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Synthesis and investigations of substituted semibullvalenes

Connelly, Mercedes B., Ph.D.

City University of New York, 1993

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SYNTHESIS AND INVESTIGATIONS OF SUBSTITUTED SEMIBULLVALENES

by

Mercedes B. Connelly

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 NewYork.

1993

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.

4-12-93
Date

Chair of Examining Committee

4/27/93
Date

Executive Officer

Supervisory Committee

The City University of New York

Abstract

Synthesis and Investigations of Substituted Semibullvalenes

by

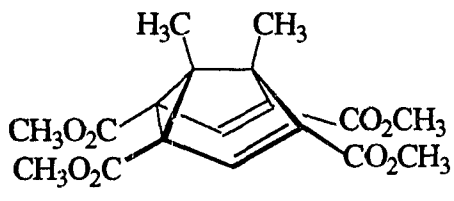
Mercedes B. Connelly

Advisor: Professor Klaus Grohmann

The concept of homoaromaticity, introduced into organic chemistry by Saul Winstein in 1959,[1] has stimulated and intrigued many chemists over the last three decades. Homoaromaticity is a term used to describe systems in which the σ backbone of an aromatic species is interrupted by a saturated center and in which the geometry continues to favor overlap of the π system.

1,5-Dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene **1**,[2] undergoes the fastest Cope rearrangement known to date. This prompted us to investigate semibullvalenes further. The main premise of our work is to further lower the energy of activation for the Cope rearrangement in semibullvalene, thus reaching a "transition state" of lower energy than the "ground state". It has been the goal of this thesis project to synthesize the first neutral bis-homoaromatic molecule. Both planar 1,5-annulated, such as **2** and **3**, as well as non-annulated systems will be disscussed.

A method was developed for the synthesis of 2,6-dicarbomethoxy-1,5-dimethyl-semibullvalene **4** the resulting key intermediates **74** and **75** can be used as the starting material for the synthesis of differently substituted novel semibullvalenes. Solution state VT ^{13}C NMR studies, ranging from room temperature down to 163K, indicate that **4** undergoes a very fast Cope rearrangement.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CH3O2C
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CO2CH3

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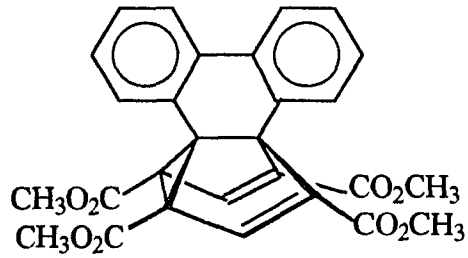
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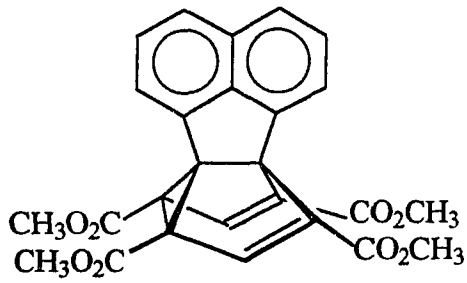
CH3O2C
CO2CH3
CO2CH3

2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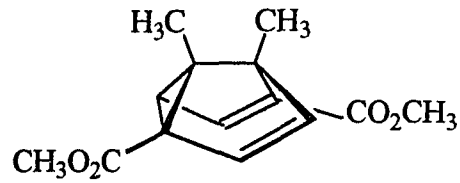
CO2CH3

3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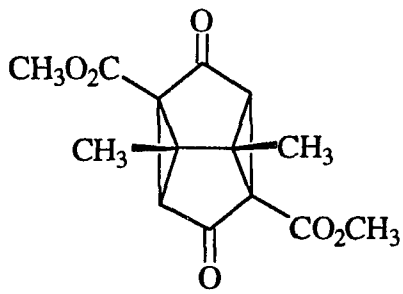
CH3O2C
CO2CH3

4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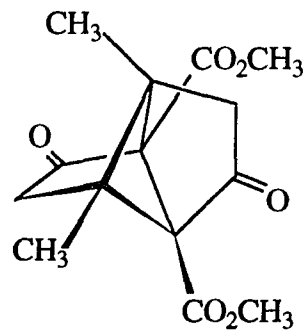
CH3
CH3
CO2CH3
O

74


CH3
CO2CH3
O
O
CH3
CO2CH3

75

In memory of Alice Rich Northrop.

Acknowledgments

I would like to thank my mentor Dr. Klaus Grohmann for giving me the experience of a lifetime. Dr. Grohmann has taught me so much about chemistry, teaching, patience (which I am still working on!) life in general, and trough it all he always made things fun. I consider myself fortunate to know him. I can only hope to have learned enough to be half the person he is.

I would like to thank Professors William Berkowitz, Richard Franck, and Ruth Stark for being on my committee and offering valuable and insightful advice on my project.

I would like to thank Dr. Michael Blumenstein for all his invaluable help and advice on the writing of this manuscript as well as his help in the area of NMR.

I would like to thank all of my fellow labmates for giving many reasons to remember them: Derek, Sassan, Carlos, Richard, Tanos, Xioa Xia, and Ronnie. Very special thanks to Marcella and Mahoney for their contagious enthusiasm and assistance in the lab during the last six months.

I would like my best friend Dr. Paula A. Longo for everything. For the great feedback, laughter, enthusiasm and insight thank you. I would also like to thank Sister Mary Maire, Georgia Boothe, and Pauline Hamilton for their friendship and support throughout.

I would also like to thank my husband, Brendan D. Connelly for being my rock of Gibraltar. Brendan has been supportive, loving and very patient. I could not have done it without him. As far as everyone in the lab is concerned Brendan is a saint, for once I agree with the male majority. I would like thank my family in law for everything.

Lastly, I would like to thank my mother and father, Hilda and Gilberto, for their undying belief , love and support. Thank you.

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INTRODUCTION AND BACKGROUND

CHAPTER 1: INTRODUCTION

THE COPE REARRANGEMENT

Since its discovery over five decades ago, the Cope rearrangement has continued to generate a great deal of discussion.[3] As shown in Figure 1, a Cope rearrangement involves the breaking of a σ bond, (C_3-C_4), and the formation of a new σ bond, (C_1-C_6), along with the migration of two π systems. In 1965 Woodward and Hoffmann,[4] in their now classic paper, defined the Cope rearrangement as a pericyclic reaction, specifically, a [3,3] sigmatropic shift.

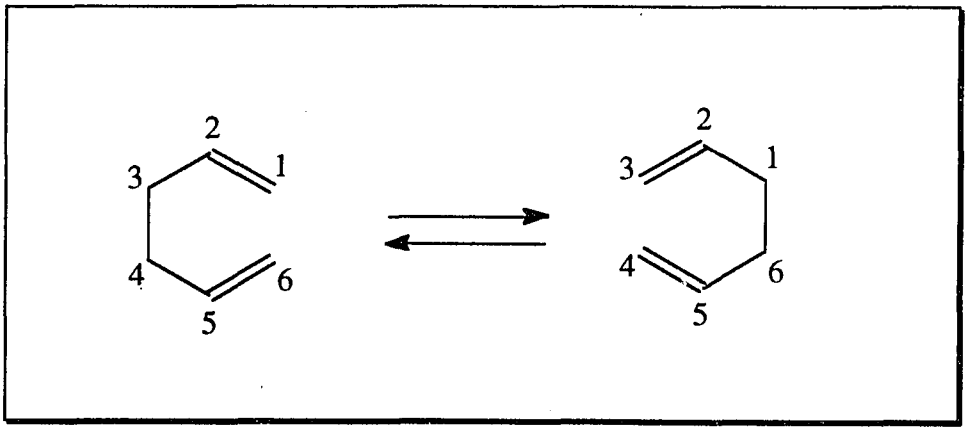


Figure 1: The Cope Rearrangement of 1,5-Hexadiene.

When the diene is symmetrical, both product and starting material are identical and the rearrangement is therefore referred to as degenerate. At equilibrium only one product will be formed. When a diene is not symmetrical, the product is different from the starting material and the rearrangement is therefore referred to as non-degenerate. In the

case of a non-degenerate rearrangement, an unequal mixture of both isomers at equilibrium will be observed with, the thermodynamically most stable isomer being favored.[5]

Table 1 shows a series of molecules that contain a 1,5-hexadiene backbone, and the corresponding energy of activation required for Cope rearrangement. As can be seen from Table 1, the barrier of this rearrangement changes as the skeleton of the 1,5-diene becomes more restricted. For example homotropylidene (Figure 2) is unrestricted and can, therefore, undergo a ring inversion. In comparison, a bridged homotropylidene, such as semibullvalene (Figure 3) cannot undergo a ring inversion.

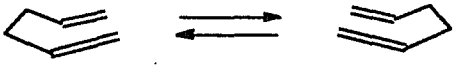
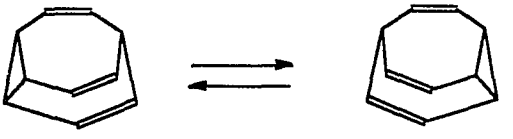
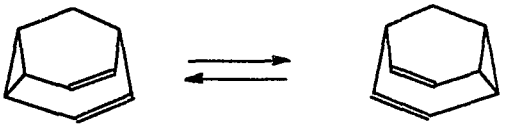
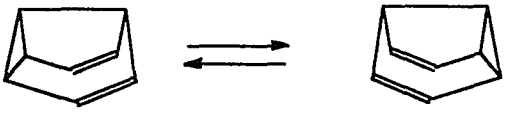
			$\Delta G^{\ddagger}$
1)		1,5-Hexadiene	36 Kcal/mol
2)		Homotropylidene	13.6 Kcal/mol at 220 K
3)		Bullvalene	12.5 Kcal/mol at 273 K
4)		Barbaralane	7.8 Kcal/mol at 202 K
5)		Semibullvalene	5.5 Kcal/mol at 173 K

Table 1: Selected Molecules Which Undergo the Cope Rearrangement and Their Energies of Activation.

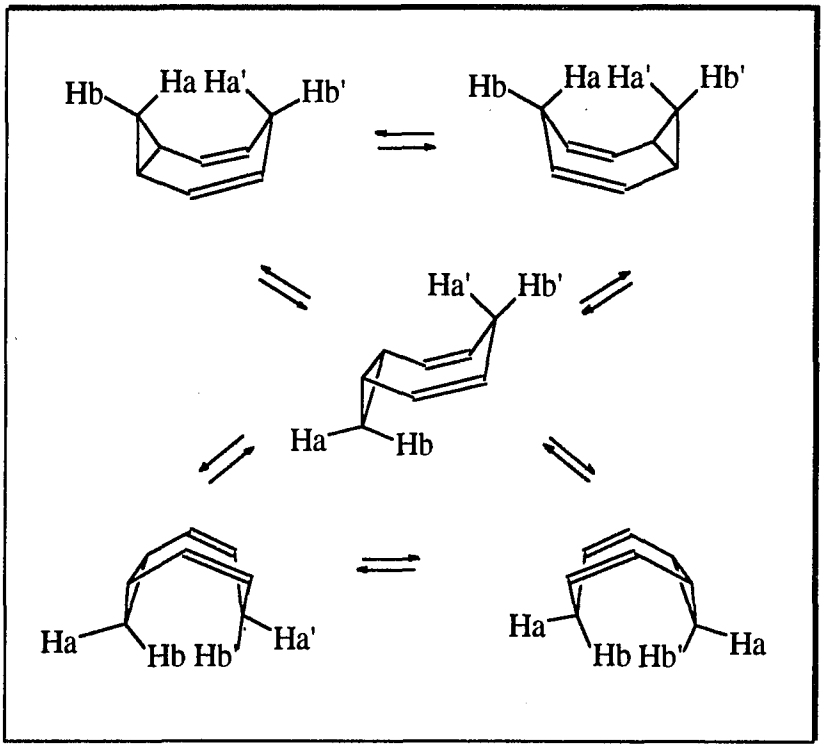


Figure 2: Homotropylidene Undergoes an Unrestricted Cope Rearrangement.

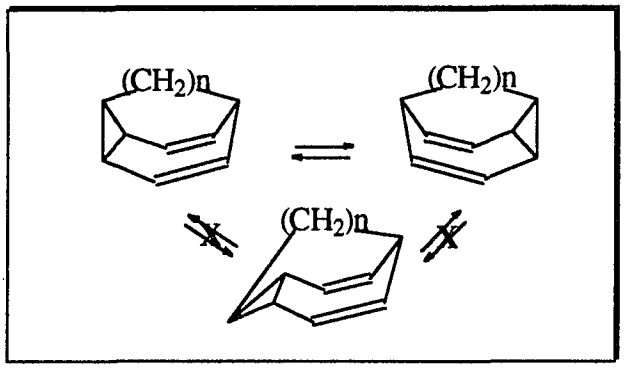


Figure 3: Bridged Homotropylidenes Undergo a Restricted Cope Rearrangement.

The nature of the transition state (TS) of the Cope rearrangement and its possible geometry has continued to be of great interest to chemists over the years.[6] There are three extreme TS's:

1. Where the (C_3-C_4) bond breaks forming a bis allyl radical before the (C_1-C_6) bond is made. (Figure 4a)

2. Where bond breaking and bond making occur simultaneously in a concerted mechanism. (Figure 4b)

3. Where the (C_1-C_6) bond is made before the (C_3-C_4) bond breaks, forming a cyclohexyl-1,4-diyl diradical. (Figure 4c)

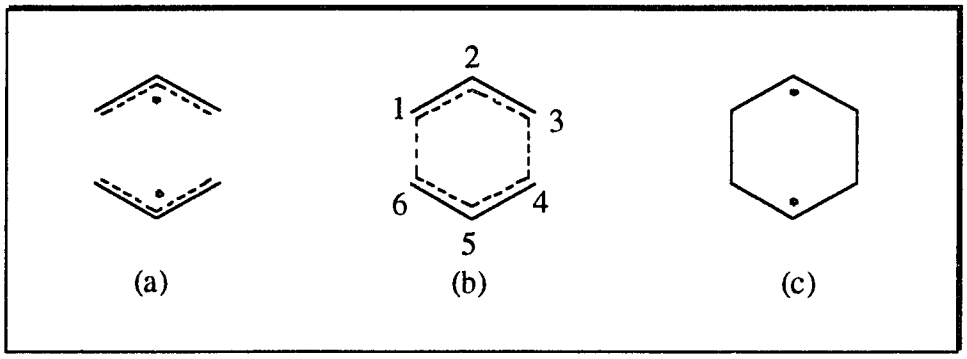


Figure 4: Three Possible Transition States of 1,5-Hexadiene.

Finding the exact nature of the TS for the Cope rearrangement has been the source of intense research by both experimentalists and theoreticians. Doering approached the problem, of TS geometry, from an experimental point of view, while Hoffmann and Woodward attacked it theoretically.[7] Both studies led to conclusions that an acyclic 1,5-hexadiene will have a preference for the chair TS, whereas a restricted 1,5-hexadiene, which will not be able to assume a chair geometry, will be locked into the boat geometry.[8]

Doering and Roth first suggested in 1963[9] that the Cope rearrangment, as the result of a non-concerted mechanism, might be of the type in Figure 4c. In this case radical stabilizing groups in the 2,5 position will have a stabilizing effect on the transiton state and therefore increase the rate of its Cope rearrangement. Dewar found that 2-phenyl and 2,5-diphenyl-1,5-hexadiene rearrange 40 and 1600 times more rapidly than 1,5 hexadiene.[10] Gajewski[11] concluded, based on studies of α-secondary deuterium kinetic isotope effects, that the transition state structure changes with substitution. AM1[12] calculations by Dewar on the chair Cope rearrangement of 1,5-hexadiene and a number of its derivatives seem to confirm a diradical TS of the type in Figure 4c.

Studies on the rate of rearrangement of restricted 1,5-hexadienes, such as barbaralane, have discounted the cyclohexyl-1,4-diyl TS. A number of substituted barbaralanes, (Figure 5) that would have stabilized the biradical TS have been studied, but none of the substitution patterns resulted in lowering the barrier to the Cope rearrangement.[13,14] Gajewski has reasoned that the TS for the Cope rearrangement in the bridged polycyclic systems such as barbaralane and semibullvalene should involve more bond breaking since a bis allyl diradical would be more stable in these systems than the diyl alternative. A thermochemical argument rendered the 1,4-diyl alternative unlikely. AM1 calculations by Dewar in 1988 and 1992[15] predicted that the Cope rearrangement for restricted 1,5-hexadienes, which have an inherent boat geometry, takes place via a typical aromatic pericyclic TS. (Figure 6b)

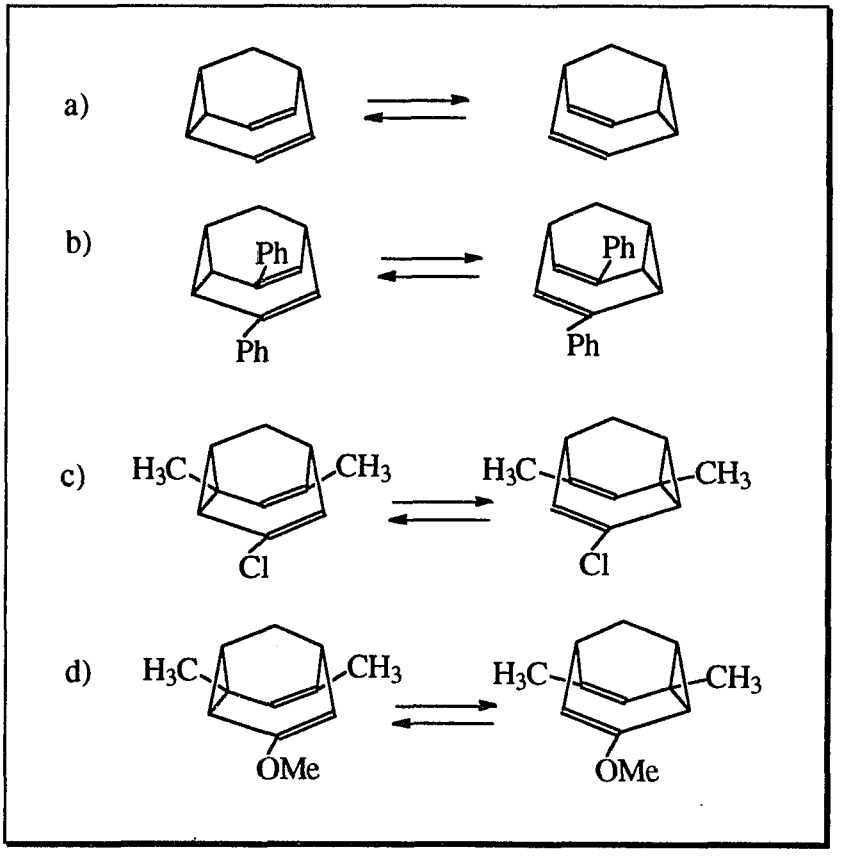


Figure 5: Substituted Barbaralanes (b), (c) and (d) Exhibit a Slower Rate Toward the Cope rearrangement in Comparison to Barbaralane (a).

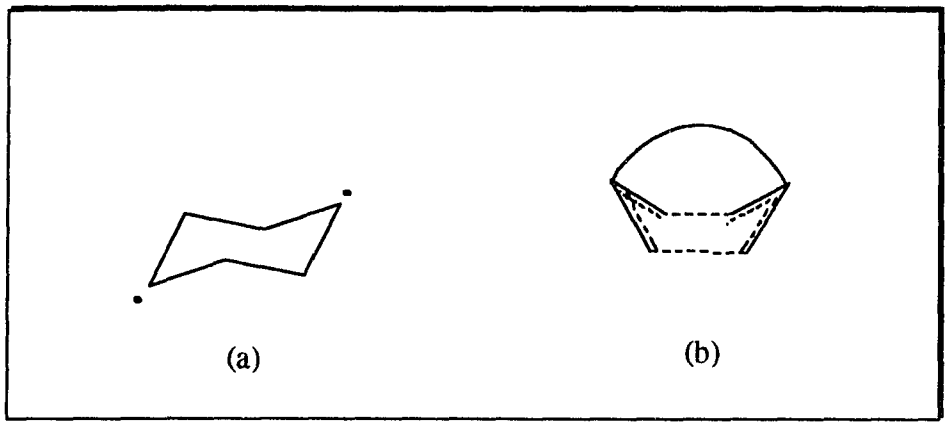


Figure 6: The Possible Transition States for the Cope Rearrangement of Unrestricted and Restricted 1,5-Hexadienes.

A molecule which isomerizes rapidly from one structure to another is said to be fluxional and to exhibit valence tautomerism. The Cope rearrangement is an example of valence tautomerism. Valence tautomerism can be studied through the use of variable temperature ^{13}C- and ^{1}H-NMR and well as IR. Homotropylidene (Figure 2) has been used to study valence tautomerism through the use of variable temperature NMR. At room temperature only one valence isomer of bicyclo[5.1.0]octa-2,5-diene, homotropylidene, is observed. At 180°C the ^{1}H NMR spectrum shows an equilibirum between the tautomers.[16]

Bullvalene,[17] is an example of a restricted degenerate Cope rearrangement.[18] (Figure 7) Bullvalene is a threefold symmetric molecule that undergoes an infinitely degenerate Cope rearrangement. In fact, at any given time the carbons in the cyclopropane ring can be any of three carbons of the bullvalene molecule.

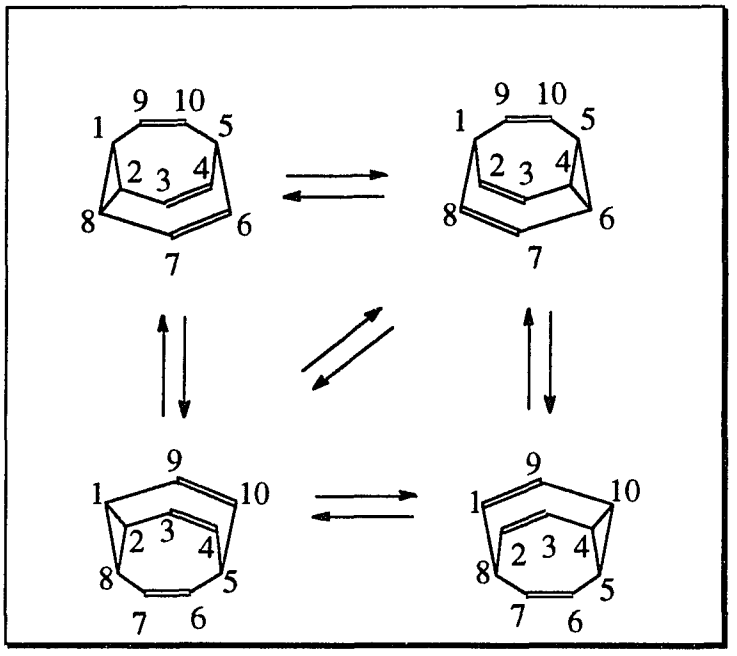


Figure 7: Bullvalene Undergoes an Infinitely Degenerate Cope Rearrangement.

Semibullvalene undergoes the fastest Cope rearrangement (Table 1). The potential energy diagram of this rearrangement is depicted in Figure 8. The prospect of further lowering the energy of the barrier to the Cope rearrangement for 1,5-dienes has been the goal of many chemists. Hoffman and Stohrer[19] stated that to stabilize the transition state and/or destabilize the tautomers would lower the barrier to the Cope rearrangement. They noted that the simultaneous accomplishment of these goals would result in the most favorable results. The potential energy diagram of the resulting molecule would resemble that of benzene, as shown in Figure 9.

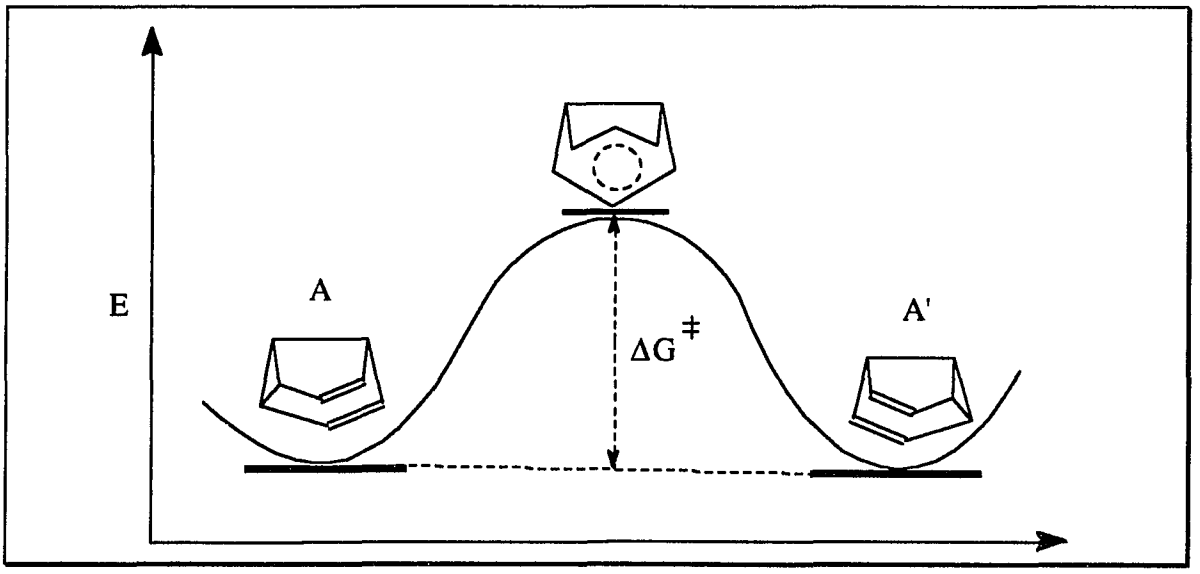


Figure 8: The Degenerate Cope Rearrangement of Semibullvalene.

