemization of Optically Active 2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) Using Triglyme as the Solvent.

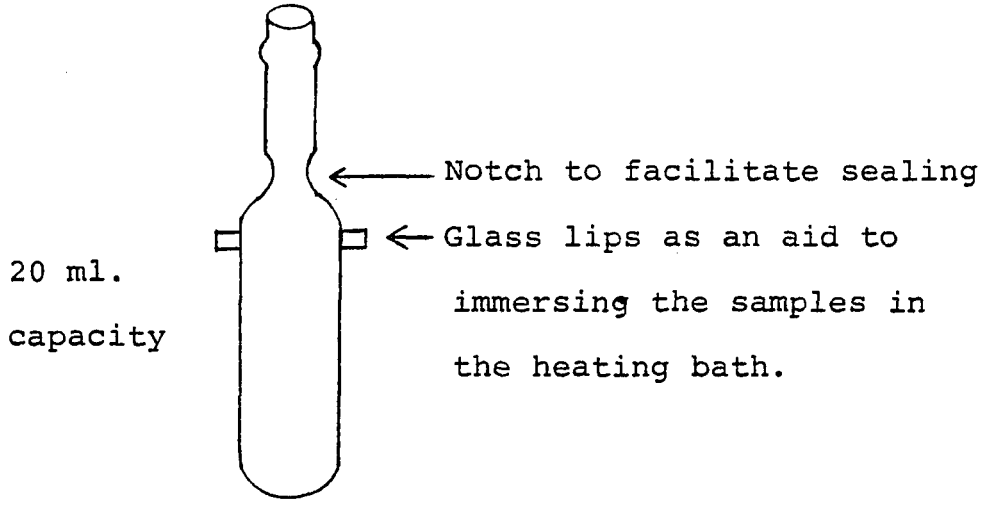
A. Racemization of (+)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of Oxygen.

1. Preparation of Racemization Samples.

Triglyme was purified by gradually adding $LiAlH_4$ (about 1 g. per 100 ml. triglyme) until the color of the mixture became dark gray. Vigorous bubbling could be expected during the addition of $LiAlH_4$. The resulting mixture was stirred overnight, with a drying tube mounted on the mouth of the round bottom flask containing the mixture, and was then distilled under reduced pressure.

Each sample contained about 0.5 g. of (+)2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) dissolved in 10 ml. of triglyme, in a specially made tube (Figure IV). Oxygen gas was

Figure IV Racemization Tube



bubbled through the solution for 30 min. at room temp. The tube was then immediately sealed, while it was being cooled in an ice bath. In order to prevent the air from diffusing into the tube, a balloon filled with oxygen was put onto the mouth of the tube prior to sealing.

All samples of a run were prepared at the same time from one stock solution, and thus had the same initial optical ratations.

2. Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl Ia

All samples of a run* were simultaneously immersed in a constant temp. silicone oil bath.** The samples were heated at 148.8 ± 0.1°C. Samples were removed at intervals of time, cooled, opened and their optical rotations taken. The data from a typical run is shown in Table IV and plotted in Figure V .

---

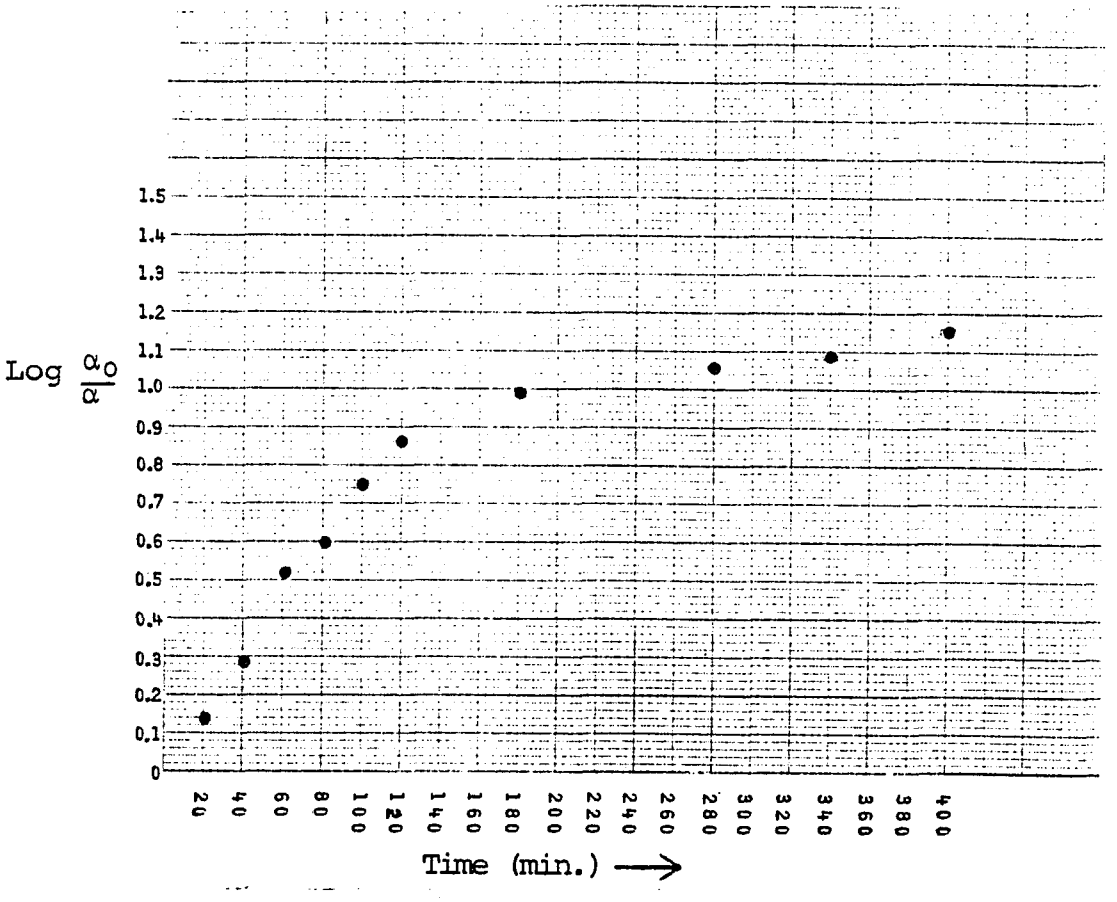
* Our apparatus could accommodate as many as twelve samples per run.

** HAAKE constant temp. circulator (Model NBS, HAAKE Instrument Corp.), equipped with an aluminum rack to hold the samples in a vertical position.

Table IV

Heating Time (Min.)	10	20	40	62.5	81	100	120	180	280	340	400
$\log \frac{\alpha_o}{\alpha}$	0	0.144	0.291	0.532	0.604	0.758	0.881	0.967	1.065	1.086	1.151
Racemization (%)	0	28.2	48.8	70.6	75.1	82.5	86.9	89.2	91.4	90.1	92.9

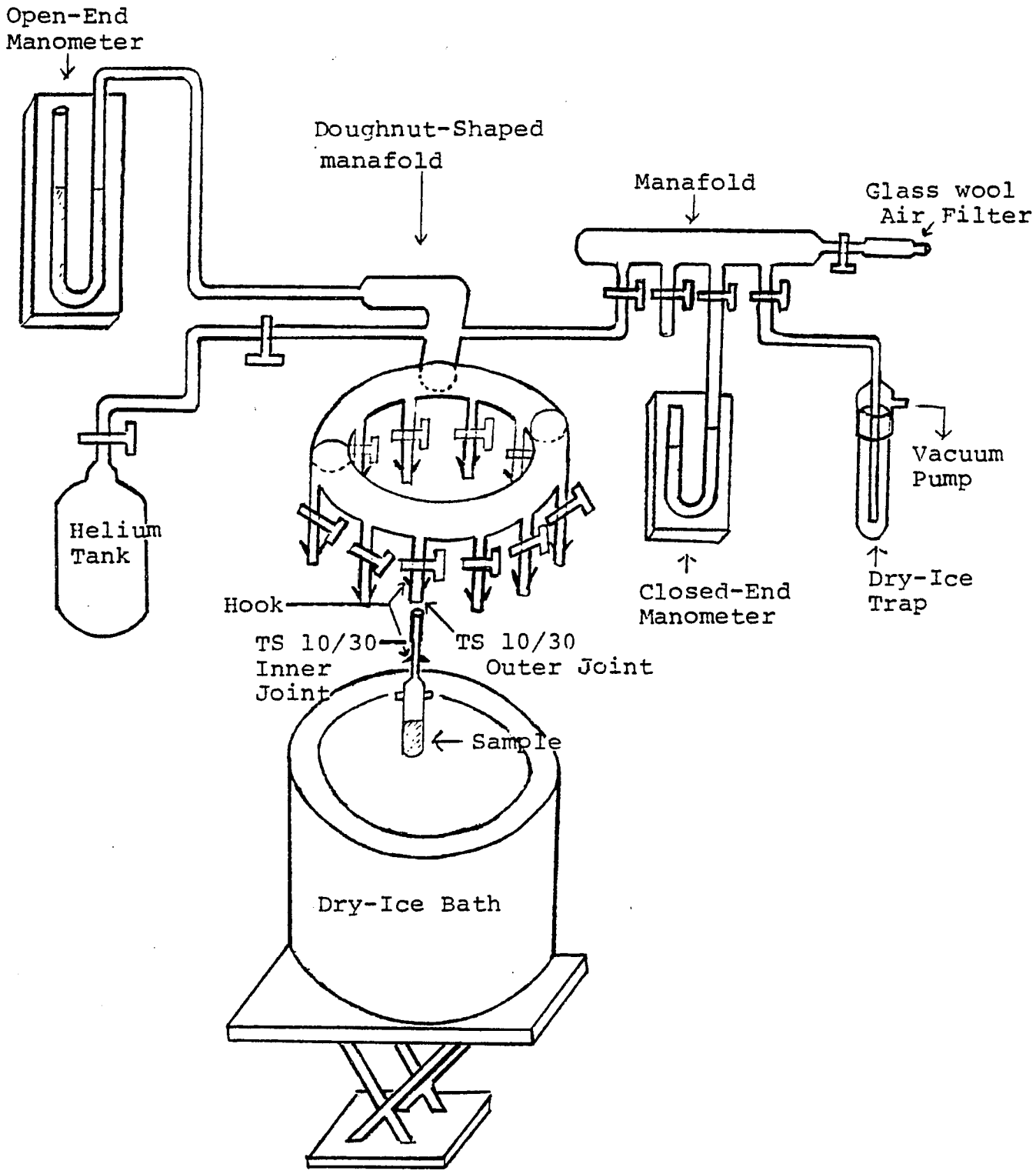
Figure V



B. Racemization of (+)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Absence of Oxygen. Freeze-Pump-Thaw Procedure.

Each sample contained about 0.03 g. of (Ia) in 10 ml. of triglyme (the purification procedure is described in each of the subtitles in the following paragraphs). All samples were degassed by a freeze-pump-thaw procedure (see Figure VI) as follows: The apparatus consisted of ten stopcocks, each connected to one TS 10/30 outer joint, and annexed to a Doughnut-Shaped manafold leading to a vacuum pump, an Open-End manometer, a Closed-End manometer and a helium gas tank. Ten sample tubes, each with an inner TS 10/30 joint, were attached to the TS 10/30 outer joints. The samples were frozen in a dry ice-acetone bath and the system evacuated. After minimum pressure was obtained, the stopcock to the vacuum system was closed and the dry ice-acetone bath was removed, allowing the solution to melt. Mild boiling could be expected during the melting process. After the melting was complete and the samples approached room temp., the dry ice-acetone bath was replaced to freeze the samples again and the stopcock was reopened. After pumping for a few minutes the process was repeated. Finally the stopcock leading to the vacuum pump was closed. Helium was introduced until a pressure equivalent to the atmosphere pressure

Figure VI Freeze-Pump-Thaw System



was obtained. The system was evacuated again and helium was re-introduced to the desired pressure.* The tubes were sealed off while the samples were frozen in the dry ice-acetone bath.