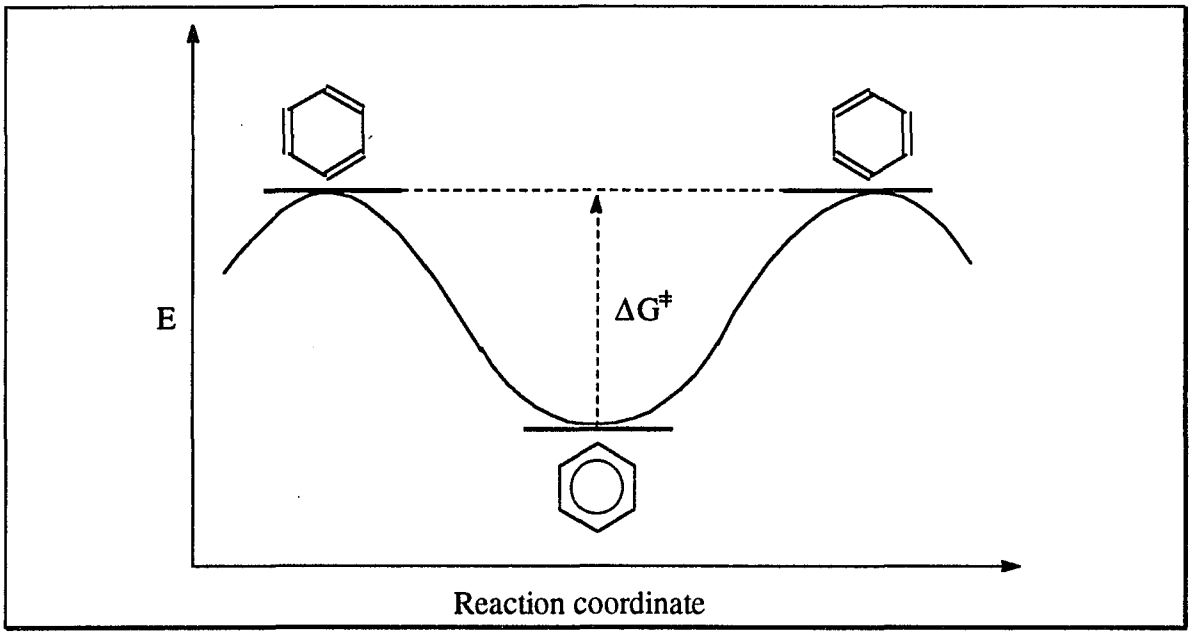


Figure 9: The Potential Energy Diagram for the Resonance of Benzene.

Semibullvalenes that undergo the Cope rearrangement through a mechanism that involves a symmetric transition state with synchronous bond making and bond breaking, (Figure 10), will result in a closed loop of (4n+2) π electrons: a so called homoaromatic system.

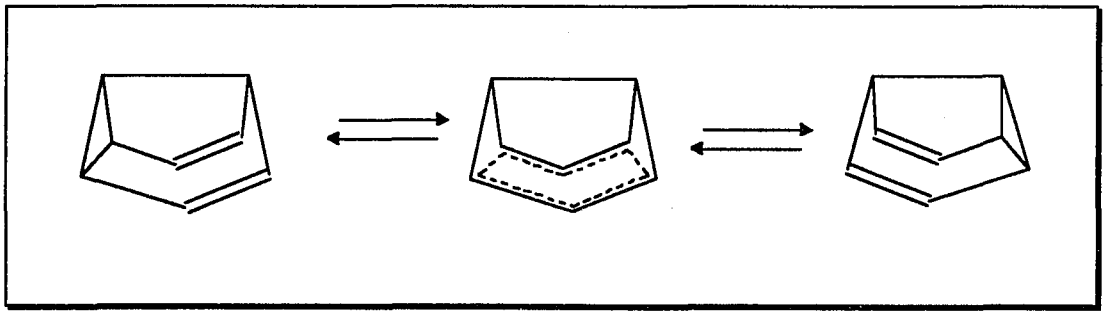


Figure 10: Semibullvalene Undergoes a Restricted Cope Rearrangement.

HOMOAROMATICITY

Homoaromaticity, first discovered by Winstein in 1967,[20] is a term which is used to describe systems in which the σ backbone of an aromatic species is interrupted by a saturated center, and in which the geometry continues to favor overlap of the π system. In an aromatic system electron delocalization is maintained because p orbitals are parallel to one another (Figure 11a). When a (4n+2) cyclic array of these orbitals is interrupted, to accomodate an sp^3-hybridized center, electron delocalization can only be maintained if the two interrupted p-atomic orbitals are able to tip toward one another, and are close enough to result in positive orbital overlap (Figure 11b). The resulting orbital overlap lies between pp-π and pp-σ. Further alteration of the p orbitals can lead to the overlap types shown in Figures 11c and 11d. When two saturated atoms are present the term bis-homoaromatic is applied.

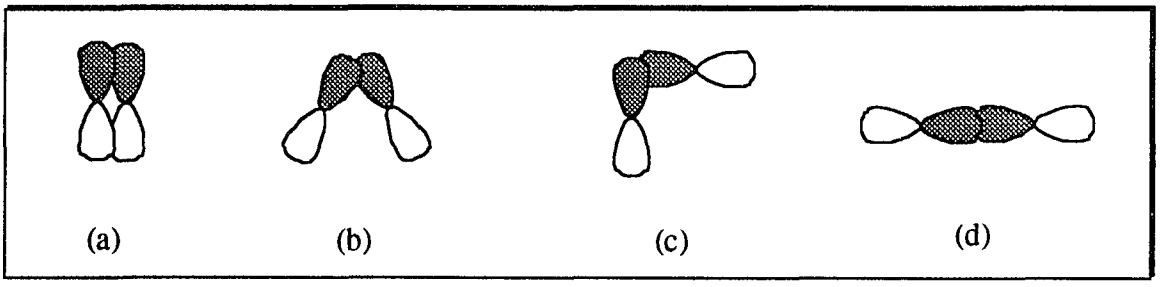


Figure 11: Orbital Interactions.

The aromatic properties of benzene are due to the presence of a (4n+2) closed loop of electrons, which sustain an induced ring current. Compounds with this capability are called diatropic. As shown in Figure 12, when an aromatic molecule is subjected to an external magnetic field the closed loop of aromatic electrons circulates in a

diamagnetic ring current fashion and produces a magnetic field of its own. This induced field deshields any hydrogens directly attached to the aromatic ring and shields any hydrogens above or within it, as seen in Figures 13. Therefore, based on the NMR chemical shifts, it is possible to determine whether a molecule is sustaining a ring current.

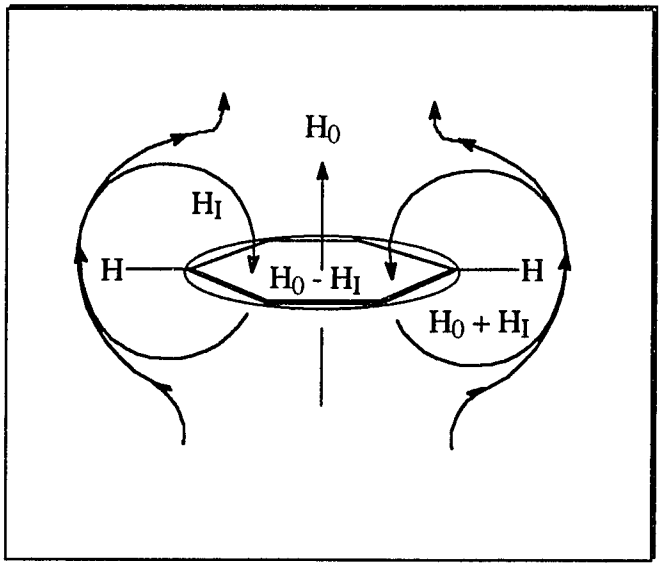


Figure 12: Diamagnetic Anisotropy in Benzene.

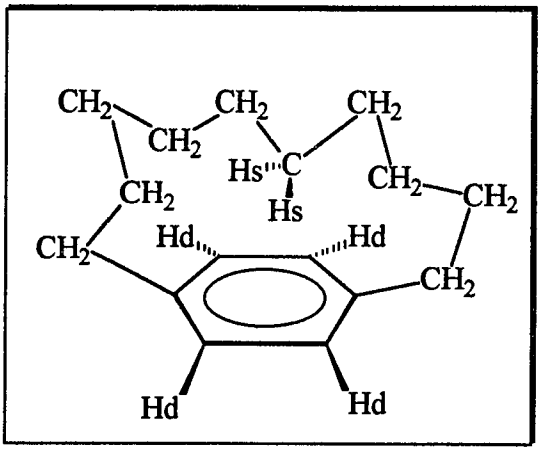


Figure 13: The Effects of Anisotropy in a 10-Cyclophane.

A homoaromatic molecule can sustain an induced diamagnetic current and this can be studied by NMR. To date there is no reported example of a neutral homoaromatic species. However, there are many examples of homoaromatic ions.[21,22] As shown in Figure 14, cyclobutenyl cation studied first by Olah, is the simplest ion exhibiting homoaromaticity. Homotropylidene cation, Figure 15, the classic example of a homoaromatic ion, was first made by Pettit in 1962[23] by treating cyclooctatetraene with concentrated sulfuric acid or with antimony pentachloride and HCl in nitromethane. ^{1}H and ^{13}C NMR[24] spectra of this cation have been used to determine the effect of the ring current on H_a and H_b. The hydrogen above the ring, H_a, current will be shielded and H_b will have the expected NMR chemical shift.

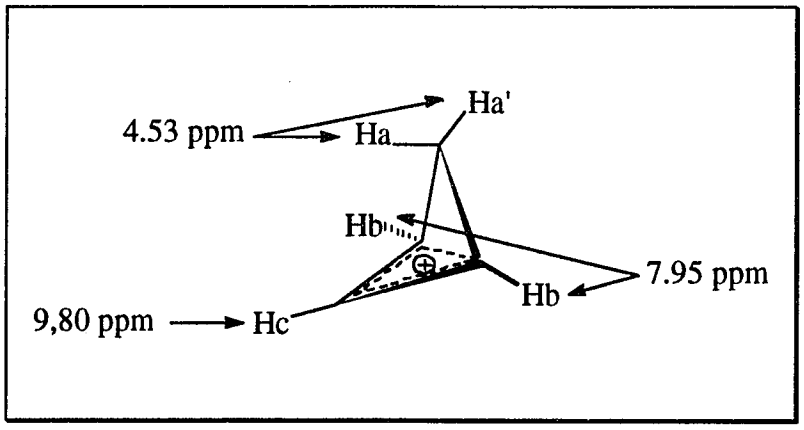


Figure 14: Cyclobutenyl Cation.

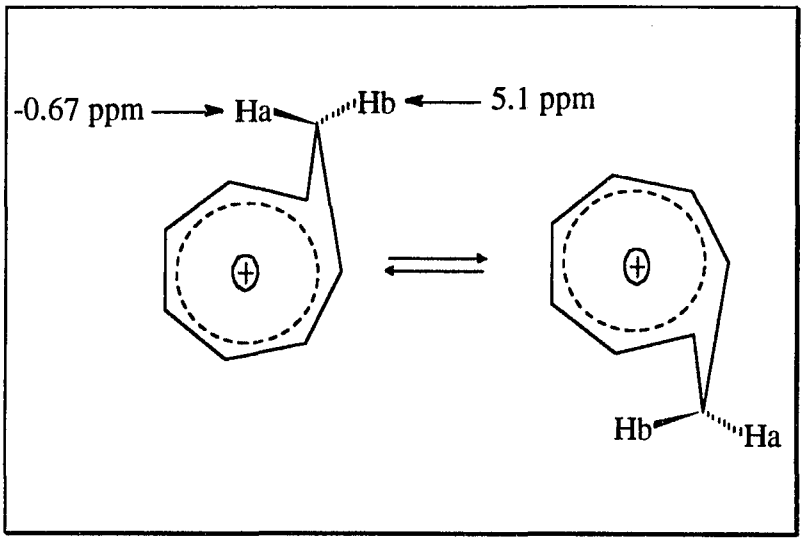


Figure 15: Homotropylidene Cation.

Semibullvalenes can be considered molecules approaching a homoaromatic state. Substituents on the semibullvalene skeleton that do not perturb the σ backbone severely enough to disrupt homoconjugation, but rather enhance it, will result in the orbital overlap necessary for an electron delocalization that is not pp–π, but an intermediate of σ and π[25].

The central problem in the characterization of a homoaromatic system is the proper assesment of the extent of the cyclopropane participation and the 1,3-π-overlap leading to a [4n + 2] perimeter.[26] In an effort to replace the σ bond by a pair of π electrons Paquette examined the effect of bridging the semibullvalene skeleton at C_2 and C_8 with a 1,3-butadienyl moiety. Elassovalenes, as seen in Figure 16, show some evidence for homoconjugative overlap between C_{4a} and C_{8a} and even between C_2 and C_6 in compound (b),[27]but this interpertation has been subject to dispute.[28]

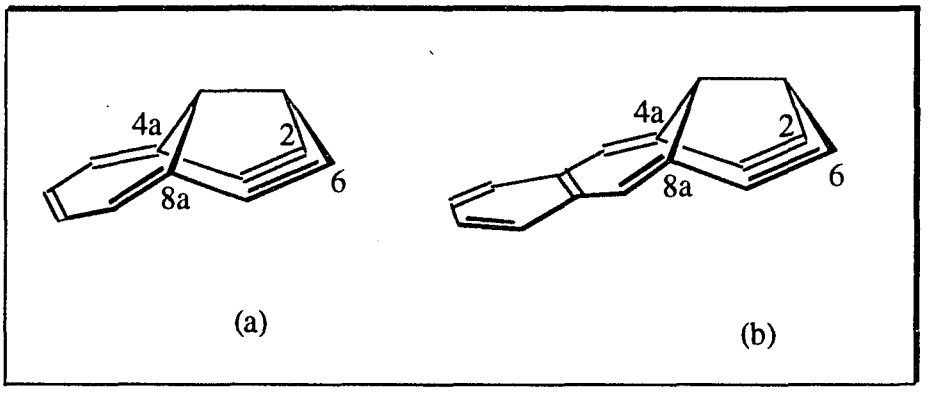


Figure 16: Elassovenes.

Paquette and coworkers[29] reported thermo-chemical measurments on triquinacene which suggest that there is homoaromatic stabilization of this molecule relative to model compounds. Paquette reported that mutually canted carbon atoms can still interact when separated by internuclear distances as large as 2.54 Å. This conclusion was based on calculations of the overlap intregal between C_2 and C_3 in molecule (b) from the x-ray data using a modification of the Mulliken procedure. There has been some controversy concerning this conclusion. Houk[30] reported, based on MINDO/3 and ab initio STO-3G methods, that neutral molecules designed to provide maximum overlap increased the interactions between filled orbitals and would therefore destabilize rather than stabilize the molecule.

The transition state for the Cope rearrangement of semibullvalene could be described as a bishomoaromatic structure,[31] with the six electrons involved in the rearrangment delocalized among the six carbons.[32] The amount of bond breaking at one end (C_2-C_8) is equal to the amount of bond making (C_4-C_6) at the other end of the molecule. An alternative transition state is the bis allyl type. The bond breaking, is more advanced than the bond forming. The third possibility, the diyl transition state which involves bond formation between C_4 and C_6 before bond breaking is less likely because

of molecular strain. Some interactions between the ends of the bis allyl system (C_2-C_8) and (C_4-C_6) would still be possible. As seen in Figure 17, the difference in the distance between (C_2-C_8) and (C_4-C_6) would be the distinguishing feature between an allyl biradical type of a TS and the symmetric TS.

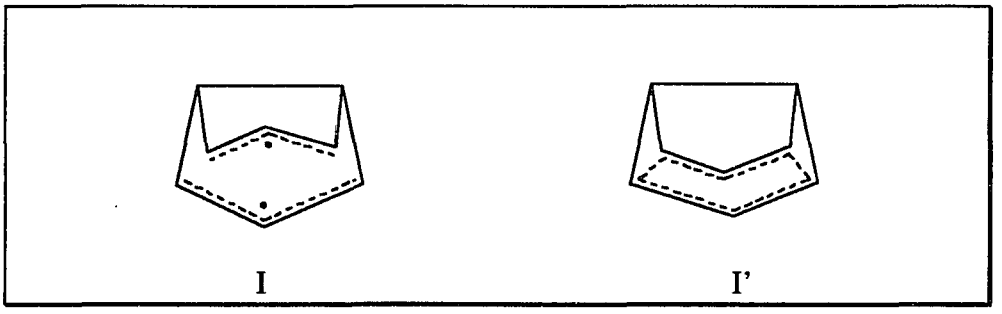


Figure 17: Possible Transition States for Semibullvalene.

Semibullvalene was first prepared in 1966 by Zimmerman.[33] Its NMR spectrum showed only averaged signals for H_1 and for H_5 and $H_{2,4,6,}$ and H_8 at -110°C. UV spectral data and semiempirical calculations did not support the view that semibullvalene was an example of a homoaromatic molecule. Anet determined the activation energy for the Cope rearrangement of parent semibullvalene using low temperature ^{13}C-NMR to be 5.5 kcal/mol at -130°C.

In the early 1970's theoreticians utilized several different methods to calculate the geometries of the ground and transition states for the various semibullvalenes and made predictions about the energies of activation for the Cope rearrangement of substituted semibullvalenes. MINDO/2 calculations were carried out by Dewar and his coworkers on the Cope rearrangement of bullvalene, barbaralane and semibullvalene series.[34] They calculated the energy of activation for the Cope rearrangement of semibullvalene to be 2.3 Kcal/mol, and the transition state geometry, in which C_2-C_8 and C_4-C_6 bonds were

found to be 1.752 Å apart. MINDO/2 is known to overestimate the stability of compounds, and therefore these values were thought to be low. In a later study using MINDO/2, Dewar recalculated the Eact as 3.6 Kcal/mol.[35]

Hoffman and Stohrer used extended Hückel calculations to asses the effects of π donating or withdrawing substituents on the ground state and the transition state energies for the Cope rearrangement of semibullvalene.[36,37] They constructed a set of orbitals for semibullvalene by combining the Walsh orbitals of a penta-1,4-diene unit corresponding to the same geometry as the C_3 to C_7 portion of semibullvalene. The interaction of the orbitals of appropriate symmetry from π-electron donating and π-electron withdrawing susbstituents with the correct semibullvalene orbitals were assessed. This allowed them to assess the relative stabilization or destabilization of the substituted ground state with respect to the unsubstituted semibullvalene.

They concluded that the pattern of substitution shown in Figure 18 would weaken the C_2-C_8 bond in the reactant and product. When the same substitution pattern was used to study the transition state, it was stabilized to a greater extent than the ground state. In conclusion they stated that this pattern of substitution would result in the ideal stabilization of a neutral "homoaromatic" geometry. Anet, using the Eact of semibullvalene that he found, in combination with the predictions that Hoffmann and Stohrer made about the Eact of several model semibullvalenes, calculated the energy of activation of -2.8 Kcal/mol for 2,4,6,8-tetracyanosemibullvalene and -8.7 Kcal/mol for the 1,5-difluoro-2,4,6,8 tetracynano semibullvalene.[38] These molecules should therefore exist as neutral bis-homoaromatic structures as seen in Figure 19.

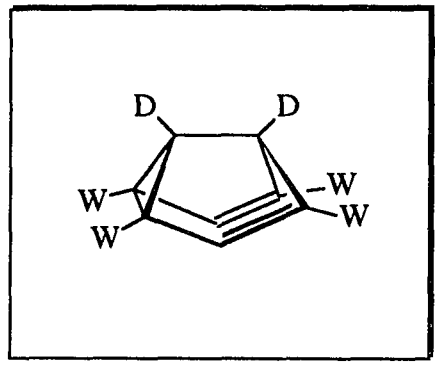


Figure 18: Hoffmann and Dewar's Design of a Delocalized Bishomoaromatic Semibullvalene.

Where D = π-electron donating group; W = π-withdrawing group.

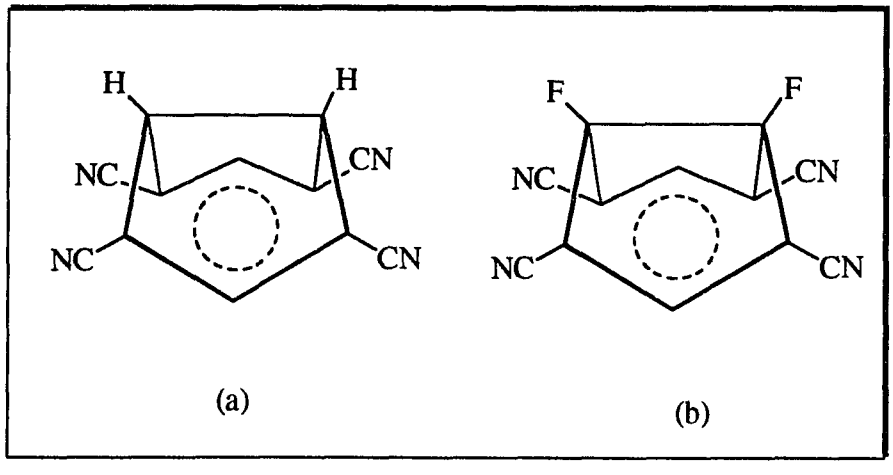
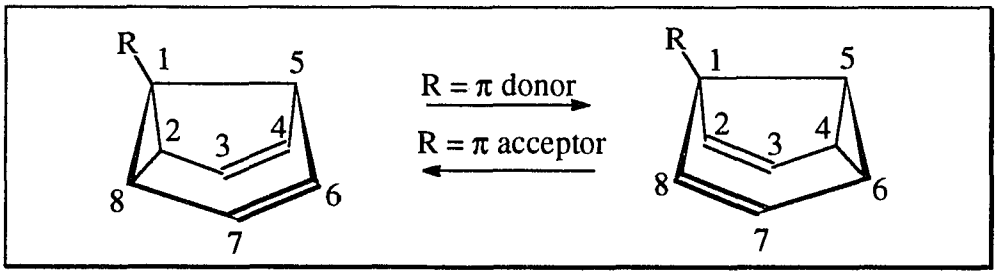


Figure 19: : Hoffmann and Dewar's Design of a Delocalized Bishomoaromatic Semibullvalene.

Mono-substituted semibullvalenes such as those in Figure 20 prepared by Paquette and co-workers[39] confirm predictions made by Hoffmann and Stohrer.[40] The two valence isomers are not equivalent and therefore the most stable thermodynamic isomer prevails. In the case where an electron withdrawing group is in the 1 position the equilibrium is toward structure (a). Hoffmann and Stohrer predicted this would be so

because an electron withdrawing group strengthens the cyclopropyl bond. On the other hand an electron donating group such as a methoxy group would weaken the cyclopropyl bond and would therefore prefer isomer b. In the case of 1-methoxy semibullvalene the predicted isomer (b) prevails. Since these examples result in a non-degenerate rearrangement, it is not suitable for lowering the Eact for the Cope rearrangement.



Figrue 20: The Effect of π-Donors or π Acceptors on the Equilibrium of the Cope Rearrangement.

Table 2 lists a number substituted semibullvalenes and their corresponding Cope rearrangement as determined by low temperature NMR studies. Since it is not possible to run solution spectra at temperatures lower than -160 +/- 10°C., it may not be possible to reach a temperature low enough to visualize the "freezing out" of the Cope rearrangement if the Eact is very small. However, it is possible to observe a similar process through the use of low temperature x-ray and variable temperature solid state NMR. A semibullvalene with a homoaromatic transition state for the Cope rearrangement has C_{2v} symmetry. The distances between C_2-C_8 and C_4-C_6 are therefore equal. A determination of the geometry of the molecule by low temperature x-ray studies yields the information concerning the presence or absence of a symmetric intermediate Figure 20.

Semibullvalene	$\Delta G^{\neq}$ kcal/mol	Temp. K
Parent-[41]	5.5	130
Octamethyl-[36]	6.4	132
1,5-Dimethyl-2,4,6,8-tetracarbomethoxy-[42]	3.8	113
1,5-Dimethyl-[43]	4.5	298
1,5-Dimethyl-2,6-dicyano-[44,45]	3.1	115
1,5-Cyclopentano-2,4,6,8-tetracarbomethoxy-[46]	NA	
1,5-Cyclohexano-2,4,6,8-tetracarbomethoxy-	NA	
1,5-Cycloheptano-2,4,6,8-tetracarbomethoxy-[47]	NA	
1,5-Cyclooctano-2,4,6,8-tetracarbomethoxy-	NA	
1,5-Cyclododecatano-2,4,6,8-tetracarbomethoxy-	NA	
1,5-Dimethyl-2,6-dibromo-[48,49]	7.4	298
1,5-Dimethyl-2,6-diphenyl-[50,51]	NA	

Table 2: Substituted Semibullvalenes and their Energies of Activation.

Another method which has been applied to the problem of differentiating between delocalized structure and one that is undergoing a rapid degenerate rearrangement was developed by Saunders and coworkers.[52] Askani[53] and Klumpp[54] applied the technique to the semibullvalene system. In addition to the intrinsic change in the ^{13}C chemical shift which is due to simply the presence of deuterium in the molecule, there will also be a shift in the equilibrium of a rapidly rearranging system caused by the deuterium. This will not happen if the compound exists solely in the delocalized structure. This new equilibrium constant can be determined from the change in the chemical shifts of the same carbons in the frozen out, non-equilibrating, compound. If the compound is delocalized and not equilibrating there will only be a very small change in the chemical shifts due to the "isotopic perturbation of resonance"[55] The ratio of the change in chemical shifts due to deuterium, to the difference in chemical shifts for that particular carbon in the two frozen out states, is considered a measure of the delocalization.

When applied to the semibullvalene system Askani found that it did not exist as a single delocalized structure, but rather that semibullvalene undergoes a the degenerate rearrangement. The technique involves introducing a deuterium atom into the molecule and studying the ^{13}C chemical shifts of a mixture of deuterated and undeuterated compounds.

The first donor acceptor semibullvalene was synthesized by Miller[56]. Todaro carried out the x-ray crystallographic studies on the molecule to determine its structure[57]. Based on its bond lengths 1,5-dimethyl-2,4,6,8-tetracarbomethoxy semibullvalene can be described as a molecule approaching a symmetrical structure (Table 4).

Semibullvalene	C_2-C_8	C_2-C_3	C_1-C_5	C_4-C_6.	$\Delta G^{\neq}$
1,5-Dimethyl-2,4,6,8-tetracarbo-methoxy-	1.782 Å	1.42 Å	1.581 Å	2.21 Å	3.8 kcal /mol
Parent[58]	1.60	1.53	1.49	2.36	5.5
1,5-Dimethyl-2,6-dicyano	1.722			2.249	3.1
1,5-Dimethyl-3,7-dicyano	1.835			2.048	6.0[59]

Table 3: Substituted Semibullvalenes and Selected Bond Lengths.

A homoaromatic species should have the C_2-C_8 distance equal to the C_4-C_6 distance (about 1.99 Å). Therefore investigations of the transition of semibullvalenes focus on the determination of those bond lengths as well as finding the energy of activation for the Cope rearrangement.

The x-ray structure of 1,5-dimethyl-2,4,6,8-tetracarbomethoxysemibullvalane revealed that the four ester groups are arranged in two orthogonal planes with only two of them in conjugation with the cyclopropane ring and double bond. Despite the orientation of the ester groups, there is a significant drop in the Eact for the Cope rearrangement of 1,5-dimethyl-2,4,6,8-tetracarbomethoxysemibullvalane in comparison to parent semibullvalene.[60]

As shown in Table 3, the C_2-C_8 bond length in 1,5-dimethyl-3,7-dicyano semibullvalene is the longest cyclopropane bond reported, for these types of compounds, so far. In addition, this compound also exhibits a very short non-bonded C_4-C_6 distance indicating the possibiltity of a homoaromatic transition state. However, 1,5-Dimethyl-3,7-dicyano semibullvalene has a higher energy of activation for the Cope rearrangement

than semibullvalene or the isomeric 2,6-dicyano compound. These results indicate the need for more complete data such as that gathered from a variable temperature x-ray study.

In 1987 Miller[61] studied the effect of differently placed substituents on the relative energies of the ground and transition states in semibullvalene based on MNDO calculations. The results, as summarized in Table 4, predicted the strong stabilizing effect of annulation at positions 1 and 5. The effect of a three membered ring in the 1,5-position in particular was predicted to have a great stabilizing effect.

Semibullvalene	GS C_2-C_8	GS C_4-C_6	TS C_2-C_8	TS C_4-C_6	Eact
Parent	1.57 Å	2.44 Å	2.46 Å	2.46 Å	5.7 kcal/mol
1,5-cyclopropa	1.60	2.48	2.47	2.47	-9.1
1,5-cyclobuta-	1.58	2.44	2.41	2.41	5.4

Table 4: Substituted Semibullvalenes and Selected Bond Lengths.

CHAPTER 2: BACKGROUND

NMR BACKGROUND

Intramolecular rearrangements such as the Cope rearrangement give rise two species, A and B, which are equivalent (Figure 21).

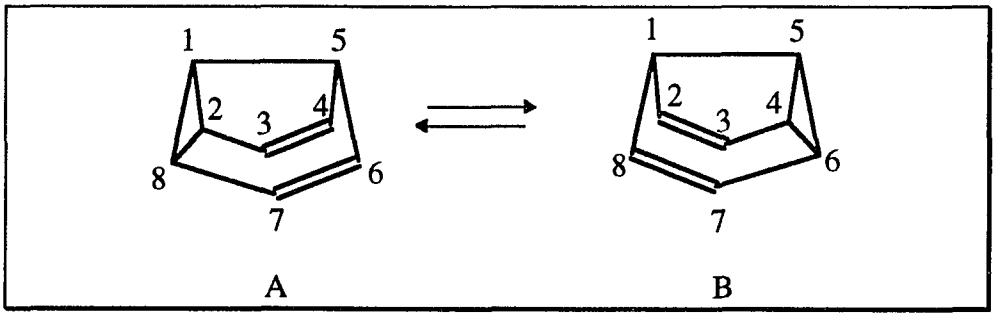


Figure 21: The Valence Tautomerism of Semibullvalene.

Such species exist in equilibrium and their concentrations are dependent on T(K) and the free energy of activation $\Delta G^{\neq}$. The rate constant k_r of isomerization is given by Eyring Equation 1.[62,63]

$$k_r = \frac{kT}{h} e^{-\Delta G^{*} / RT} \qquad \text{Equation 1}$$

The rearrangement of semibullvalene at room temperature is faster than the NMR time scale and therefore ^{13}C-NMR spectra show $C_{2,4,6,8}$ as one signal. If this rearrangement were slow on the NMR time scale $C_{2,8}$ and $C_{4,6}$ would give rise to two separate signals.

In order to have two separate signals for the same nucleus the following conditions must be met.

1) $C_{2,8}$ and $C_{4,6}$ must have different chemical environments.

2) The k_r of the Cope rearrangement must be slow so that k_r is smaller than the chemical shift difference.

3) Most important to our work, the chemical shift difference (υ_A - υ_B) of $C_{2,8}$ and $C_{4,6}$ in the rearrangment of A and B should be large relative to its line width $\Delta\upsilon_{1/2}$ = $((\upsilon_A - \upsilon_B) >> \Delta\upsilon_{1/2})$.

The temperature dependence of chemical shifts and the line shape due to intramolecular mobility is illustrated in (Figure 22).

At low temperature, k_r is small compared to the chemical shift difference (υ_A - υ_B) and two separate signals emerge for the corresponding nuclei in A and B (Figure 22a). As the temperature increases kr increases and the line widths of the corresponding signals increase. As k_r approaches the magnitude of the chemical shift difference (υ_A - υ_B). Consequently the signal maxima approach one another, and join at the temperature of coalescence T_c (Figure 22c). At coalescence, the rate constant is related to the chemical shift difference by Equation 2.

$$k_r = \frac{\pi}{\sqrt{2}}(\upsilon_A - \upsilon_B) \qquad \text{Equation 2}$$

At high temperature k_r is larger than (υ_A - υ_B) and a line width of $\Delta\upsilon_{1/2}$ is reached(Figure 22e).

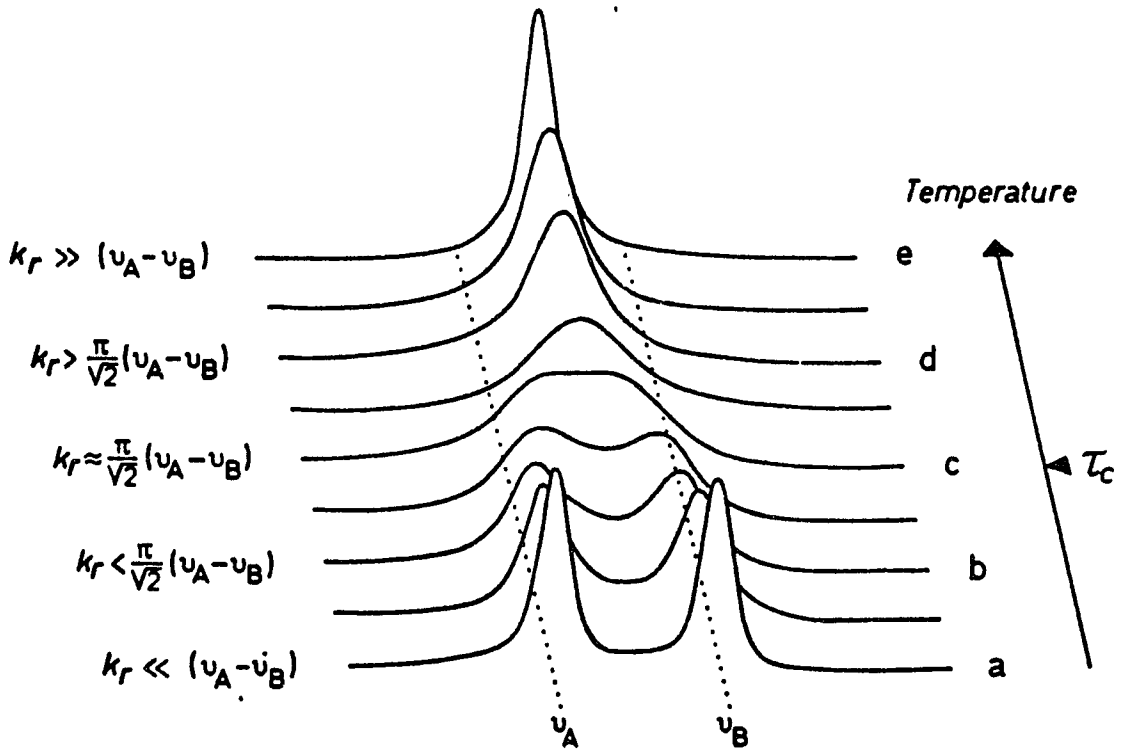


Figure 22: Temperature Dependence and Line Shapes Due to Intramolecular Mobility.

Brietmaier, E., Voelter, W., "^{13}C-NMR Spectroscopy" Verlag Chemie, **1987**, 127

Through the use of variable temperture ^{13}C NMR spectra the energy of activation for the Cope rearrangement can be determined. If the coalescence temperature is known, k_r can be calculated using Equation 2. However, as a rough estimate, the rate constant can be estimated by measuring the line widths at half height near T_c (where T_c is the temperature at which some line broadening occurs), $\Delta\upsilon_{1/2}$ (T_c), and using Equation 3.

$$k_r \cong 2\Delta\upsilon_{1/2(Tc)} \quad (\text{near } T_c) \qquad \text{Equation 3}$$

Once the value for k_r is determined, $\Delta G^{\neq}$ can be calculated for the equilibrium using Equation 4.[64,65]

$$\Delta G^{*}_{(Tc)} = 4.57T_c\left(10.32 + \log\frac{T_c}{k_r}\right)cal/mol \qquad \text{Equation 4}$$

Other thermodynamic data that may be obtained include the energy of activation by the use of the Arrhenius Equation 5, the enthalphy of activation by Equation 6 and the entropy of activation may be obtained by the Gibbs-Helmholtz Equation 7.

$$k_r = Ae^{-\Delta E_n/RT} \qquad \text{Equation 5}$$

$$\Delta H^{*} = \Delta E_n - RT \qquad \text{Equation 6}$$

$$\Delta G^{*} = \Delta H^{*} - T\Delta S^{*} \qquad \text{Equation 7}$$

At low temperatures, lines may broaden for reasons other than changes in the rate constant, e.g. changes in the relaxation time due to decreased tumbling of slow moving

molecules[66] solvation viscosity, field inhomogeneity. These factors must also be taken into account when interpreting low temperature NMR data.

The chemical shift differenences between carbons in different environments span a large range (200 ppm). Because the chemical shifts are proportional to the applied magnetic field strength, the shift difference between two exchanging sites is a function of the external magnetic field. The advent of high field spectrometers has aided in the accurate determination of this paramenter (Equation 8) [67]

$$\delta_{ppm} = \frac{\upsilon_{obs} - \upsilon_{std}}{\upsilon_1} \quad (\upsilon_1 = {}^{13}C \text{ radiofrequency used}) \qquad \text{Equation 8}$$

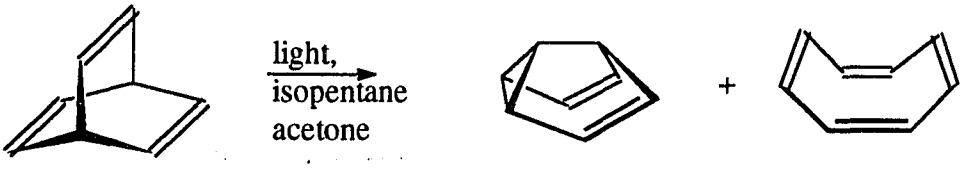
The difference in Hz between two signals differing by the same number of ppm will be larger when a higher field instrument is used. Because of this, coalescence will occur at a higher temperature. Systems whose T_c is below the range of measurement using a 62.5 MHz ^{13}C spectrometer might be measured using one at 100.6 MHz.

The lower temperature limit for the determination of a spectrum is dependent upon several factors; solvent viscosity, solubility of the solute in the solvent at that temperature, ability to maintain temperature at the probe. At present time the lower limit for solution 13C-NMR using a typical commercial instrument 100.6 MHz spectrometer is -160 to -170°C.

PREVIOUS SYNTHETIC METHODS

PHOTOCHEMISTRY

Semibullvalene was first synthesized in 1966 by Zimmerman[68] by reacting barrelene **5**, a C_8H_8 isomer, with acetone as a sensitizer in isopentane as a solvent (Scheme 1). The use of this method in the synthesis of substituted semibullvalenes is limited by the availability of a properly substituted barrelene.

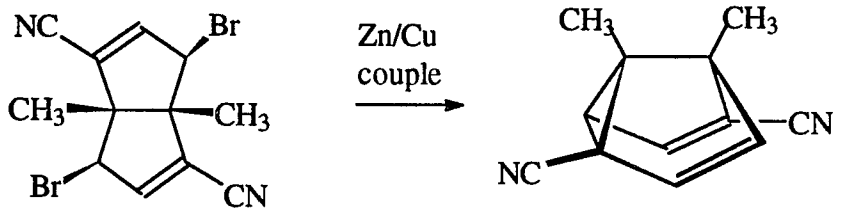


5 **6** **7**

Scheme 1

RING CLOSURE METHOD

Quast[69] and his group have used this short variation of their method to synthesize 2,6-dicyano-1,5-dimethyl semibullvalene. However, this approach has failed in the synthesis of 1,5-annulated semibullvalenes.[70]

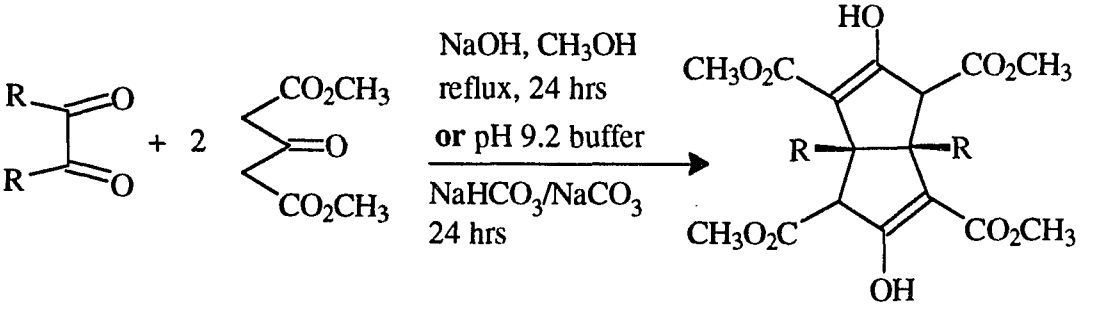


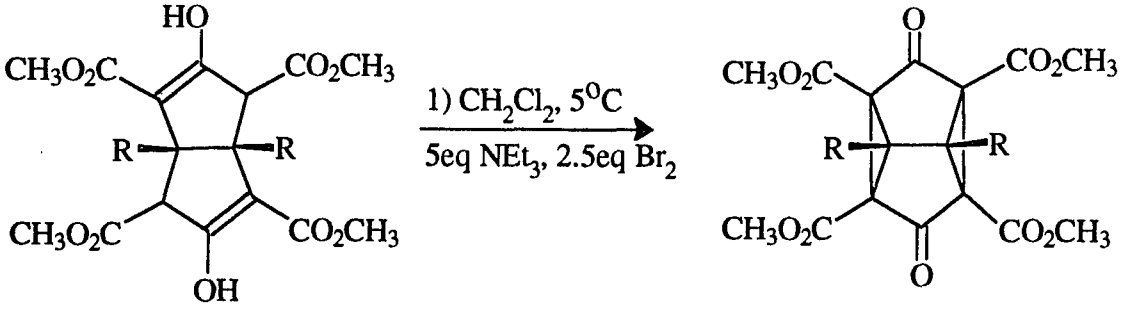
8 **9**

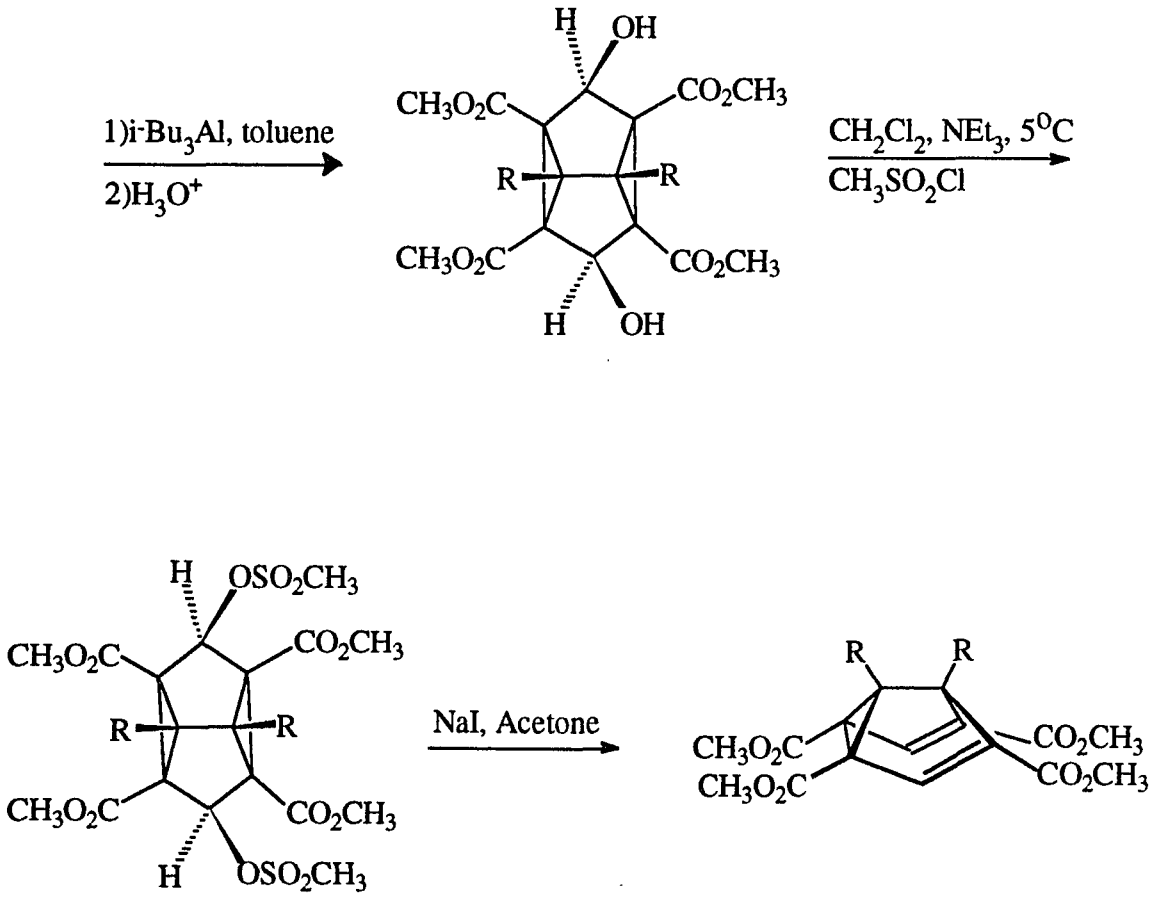
Scheme 2

RING OPENING METHOD

L. Miller,[71] reported in 1981, the synthesis of the first donor-acceptor substituted semibullvalene. R. Iyengar,[72] reported in 1986 the annulation of the 1,5-position on the 2,4,6,8-tetracarbomethoxysemibullvalene. The general method detailed in Scheme 2.3 is the general method used in both approaches.






1)i-Bu3Al, toluene
2)H3O+
CH2Cl2, NEt3, 5°C
CH3SO2Cl
NaI, Acetone
H
OH
CH3O2C
CO2CH3
R
OSO2CH3

Scheme 3

PURPOSE AND STRATEGY

PURPOSE

The goal of this thesis is to continue efforts toward lowering the energy of activation for the Cope rearrangement in semibullvalenes. As discussed above, annulation of the 1,5-positions of 2,4,6,8-tetracarbomethoxy semibullvalene has led to some promising results. The results section of this thesis is divided into two parts: first, the attempted synthesis of 1,5-phenanthra- and 1,5-acenaphtha-2,4,6,8-tetracarbomethoxy semibullvalene. Second, the synthesis of 1,5-dimethyl-2,6-dicarbomethoxy semibullvalene. Variable temperature NMR was used to study the Cope rearrangement of 1,5-dimethyl-2,6-dicarbomethoxysemibullvalene. Variable temperature ^{13}C-NMR, solid state NMR, and x-ray structure determination can also be used to study the properties of these molecules.

BACKGROUND ON 1,5-ANNULATED-2,4,6,8-TETRACARBOMETHOXY SEMIBULLVALENES

Iyengar[73] studied the effect of annulation on the Cope rearrangement of semibullvalenes. In the case of the 1,5-cyclooctano compound, the movements of the cyclooctane (Figures 23, 24 and 25) are complicated. Semibullvalenes of this type rearrange in two distinct ways, by ring flipping as well as the Cope rearrangement; therefore their study by NMR is far more complicated.[74]

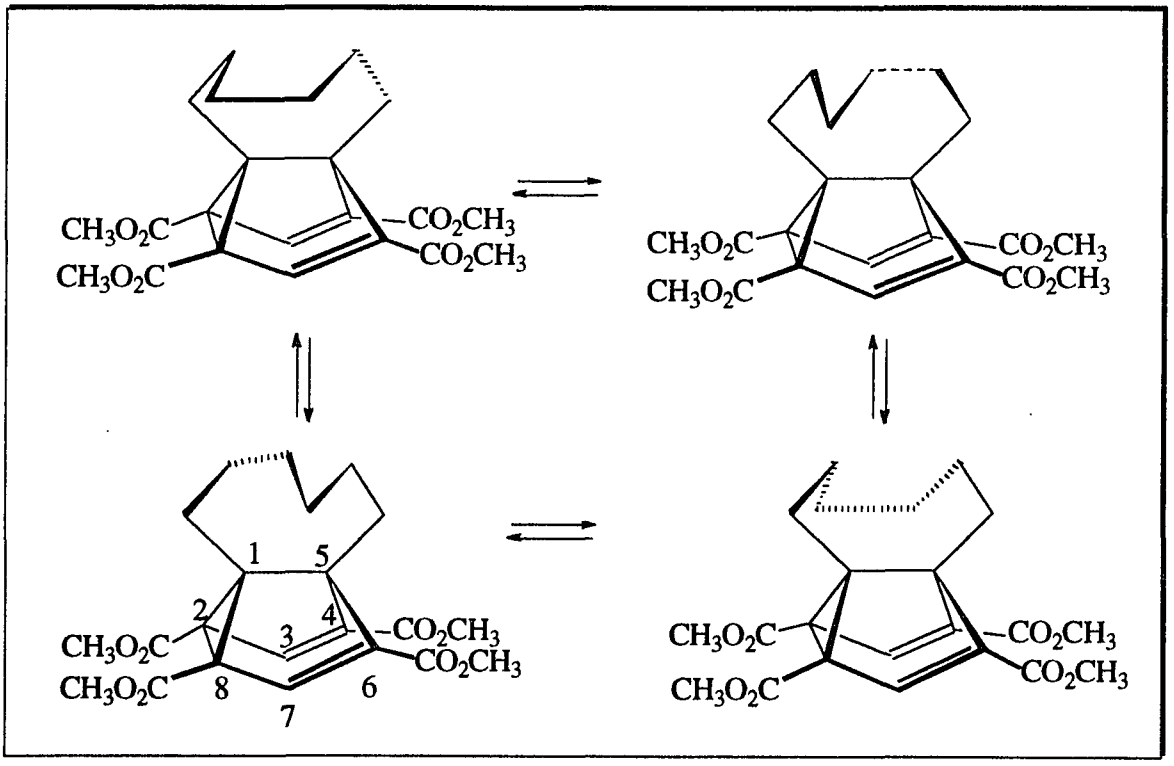


Figure 23: 1,5-Cyclooctano-2,4,6,8-Tetracarbomethoxy Semibullvalene.

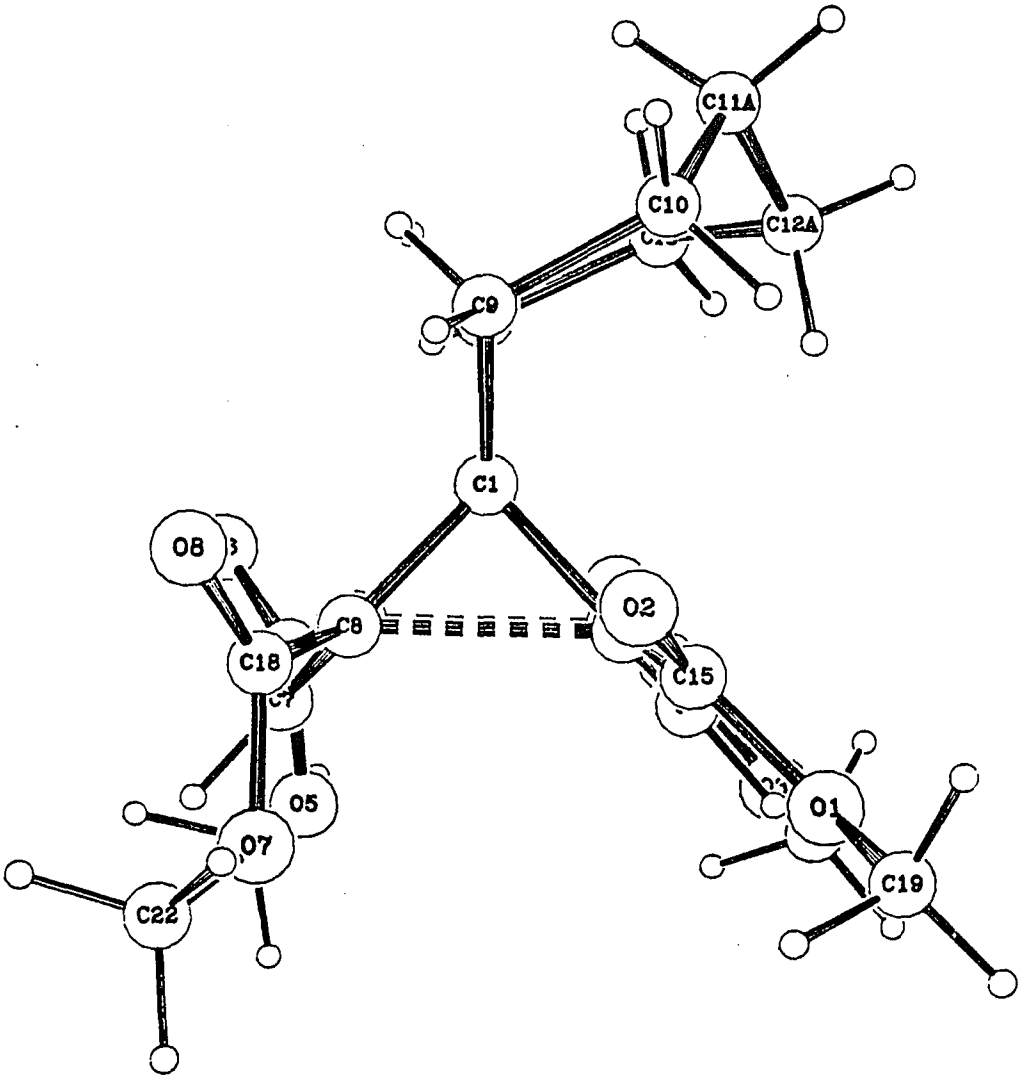


Figure 24: Room Temperature X-ray Structure of Cyclooctano-2,4,6,8-Tetracarbomethoxy Semibullvalene.