The following samples were studied:

1. The triglyme was previously purified by treatment with $LiAlH_4$ and distillation under reduced pressure. It was stored in a tightly closed bottle.

After three hr. heating at 148 ± 0.1° C, the extent of racemization was as high as 39 %.

2. The triglyme was purified as in 1, in order to remove peroxides,** followed by passage through a column of

---

* Less than atmospheric pressure. The pressure chosen was that estimated to result in a pressure of one atmosphere at the temperature of the racemization reaction.

** To detect the presence of peroxides, a reagent was prepared as follows: $FeSO_4 \cdot 7H_2O$ (9 g., 3.2×10^{-2} mole) was dissolved in 50 ml. of 18 % HCl. To this solution about 3 g. of granular Zn was added, then 5 g. (3.2×10^{-2} mole) sodium thiocyanate. When the transient red color faded, 12 g. of sodium thiocyanate was added and the solution decanted away from the unused Zn into a storage bottle. In the presence of peroxides, the color of this reagent changes from colorless to the deep red color of $Fe(CNS)_3$.

alumina.* The purified triglyme was stored over alumina, under a N_2 atmosphere in a tightly closed bottle. When used, the triglyme gave a faint pink color in the test for peroxides.

After three hr. heating at 148.8 ± 0.1°C, the racemization was 19%.

3. The triglyme was purified as in 2, and used immediately. After 3 hr. of heating at 148.8 ± 0.1°C, the average racemization of several runs was 2.0%. In each run, another sample in the presence of an oxygen atmosphere showed 97% racemization.

---

* Triglyme was eluted through a column which contained 60 g. Al_2O_3 (Grade 1, ICN Pharmaceuticals). The purified triglyme was dripped directly into a three-necked flask without contact with the atmosphere. Two of the three necks were used as inlet and outlet for N_2 gas during the purification process.

C. Racemization of (-)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of Oxygen and a Radical Inhibitor.

Triglyme was purified as on p. 95.

Two samples were prepared by the same procedure as on p. 94 except that 2,6-di-tert-butyl-p-cresol* (0.12 g 5.4×10^{-4} mole) was added to the first sample.

After heating for 4.5 hr. at 148 ± 0.1°C, the first sample (with inhibitor) showed 2.6% racemization, while the second sample showed 95% racemization.

---

* The molar ratio of 2,6-di-tert-butyl-p-cresol to (-)2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) was 6.4:1

D. Racemization of (+)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) under a Helium Atmosphere in Triglyme Exposed to the Atmosphere.

Triglyme was purified as on p. 100, No 2 and stored overnight under a nitrogen atmosphere. Different samples (with the same optical rotation) were prepared by allowing the triglyme solution to be exposed to the air* for different periods of time. All samples were degassed by the freeze-pump-thaw procedure, p. 98, helium was then introduced and the samples were sealed off.

Eight samples were heated at 148.8 ± 0.1°C for different periods of time. The results are shown in Table V.

---

* This was done by putting a piece of cotton in the mouth of the erlenmeyer flask containing the triglyme solution. The solution was allowed to stand for different periods of time before being sealed into the racemization tubes.

Table V

Sample	Length of Time That Triglyme Was Exposed to Air	Heating Period (hr.) at 148.8 ± 0.1°C	Degree of Racemization (%)
1	without exposure	3	11
2	without exposure	6	18
3	24 hr.	3	21
4	24 hr.	6	37
5	48 hr.	3	41
6	48 hr.	6	49
7	72 hr.	3	56
8	72 hr.	6	56

E. Racemization of (-)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of a Radical Inhibitor Under a Helium Atmosphere in Triglyme Exposed to the Atmosphere.

Triglyme was purified as on p. 100, No. 2. Sample No. 1, with 2,6-di-tert-butyl-p-cresol* (0.12 g, 5.4×10^{-4} mole), and No. 2 were prepared immediately after the purification of the triglyme. Samples No. 3 through 6 (with the same optical rotation as No. 1 and 2) were prepared by allowing each of the triglyme solutions to be exposed to air for different lengths of time before the samples were sealed under a helium atmosphere. The sample preparation procedure was the same as in D, p. 103.

The results, after 4.5 hr. heating at 148.8 ± 0.1°C, are shown in Table VI.

---

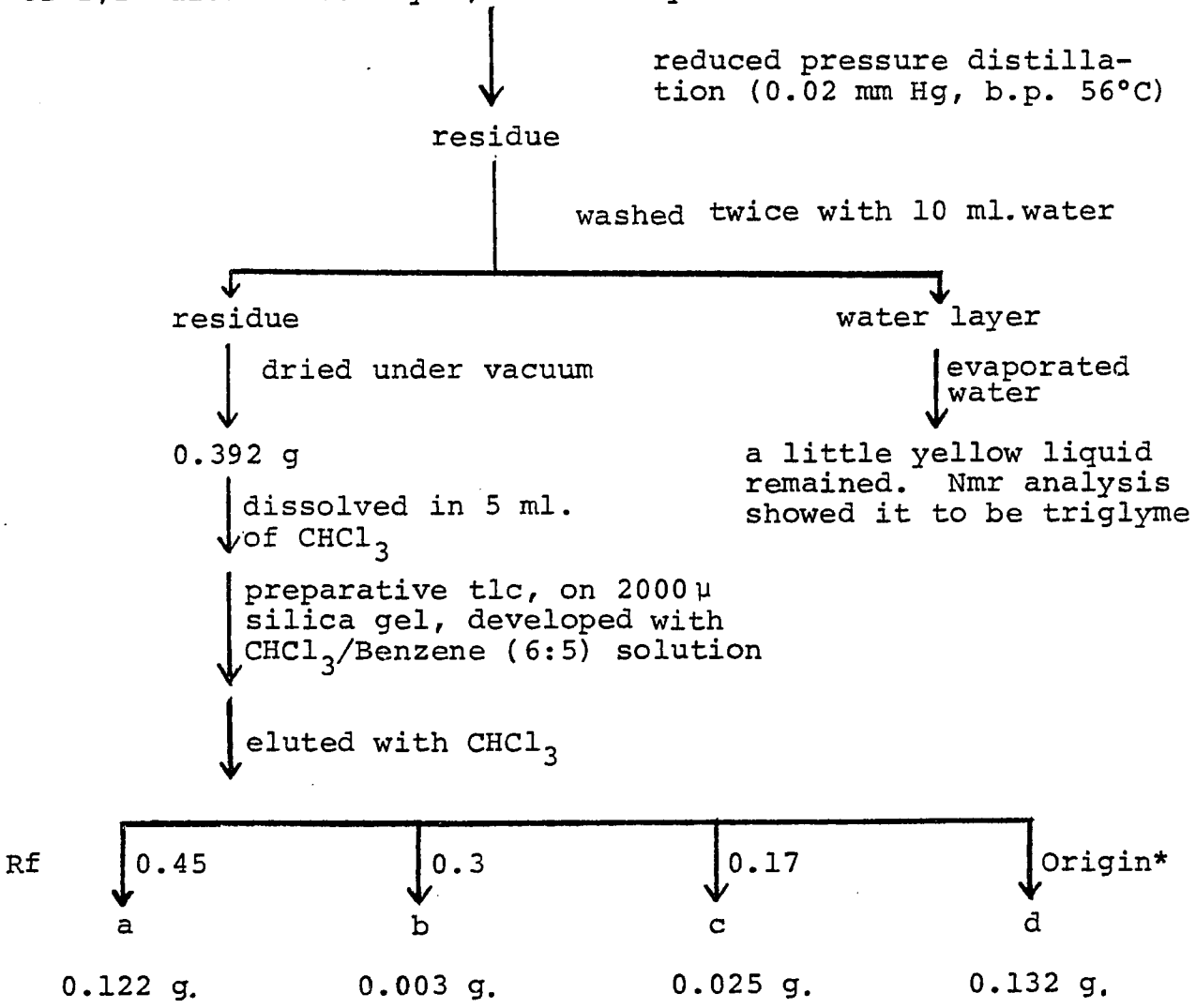
* The molar ratio of 2,6-di-tert-butyl-p-cresol to (-)2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) was 6.4:1.

Table VI

Sample	With 2,6-Di-tert-butyl-p-cresol (mole)	Atmosphere	Length of Time that Triglyme Was Exposed to Air	Degree of Racemization (%)
1	5.4×10^{-4}	He	0	0.10
2	0	He	0	0.40
3	5.4×10^{-4}	He	24 hr.	0.10
4	0	He	24 hr.	59
5	5.4×10^{-4}	He	72 hr.	0.60
6	0	He	72 hr.	79

F. Investigation of the Products of the Racemization of (-)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) under O_2.

1. The following work-up procedure was used on the racemized (85%) sample (after 2.5 hr. of heating at 148.8 ± 0.1°C) which consisted of 60 ml. of triglyme solution containing 0.3 g. of 2,2'-dicarbomethoxy-9,9'-bianthryl.



* The absorbent at the origin retained a yellow color after elution with $CHCl_3$.

2. Properties of the four components:

   a. The same Rf as the starting material; 40.6% recovery; $[\alpha]_{589}^{23°C}$ = -59.67° (c 0.3, $CHCl_3$; 62.4% racemized (based on the rotation of the starting material). Nmr, ir, and ms virtually identical to those of the starting material.

   b. Ir showed some differences between a and b. The major difference was at 2900 cm^{-1}. This band, the aliphatic C-H stretching band, was much bigger than in a. Also, each peak on the spectrum was broader. Ms showed peaks up to m/e 514. The molecular weight of the starting material is 470.

   c. Nmr was similar to a, except at δ 3.38 and 3.62 where typical triglyme-type absorptions appeared. These peaks were small. The appearance of the aromatic proton region was similar but not identical to a. Ms showed peaks up to m/e 558.

   d. Ir was very similar to b , but the absorption at 2900 cm^{-1} was much more intense than in b. Nmr was the same as c except that the δ 3.38 and 3.62 peaks were more intense. Ms showed peaks up to m/e 528. $[\alpha]_{589}^{23°C}$ = -8.6 (c 1.27, $CHCl_3$). It was 95% racemized based on the assumption that the original specific rotation was the same as that of the starting material (Ia).

III. Racemization of Optically Active 2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of Diphenyl Disulfide Using Triglyme as the Solvent.

A. Racemization of (-)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) and Recovery of the Racemized Material.

A typical reaction was carried out by dissolving 0.03 g. (6.4×10^{-5} mole) of (-)2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) and 0.07 g. (3.2×10^{-3} mole) of diphenyl disulfide in 10 ml. of freshly purified triglyme.* This solution was placed in a 20 ml. tube** and degassed using a Freeze-Pump-Thaw procedure (p. 98). Helium was introduced, while the

---

* To purify triglyme, $LiAlH_4$ was gradually added to 200 ml. of triglyme solution, with stirring, in a 250 ml. round bottom flask, until vigorous bubbling ceased. The resulting dark gray mixture was stirred overnight with drying tube mounted on the mouth of the flask, and then distilled under reduced pressure and used immediately.

** Same tube as on p. 95, Figure IV except that a TS 10/30 inner joint formed the mouth of the tube.

sample was being cooled in a dry ice-acetone bath, to a pressure of 538 mm Hg. The tube was sealed off. After 96 hr. heating at 196.6°C, the degree of racemization was 44.5%.

Preparative tlc analysis of the racemized material showed 78% recovery of chemically unchanged starting material with 45% racemization.

B. Racemization of (-)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) with varying concentrations of Diphenyl Disulfide.

Ten samples were prepared by the same procedure as on p. 109 except that the samples contained varying amounts of diphenyl disulfide.

The results, after 48 hr. heating at 197 ± 1°C, are shown in Table I .