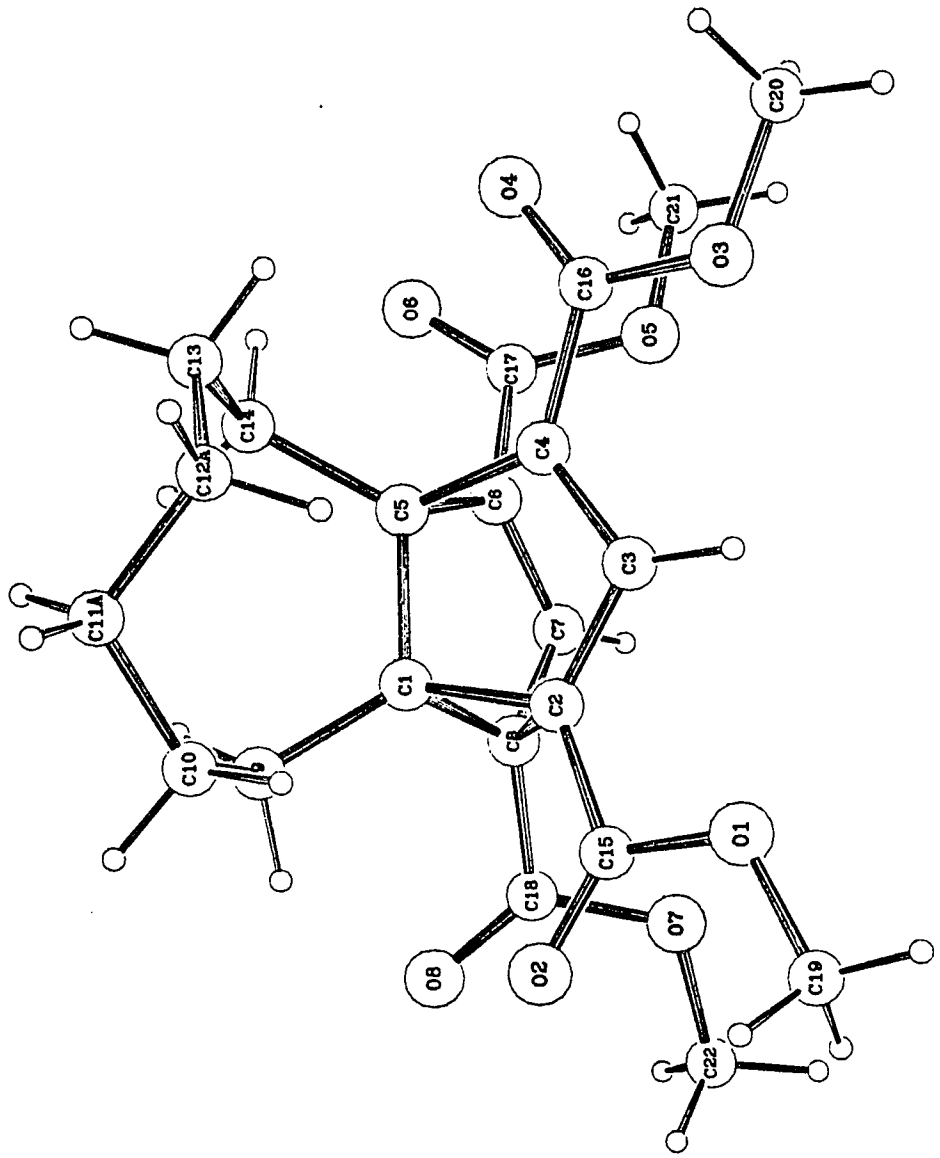
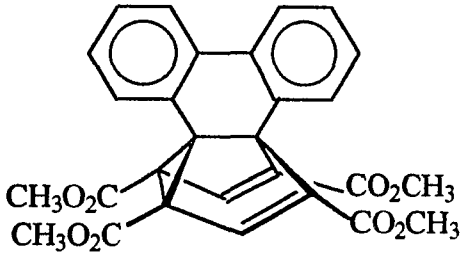


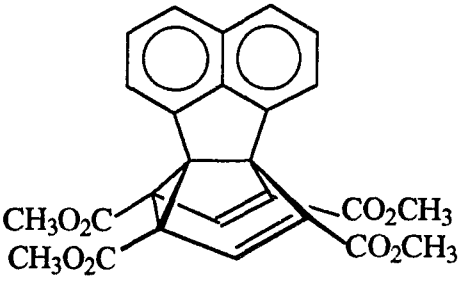
Figure 25: 178K X-ray Structure of Cyclooctano-2,4,6,8-Tetracarbomethoxy Semibullvalene

At room temperature, 298K, in solution, these dynamic processes is rapid on an NMR time scale and thus there is no observable difference in the resonances for C_2, C_4, C_6 and C_8. However, at 240K the ring folding is slowed down relative to the NMR time scale. Therefore, C_2, C_4 and C_6, C_8 experience different environments and this results in a broadening of the peak for $C_{2,4,6,8}$. At 178K the peak for $C_{2,4,6,8}$ splits into two broad peaks due to the folding of the cyclooctane ring. In addition, the folding of the cyclooctane ring causes differences in C_3 and C_7 at 240K. The peak for C_3 and C_7 begins to broaden, resulting in two separate signals at 174K. The remaining signals remain sharp at 174K. Based on the structure determination studies, Ivenger concluded that the broadening is related to the motion of the cyclooctane ring rather than the Cope rearrangement.

As mentioned earlier we sought to continue investigations into the effects of annulation of the 1,5-positions of semibullvalenes, specifically of rigid symmetric rings. Therefore, we decided on 1,5-annulation with aromatic rings such as phenanthrene and acenapthene. The results are divided into two chapters: chapter 3 deals with our attempts to synthesize 1,5-phenanthra-2,4,6,8-tetracarbomethoxysemibullvalene **2** and our attempts to synthesize the 1,5-acenaphtha-2,4,6,8-tetracarbomethoxysemibullvalene **3**. Chapter 4 deals with the synthesis and investigations of 2,6-dicarbomethoxy-1,5-dimethyl semibullvalene **4.**



2



3

BACKGROUND ON 1,5-DIMETHYL-2,6-DICARBOMETHOXY SEMIBULLVALENES

As one can see from the x-ray of 1,5-dimethyl-2,4,6,8-tetracarbomethoxy semibullvalene **1**, shown in Figure 26, the four carbomethoxy groups are arranged in two orthogonal planes.

It appears that perhaps full rotation of the ester groups could be hindered by their proximity to one another. In order for electron withdrawing groups, such as esters, to lower energy of activation for the Cope rearrangement the carbonyls must bisect the cyclopropane bond. If only two of the four carbomethoxy groups are able to be in the correct conformation at any given time, then perhaps the effect of two carbomethoxy groups will be equivalent to the effect of four carbomethoxy esters.

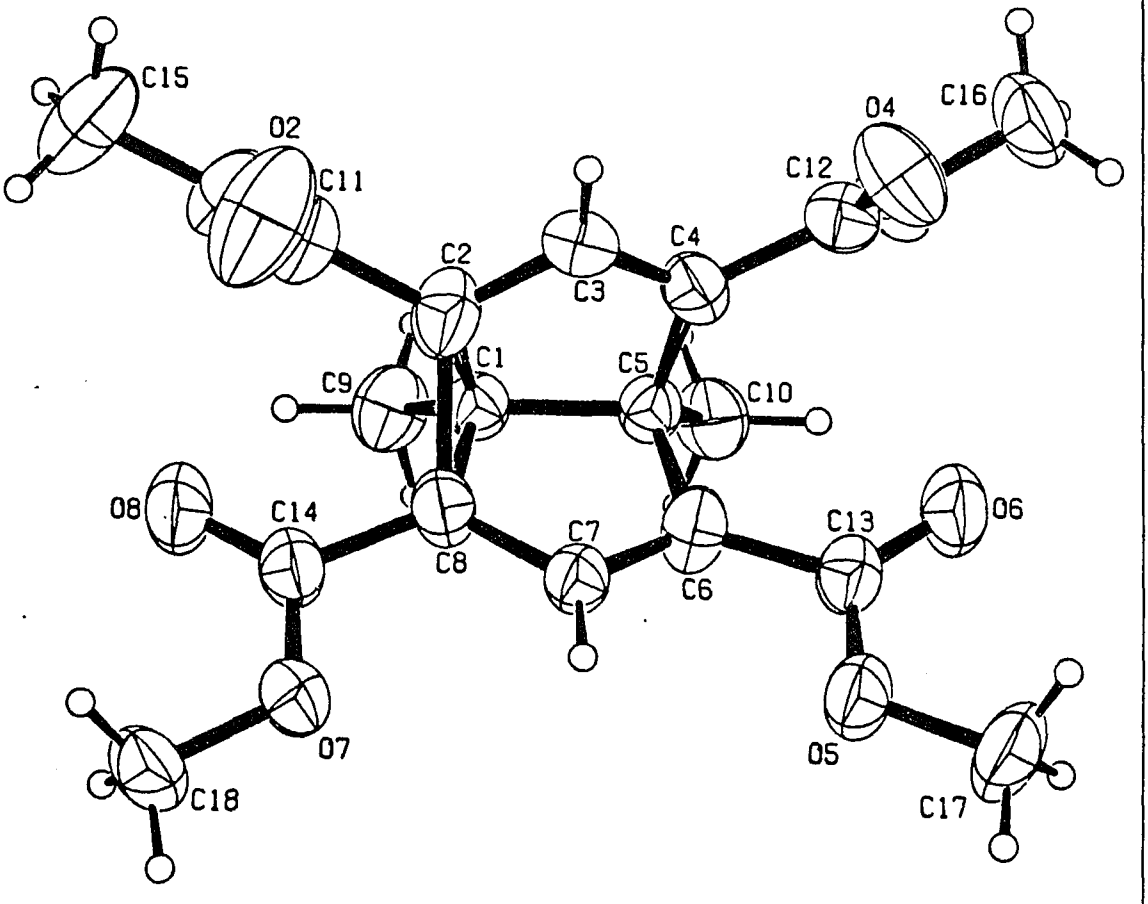
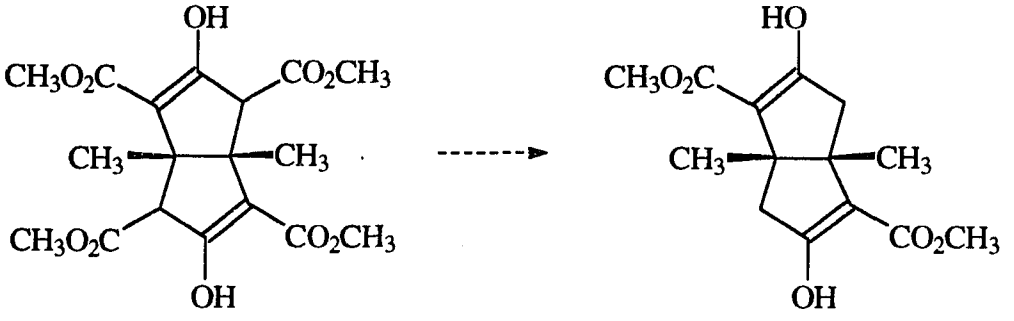


Figure 26: X-ray Structure of 1,5-Dimethyl-2,4,6,8-Tetracarbomethoxy Semibullvalene.

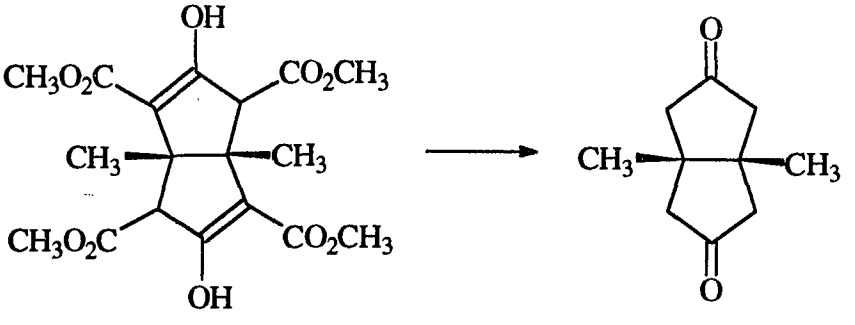
1,5-dimethyl-2,4,6,8-tetracarbomethoxy semibullvalene was previously synthesized by L. Miller[75] using the route shown in Scheme 3.[76] At first it seemed reasonable to follow this exact scheme with the assumption that the selective decarboxylation of tetracarbomethoxy enol **10** to the 2,6-dicarbomethoxy enol **11** would be successful (Scheme 4).



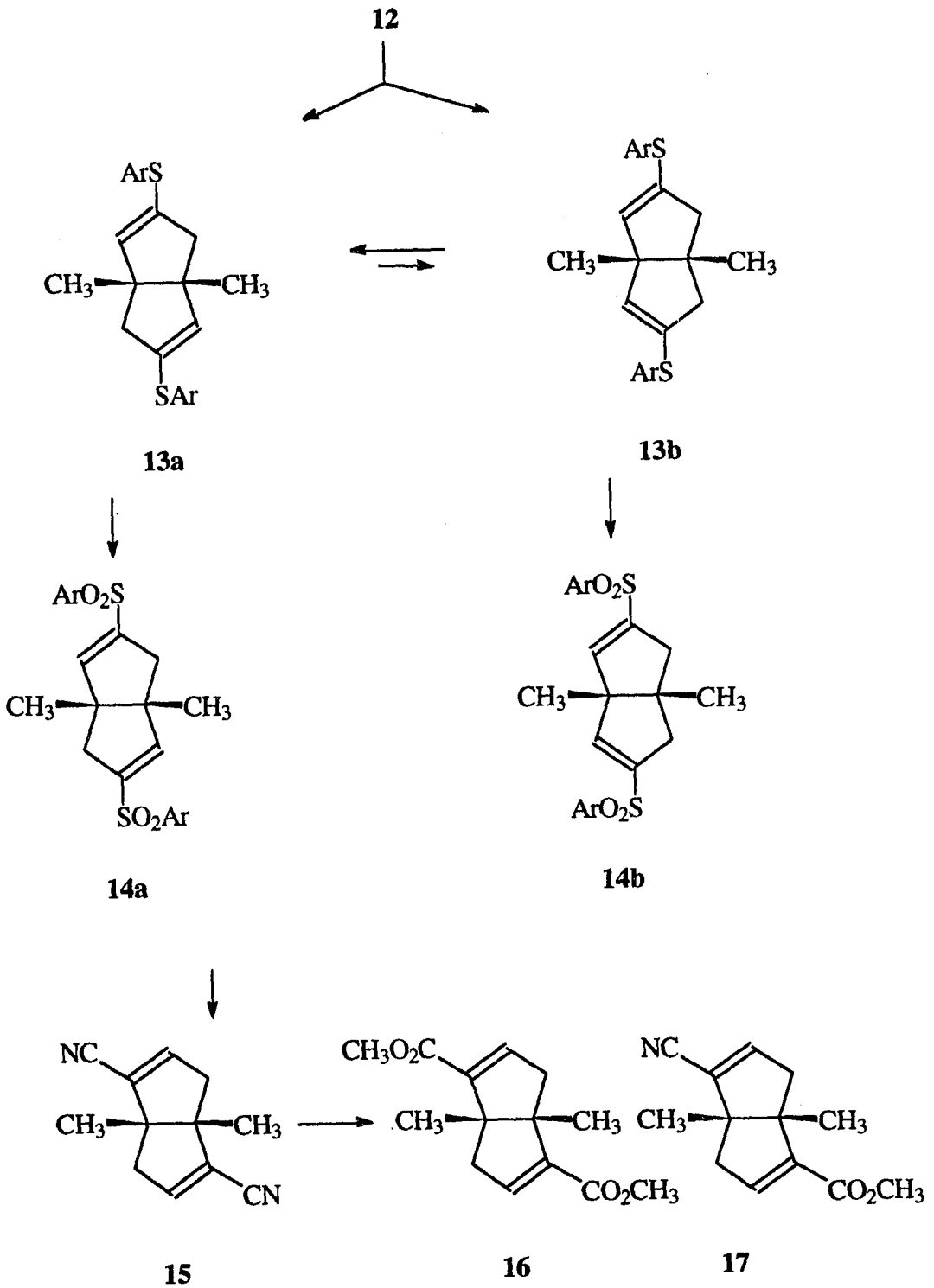
10 **11**

Scheme 4

Recently, Quast[77] and coworkers reported the synthesis of 2,6-dicarbomethoxy-1,5-dimethyl semibullvalene **2** by their Zn-Cu couple approach shown in Scheme 2.3.



10 **12**


12
ArS
CH3
CH3
SAr
13a
ArS
CH3
CH3
ArS
13b
ArO2S
CH3
CH3
SO2Ar
14a
ArO2S
CH3
CH3
ArO2S
14b
NC
CH3
CH3
CN
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CH3O2C
CH3
CH3
CO2CH3
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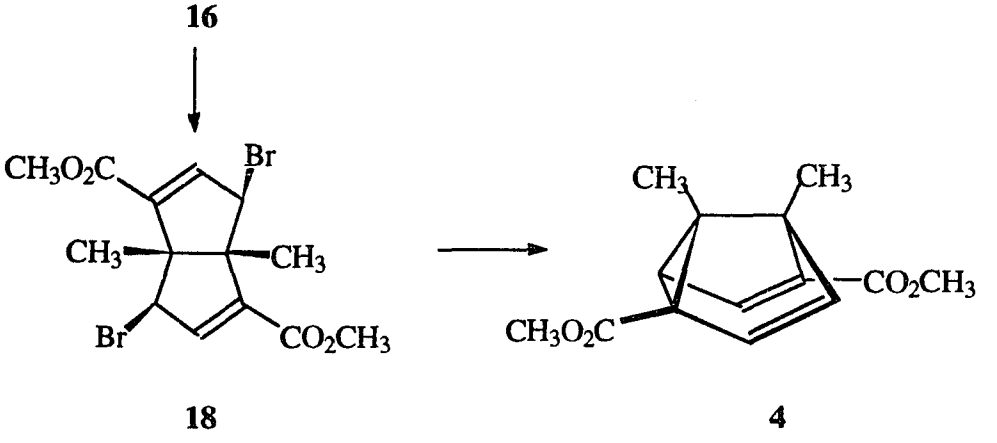
NC
CH3
CH3
CO2CH3
17



Scheme 5

The dinitrile **15** is the key intermediate in Quast's approach to 2,6-dicarbomethoxy-1,5-dimethyl semibullvalene as shown in Scheme 5 above. This synthesis starts with diketone **10** and 4-chlorothiophenol in the presence of titanium tetrachloride and triethylamine to produce a 1:1 mixture of vinyl sulphides **13a** and **13b**. Acid catalyzed equilibration of these vinyl sulphides resulted in a ratio of 73:27 in favor of the **13a** isomer. This ratio is preserved during oxidation with sodium perborate tetrahydrate leading to vinyl sulphonyls **14a** and **14b**.

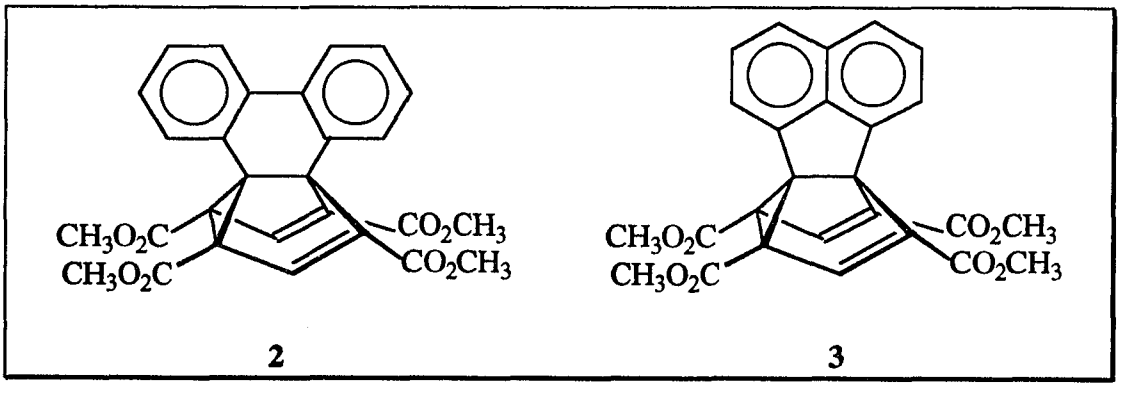
Dinitrile **15** was eluted from an aluminum oxide column impregnated with potassium cyanide when a mixture of **14a** and **14b** was washed through the column. Prolonged treatment of dinitrile **15** with hot methanol in the presence of hydrochloric acid resulted in dicarbomethoxy diene **16**. Unsaturated ester **16** was brominated in the presence of NBS to exo-exo dibromide **17**. Reductive ring closure of the exo-exo dibromide to the semibullvalene **4** was afforded in the presence of zinc-copper couple.

RESULTS

CHAPTER 3: APPROACHES TOWARD 1,5-PHENANTHRA- AND 1,5-ACENAPHTHA-2,4,6,8-TETRACARBOMETHOXY SEMIBULLVALENES

INTRODUCTION

Our investigations into the effects of annulation of the 1,5-positions of semibullvalenes, specifically with rigid symmetric rings, such as phenanthrene and acenapthene are outlined in this chapter. This chapter is divided into two parts: the first part deals with our attempts to synthesize 1,5-phenanthra-2,4,6,8-tetracarbomethoxy semibullvalene **2** and the second part deals with our attempts to synthesize the 1,5-acenaphtha-2,4,6,8-tetracarbomethoxysemibullvalene **3**.

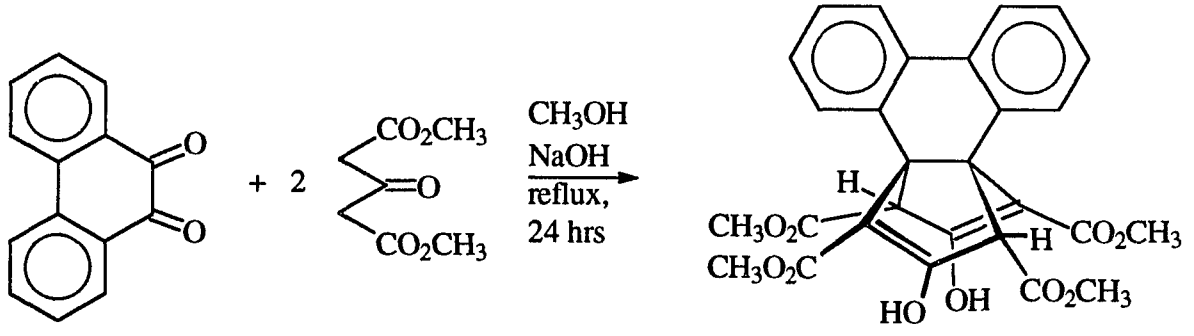


2 **3**

PART 1:

APPROACH TOWARD THE SYNTHESIS OF 1,5-PHENANTHRA-2,4,6,8-TETRACARBOMETHOXY SEMIBULLVALENE

As discussed previously in Chapter 2, the general procedure used to synthesize semibullvalenes begins with building the appropriately 1,5-substituted-2,4,6,8-tetracarbomethoxy-bicyclo-[3.3.0]-octane-3,7-dione skeleton, eg **41,** through the use of the Weiss reaction. As shown in Scheme 6, 1,5-phenanthra-bicylo-[3.3.0]-octane-3,7-dione **41** was first synthesized by Cook and coworkers in 54% yield. Purification was achieved on an analytical scale only.[78] In our hands, the yield ranged from 10% to 60% and sometimes the reaction would not work at all. Attempts to recrystallize the beige powder on a large scale, as per Cook et al, were unsuccessful. Crude compound **41** was dried under vacuum and used without further purification.

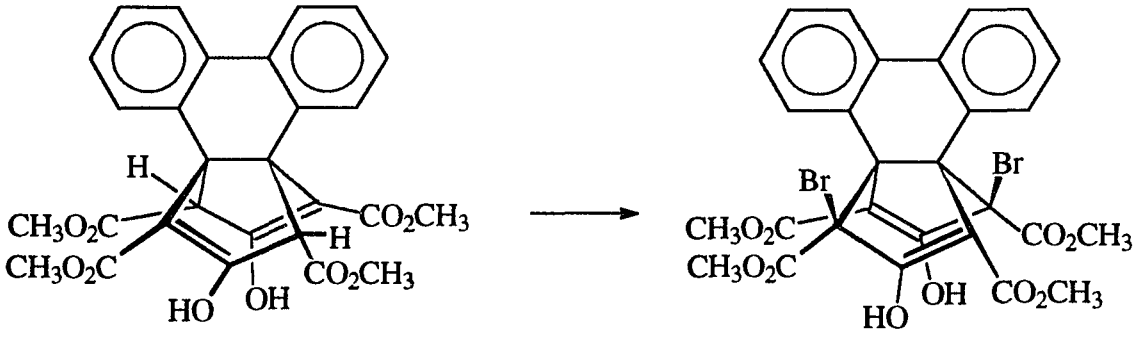


39 **40** **41**

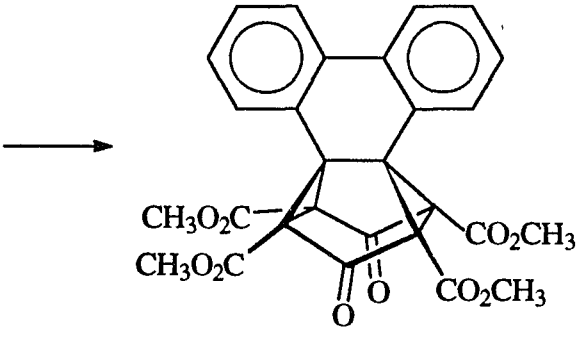
Scheme 6

The second step in the sequence is the cyclization of the Weiss compound to a tetracyclic dione. In previous cases this was accomplished by bromination of the Weiss

compound to isolate a dibromo adduct and subsequent dehydrobromination to the tetracyclic key intermediate in the presence of a strong base such as triethylamine or DBU, as shown in Scheme 7.