Table I

Sample	PhSSPh (mole x 10^6)	$\frac{\text{PhSSPh}}{\text{Bianthryl}}$	Racemization (%)
1	320	5.0	35
2	260	4.1	35
3	190	3.0	39
4	130	2.0	40
5	64	1.0	40
6	32	0.50	41
7	16	0.25	39
8	8	0.13	36
9	4	0.063	40
10	0	0	7.6

C. Racemization of (+)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of Diphenyl Disulfide and Benzenethiol.

Eight samples were prepared by the same procedure as on p. 109 except that the samples contained varying amounts of diphenyl disulfide and benzenethiol.

The results, after heating for 48 hr. and 96 hr. periods at 195.4 ± 0.1°C, are shown in Table VII.

Table VII

Sample	PhSSPh (mole)	PhSSPh[a] / BH	PhSH (mole)	PhSH[a] / BH	Heating Time (hr.)	Racemization (%)
1	0	0	0	0	48	53
2	3.2×10^{-4}	5.0	0	0	48	33
3	3.2×10^{-4}	5.0	3.3×10^{-4}	5.2	48	15
4	0	0	3.3×10^{-4}	5.2	48	6.5
5	0	0	0	0	96	58
6	3.2×10^{-4}	5.0	0	0	96	46
7	3.2×10^{-4}	5.0	3.3×10^{-4}	5.2	96	25
8	0	0	3.3×10^{-4}	5.2	96	9.6

[a] BH stands for 2,2'-dicarbomethoxy-9,9'-bianthryl.

D. Racemization of (+)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of Diphenyl Disulfide and Varying Concentrations of Benzenethiol.

Ten samples were prepared by the same procedure as on p. 112 . The samples contained varying amounts of benzenethiol in addition to diphenyl disulfide (0.07 g, 3.2×10^{-4} mole in each sample).

The results, after heating for 48 hr. and 96 hr. at 195.4 ± 0.1°C are shown in Table VIII.

Table VIII

Sample	PhSSPh (mole)	PhSH(mole)	PhSH / PhSSPh	PhSSPh[a] / BH	Heating Time(hr.)	Racemization(%)
1	3.2×10^{-4}	0	0	5.0	48	30
2	3.2×10^{-4}	1.2×10^{-4}	0.38	5.0	48	23
3	3.2×10^{-4}	3.4×10^{-4}	1.1	5.0	48	17
4	3.2×10^{-4}	6.5×10^{-4}	2.0	5.0	48	12
5	3.2×10^{-4}	1.0×10^{-3}	3.1	5.0	48	7.9
6	3.2×10^{-4}	0	0	5.0	96	42
7	3.2×10^{-4}	1.2×10^{-4}	0.38	5.0	96	35
8	3.2×10^{-4}	3.4×10^{-4}	1.1	5.0	96	26
9	3.2×10^{-4}	6.5×10^{-4}	2.0	5.0	96	18
10	3.2×10^{-4}	1.0×10^{-3}	3.1	5.0	96	14

[a] BH stands for 2,2'-dicarbomethoxy-9,9'-bianthryl.

E. Racemization of (-)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence and Absence of Diphenyl Disulfide under Air and Helium Atmospheres.

Samples were prepared by the same procedure as on p. 108. Samples having air as an atmosphere were sealed off, while being cooled in a dry ice-acetone bath, with the mouth of the tube open to air. The results of two similar runs are shown in Table IX and Table X, p. 115.

In other similar runs, the percent racemization of the reference sample (No. 1 in Tables IX and X) was found to be as high as 63%, No. 2 sample consistently remained at 34%.

Table IX

Sample	Atmosphere	PhSSPh(mole)	Racemization(%)[a]
1	He	0	5.7
2	He	3.2×10^{-4}	34
3	Air	3.2×10^{-4}	34
4	Air	0	83

[a] After heating at 197.4 ± 0.5°C for 48 hr.

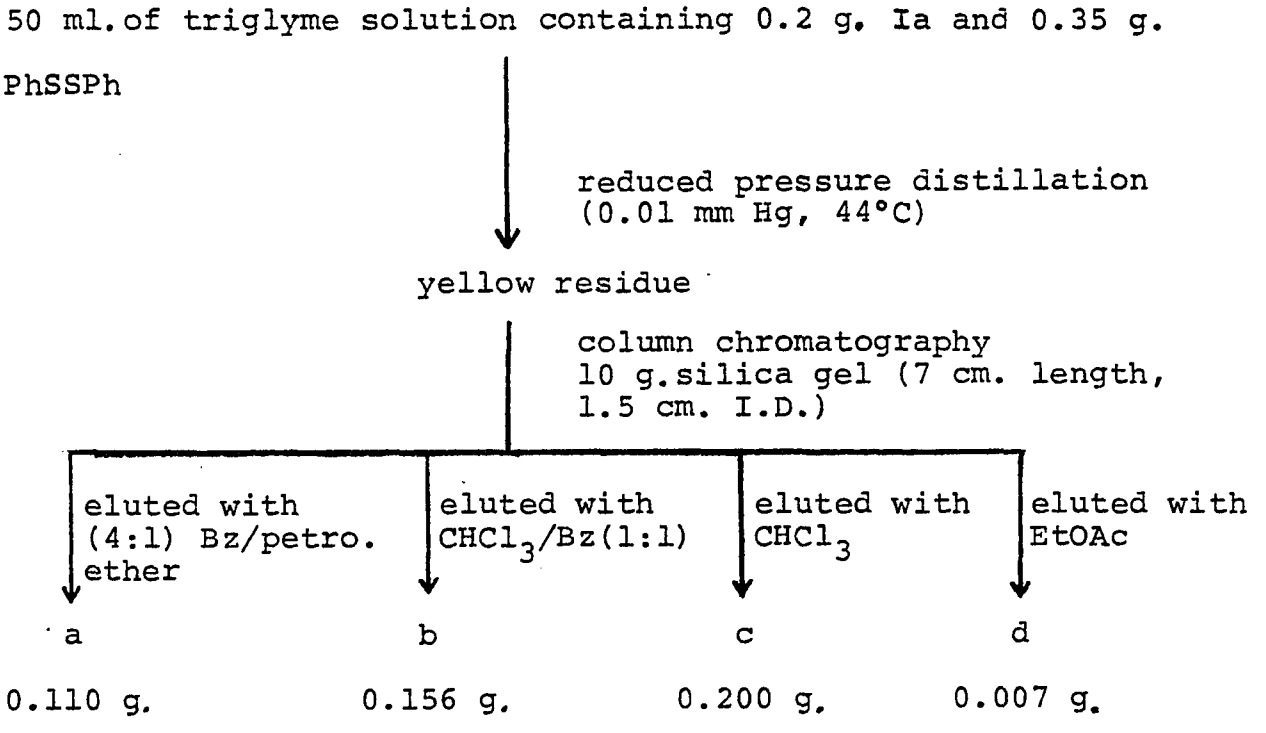
Table X

Sample	Atmosphere	PhSSPh(mole)	Racemization(%)[a]
1	He	0	20
2	He	3.2×10^{-4}	34
3	Air	3.2×10^{-4}	34
4	Air	0	77

[a] After heating at 196.7 ± 0.3°C for 48 hr..

F. Investigation of the Products of the Racemization of (+) 2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia).

A large scale experiment, similar to that described on p. 109, was conducted on a sample containing 50 ml. of triglyme, 0.2 g. of Ia, and 0.35 g of PhSSPh. This sample showed 43.4% racemization. The following separation scheme was used on this racemized sample.



Properties of the four fractions:

a. Tlc and nmr showed this fraction to be diphenyl disulfide. In a control test starting with 0.35 g. of diphenyl disulfide, 0.30 g. was recovered after reduced pressure distillation. The recovery of 0.11 g. of the original 0.35 g. diphenyl disulfide thus corresponds to about 37 %.

b. Chemically unchanged (+)2,2'-dicarbomethoxy-9,9'-bianthryl (Ia).in 78 % recovery. This material was 43.9% racemized. A control test (without heating) showed 97.5% recovery.

c. Nmr, ir, and ms showed it to be substitution products of the phenylthiyl group on triglyme. Mass spectrum, m/e (rel. intensity using linear mass scan) 286(12.5), 177(95.0), 110(93.0), 109(82.0), 103(98.0), 59(100), 15(77.0). Since m/e=59 could not possibly be a fragmentation peak from m/e=103, this fraction could possibly be a mixture of positional isomers (XXXVI, p.49).

d. Tlc and nmr showed it to be an substitution product of the homolytic aromatic substitution of Ia by triglyme radical. The peaks in the nmr spectrum were unusually broad, which implied the presence of a mixture. $[\alpha]_{589}^{23^{\circ}C} = -41$ (c 0.74, $CHCl_3$). It was 74% racemized based on the assumption that the original specific rotation was the same as that of the starting material (Ia).

G. Racemization of (-)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of Diphenyl Disulfide.

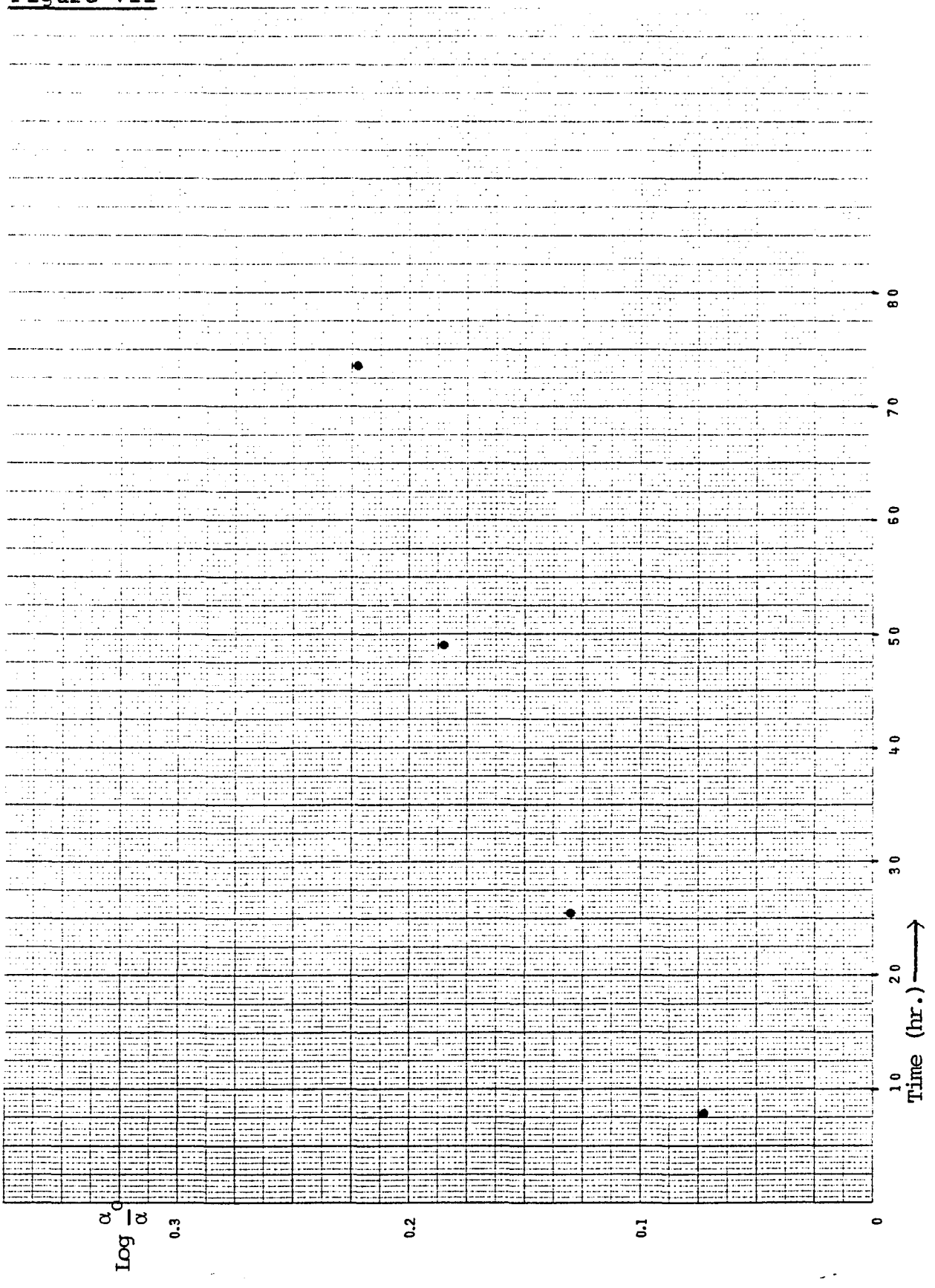
Samples were prepared by the same methods as on p. 109. All samples of a run were prepared at the same time, from one stock solution, and thus had the same initial optical rotation.

All samples of a run were simultaneously immersed in a constant temperature silicone oil bath. The samples were heated at 196.6 ± 0.5°C. Samples were removed at intervals of time, cooled, opened and their optical rotations taken. The results from a typical run are shown in Table XI and plotted in Figure VII, p. 119.

Table XI

Sample	PhSSPh(mole)	Heating Time(hr.)	Racemization(%)	Log $\frac{\alpha_0}{\alpha}$
1	3.2×10^{-4}	8	15	0.072
2	0	8	12	
3	3.2×10^{-4}	25.3	26	0.130
4	0	25.3	12	
5	3.2×10^{-4}	49	35	0.185
6	0	49	12	
7	3.2×10^{-4}	73.5	40	0.223
8	0	73.5	13	

Figure VII



IV. Racemization of (+)2,2'-Dicarbomethoxy-9,9'-bianthryl (I_a) in the Presence of Diphenyl Disulfide.

A. Using Dimethyl Suberate as the Solvent With and Without 2,6 -Di-tert-butyl-p-cresol.

Each sample contained 0.03 g. (6.4×10^{-5} mole) of Ia in 10 ml. of dimethyl suberate* with or without added diphenyl disulfide (Eastman Organic Chemicals, Rochester, N.Y.) or 2,6-di-tert-butyl-p-cresol (Matheson Coleman and Bell, East Rutherford, N.J.). All samples were degassed by a Freeze-Pump-Thaw procedure (p. 98). Nitrogen (O_2 < 5 ppm, Matheson, Lyndhurst, N.J.) was then introduced to a pressure of 480 mm Hg and the samples were sealed off.

The results after heating at 196.3 ± 0.1°C for 48 hr. are shown in Table XII.

Table XII

Sample	PhSSPh(mole)	2,6-Di-tert-butyl-p-cresol(mole)	Racemization(%)
1	0	0	8.3
2	0	6.4×10^{-4}	1.4
3	3.2×10^{-4}	0	10

* Dimethyl suberate was purified by washing two times with 10% Na_2CO_3 solution, followed by drying over anhydrous $MgSO_4$. Cuprous chloride (about 1 g. per 200 ml. of dimethyl suberate) was added to the dried dimethyl suberate. The resulting solution was stirred overnight at 50°C, distilled and used immediately.

B. Racemization of (+)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of Diphenyl Disulfide Using Diphenyl Ether as the Solvent.

Each sample contained 0.03 g (6.4×10^{-5} mole) of Ia in 10 ml.of diphenyl ether* with or without added diphenyl disulfide (0.07 g., 3.2×10^{-4} mole). After heating at 195.8 ± 0.1°C for 48 hr. both samples showed no racemization.

---

* Purified by reduced pressure distillation.

C. Racemization of (+) 2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of Diphenyl Disulfide Using Dimethyl Phthalate as the Solvent.

Each sample contained 0.03 g. (6.4×10^{-5} mole) of Ia in 10 ml. of dimethyl phthalate* with or without added diphenyl disulfide (0.07 g., 3.2×10^{-4} mole). After heating at 195.8 ± 0.1°C for 48 hr. both samples showed no racemization.

---

* Purified by washing with $NaHCO_3$ (10%) solution twice, and drying over anhydrous $MgSO_4$. This material was distilled under reduced pressure prior to use.

V. Racemization of Optically Active 2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of Dibenzyl Mercury Using Dimethyl Suberate as the Solvent.

A. Racemization of (+)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of Dibenzyl Mercury.

Eight samples were prepared at the same time. Each sample contained mercury dibenzyl (0.122 g., 3.2×10^{-4} mole) and (+)2,2'-dicarbomethoxy-9,9'-bianthryl (0.03 g., 6.4×10^{-5} mole) in 10 ml. of dimethyl suberate* in a specially made tube.** All samples were degassed by a Freeze-Pump-Thaw procedure (p. 98). Helium was introduced to a pressure of 700 mm Hg and the samples were sealed off at -79°C (dry ice-acetone bath). All samples of a run were simultaneously immersed in a constant temperature silicone oil bath. The temperature of the oil bath was kept at 186.8 ± 0.1°C. Samples were removed at intervals of time, cooled, opened and their optical rotations taken. The results from a typical run are shown in Table XIII and Figure VIII.

---

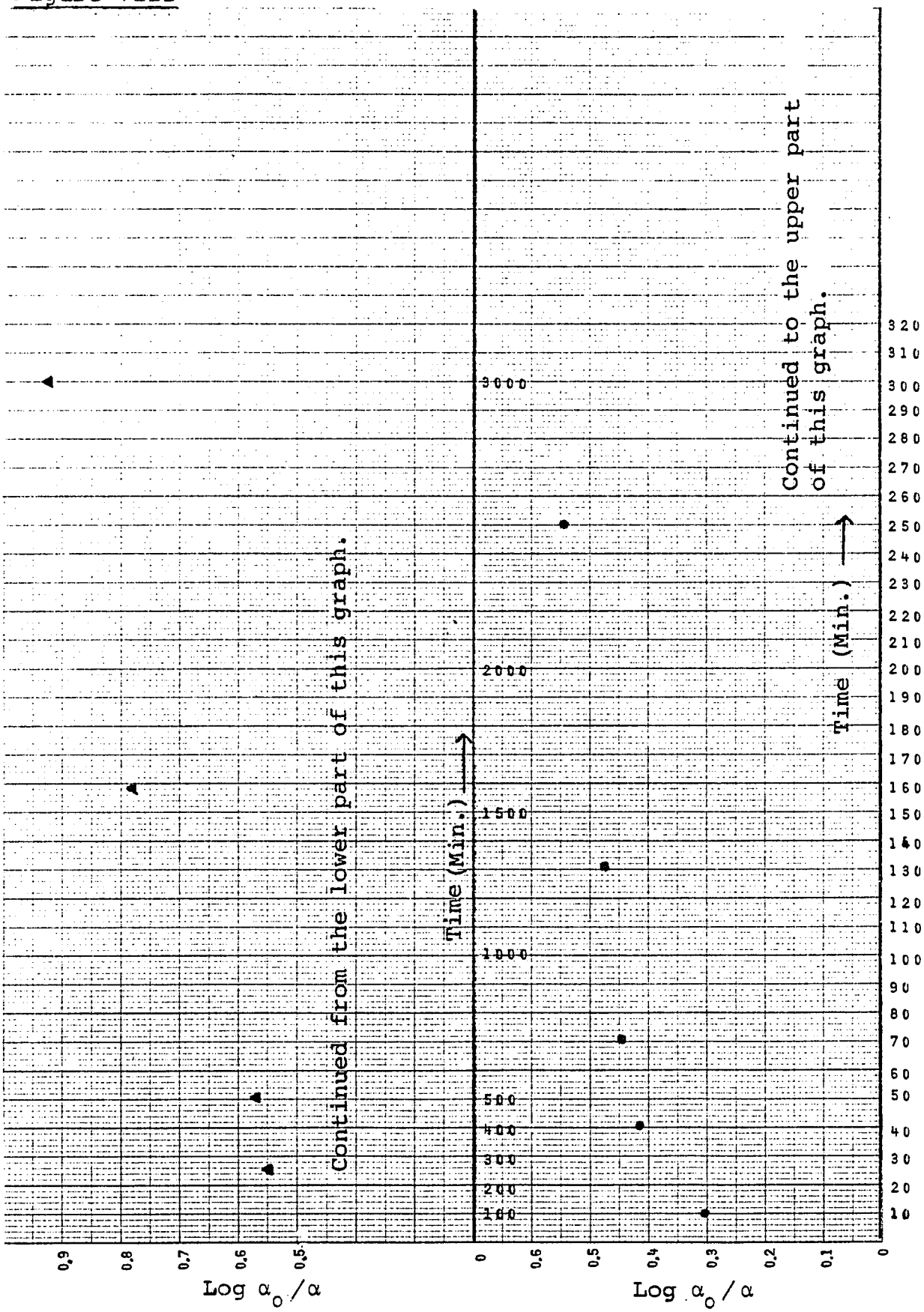
* Purified by the same procedure as on p.119.

** The same as Figure IV , p. 95 , except that a 10/30 inner joint was put on the mouth of the tube.

Table XIII

Sample	Heating Time (min.)	Racemization(%)	$\log \frac{\alpha_o}{\alpha}$
1	10	50	0.303
2	40	62	0.416
3	70	64	0.442
4	130	66	0.474
5	250	72	0.548
6	490	73	0.565
7	1570	83	0.771
8	3010	88	0.923

Figure VIII


Continued from the lower part of this graph.
Time (Min.)
3000
2000
1500
1000
500
400
300
200
100
0.9
0.8
0.7
0.6
0.5
Log α_o / α
0
0.6
0.5
0.4
0.3
0.2
0.1
0
Log α_o / α
Continued to the upper part of this graph.
Time (Min.)
320
310
300
290
280
270
260
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

B. Racemization of (+)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of Mercury.

The procedure for the preparation of the samples was the same as on p. 123 except that mercury (0.06 g., 3×10^{-4} mole) was added instead of dibenzyl mercury.

The results, after heating at 187 ± 0.1°C for two hours, showed that no racemization of Ia had occurred in the presence of mercury. In the same run, a reference sample (without added mercury) also showed no racemization.

C. Racemization of (+)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of Varying Concentrations of Dibenzyl Mercury.

The procedure for the preparation of samples was the same as on p. 123 except that each sample contained a different amount of dibenzyl mercury.

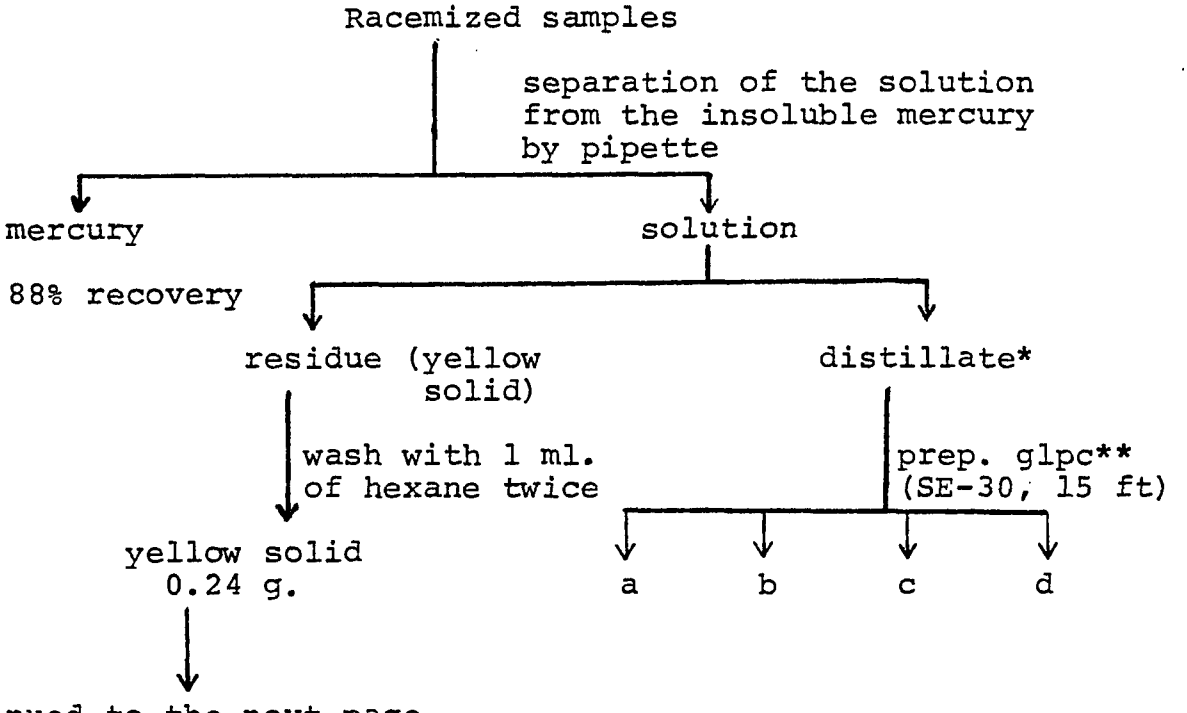
The results, after heating at 186.3 ± 0.1°C for 2 hr., are shown in Table II.