41 **42**



43

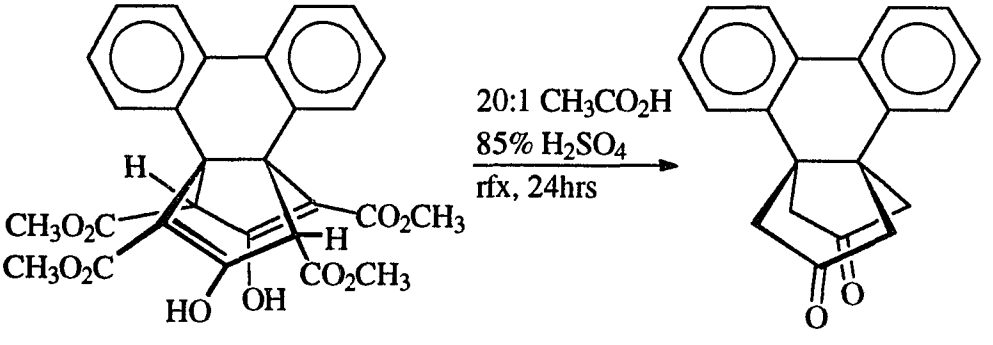
Scheme 7

Our approaches toward the dibromide **42** were based on three general conditions and the effect that temperature and time had on the course of the reactions. Neutral conditions involved the addition of 2.5 equivalents of bromine to a solution of enol **5** in either carbon tetrachloride, chloroform, or methylene chloride, and resulted in no

reaction at room temperature or gentle reflux. Acidic conditions involved the addition of bromine to a solution of glacial acetic acid and either carbon tetrachloride, chloroform, or methylene chloride, and resulted in the formation of a mixture of compounds that were inseparable and unidentifiable. Bromination of enol **41** under basic conditions involved the addition of bromine to a solution of enol **41** in methylene chloride and 6 equivalents of triethylamine and resulted in a complicated mixture of inseparable products.

Attempts to synthesize the tetracyclic compound **43** directly from enol **41** focused on bypassing the isolation of the dibromide by adding triethylamine to the reaction, a condition which we have used successfully to make similar compounds (see Chapter 4). However, this resulted in a complicated mixture of products which were inseparable. To date all attempts to synthesize the dibromide **42** or tetracyclic **43** have been unsuccessful.

Our next approach was to attempt the synthesis of the more simple decarboxylated 1,5-phenanthro-bicyclo-[3.3.0]octane-3,7-dione **44**. Tetracarbomethoxy compound **5** was decarboxylated in a refluxing mixture of 20:1 glacial acetic acid and phosphoric acid. After column chromatography dione **44** was isolated in 50% yield.

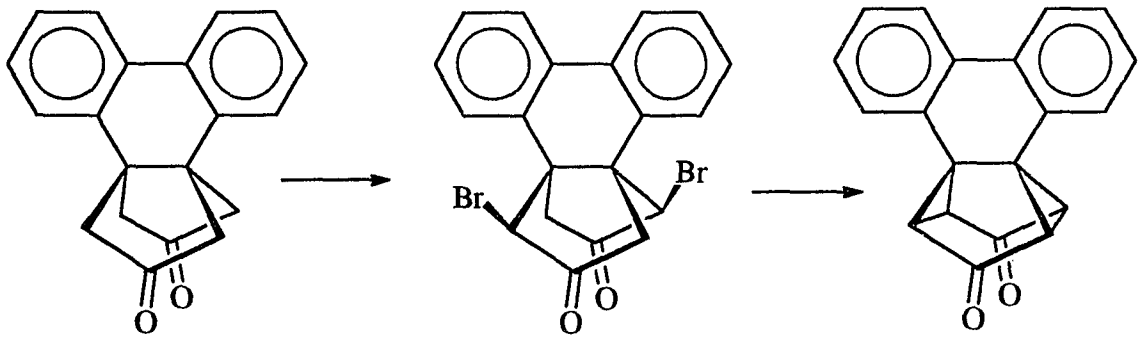


41 **44**

Scheme 8

Attempts at the synthesis of the dibromo adduct **45** concentrated on bromination, with 2.5 equivalents of bromine, of the dione under neutral, acidic or basic (triethylamine) conditions and the effect that temperature as well as time had on the outcome of the reactions. Neutral conditions gave no reaction and the starting material was recovered. Acidic conditions such as dissolving the dione in glacial acidic acid or a mixture of glacial acetic acid and either carbon tetrachloride, chloroform, or methylene chloride, resulted in the formation of a mixture of compounds that were inseparable and unidentifiable.

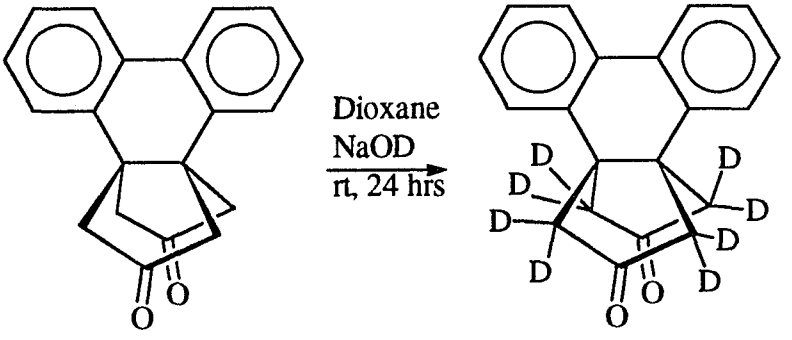
In the cases where bromination led to the formation of diverse mixtures, subsequent treatment with trietylamine or DBU did not result in a visible change in the NMR spectrum after workup. On several occasions our attempts to separate these mixtures into their individual components led to more complicated mixtures.



44 **45** **46**

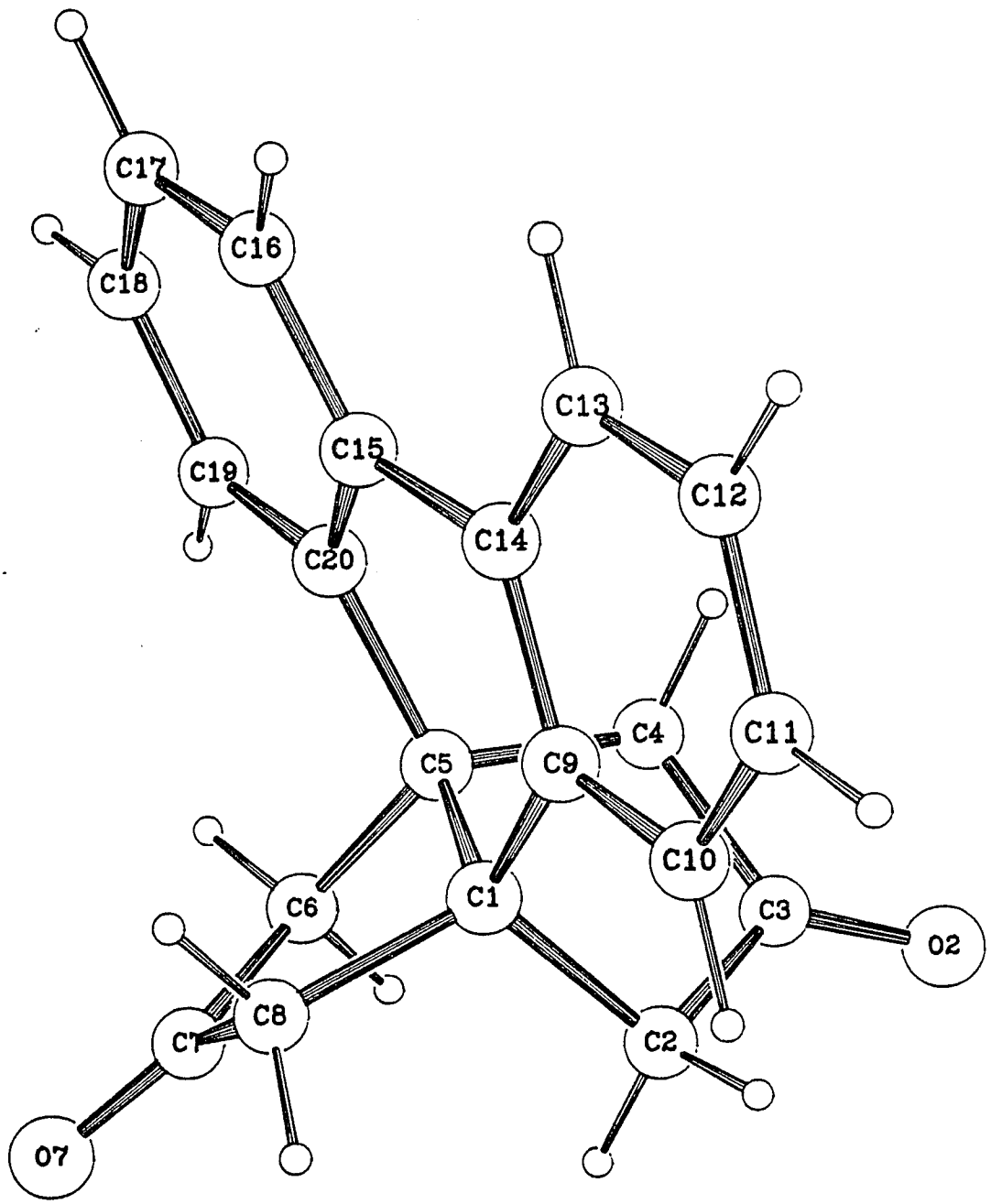
Scheme 9

In order for bromination of dione **44** to occur the enolate must be formed. As shown in Scheme 10, a simple way to check whether dione **44** forms enolate would be to see if there is an exchange of hydrogens with deuterium in D_2O and base to form dione **47**. A solution of dione **44** in a solution of dioxane and NaOD was stired for 24 hours and the deuterated dione which was isolated characterized by ^{1}H-NMR. The ^{1}H-NMR spectrum of **47** lacks the ab quartet present in the ^{1}H-NMR of dione **44** representative of the eight hydrogens. However, all attempts to synthesize the dibromide **45** or tetracyclic **46** have been unsuccessful.



44 **47**

Scheme 10

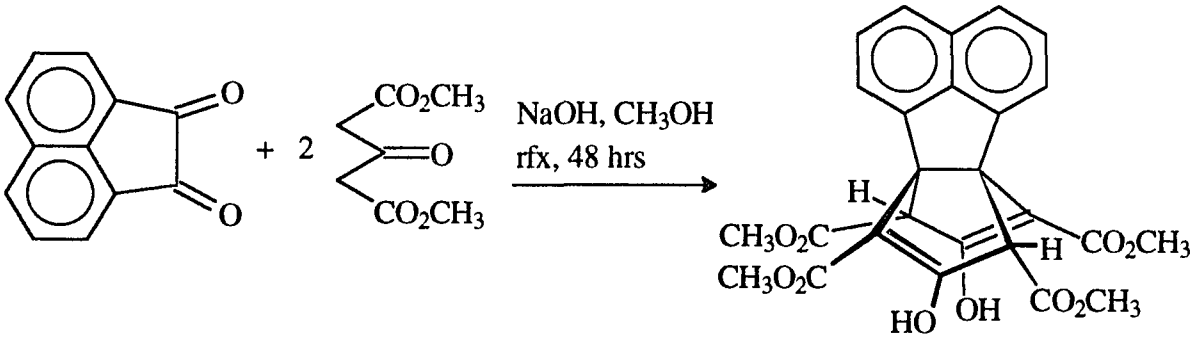


X-ray structure of dione **44**

PART 2:

APPROACH TOWARD THE SYNTHESIS OF 1,5-ACENAPHTHA-2,4,6,8-TETRACARBOMETHOXY SEMIBULLVALENE

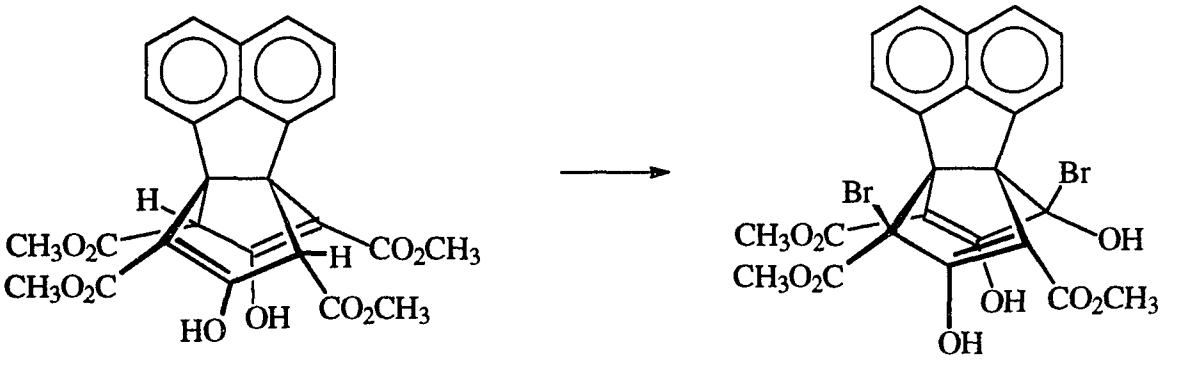
The first step in the synthesis of 1,5-acenaphtha-2,4,6,8-tetracarbomethoxy semibullvalene was the Weiss reaction in which acenaphthenequinone **48** reacted with two equivalents of 1,3-dimethylacetonedicarboxylate **40** with sodium hydroxide in refluxing methanol for two days. The resulting Weiss compound **49** was previously unknown and its ^{13}C NMR at room temperature shows a symmetric molecule which exists as the enol ester.



48 **40** **49**

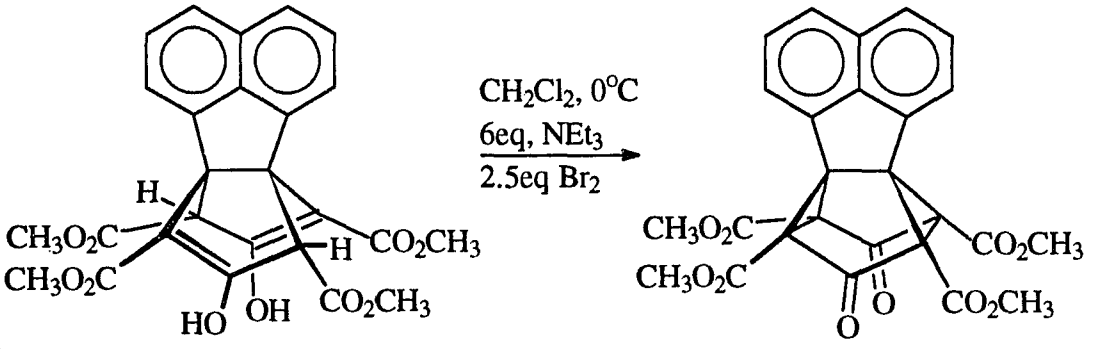
Scheme 11

Synthesis of the key tetracyclic intermediate dibromo adduct **50** was similarly unsuccessful. However, bromination in the presence of triethyl amine led to the formation of the tetracyclic **51** directly from enol **49** in one step.



49 **50**

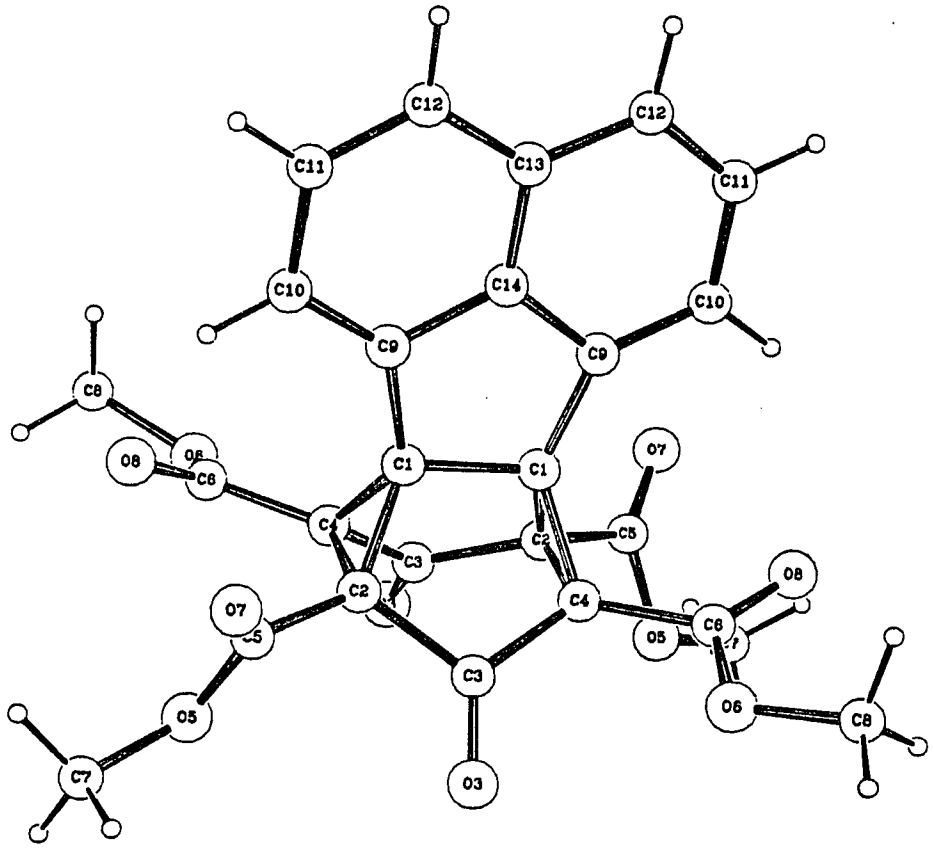
Scheme 12



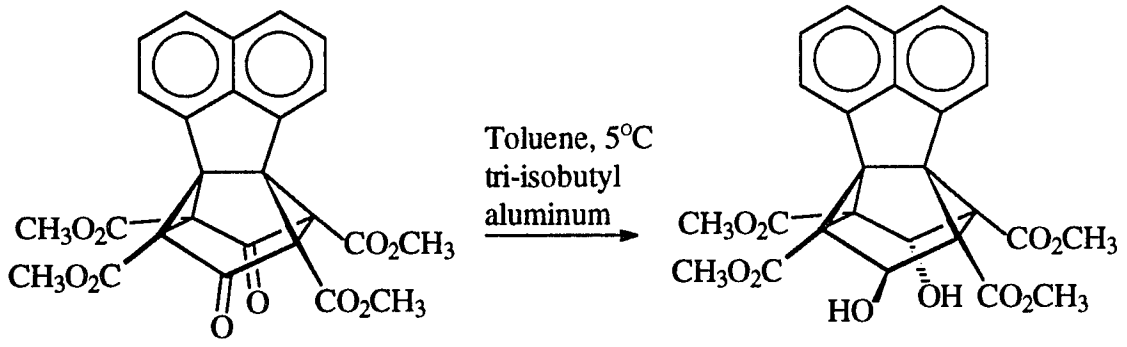
49 **51**

Scheme 13

Diketo-tetraester **51** was reduced with tri-isobutylalumunium in toluene at ice bath temperature and, after hydrolysis with 6M HCl. The aqueous layer was subjected to continous extraction with ethyl acetate for 5 days to yield diol **52**. The x-ray structure of **51** shows that the 1,5-acenaphtha group is compleatly planar.



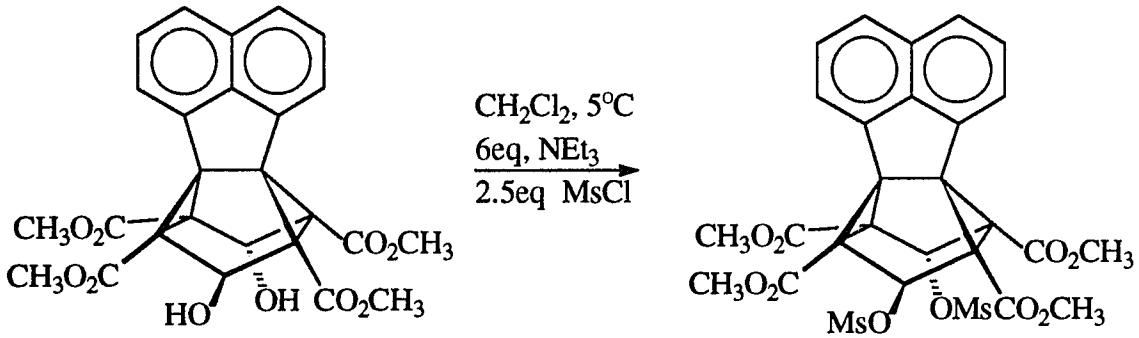
X-ray structure of tetracyclic dione **51**.



51 **52**

Scheme 14

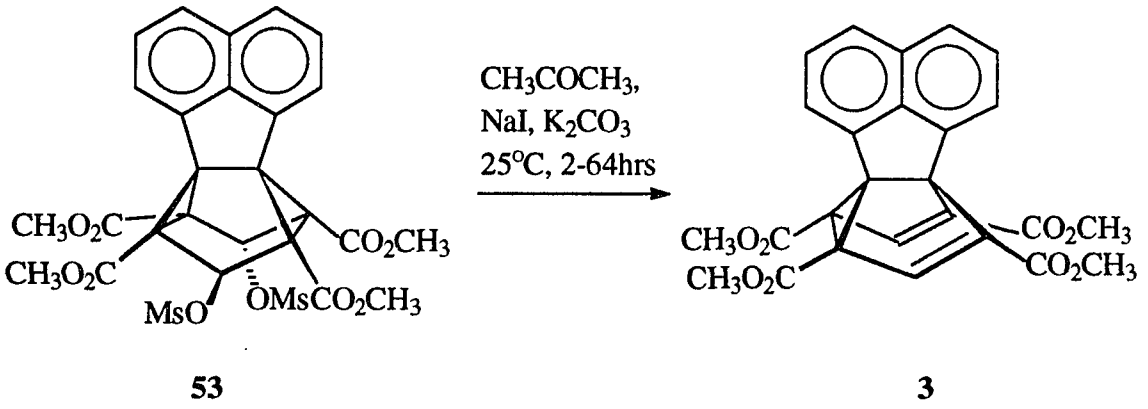
Diol **52** was first dried under vacuum overnight, and coverted to dimesylate **53** then treated with 3eq of triethylamine and methyl sulphonyl chloride in methylene chloride.



52 **53**

Scheme 15

Subjecting dimesylate **53** to the Grob fragmentation by sodium iodide in acetone resulted in a mixture of unknown and inseparable compounds in which we believe is a small quantity of semibullvalene **3**.



53 **3**

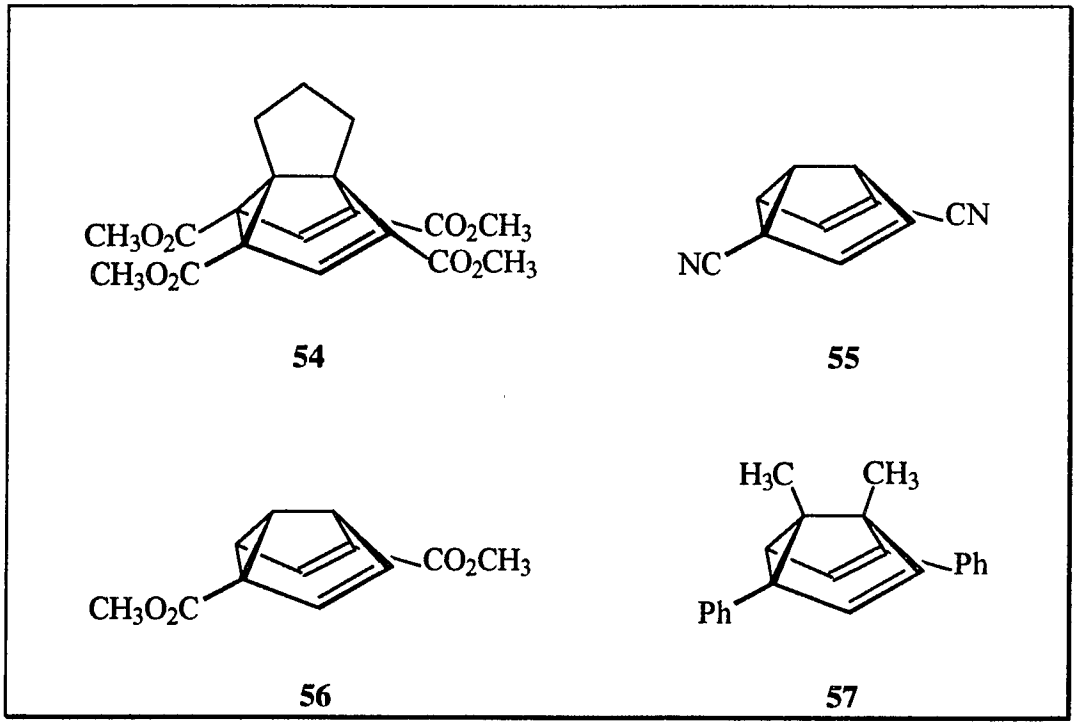
+ inseparable mixture of unknowns.

Scheme 16

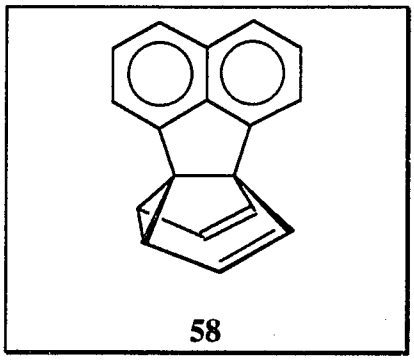
Our investigation into the nature of this reaction has excluded oxygen, light and water from the reaction vessel and the workup was carried out under a cloud of carbon dioxide in the dark. All chromatographic procedures were carried out under nitrogen or argon. There is a typical peak for the olefinic protons $H_{3,7}$ at about 6.2- 6.4 ppm. While our spectra show a mixture of compounds, a small peak in the same area is clearly observed and indicative of the presence for a semibullvalene.

Chromatography of the mixture resulted in the rapid decomposition of its components we speculate that decomposition was due to oxidation. It is not unusual for semibullvalenes to exhibit high reactivity. Quast and coworkers reported that 2,6-dicyano semibullvalene **55**,[79] 2,6-dicarbomethoxy semibullvalene **56**[80] and 1,5-dimethyl-3,7-diphenylsemibullvalene **57**[81] are extremely air sensitive and isolation has been extremely difficult. Quast and coworkers suggest that the instability of these semibullvalenes might be the result of polymerization resulting from the cleavage of the C_2-C_8 cyclopropane and speculate that this may be the initial step in such a reaction. On the other hand, 1,5-cyclopentano-2,4,6,8-tetracarbomethoxysemibullvalene **54**, isolated by Iyengar[82] found

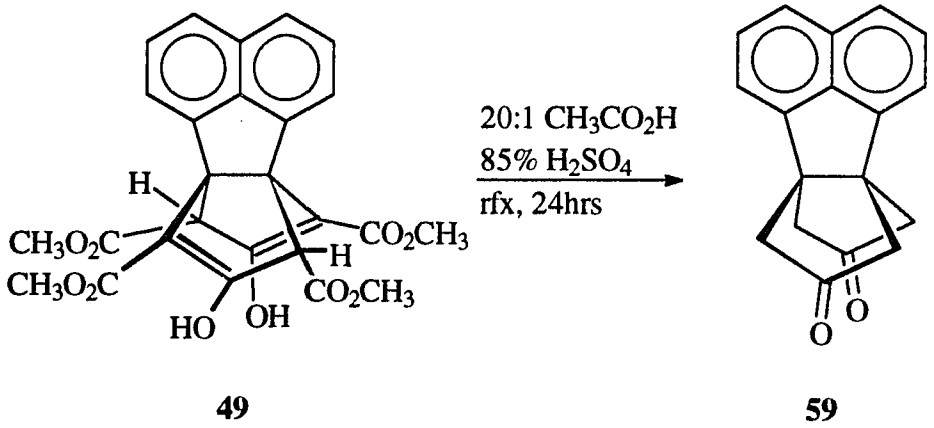
that a mixture of two compounds was formed[83]. These two compounds have been identified as two isomers of peroxides formed from the addition of oxygen to the semibullvalene.



Our next approach was to attempt the synthesis of the simpler decarboxylated semibullvalene **58**. As seen in Scheme 17, enol **49** was converted to dione **59** by refluxing in a mixture of 20:1 glacial acetic acid and phosphoric acid overnight.



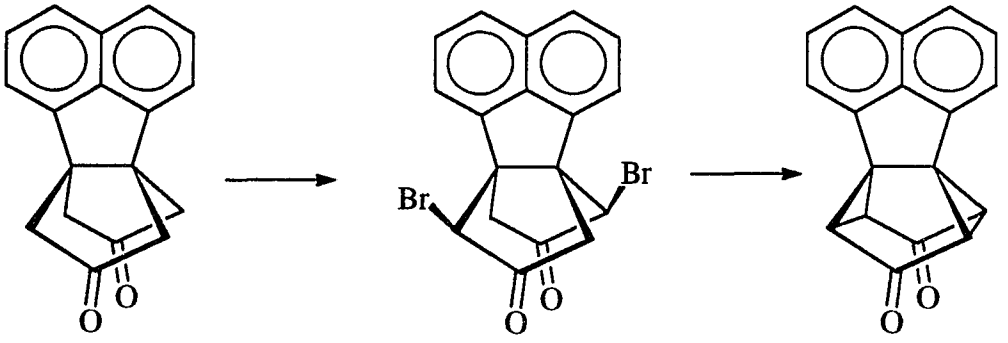
58



49 **59**

Scheme 17

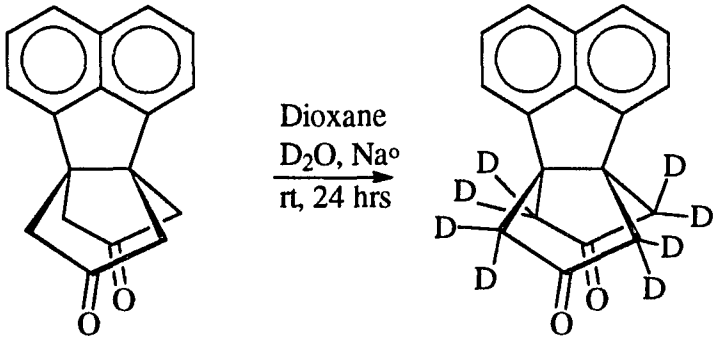
Attempts to brominate dione **59** to dibromo **60** included using bromine under neutral, acidic and basic conditions as well as $CuBr_2$ in ethyl acetate and chloroform. As was the case in the phenanthro system these attempts were unsuccessful.



59 **60** **61**

Scheme 18

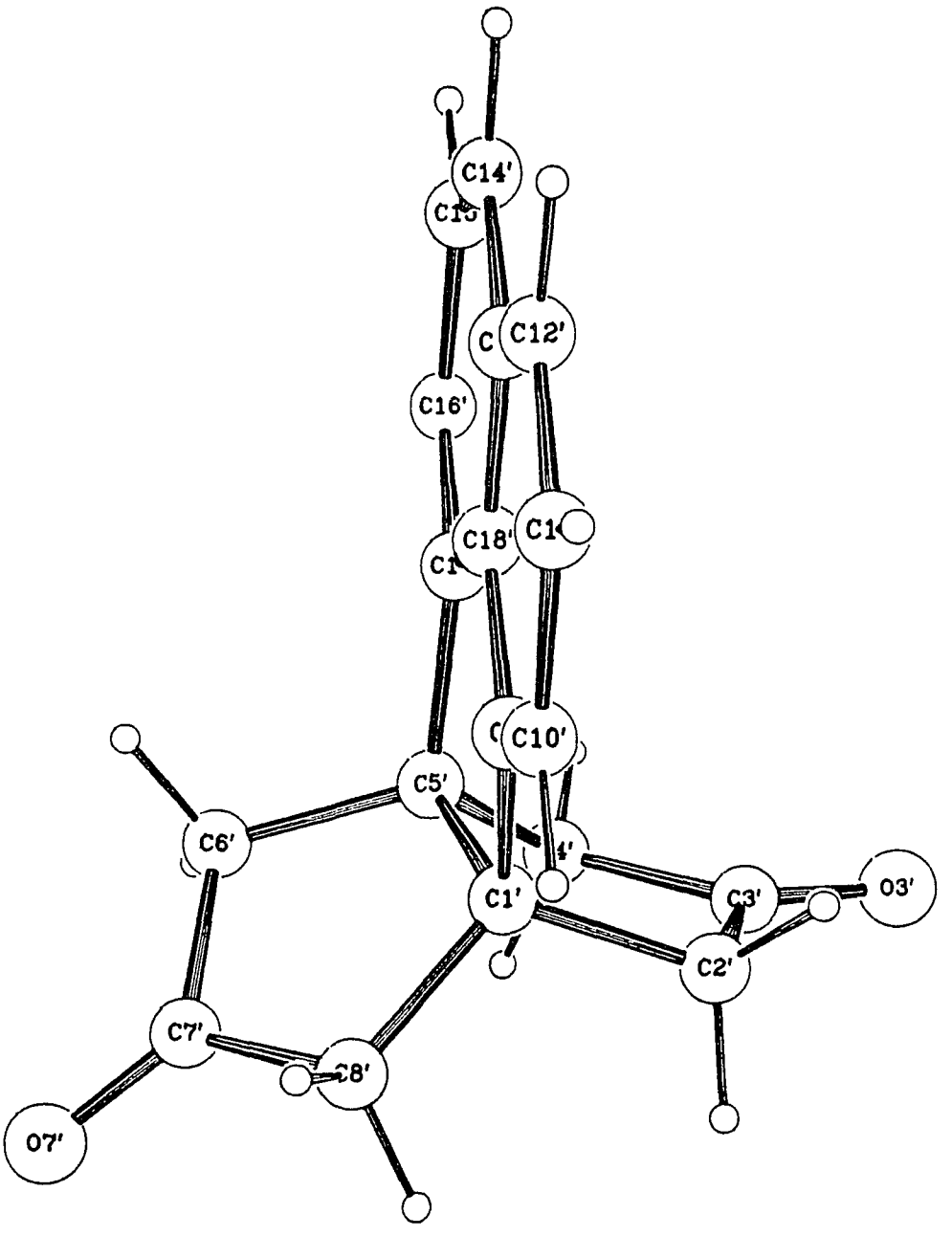
As before deuteration of **59** with NaOD in dioxane gave the deutero analog **62**, proving that the enolate did indeed form. The ^{1}H-NMR spectrum of deutero **62** lacks the ab quartet representative of the eight hydrogens in dione **59**. However, all attempts to synthesize the dibromide **60** or tetracyclic **61** have been unsuccessful. We do not have an explanation for this.



59 **62**

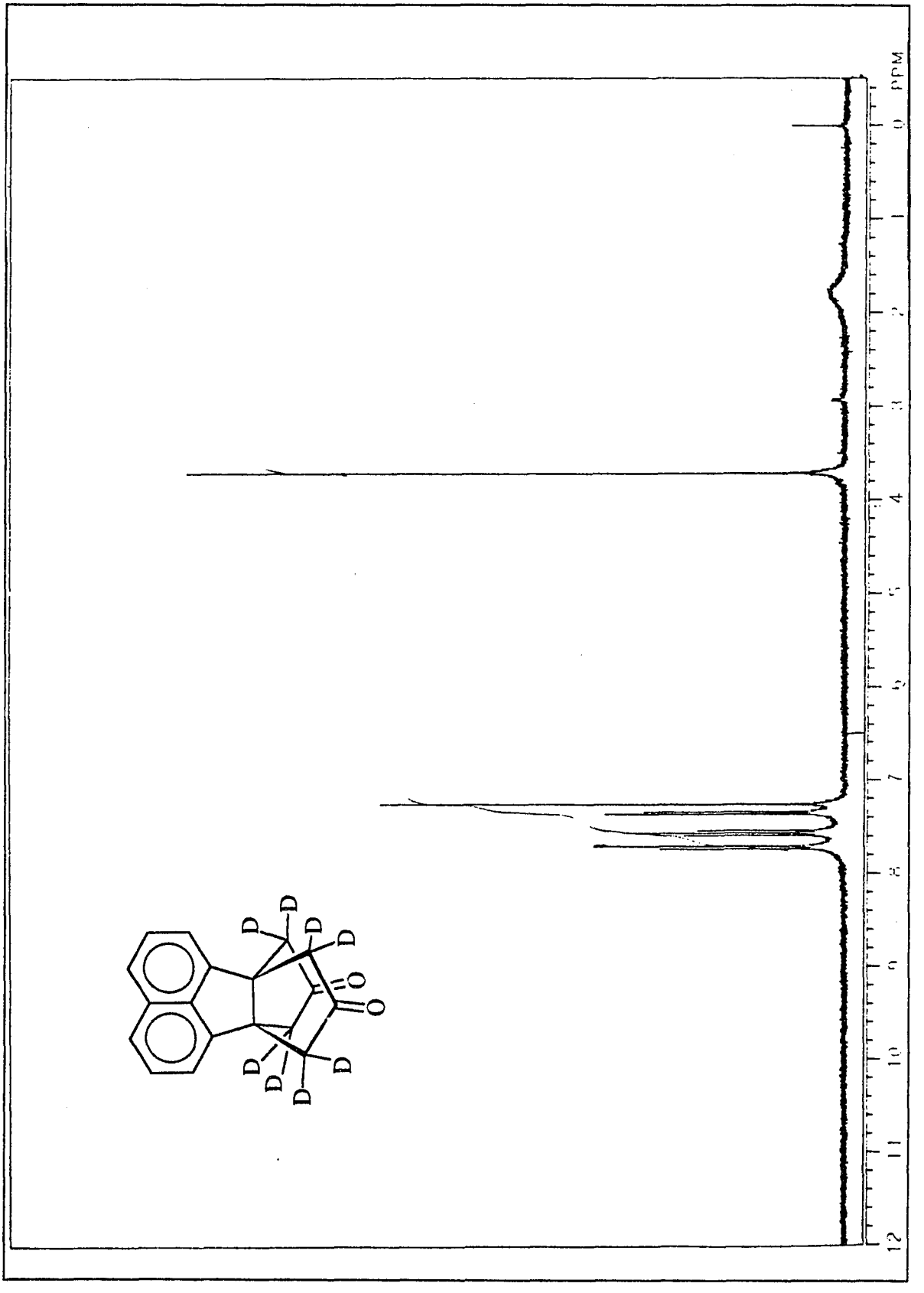
Scheme 19

The structure of dione **59** was elucidated by x-ray studies and its ^{1}H-300MHz NMR shows a characteristic ab quartet for the eight hydrogens. The ^{1}H-300MHz NMR of deutero analog **62** lacks this quartet.



X-ray of dione **59**.

^{1}H-300MHz NMR of dione **59**.


PPM
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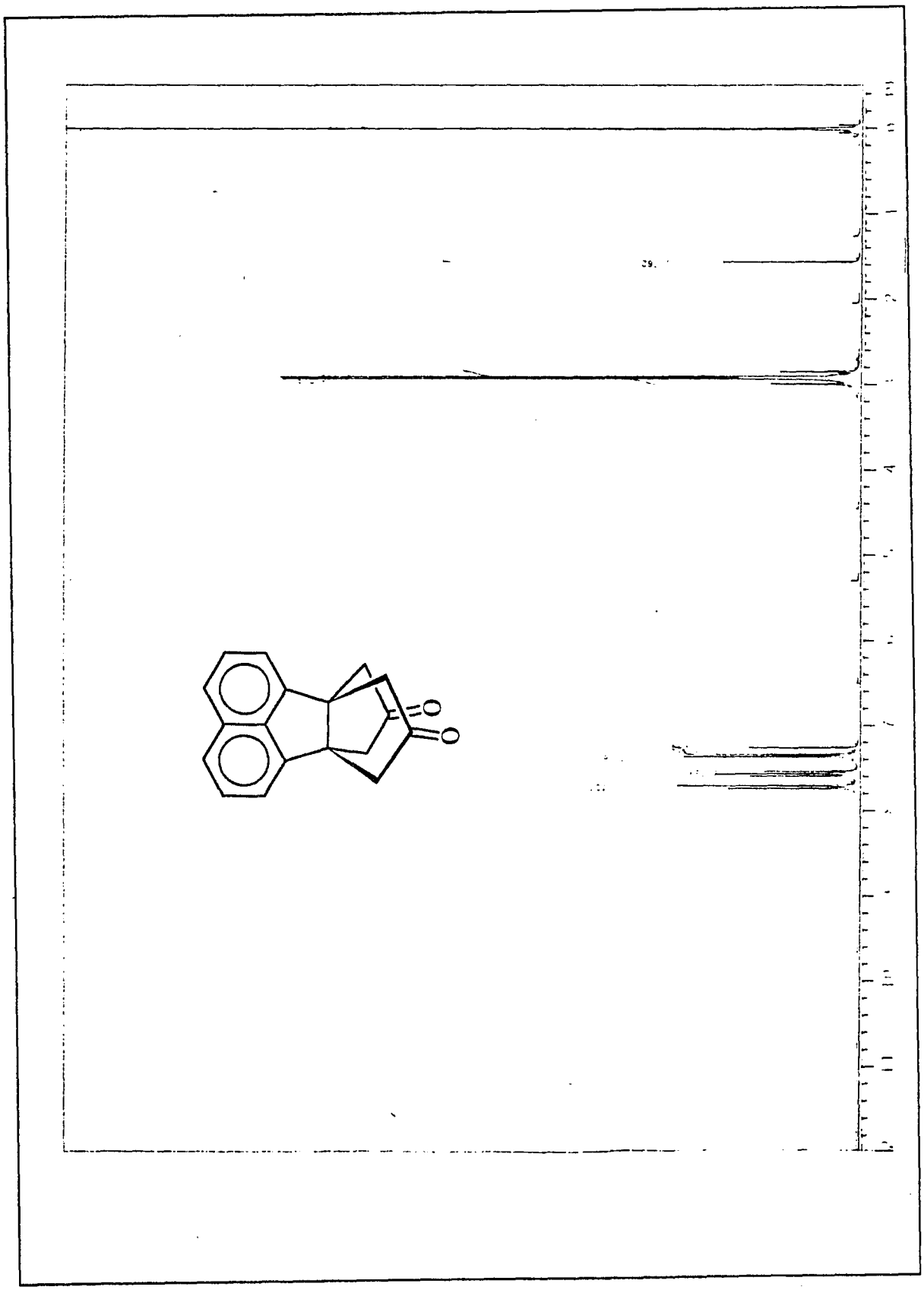
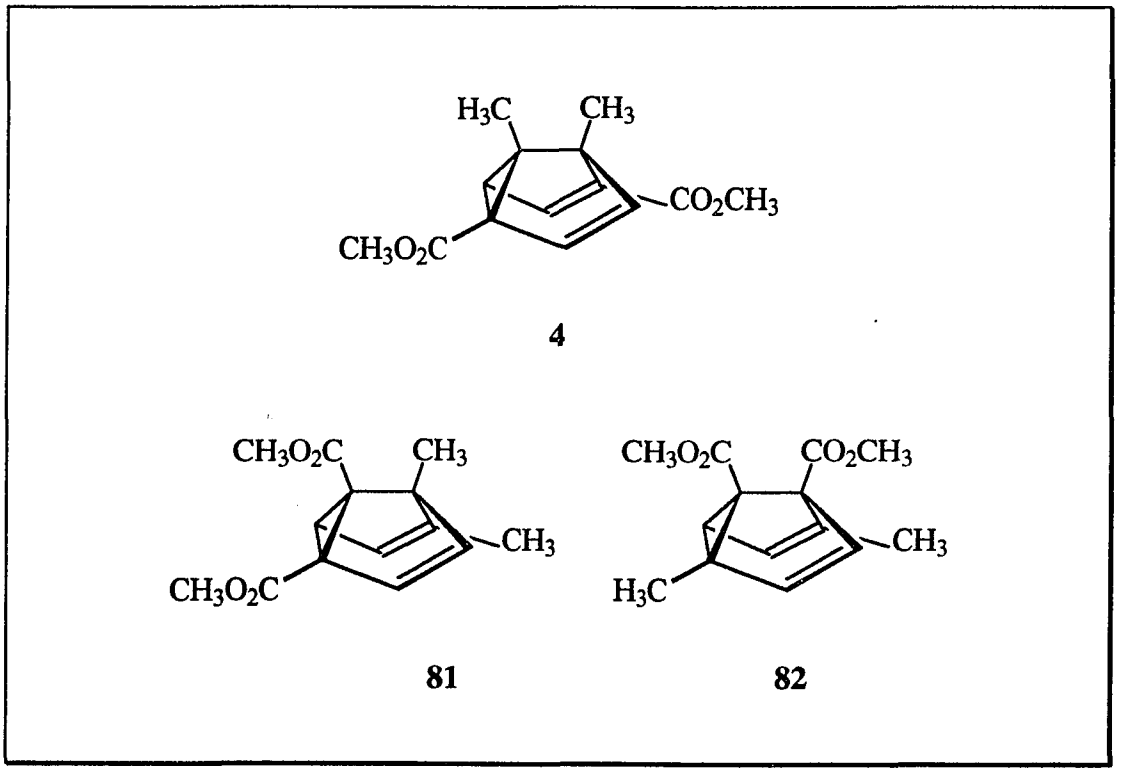
^{1}H-300MHz NMR of dione **62**.



CHAPTER 4: SYNTHESIS AND INVESTIGATIONS OF 1,5-DIMETHYL-2,6-DICARBOMETHOXY SEMIBULLVALENE

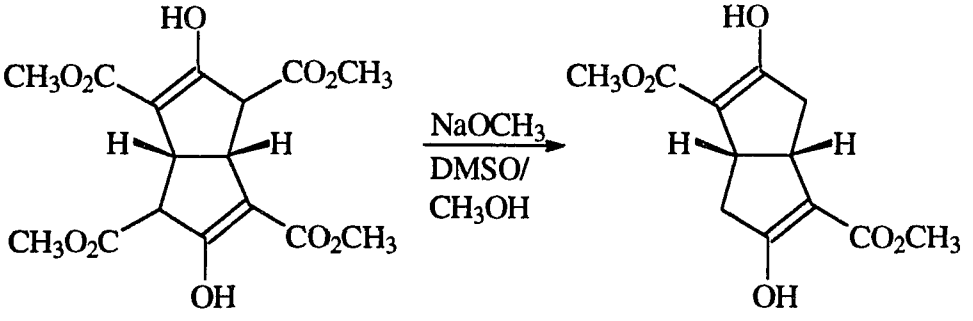
INTRODUCTION

This section details our synthetic approach and our investigation of the Cope rearrangement of semibullvalene **4**, and it details a new approach to a different substitution pattern previously inaccessible such as **81**.



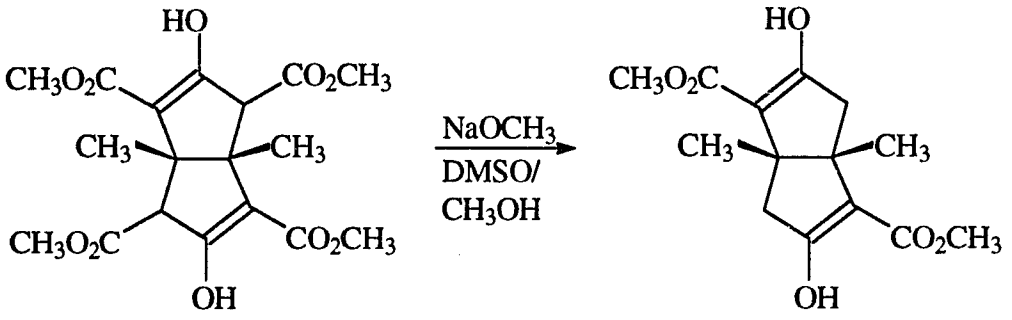
SYNTHESIS

As reported, and shown in Scheme 20, tetraester **63** has been reported to be decarboxylated by sodium methoxide in dimethyl sulphoxide to afford the diester **64** in 90% yield. Homologous ester **65**, Scheme 21, can be envisioned as undergoing the same degradation to diester **66**. However, several attempts at the decarboxylation of tetraester **65** met with failure. The problem seems to be that tetraester **65** is completely decarboxylated under any of the conditions we employed. Therefore, as can be seen in Scheme 22, we attempted to modify the Weiss reaction in order to arrive at the diacid diester **71**. A similar approach has been used by Willstätter in 1923 in the synthesis of ecgonine.[84]



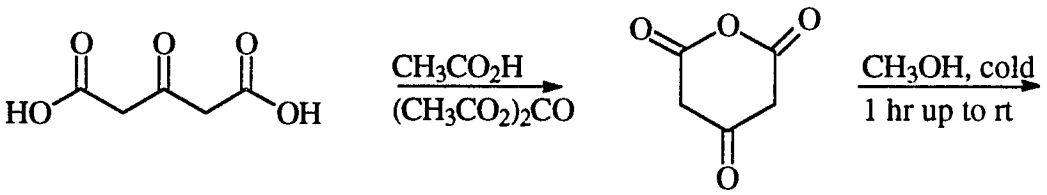
24 **25**

Scheme 20

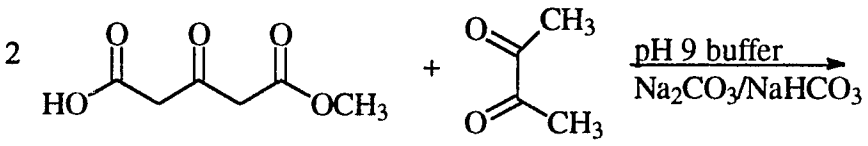


65 **66**

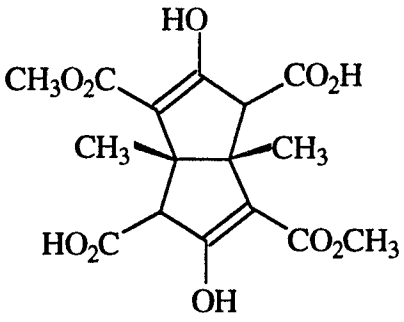
Scheme 21



67 **68**



69 **70**

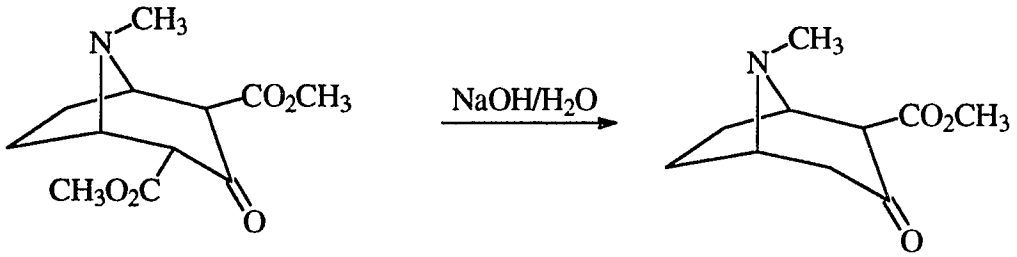


71

(not observed)

Scheme 22

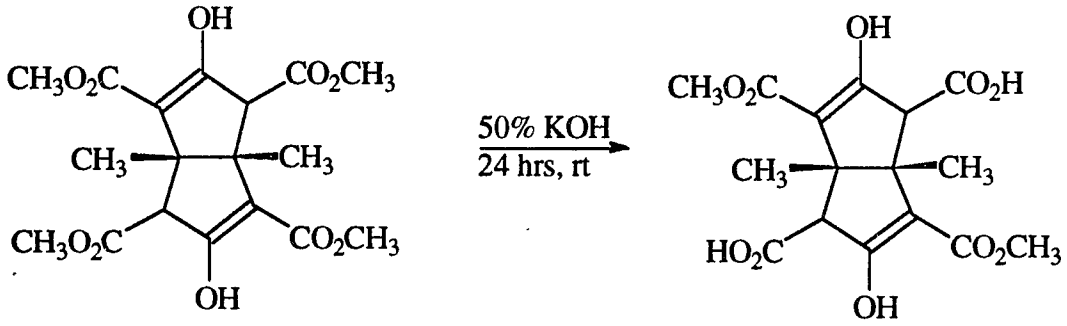
Findlay and coworkers developed a synthetic pathway to selectively decarboxyalate 2,4-dicarbomethoxytropinone **72** to 2-carbomethoxytropinone **73**, as shown in scheme 4.7. The intermediate mono acid was formed through selective saponification of diester **72** by sodium hydroxide solution and immediately decarboxylated to ester **73**. Similar selective hydrolysis and decarboxylation has been reported by Winterfelt on the synthesis of bicycloocatane.[85]



72 **73**

Scheme 23

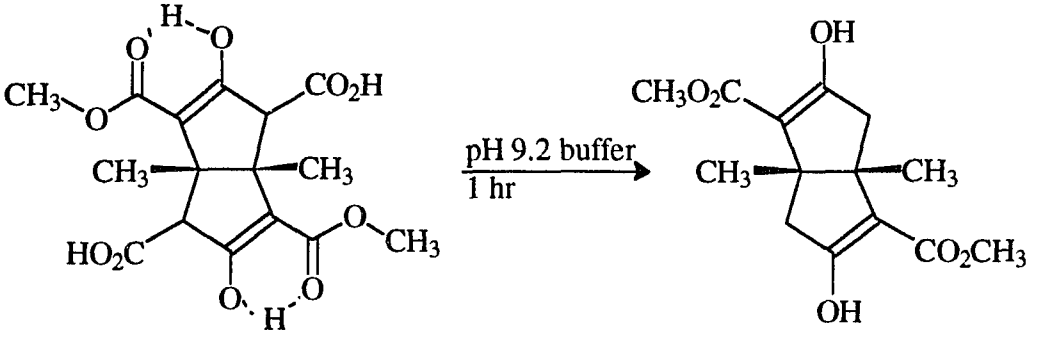
Selective saponification of tetraester **65** was achieved in the presence of 50% KOH solution overnight at room temperature in 51% yield. This reaction is successful in differentiating between the two sets of esters because the ketone exists exclusively as the C_2 symmetric bis enol. Formation of the dienolate anion renders the conjugated ester group.