Table II

Sample	Mercury Dibenzyl(mole)	Mercury Dibenzyl / Bianthryl	Racemization(%)
1	6.4×10^{-4}	10	75
2	3.2×10^{-4}	5.0	69
3	1.9×10^{-4}	3.0	66
4	6.4×10^{-5}	1.0	54
5	3.2×10^{-5}	0.50	43

D. Investigation of the Products of the Racemization of (+)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia).

Racemization of 50 ml of dimethyl suberate solution, containing Ia (0.4 g., 3.2×10^{-4} mole) and dibenzyl mercury (1.22 g., 1.6×10^{-3} mole) was carried out at 187 ± 0.1°C, for 2 hr.. The following work-up procedure was used on the racemized sample (70% racemized).



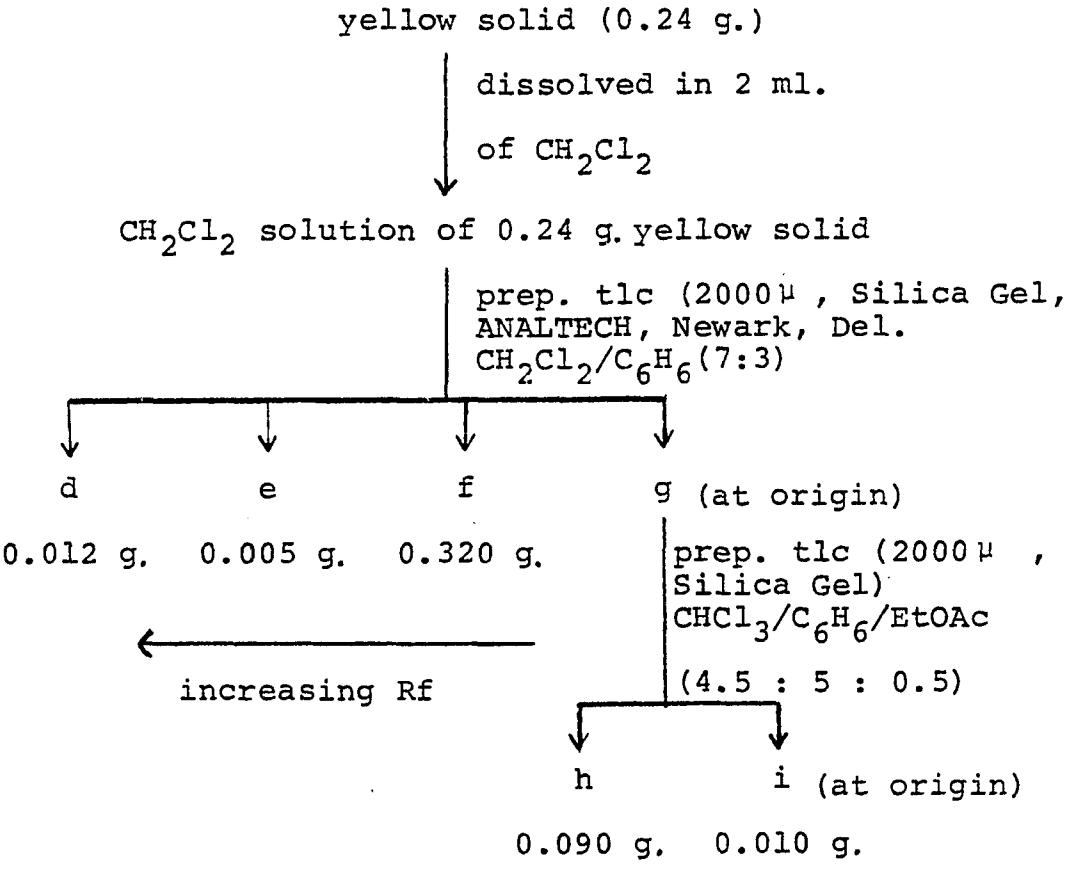
continued to the next page

---

* The receiver was cooled in a dry ice-acetone bath.

** Column temp. 254°C. Flow rate 70 cc/min.

Continued from the last page



Properties of the components:

a. Retention time is 1.9 min., identical to that of toluene.

b. Retention time is 4.3 min.. (See p. 132.)

c. Retention time is 7.5 min., identical to that of dimethyl suberate. Nmr spectrum is also identical to that of dimethyl suberate.

d. Retention time is 10.7 min, identical to that of the bibenzyl.

e. Mass spectrum showed m/e (rel. intensity using linear mass scan) 272(5), 181(26), 91(29), 28(100). Nmr ($CDCl_3$), δ 2.72-2.88 (m, 1 H, -CH-), 3.9 (doublet, 4 H, CH_2-), 7.08 (broad, 15 H,aromatic H).

f. Tlc analysis indicated it was a single compound. Mass spectrum, m/e (rel. intensity using linear mass scan) 560(100), 470(31), 468(27), 350(20). Nmr ($CDCl_3$), δ3.48 (s, 3 H, CH_3O), 3.70 (s, 3 H, CH_3O), 4.48 (s, 2 H, $PhCH_2$-), 6.9-7.6 (m, 11 H, aromatic H), 7.8-8.2 (m, 7 H, aromatic H), 8.54 (s, 1 H, aromatic H at C-10), 8.66 (s, 1 H, aromatic H at C-10'). Optical rotation was zero.

g. Tlc analysis showed it had the same Rf value as the starting material, (+)2,2'-dicarbomethoxy-9,9'-bianthryl (Ia); $[\alpha]_{589}^{23°C}$ = +39 (c 0.30, $CHCl_3$); 71.6% racemized (based on the rotation of the starting material). Nmr, ir and ms were virtually identical to those of the starting material (Ia).

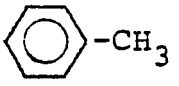
h. Tlc analysis indicated it to be a single compound: Mass spectrum, m/e (rel. intensity using linear mass scan) 670(100), 470(9), 350(11); nmr ($CDCl_3$), δ 1.38-2.39

(m, 11 H, $-\underline{CH_2}-COOCH_3$), 3.64-3.70 (overlapping singlets, 12 H, CH_3O), 6.9-8.2 (m, 13 H, aromatic H), 8.64 (s, 1 H, aromatic H at C-10), 8.68 (s, 1 H, aromatic H at C-10'). Optical rotation was zero.

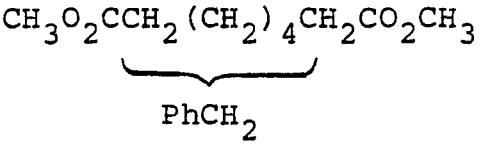
i. Nmr ($CDCl_3$), δ 0.8-2.6 (m, 22 H, $-\underline{CH_2}-COOCH_3$), 3.64-3.68 (overlapping singlets, 12 H, CH_3O-). Mass spectrum (rel. intensity using linear mass scan), 371(3.3), 215(5.5), 202(10.4), 69(40.4), 59(44.4), 55(100), 43(77.8).

Possible structures of the compounds:

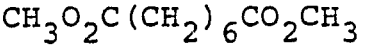
a.



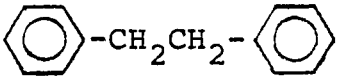
b.



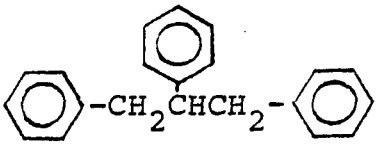
c.



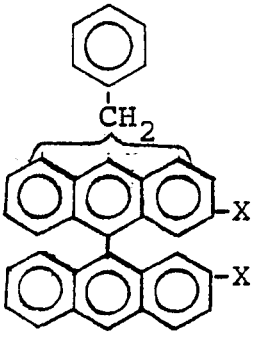
d.



e.

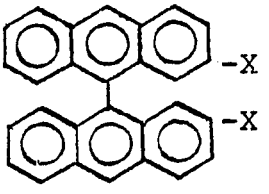


f.



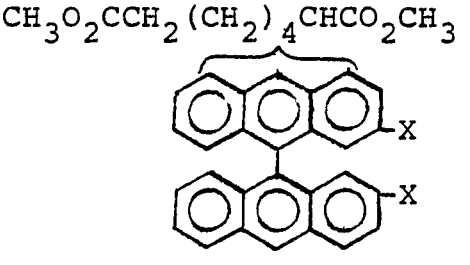
X = $COOCH_3$

g.

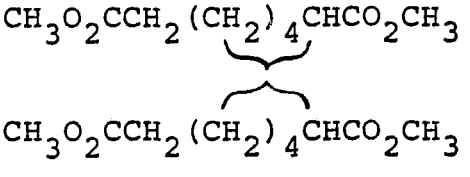


Ia

h.



i.



VI. Racemization of Optically Active 2,2'-Dicarbomethoxy-9.9'-bianthryl (Ia) in the Presence of tert-Butyl Peroxide Using Dimethyl Suberate as Solvent.

A. Racemization of (+)2,2'-Dicarbomethoxy-9,9'-bianthryl.

All samples of a run were prepared at the same time, from one stock solution, and thus had the same initial optical rotation.

Each sample contained (+)2,2'-dicarbomethoxy-9,9'-bianthryl (Ia) (0.03 g, 6.4×10^{-5} mole) and tert-butyl peroxide (0.10 ml., 1.1×10^{-3} mole), dissolved in 10 ml. dimethyl suberate,* in a specially made tube (Figure p. 95). Helium gas was bubbled through the solution for 15 min.at room temp., The tube was then immediately cooled in a dry ice-acetone bath and sealed.

All samples of a run were simultaneously immersed in a constant temperature silicone oil bath. The samples were heated at 124.7 ± 0.1°C. Samples were removed at intervals of time, cooled, opened, and their optical rotation taken. The result from a typical run are shown in Table XIV and plotted in Figure IX.