65 **71**

Scheme 24

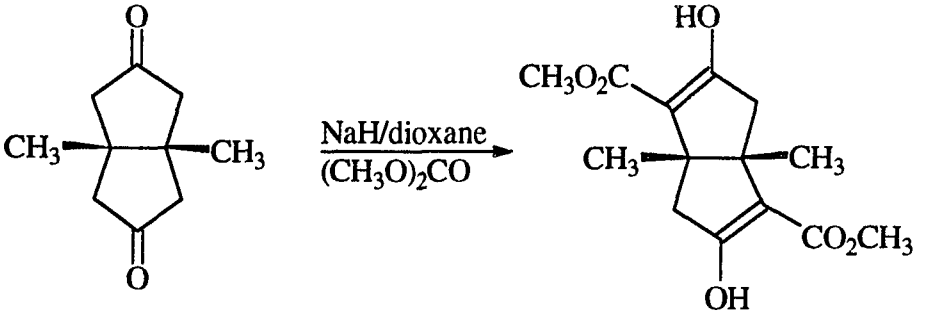
Selective decarboxylation of diacid **71** to the desired diester **66** was achieved by a gentle reflux of **71** in carbonate/bicarbonate buffer pH 9.2 for about 1 to 2 hours. This approach is the highest yielding of all the methods we tested.



71 **66**

Scheme 25

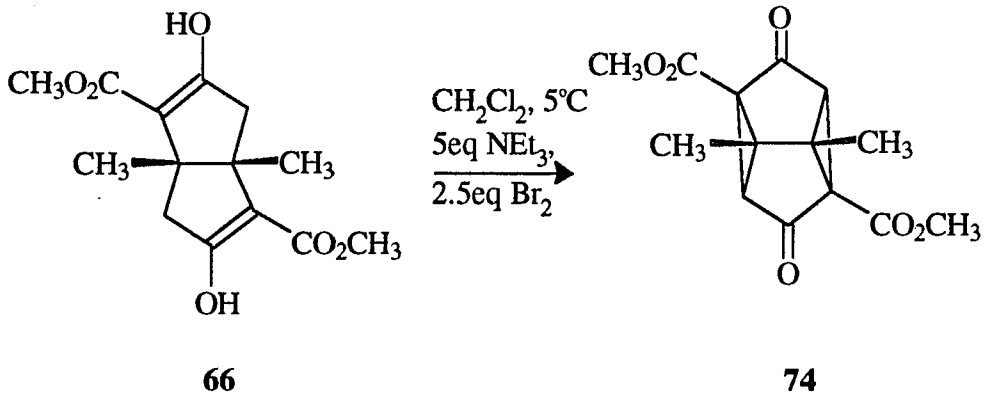
Another successful approach toward **66** was the addition of dimethylcarbonate to dione **12** in a 10% yield Scheme 26.



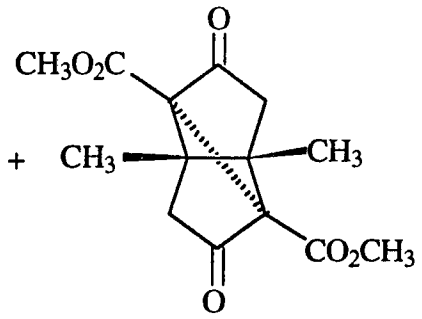
12 **66**

Scheme 26

In the presence of triethylamine bromination and dehydrobromination of diester **66** to tetracyclic **72** occured in one step . The dibromide intermediate **74** was not isolated and the excess triethlyamine causes the dehydrobromination as **74** was formed. Two side products were collected in about 40% yield as a 1:1 mixture of tetracyclic **74** and cyclobutane **75** (Scheme 27).



66 **74**

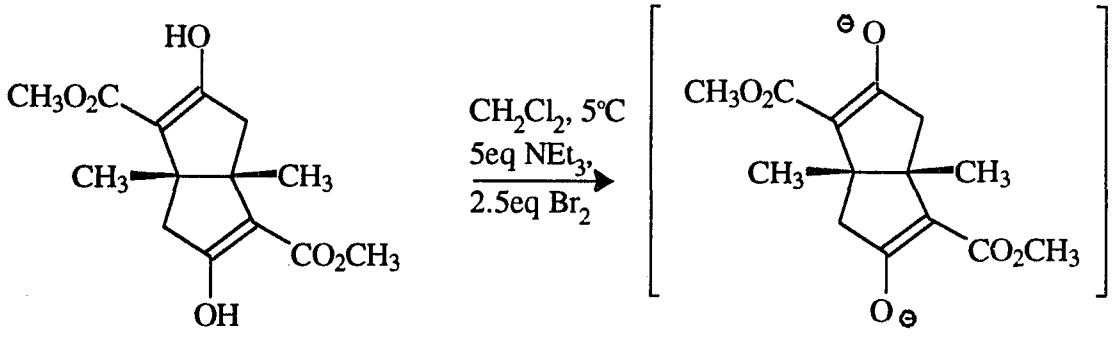


75

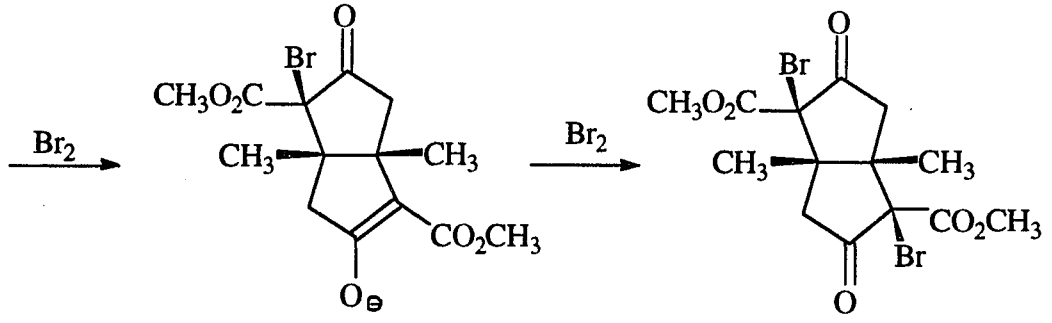
Scheme 27

It appears that there is a competition reaction between the dehydrobromination of monobromide **76** and the bromination of this monobromide to a dibromide **77** (Scheme 28). Monobromide could dehydrobrominate to tricyclic **78** or tetracyclic **75**. In one case a

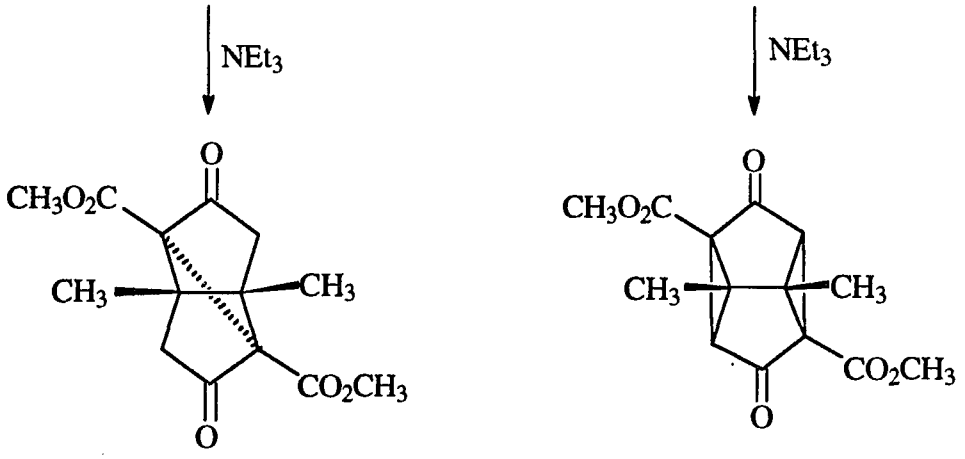
three membered ring is formed and in the other case a four membered ring is formed, we see the cyclobutane tricylic **75** formed.



66



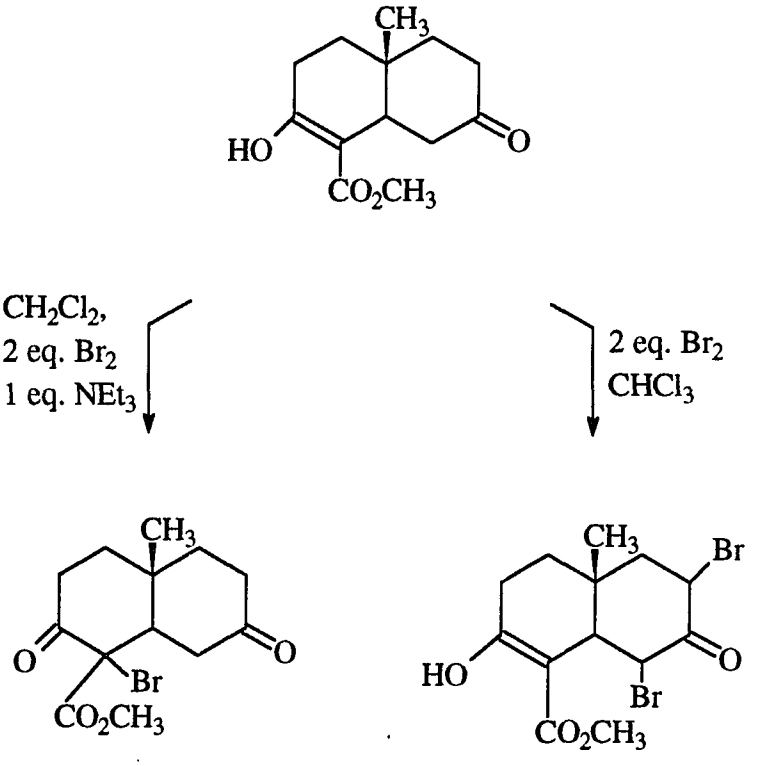
76 **77**



75 **74**

Scheme 28

Mechanistic studies directed toward the isolation and characterization of the monobromide **76** and/or the dibromide **77** have been unsuccessful. However, acid catalyzed bromination **66** in methylene chloride led exclusively to bromination of at positions 4 and 8 as indicated by the disappearance of the ab quartet and the appearance of a new peak at 5.1. Subsequent addition of triethylamine to this dibromide results in tetracyclic **74** exclusively and no cyclobutane **75**. Similar reports were reported by Karimi[86] in the bromination of cis-6-metylbicyclo[4.4.0]deca-4,7-diene-3,9-dione Scheme 29.

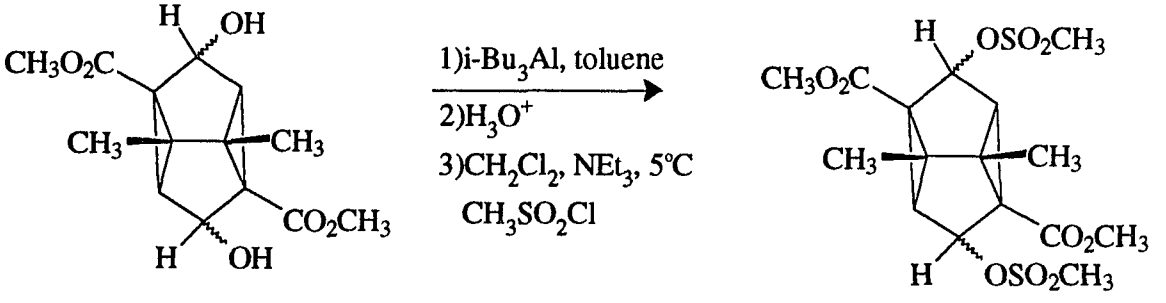


Scheme 29

The isolation of tricyclic cyclobutane **75** from the mixture of **74** and **75** was achieved by repeated recystallization of the white crystals collected from methanol and acetone. Since these compounds have very similar R_f's and are difficult to chromatograph. The importance of this side product is disscussed later in this thesis.

Tetracyclic dione **74** is an important intermediate toward the synthesis of symmetrically tetrasubstituted semibullvalenes, e.g. diagonally symmetrical di- and tetrasubstituted semibullvalenes. Nucleophilic reagents such as copper I cyanide and diphenyl copper lithium are expected to open the activated cyclopropane ring in **74**.

The next step in the synthesis of ?,6-dicarbomethoxy-1,5-dimethyl-semibullvalene was the reduction of the tetracyclic dione **72** to a mixture of diols **79** by reaction with tri-iso-butylaluminum at ice bath temperature. These were recrystallized and used as a mixture to form a mixture of dimesylates **80** by reaction with methanesulfonyl chloride and triethylamine in methylene chloride.

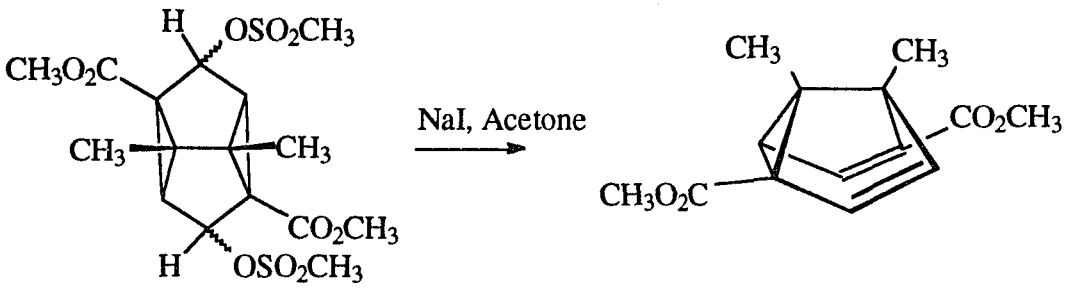


79 **80**

Scheme 30

The ring opening of dimesylate **80** was caused by the Grob fragmentation to afford semibullvalene **4** as part of a mixture of air sensitive compounds. After flash

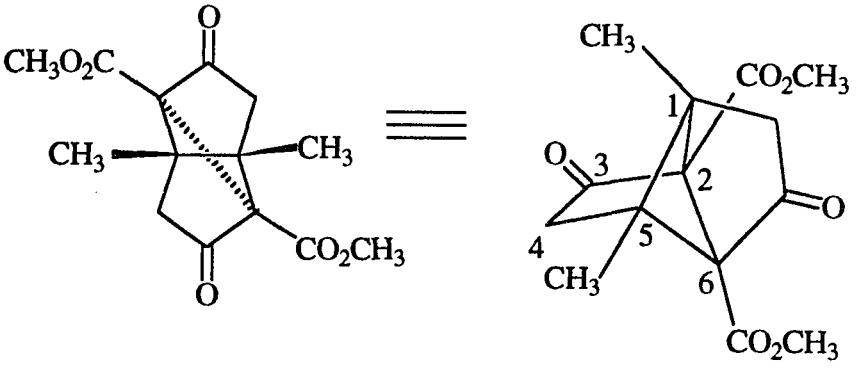
chromatography semibullvalene **4** was isolated from the mixture and temperature dependent solution NMR studies were performed. These studies are discussed in the following section.



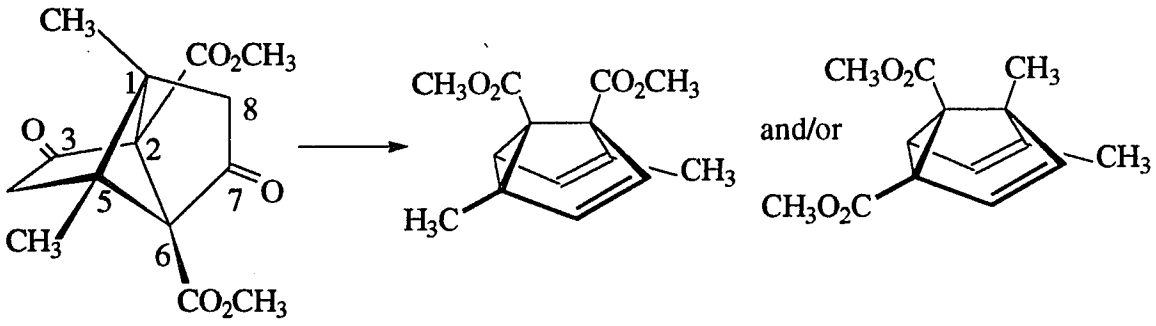
80 **4**

Scheme 31

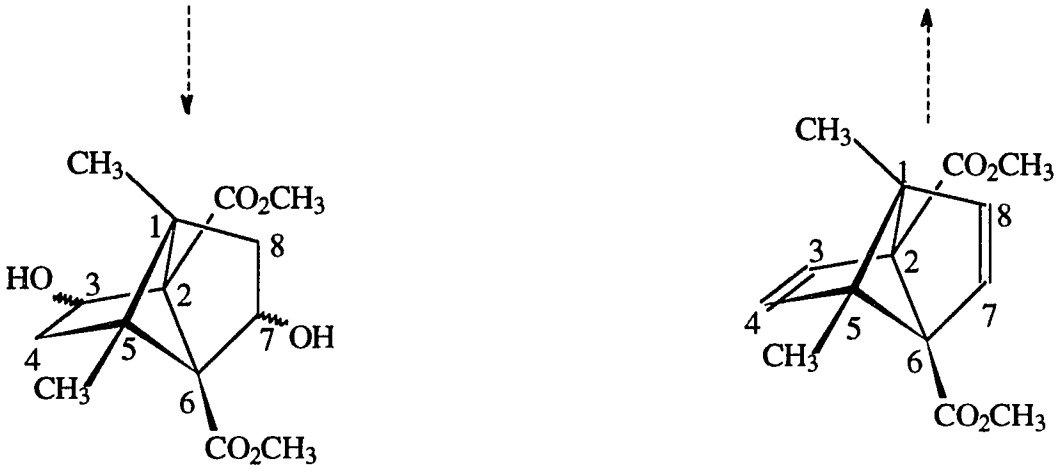
The bromination and dehydrobromination of diester **66** led to the desired tetracyclic dione **74** and compound **75**. We are currently in the process of investigating the mechanism for its formation. Cyclobutane **75** is a very interesting and unusual side product that could be converted to a semibullvalene by converting its dimesylate derivative to a diene. The diene can then be heated mildly to the corresponding semibullvalene Scheme 33. This procedure is based on known methodology in the literature.



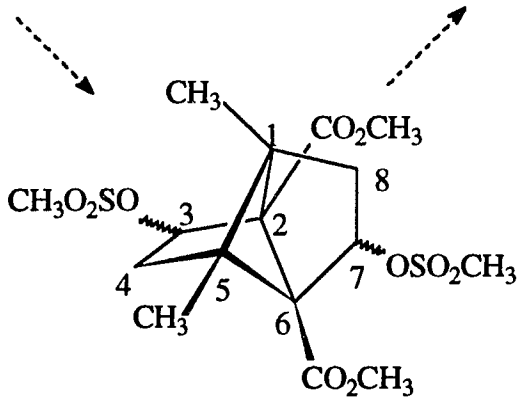
75



75 **81** **82**

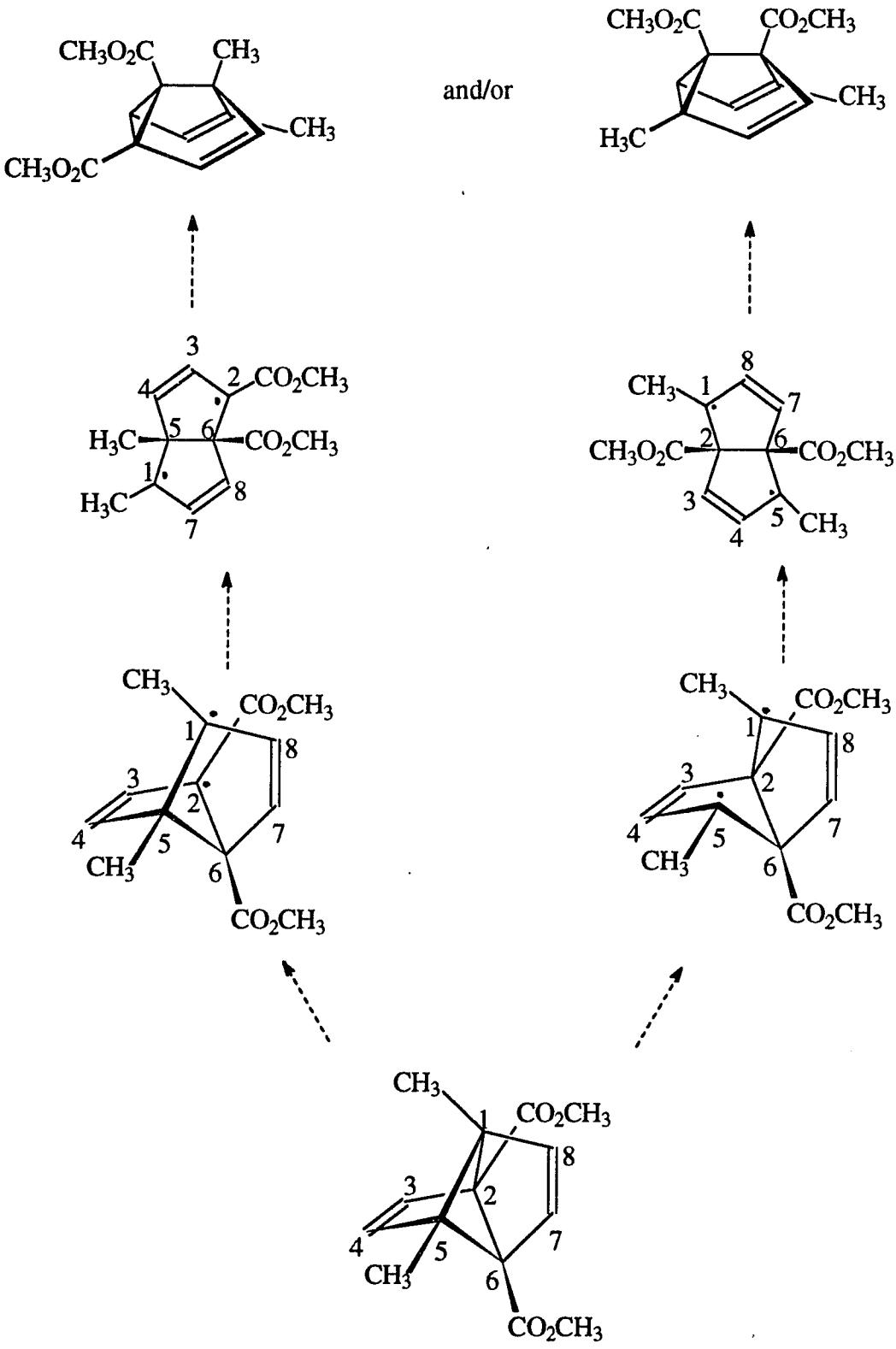


83 **85**



84

Scheme 32


CH3O2C
CH3
CH3
CH3O2C
and/or
CH3O2C
CO2CH3
CH3
H3C
CO2CH3
H3C
CO2CH3
CH3
CO2CH3
CH3
CO2CH3
CH3
CO2CH3
CO2CH3

Scheme 33

NMR STUDIES

Variable temperature NMR spectroscopy has been an extremely effective tool in the study of equilibrating systems. Low temperature ^{13}C NMR has been used to determine the barrier to rapidly rearranging systems like the Cope rearrangment. Before analyzing the low temperature ^{13}C NMR of semibullvalene **4** an interpretation of the room temperature spectra is necessary.

Room temperature ^{1}H and ^{13}C studies of semibullvalene **4** are shown in Figures 27 and 28. The ^{1}H spectrum shows four averaged resonances at δ 1.28, 3.76, 4.77, 5.83 ppm, which are assigned to $2(CH_3)$, $2(OCH_3)$, (H_1, H_5) and (H_3, H_7) respectively. Although H_1 is a cyclopropyl proton and H_5 is a an olefinic proton, both H_1 and H_5 appear together at δ ppm which is the direct result of rapidly equilibrating structurally indistinguishable valence tautomers.

The ^{13}C spectrum of semibullvalene **4** at room temperature consists of seven resonances at δ 12.4, 52.9, 66.9, 100.2, 101.5, 126.5 and 168.4 ppm, assigned to carbons CH_3, $2(OCH_3)$, $C_{1,5}$, $C_{3,7}$, $C_{6,8}$, $C_{2,4}$, 2(C=O) respectively. The ^{13}C NMR of semibullvalene **4** indicates that $C_{1,5}$, $C_{2,6}$ and $C_{4,8}$ resonances are the average between the cyclopropyl, and vinyl resonances expected in the static structure.

In solution at temperatures ranging from 25° to -113°C, shown in Figure 29, the Cope rearrangement is faster than the ^{13}C 400 MHz NMR time scale. Lowering the temperature will slow down the rearrangement relative to the NMR time scale, depending on the limit of the probe. When there are both valence tautomers are observable $C_{1,5}$, $C_{2,6}$ and $C_{4,8}$ will result in individual signals, this phenomenon is called decoalescence.

Variable temperature solution ^{13}C 400 MHz NMR spectra of **4** was measured in tetrahydrofuran-d_8. Due to our JEOL 400 MHz probe limitations low temperature NMR studies below -113°C were unattainable. As explained in Chapter 2 it is necessary to know the temperature of coalescence T_c (decoalescence in our case) in order to calculate the Eact. To date the Eact for the Cope rearrangement is not known.