---

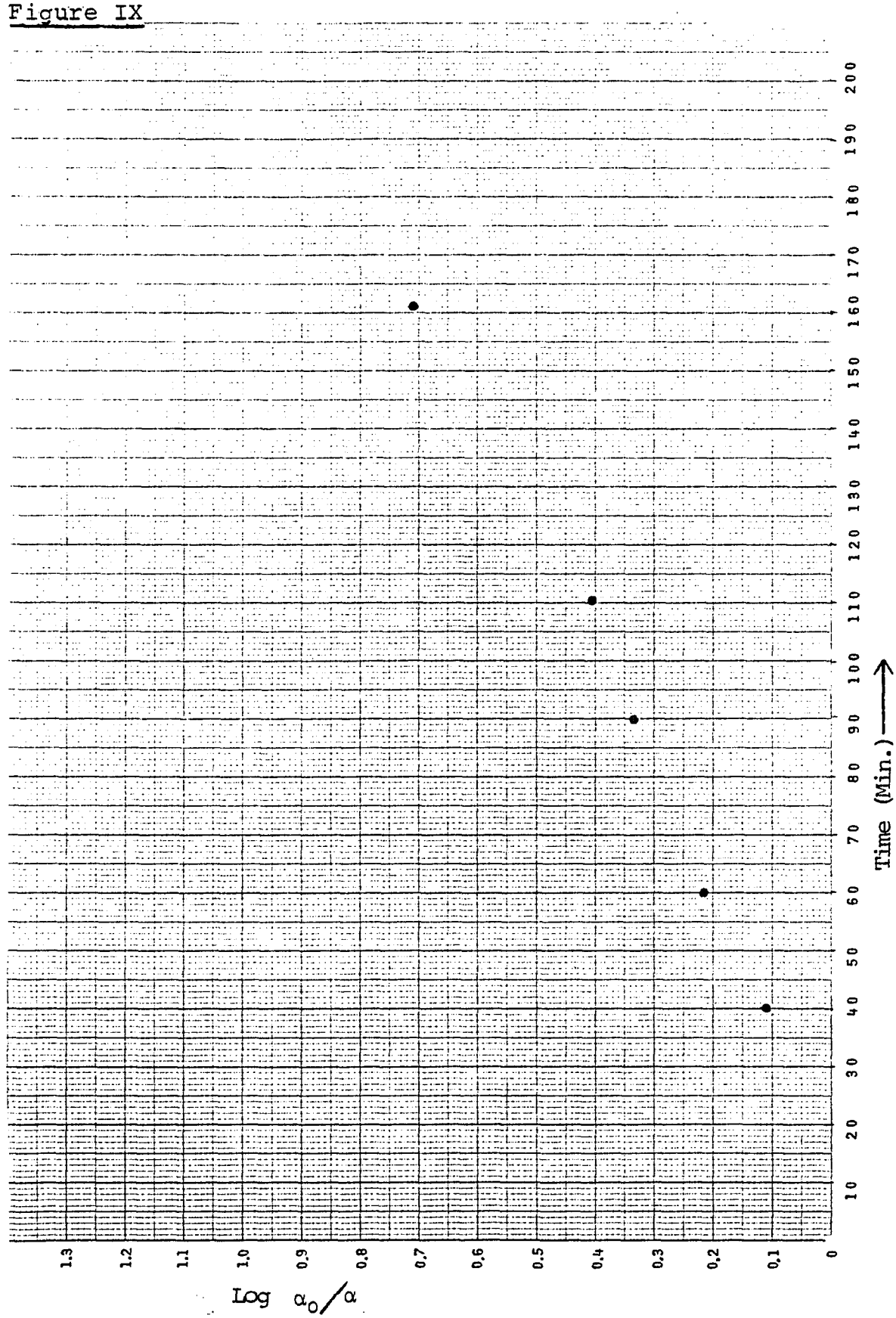
* Purified by the procedure on p. 120.

Table XIV

Sample	Heating time (min.)	Racemization(%)	Log $\frac{\alpha_o}{\alpha}$
1	10	10	0
2	40	32	0.119
3	60	45	0.215
4	90	59	0.336
5	110	65	0.404
6	161	83	0.710
7	225	97	1.530
8	225	0	

* Sample No. 8 is a reference sample (without tert-butyl peroxide).

Figure IX


Time (Min.)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Log α_0/α

B. Racemization of (+)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) and the Recovery of the Racemized Material.

A solution of dimethyl suberate* (50 ml.),containing (+)2,2'-dicarbomethoxy-9,9'-bianthryl (0.20 g., 4.3×10^{-4} mole) and tert-butyl peroxide (0.50 ml., 2.6×10^{-3} mole) was prepared. This solution was transferred into five tubes** and degassed by a freeze-pump-thaw procedure (p. 98). Helium was introduced to a pressure of 700 mm Hg and the tubes were sealed off.

After heating in a constant temp. silicone oil bath at 125.2 ± 0.1°C for 3 hr, the samples were removed, cooled, opened, combined and the optical rotation taken. The combined solution which showed 64% racemization was subjected to reduced pressure distillation, to yield a yellow colored residue. This viscous liquid was dissolved in 5 ml. of $CHCl_3$ and chromatographed on prep. tlc plates. The recovered, chemically unchanged 2,2'-dicarbomethoxy-9,9'-bianthryl weighed 0.05 g.(25%). It was 40.6% racemized (based on the rotation of the starting material).

---

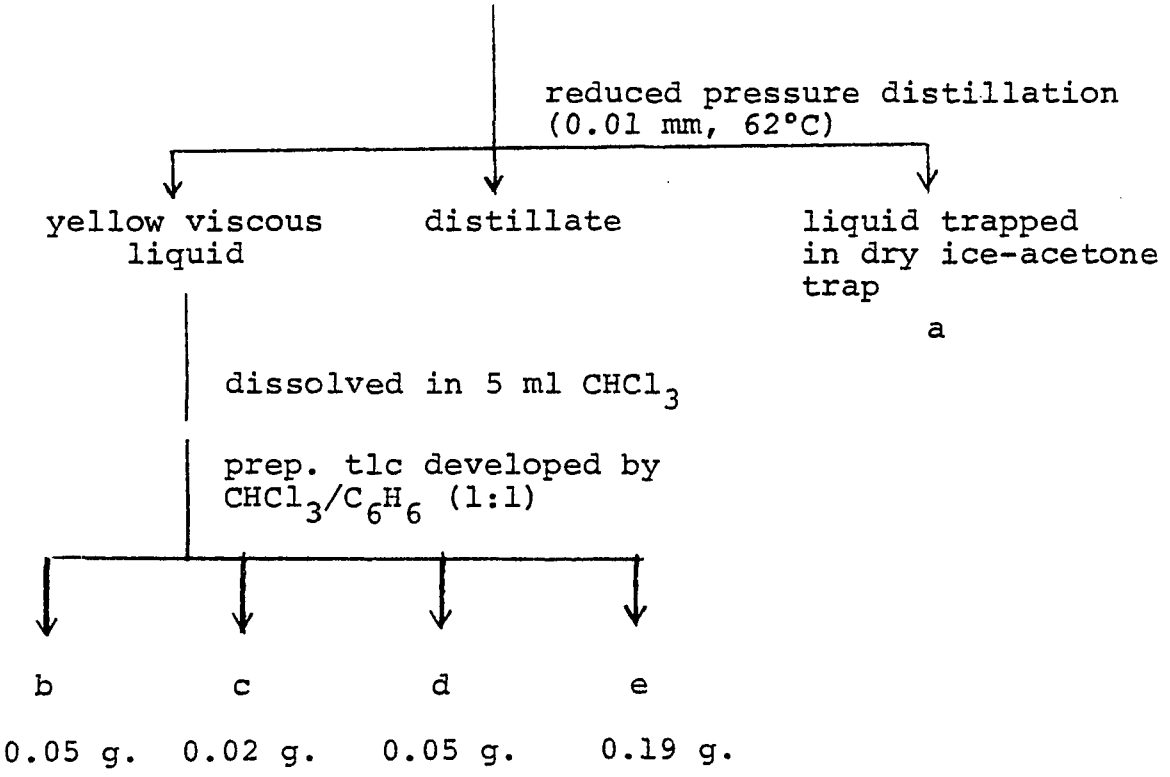
* Purified by the procedure on p. 120.

** Same tube as on p. 95, Figure IV except that a TS 10/30 inner joint formed the mouth of the tube.

C. Investigation of the Products of the Racemization of 2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia).

The following work-up procedure was used on the racemized sample (64% racemized) (after heating at 125 ± 0.1°C for 3 hr.).

50 ml. of dimethyl suberate solution containing (+) 2,2'-dicarbomethoxy-9,9'-bianthryl (0.20 g., 4.3×10^{-4} mole) and tert-butyl peroxide (0.5 ml., 2.6×10^{-3} mole)



Properties of the five components:

a. Nmr showed it to be tert-butyl peroxide.

b. Tlc analysis showed it had the same Rf values as the starting material; 25% recovery; $[\alpha]_{589}^{23^{\circ}C} = +79.0 \pm 0.2$ (c 0.5, $CHCl_3$; 42.6% racemized (based on the rotation of the starting material). Ms, ir, nmr were virtually identical to those of the starting material.

c. Mass spectrum, m/e (rel. intensity using linear mass scan) 670(100), 470(9), 350(11); nmr ($CDCl_3$), δ 1.30-2.32 (m, 11 H, methylene H), 3.51-3.62 (overlapping singlets, 12 H, $-\overset{O}{\overset{\|}{C}}-OCH_3$), 6.9-8.2 (m, 13 H, aromatic H), 8.60(s, 1H, C_{10}-H), 8.64 (s, 1 H, $C_{10'}$-H); ir, 3010(w) 2985 (m), 1725 (s, broad, C=O), 1630 (m), 1440 (s, broad), 1100,(s), 765(s), 750 (s), 735 (s). Optical rotation was zero.

d. Mass spectrum, m/e (rel. intensity using linear mass scan) 670(4.2), 470(100), 350(26); nmr ($CDCl_3$), δ 1.4-2.48,(m, broad), 3.28-3.98 (overlapping singlets), 6.90-8.36 (m, broad), 8.62 (s), 8.66 (s), 8.74 (s); ir was virtually identical to that of c.

e. Nmr and ir showed the same patterns as d. $[\alpha]_{589}^{23^{0}C}$ = + 13 (c 1.9, $CHCl_3$). Based on the assumption that the original specific rotation was the same as that of the starting material (Ia), this value represented 91% racemization. Tlc analysis showed (with tailing) that it contained three components (CH_2Cl_2/EtOAc/HAc, 9:1:0.1), Rf 0.35, 0.62, 0.78. The Rf value of dimethyl suberate was 0.75 under the same condition.

VII. Racemization of (-)6,6'-Diethyl-2,2'-dicarbomethoxybiphenyl (LXV).

A. Preparation of (-)6,6'-Diethyl-2,2'-dicarbomethoxybiphenyl. Esterification of (-)6,6'-Diethyl-2,2'-dicarbomethoxybiphenyl.

Ethanol (95%, 25 ml.) was added to a solution of potassium hydroxide (5 g., 8.9 x 10^{-2} mole) in water (8 ml. in a 100-ml distilling flask, fitted with a Claisen distilling head to which a 250 ml. pressure-equalizing addition funnel and a water-cooled condenser, set downward for distillation, were connected. The condenser was connected to two receiving flasks, in series, cooled by an ice-salt bath. The second of the two flasks contained 50 ml. of ether. The inlet tube of the second receiver dipped below the surface of the ether. The first receiving flask was a 1 l. erlenmeyer flask containing 5.2 g. (1.74 x 10^{-2} mole) (-)6,6'-diethyl-2,2'-dicarboxybiphenyl* 200 ml. anhydrous ether and a magnetic stirrer.

The flask containing the potassium hydroxide solution was heated in a water bath at 65°C. A solution of 21.6 g. (0.1 mole) of Diazald (N-methyl-N-nitroso-P-toluenesulfonamide) (Aldrich Chem. Co., Milwaukee, Wisconsin) in 200 ml.

---

*Prepared by Dr. R. Gupta.

of ether, contained in the pressure-equalizing addition funnel, was added over a period of 2 hr.. The rate of addition was set approximately equal to the rate of distillation. Another 20 ml. of ether was subsequently slowly added through the addition funnel, and distillation was continued until the distillate was colorless.

The resulting solution was stirred for an additional hour, and then 5 ml. of acetic acid was added. The ether solution was subjected to simple distillation to yield 5.3 g. of a viscous liquid. This liquid was chromatographed on 200 g. of silica gel (100-200 mesh, Davison Chem. Co., Baltimore, Maryland). The column was eluted with a mixture of ether and hexane (1:9). The solution was evaporated to yield 4.8 g (-)6,6'-diethyl-2,2'-dicarbomethoxybiphenyl (LXV); b.p., 166-167/0.2 mm (literature[99], b.p., 150-170/0.2 mm); $[\alpha]_{589}^{23°C}$ = -31.7 (c 1.52, triglyme ($CDCl_3$), δ 1.01 (t, 6 H, $-CH_2CH_3$), 2.1 (quartet, 4 H, $-CH_2CH_3$), 3.58 (s, 6 H, CH_3O-), 7.24-7.44 (m, 4 H, aromatic H), 7.78 (doublet of doublets, 2 H, aromatic H).

B. Racemization of (-)6,6'-Diethyl-2,2'-dicarbomethoxy-biphenyl (LXV) in the Presence of Oxygen Using Triglyme as Solvent.

Two samples were prepared at the same time. Each sample contained (-)6,6'-diethyl-2,2'-dicarbomethoxy-biphenyl (2.17×10^{-2} g.,6.64×10^{-5} mole) in 1 ml. freshly purified triglyme,* in a specially made tube.**

These samples were degassed by a freeze-pump-thaw procedure (p. 98). Helium was introduced to the first sample*** and the tube was sealed. In the same way, oxygen*** was introduced to the second tube before sealing.

After 2 hr. heating in a silicone oil constant temp. bath (p. 96, footnote) at 189.5 ± 0.1°C, both samples showed no racemization.

---

* See p. 95 for the purification procedure.

** Same tube as on p. 95, Figure IV except that a TS 10/30 inner joint formed the mouth of the tube.

*** Both were introduced until a pressure of 700 mm Hg was reached.

C. Racemization and Recovery of (-)6,6'-Diethyl-2,2'-dicarbomethoxybiphenyl (LXV).

Two samples were prepared at the same time. Each sample contained (-)6,6'-diethyl-2,2'-dicarbomethoxybiphenyl (LXV) (0.11 g., 3.1×10^{-4} mole) in 10 ml. triglyme,* in a specially made tube.** The subsequent procedure for the preparation of these two samples was the same as on p. 142.

After 3 hr. heating in a silicone oil constant temp. bath at 190.0 ± 0.1°C both samples showed no racemization.

After reduced pressure distillation, 0.1 g. of a viscous liquid was recovered from sample number 1 (under a helium atmosphere). Tlc analysis showed it had the same Rf value as the starting material, (-)6,6'-diethyl-2,2'-dicarbomethoxybiphenyl. Its nmr spectrum was identical to that of the starting material.

In a similar way, 0.139 g. of viscous liquid was recovered from sample number 2 (oxygen atmosphere). Prep. tlc (hexane/ether, 4:1), separated it into two parts:

---

* See p. 95 for the purification procedure.

** Same tube as on p. 95, Figure IV except that a TS 10/30 inner joint formed the mouth of the tube.

*** Both were introduced until a pressure of 700 mm Hg was reached.

Part a, 0.1 g., the same Rf value as (-)6,6'-diethyl-2,2'-dicarbomethoxybiphenyl (LXV); the nmr spectrum was identical to that of the starting material. Part b, 0.02 g., the nmr spectrum showed it to be aliphatic and a derivative of triglyme.

APPENDIXES

I. Racemization of (-)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of tert-Butyl Peroxide Using Diphenyl Ether as the Solvent.

A. Racemization of (-)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of tert-Butyl Peroxide.

A solution of 0.2 g. (4.26×10^{-4} mole) of Ia in 50 ml. of diphenyl ether (purified by reduced pressure distillation) was placed in a 100 ml. three-necked flask. Each neck was fitted with a water condenser. A 50 ml. pressure-equalizing addition funnel, containing a solution of 0.159 g. (1.1×10^{-3} mole) of tert-butyl peroxide in 2 ml.of diphenyl ether, was placed on the top of the central condenser. The other two condensers were used as inlet and oulet for nitrogen gas. The outlet for the nitrogen gas was sealed by a silicone oil bath. The pressure of nitrogen gas inside the assembly was regulated by a tee-tube. One of three openings of the tee-tube was sealed by another silicone oil bath.

tert-Butyl peroxide solution was added slowly, over a period of 3 hr., to the stirring solution in the 100 ml. flask, which was heated in a silicone oil bath at 146 ± 0.1°C. After three hours of heating the solution was allowed to cool, and the optical rotation was taken. It showed 70.5% racemization.

B. Investigation of the Products of the Racemization of (-)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia).

The solution from A (previous page) was subjected to reduced pressure distillation (0.04 mm, 73°C) to remove diphenyl ether. The yellow residue was washed with ethanol (95%) and dried under vacuum at 90°C for 20 hr..

The solid was separated, by preparative tlc ($CHCl_3$/ Benzene, 6:5), into two fractions. The first fraction had the same Rf value as the starting material (Ia); $[\alpha]_{589}^{23°C}$ = -41.3 (c 0.3, $CHCl_3$) ($[\alpha]_{589}^{23°C}$ = -158.7 (c 0.3, $CHCl_3$) for the starting material); mass spectrum m/e (linear rel. intensity), 498(20.4), 484(68.5), 470(100), 350(35.2); the nmr spectrum showed additional peaks, compared to 2,2'-dicarbomethoxy-9,9'bianthryl (Ia), at δ 1.24, 1.6, 3.24, 3.4, 3.64, 3.88, 6.6, 6.8,and 8.2-8.4; The ir spectrum showed the same pattern as the pure compound, Ia, but the shape of peaks were not completely the same, especially at 1270 cm^{-1}. The nmr spectrum of the second fraction showed δ 1.24 and 1.6 peaks larger than with the first fraction.

C. Discussion.

It appears that in the present system tert-butoxy radicals decompose substantially to form acetone and methyl radicals. Diphenyl ether (the solvent) contains non-abstractable hydrogens.[100] Thus, tert-butoxy radicals undergo decomposition rather than hydrogen abstraction. In the racemization of Ia in the presence of tert-butyl peroxide, using dimethyl suberate as the solvent, it was found that tert-butoxy radicals undergo hydrogen abstraction (pp. 76-81).

The mass spectrum of fraction one suggested that it contained methylated preducts of Ia, resulting from the attack of methyl radicals on Ia. The presence or absence of Ia could not be definitely established.

It is conceivable that a methyl radical attacks Ia (BH) to form a radical complex CH_3-BH•, which racemizes more easily than Ia (pp. 32-35). Since oxygen radicals were also present in this system, hydrogen abstraction could also take place (see p. 78) leading to substitution products.

II. Racemization of (-)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia) in the Presence of KF, or 2,6-Di-tert-butyl-p-cresol Using N-Methyl Pyrolidinone as the Solvent.

A. Racemization of (-)2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia).

Three samples were prepared, each contained 0.03 g. of Ia in 10 ml. of N-methyl pyrolidinone* with added KF (or with added 2,6-di-tert-butyl-p-cresol). Air inside the samples was removed by the Freeze-Pump Thaw procedure (p. 96). Helium was then introduced and the tubes sealed off (helium pressure at 703 mm Hg).

The samples were heated at 188.8 ± 0.1°C for 43 hr.. The results are shown in Table XV.

Table XV

Sample	2,6-Di-tert-butyl-p-cresol (mole)	KF (mole)	Racemization (%)
1	0	0	42
2	5.4×10^{-4}	0	26
3	0	6.9×10^{-4}	14

* N-Methyl pyrolidinone was purified by reduced pressure distillation.

B. Recovery and Investigation of the Racemized 2,2'-Dicarbomethoxy-9,9'-bianthryl (Ia).

The procedure for the preparation of the sample was the same as in A. A sample containing 0.16 g. (3.4×10^{-4} mole) of Ia dissolved in 40 ml. of N-methyl pyrolidinone was heated in a constant temperature bath (see p. 96) at 187.9 ± 0.1°C for 43 hr.. This sample showed 42% racemization. The solution was subjected to reduced pressure distillation to remove the solvent. A yellow solid (0.26 g.) was recovered. This solid was chromatographed on a silica gel (80 g.) column, and eluted with $CHCl_3$/Benzene (3:2). The recovery of starting material, Ia, was 54%. This recovered starting material showed 34.7% racemization. The rest of the products from this racemization experiment was not investigated.

C. Discussion

The results from the present system show that a species, which originated from N-methyl pyrolidinone (the solvent), catalyzes the racemization of Ia. The results with 2,6-di-tert-butyl-p-cresol suggest that this species could be a radical in nature. The detailed structure of this species is unknown at the present time. The role of KF is presently not understood.

References

1. Atropisomerism is defined by Eliel[3] as "... any kind of stereoisomerism due to restricted rotation about bonds where the isomers can actually be isolated."

2. Christie, J. H.; Kernner, K. J. Chem. Soc. 1922, 121, 614-620.

3. Eliel, E. L. "Stereochemistry of Carbon Compounds"; McGraw-Hill Book Co., Inc.: New York, 1962; chap. 6.

4. (a) Ref. 3 and references cited therein. (b) Grundy, J. "Stereochemistry"; Butterworths and Co. Ltd.: Washington D.C., 1964; chap. 8. (c) Harris, M. M. in "Progress in Stereochemistry"; Klyne, W. and de La Mare, P. B. D., Eds.; Butterworths and Co. Ltd.: Washington, D.C., 1958; Vol. 2, chap. 6. (d) Adams, R.; Yuan, H. C. Chem. Rev. 1933, 12, 261-337.

5. Hall, D. M.; Harris, M. M. J. Chem. Soc. 1960, 490-494, and references cited therein.

6. Bell, F.; Waring, D. H. ibid. 1949, 2689-2693.

7. Koukotas, C. Ph.D. Dissertation; The City University of New York: New York, 1968.

8. Koukotas, C.; Schwartz, L. H. J. Chem. Soc., Chem. Commun. 1969, 1400.

9. Carter, E.; Liljefors, T. Tetrahedron 1976, 32, 2915-2922, and references cited therein.

10. (a) Harris, M. M.; Lin, C. K. Chem. Ind. (London) 1962, 1378-1380. (b) Cooke, A. S.; Harris, M. M. J. Chem. Soc. 1965, 1412-1418. (c) idem, ibid. C 1967, 988-992. (d) Harris, M. M.; Mazengo, R. Z.; Cooke, A. S. ibid. C 1967, 2575-2577.

11. (a) Ling, C. C. K.; Harris, M. M. ibid. 1964, 1825-1835. (b) Harris, M. M.; Michell, R. K. ibid. 1960, 1905-1908.

12. Adams, R.; Hale, J. B. J. Am. Chem. Soc. 1939, 61, 2825-2827.

13. Baddeley, G. Nature 1946, 157, 694-695.

14. Crawford, M.; Smyth, I. F. B. Chem. Ind. (London) 1946, 346-347; J. Chem. Soc. 1954, 3464-3468.

15. Rabideau, P. W.; Paschal, J. W.; Patterson, L. E. J. Am. Chem. Soc. 1975, 97, 5700-5704.

16. Ito, O.; Hatano, M. Chem. Lett. 1976, 39-42.

17. Oki, M.; Iwamura, H.; Hayakawa, N. Bull. Chem. Soc. Jpn. 1964, 37, 1865-1870.

18. Iwaizumi, M.; Matsusaki, T.; Isobe, T. ibid. 1972, 45, 1030-1034.

19. Digregorio, S.; Yim, M. B.; Wood, D. E. J. Am. Chem. Soc. 1973, 95, 8455-8457.

20. Fahrenholtz, S. R.; Trozzolo, A. W. ibid. 1972, 94, 282-283.

21. Jordan, J. E.; Pratt, D. W.; Wood, D. E. ibid. 1974, 96, 5588-5590.

22. Satiel, J.; Curtis, H. C. ibid. 1971, 93, 2056-2058.

23. Kobayashi, M.; Minato, H.; Kobori, N. Bull. Chem. Soc. Jpn. 1969, 42, 2738.

24. Kamigata, N.; Minato, H.; Kobayashi, M. ibid. 1972, 45, 2042-2046.

25. Eliel, E. L.; Meyerson, S.; Welvart, Z.; Wilen, S. J. Am. Chem. Soc. 1960, 82, 2936-2944.

26. Smith, J. R. L.; Norman, R. O. C. J. Chem. Soc. 1963, 2897-2905.

27. For some reports of small isotope effects which have been interpreted in different ways, see (a) reference 22 and (b) Sakurai, H.; Hosomi, A. J. Am. Chem. Soc. 1971, 93, 1709-1714.

28. Berlinger, E. "Progress in Physical Organic Chemistry"; Interscience Publishers: New York, 1964; Vol. 2.

29. For leading references, see: (a) Ref. 5. (b) Kurz, M.; Kovacic, P.; Bose, A. K.; Kugajevsky, I. J. Am. Chem. Soc. 1968, 90, 1818-1822. (c) Swern, D. Ed. "Organic Peroxides"; Wiley-Interscience: New York, 1971; Vol. II. (d) Henriquez, R.; Nonhebel, D. C. Tetrahedron Lett. 1975, 3855-3856, 3857-3858.

30. (a) Atkinson, D. J.; Perkins, M. J.; Ward, P. J. Chem. Soc. C 1971, 3240-3247. (b) Perkins, M. J.; Ward, P. Tetrahedron Lett. 1971, 2379-2380.

31. Perkins, M. J. in "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1972; Vol. II, chap. 16.

32. Foote, C. S. Tetrahedron Lett. 1965, 4111-4118.

33. Nmr, ir, and ms were virtually identical to those of the starting material.

34. Davidson, R. S. Quart. Rev.,Chem. Soc. 1967, 21, 249-258.

35. Bergman, E.; Tschudnowsky, M. Ber. Disch. Chem. Ges. 1932, 65, 457-463.

36. (a) Bennett, G. M.; Glasstone, S. J. Chem. Soc. 1934, 128-129. (b) Lesslie, M. S.; Turner, E. E. ibid. 1934, 1170-1174. (c) Idem., ibid. 1935, 1268-1269; 1936, 730-731. (d) Lesslie, M. S. ibid. 1938, 1001-1003; 1949, 1183-1184. (e) Beckett, A. H.; Mulleg, B. A. Chem. Ind. (London) 1955, 146-148.

37. Turner, E. E. in "Chemistry of Carbon Compounds"; Rodd, E. H. Ed.; Elsevier Publishing Co.; London, 1951, Vol. 1, pp. 153-155.

38. Ferrier, W. G.; Iball, J. Chem. Ind. (London) 1954, 1926-1927.

39. Ternay, A. L., Jr.; Chasar, T. W.; Sax, M. J. Org. Chem. 1967, 32, 2465-2470.

40. Harvey, R. G.; Arzadon, L.; Grant, J.; Urberg, K. J. Am. Chem. Soc. 1969, 91, 4535-4541.

41. (a) Bank, S.; Bank, J.; Daney, M.; Labrande, B.; Bouas-Laurent, H. J. Org. Chem. 1977, 42, 4058. (b) Cho., H.; Harvey, R. G.; Rabideau, P. W. J. Am. Chem. Soc. 1975, 97, 1140-1145. (c) Fu, P. P.; Harvey, R. G.; Paschal, J. W.; Rabideau, P. W. ibid. . 1975, 97, 1145-1153. (d) Zeiger, H. E.; Gelbaum, L. T. J. Org. Chem. 1972, 37, 1012-1015. (e) Fabre, C.; Salem, M. H. A.; Mazaleyrat, J. P.; Tehapla, A.; Welvart, Z. J. Organomet. Chem. 1975, 87, 9-24. (f) Daney, M.; Lapayde, R.; Mary, M.; Bouas-Laurent, H. J. Organomet. Chem. 1975, 92, 267-274.

42. Non-bonded interactions with the peri hydrogens. There is general agreement that the preferred orientation of 9 or 10 substituents is quasiequatorial.

43. (a) Beckett, A. H.; Mulley, B. A. J. Chem. Soc. 1955, 4159-4168. (b) Smith, W. B.; Shoulders, B. A. J. Phys. Chem. 1965, 69, 2022-2026.

44. Brinkmann, A. W.; Gordon, M.; Harvey, R. G.; Rabideau, P. W.; Stothers, J. B.; Ternay, A. L., Jr. J. Am. Chem. Soc. 1970, 92, 5912.

45. Curtin, D. Y.; Carlson, C. G.; McCarty, C. C. Can. J. Chem. 1964, 42, 565-571.

46. Construction of the molecular model indicates that the equatorial hydrogen is severely hindered for a bi-molecular attack. The authors in ref. 43a express the same view.

47. Dickerman, S. C.; Feigenbaum, W. M.; Fred, M.; Milstein, N.; Vermont, G. B.; Zimmerman, I.; McOmie, J. P. W. J. Am. Chem. Soc. 1973, 95, 4624-4631.

48. Magelli, O.; Sheppard, C. S. in "Organic Peroxides", Swern, D. Ed.; Wiley-Interscience: New York, 1970; Vol. I, p. 15.

49. (a) Reference 48, p. 29 and p. 20. (b) Hiatt, R. reference 48, Vol. II, p. 17, 94, 96, and 97.

50. Walling, C. "Free Radicals in Solution"; John Wiley & Sons, Inc.: New York, 1957; chap. 9.

51. (a) Pryor, W. A. "Free Radical"; McGraw-Hill Co.: New York, 1966; p. 294. (b) p. 289 and the references cited therein. (c) p. 165.

52. Razuvaev, G. A.; Koton, M. M. J. Gen. Chem. (USSR) 1931, 1, 864; Ber. Disch. Chem. Ges. 1932, 65, 613-622.

53. Bass, K. C.; Nababsing, P. Chem. Ind. (London) 1965, 307-308.

54. (a) Nonhebel, D. C.; Walton, J. C. "Free Radical Chemistry": Cambridge, 1974, pp. 394-397. (b) Chap. 12. (c) Chap. 11.

55. (a) Williams, G. H. "Homolytic Aromatic Substitution"; Pergamon Press: New York, 1960, chap. 6. (b) Chap. 7.

56. Jackson, R. A. J. Chem. Soc. 1963, 5284-5287.

57. Howard, J. A. in "Free Radicals", Kochi, J. K. Ed.; John Wiley and Sons, Inc.: New York, 1973, Vol. II, p. 5.

58. Reference 57, p. 683.

59. Bass, K. C. Nature 1964, 700-701.

60. Beckwith, A. L. J.; Waters, W. A. J. Chem. Soc. 1957, 1001-1008.

61. Testaferri, L.; Tiecco, M. J. Chem. Soc., Perkin II 1975, 662-668.

62. Conway, W.; Tarbell, D. S. J. Am. Chem. Soc. 1956, 78, 2228-2233.

63. Mizashica, T.; Matsuda, M.; Iino, M. Bull. Chem. Soc. Jpn. 1975, 48, 3230-3235.

64. Miyashita, T.; Iino, T.; Matsuda, M. Bull. Chem. Soc. Jpn. 1977, 50, 317-318.

65. (a) Pryor, W. A.; Gojon, G.; Stanley, J. P. J. Am. Chem. Soc. 1973, 95, 945-946. (b) Pryor, W. A.; Gojon, G.; Church, D. F. J. Org. Chem. 1978, 43, 793-800. (c) References cited in (a) and (b).

66. (a) Kellogg, R. M. in "Methods in Free-Radical Chemistry", Huyser, E. S., Ed.; Marcel Dekker: New York, 1969; Vol. 2, chap. 1, p. 101; (b) p. 95; (c) p. 107.

67. Schmidt, U. Angew Chem., Int., Ed. Engl. 1964, 602-608.

68. Kice, J. L. in "Free Radicals", Kochi, J. K., Ed.; John Wiley and Sons, Inc.; New York, 1973, Vol. 2, p. 711.

69. Block, E. "Reactions of Organosulfur Compounds"; Academic Press: New York, 1978, chap. 5 and references cited therein.

70. The other methods of generating RS can be found elsewhere, e.g., ref. 66 and 68.

71. (a) Hawkins, W. L.; Santer, H. J. Polym. Sci. A 1963, 3499-3509: Chem. Ind. (London) 1961, 1825.

72. (a) Reference 69, p. 302. (b) Vedeneyev, V. I.; Gurvich, L. V.; Konratyey, V. N.; Medvedev, V. A.; Frankevich, Y. L. "Bond Energies, Ionization Potentials and Electron Affinities"; St. Martin's Press: New York, 1966, p. 57.

73. Budzikiewicz, H.; Dierassi, C.; Williams, H. "Interpretation of Mass Spectra of Organic Compounds"; Holden-Day Inc.: San Francisco, 1964, pp. 53-54.

74. In general, aliphatic carbon radicals are considered to be more selective than phenyl radical. It was reported (see ref. 76) that the order of selectivities were phenylation<methylation<cyclohexylation.

75. Eliel, E. L.; Welvart, Z.; Wilen, S. H. J. Org. Chem. 1958, 23, 1821-1822.

76. Shelton, J. R.; Uzelmeir, C. A. J. Am. Chem. Soc. 1966, 88, 5222-5228.

77. (a) Buratti, W.; Gardini, G. P.; Minisci, F. Bertini, F.; Galli, G.; Perchinunno, M. Tetrahedron 1971, 27, 3655-3668. (b) idem. ibid. 1971, 27, 3575-3579.

78. Alkyl radicals are generally considered to be nucleophilic in the homolytic aromatic substitution reactions, e.g., see references 79, 80, 81.

79. Mangini, A.; Spagnolo, P.; Tassi, D.; Zanirato, P. Tetrahedron 1972, 28, 3485-3488.

80. Minisci, F.; Mondell, R.; Gardini, G. P.; Porta, O. Tetrahedron 1972, 28, 2403-2413.

81. Testaferri, L.; Tiecco, M.; Spagnolo, P.; Zanirato, P. Gazz. Chim. Ital. 1975, 105, 761-775.

82. Dixon, W. T.; Norman, R.O.C.; Buley, A.L. J. Chem. Soc. 1964, 3625-3629; references cited therein.

83. Johnson, C. E., Jr.; Bovey, F. A. J. Chem. Phys. 1958, 29, 1012-1014.

84. Mcbay, H. C.; Tucker, O.; Milligan, A. J. Organomet. Chem. 1954, 19, 1003-1007.

85. Beckwith, A. L. J. Aust. J. Chem. 1960, 13, 244-255.

86. (a) Nesmeyanov, A. N.; Kocheshkov, K. A., Eds. "Methods of Elementoorganic Chemistry"; North-Holland Publishing Co.: Amsterdam, 1967, Vol. 4, p. 409, and the references cited therein. (b) idem., ibid., p. 411.

87. Billings, B. H. M.; Gowenlock, B. G. Proc. Chem. Soc. (London) 1962, 24.

88. Jensen, F. R.; Rickborn, B. "Electrophilic Substitution of Organomercurials"; McGraw-Hill Book Co.: New York, 1968, p. 137.

89. (a) Pritchard, H. O. J. Chem. Phys. 1956, 25, 267-270. (b) Russell, M. E.; Bernstein, R. B. ibid., 1959, 30, 607-612, 613-617.

90. Makarova, L. G. in "Organometallic Reactions", Becker, E. I.; Tsutsui, M.; Eds.; Wiley-Intersciences: New York, 1971; Vol. 2, p. 414.

91. Lauri, C. M.; Long, L. H. J. Chem. Soc., Faraday Trans. 1955, 51, 665-679.

92. Gray, P. ; Williams, A. Chem. Rev. 1959, 59, 239-328.

93. Moore, C. G. J. Chem. Soc. 1951, 236-237.

94. Mason, S. F.; Seal, R. H. Tetrahedron 1974, 30, 1671.

95. Komazana, H.; Stefani, A. P.; Swarc, M. J. Am. Chem. Soc. 1963, 85, 2043.

96. Majer, J. R.; Robb, J. C. J. Chem. Soc., Farady Trans. 1965, 61, 110-121.

97. Julia, M. Acc. Chem. Res. 1971, 4, 386-392.

98. Julia, M.; Mallasine, B. Tetrahedron Lett. 1971, 987-990.

99. Zimmerman, H. E.; Crumrine, D. S. J. Am. Chem. Soc. 1972, 94, 498-506.

100. In general, aromatic hydrogens are not abstracted by aliphatic radicals. For example, see reference 25.