Figure 27: Room temperature ^{1}H NMR spectrum of 1,5-Dimethyl-2,6-Dicarbomethoxy Semibullvalene

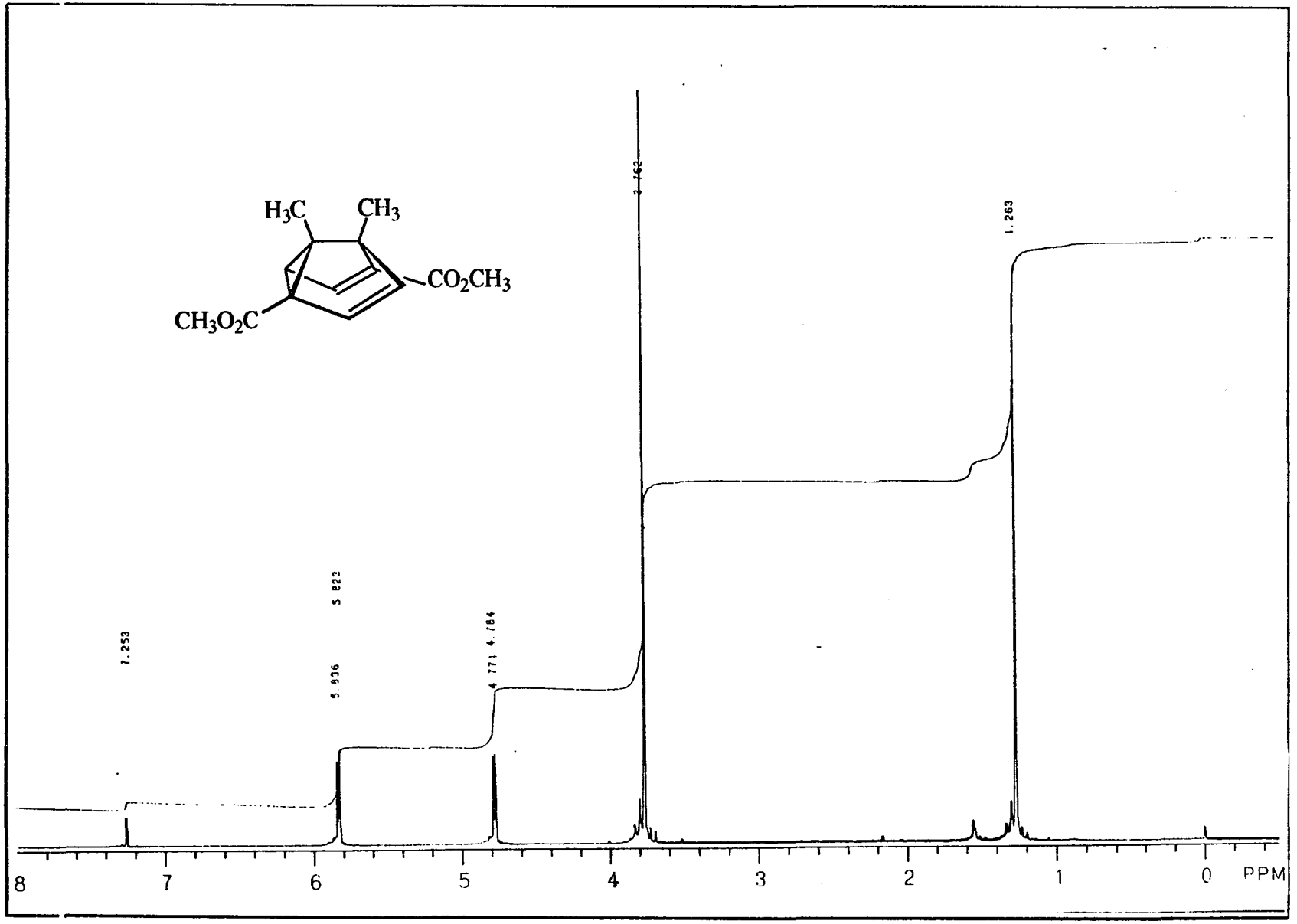

H3C
CH3
CO2CH3
CH3O2C
1.253
5.936
5.822
4.771
4.184
3.162
1.263
8
7
6
5
4
3
2
1
0
PPM

Figure 28: Room temperature ^{13}C-NMR spectrum of 1,5-Dimethyl-2,6-Dicarbomethoxy Semibullvalene

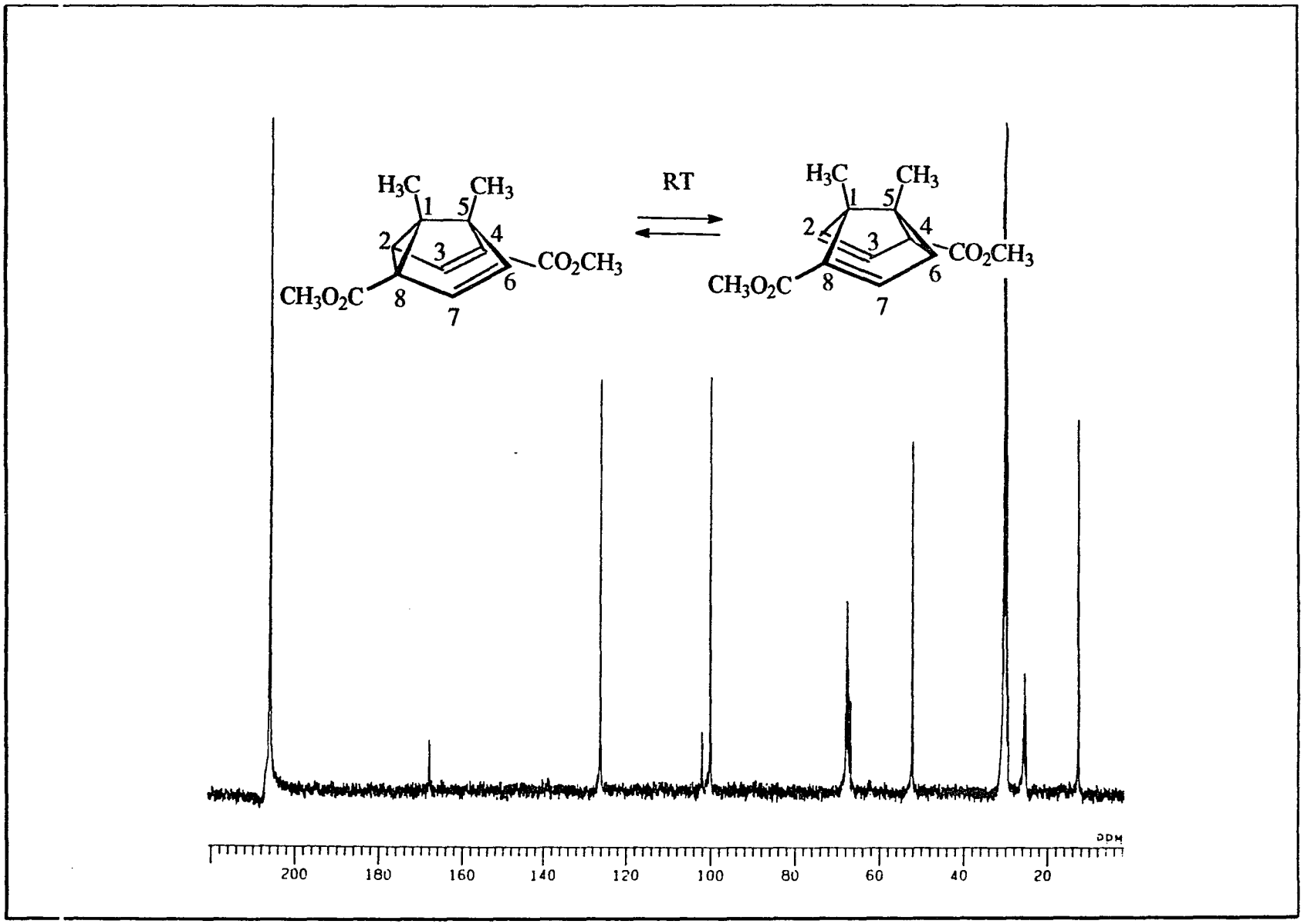

H3C
CH3
1
5
2
3
4
CO2CH3
CH3O2C
8
6
7
RT
H3C
CH3
1
5
2
3
4
CO2CH3
CH3O2C
8
6
7
PPM
200
180
160
140
120
100
80
60
40
20

Figure 29: Variable temperature ^{13}C-NMR of 2,6-Dicarbomethoxy-1,5-Dimethyl Semibullvalene

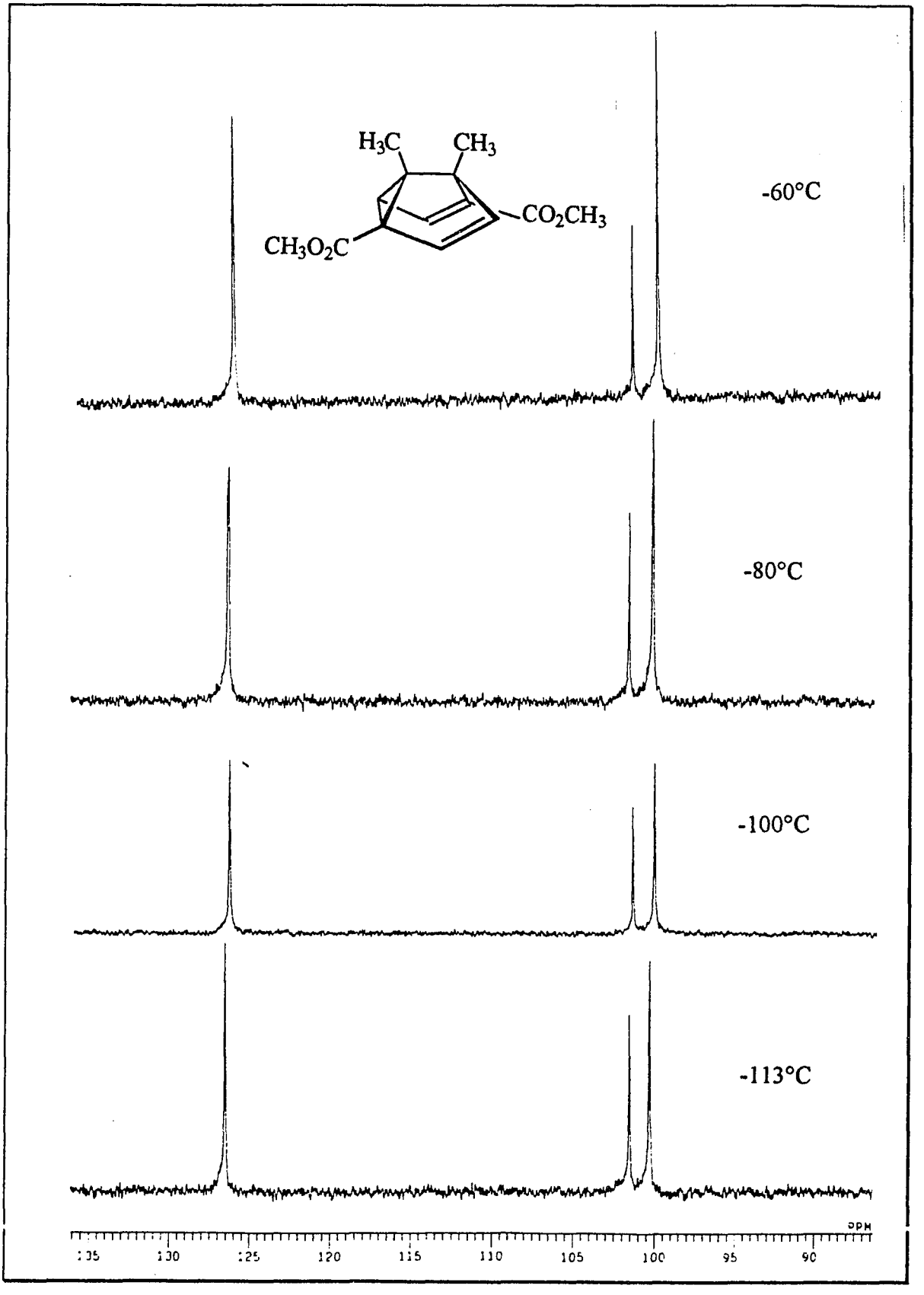
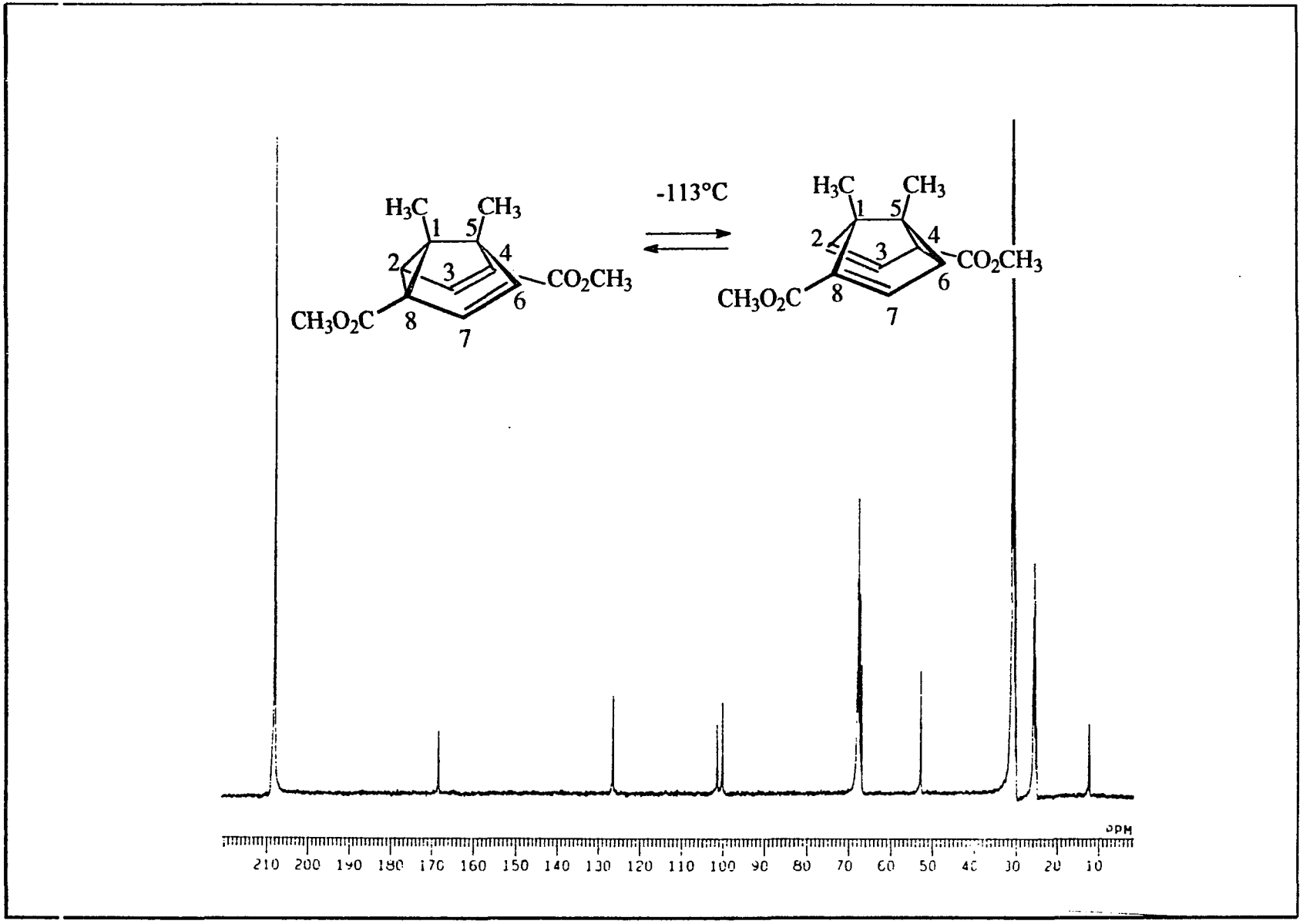

H3C
CH3
CO2CH3
CH3O2C
-60°C
-80°C
-100°C
-113°C
ppm
135
130
125
120
115
110
105
100
95
90

Figure 30: Variable Temperature ^{13}C-NMR of 1,5-Dimethyl-2,6-DicarbomethoxySemibullvalene

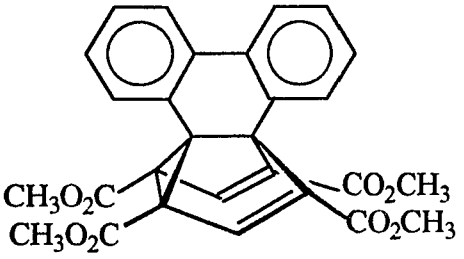

H3C
CH3
1
5
2
3
4
CO2CH3
CH3O2C
8
6
7
-113°C
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

DISCUSSION

CHAPTER 5: CONCLUSIONS

INTRODUCTION

In order to confirm theoretical predictions made by Hoffmann[87] and Dewar[88] we set out to synthesize the following donor-acceptor semibullvalenes. Our goal was to link theoretical predictions to experimental results by synthesizing the first neutral bis-homoaromatic molecule. To date a neutral homoaromatic molecule has not been made.



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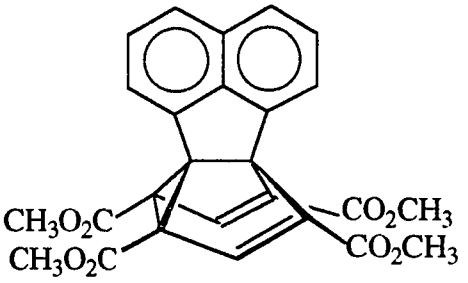
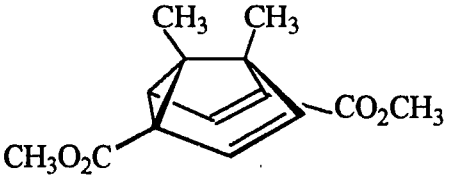


3

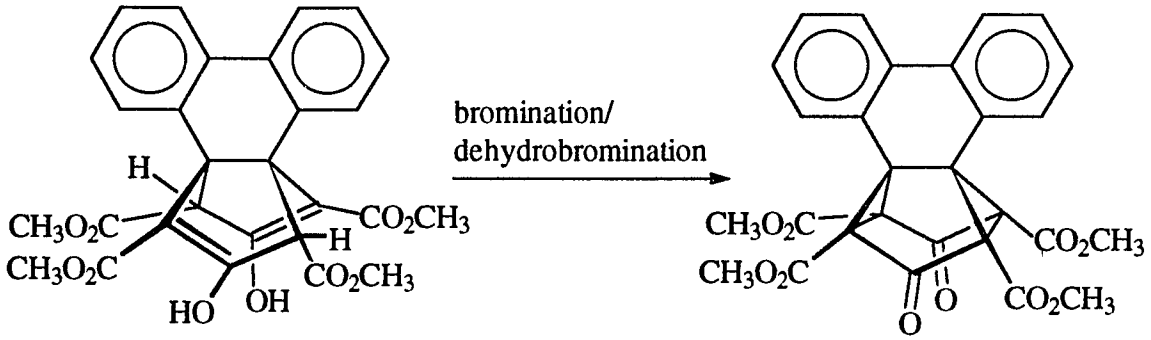


4

CONCLUSIONS

PART A

Our attempts to synthesize 1,5-phenanthra-2,4,6,8-tetracarbomethoxy semibullvalene **2** were unsuccessful. The central problem has been the synthesis of tetracyclic **43** key intermediate (Scheme 34).



41 **43**

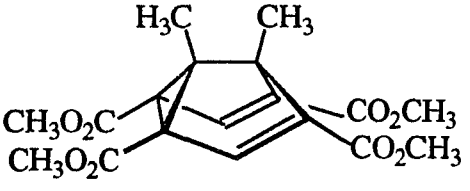
Scheme 34

PART B

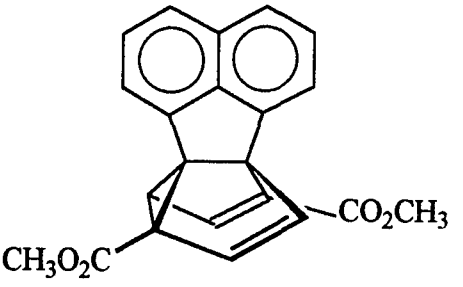
1,5-Acenaphtha-2,4,6,8-tetracarbomethoxy semibullvalene **3** was the first of its kind to be synthesized in our lab. However, it is highly reactive and therefore was not isolated form its multicomponent mixture. We have characterized it by comparing the ^{1}H-NMR spectra of the resulting mixture with the ^{1}H-NMR spectra of other semibullvalenes. The appearance of the characteristic $H_{3,7}$ at around 6.3 ppm can be used as a reference to identify other semibullvalenes.

SUGGESTIONS FOR FUTURE WORK

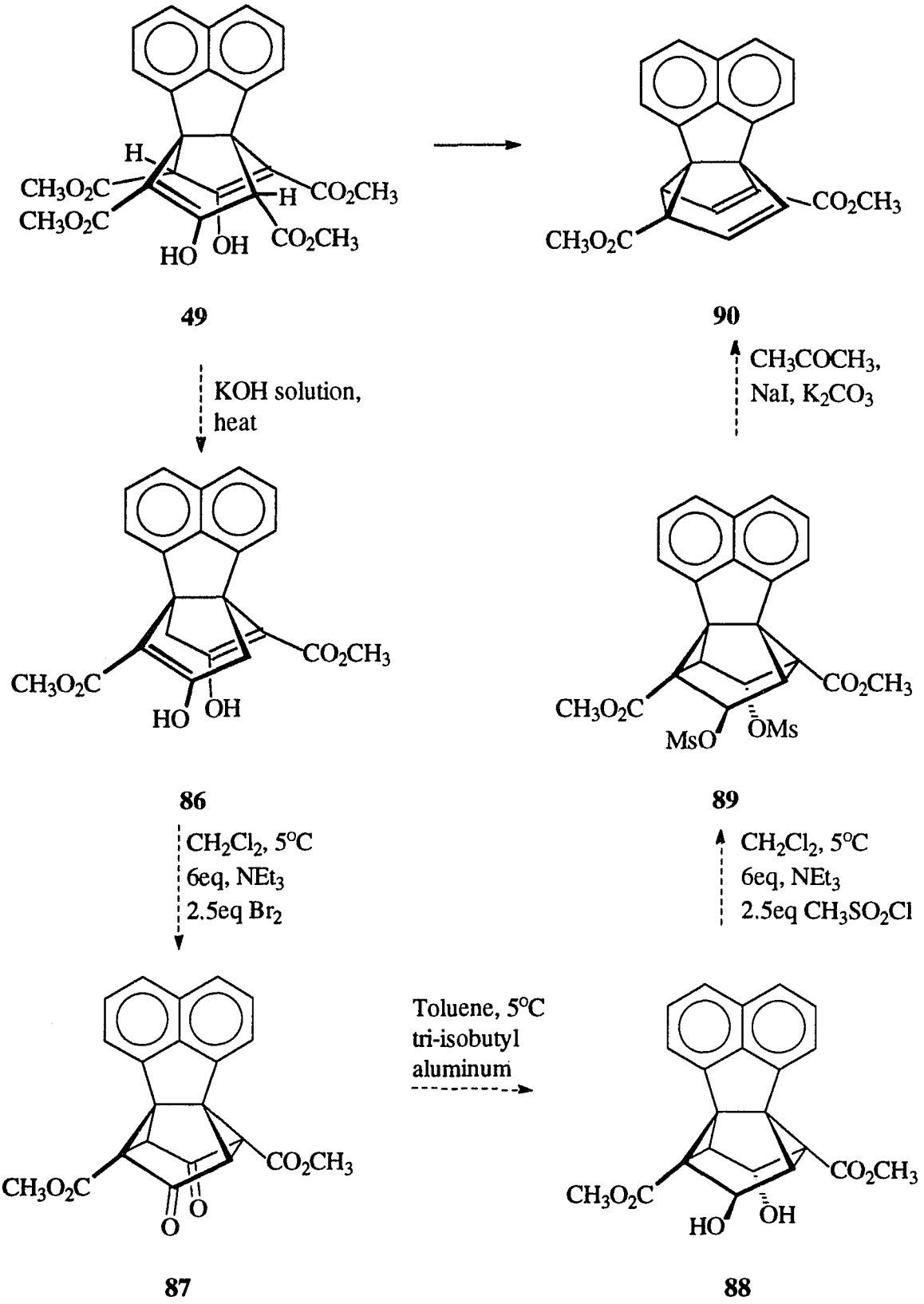
It may be possible that like 1,5-dimethyl-2,4,6,8-tetracarbomethoxy-semibullvalene **1**, in 1,5-acenaphtha-2,4,6,8-tetracarbomethoxy-semibullvalene **3**, the four esters experience a certain degree of steric hindrance which perhaps results in difficulties during the isolation of the final compound. Selective decarboxylation of **49** to the symmetric diester **86** followed by our general procedure used for making semibullvalenes should result in the first 1,5-acenaphtha-2,6-diester-semibullvalene **90**. Perhaps the 2,6-diester-1,5-annulated-semibullvalene will experience less steric hindrance than the corresponding tetraester semibullvalenes and result in an isolable semibullvalene (Scheme 35).



1



90


H
CH3O2C
CH3O2C
CO2CH3
H
CO2CH3
HO
OH
49
90
CH3COCH3,
NaI, K2CO3
KOH solution,
heat
86
89
CH2Cl2, 5°C
6eq, NEt3
2.5eq Br2
CH2Cl2, 5°C
6eq, NEt3
2.5eq CH3SO2Cl
Toluene, 5°C
tri-isobutyl
aluminum
MsO
OMs
O
O
87
88

Scheme 35.

1,5-Dimethyl-2,6-dicarbomethoxy-semibullvalene **4**, has been successfully been synthesized and characterized by solution ^{1}H and ^{13}C-NMR. The synthetic sequence developed for the synthesis of semibullvalene **4** presents a new route for the preparation of disubstituted semibullvalenes and symmetric diagonal tetrasubstituted semibullvalenes.

Semibullvalene **4** has been studied by room temperature ^{1}H and variable temperature ^{13}C-NMR. The room temperature ^{13}C NMR of **4** show averaged signals for $C_{1,5}$, $C_{3,7}$, $C_{2,6}$ and $C_{4,8}$. The low temperature ^{13}C spectra show no change in the line widths down to -113°C. This data can be interpreted as meaning that the rate of the rearrangement of semibullvalene is rapid on the NMR time scale down to at least -113°C (Figure 31).

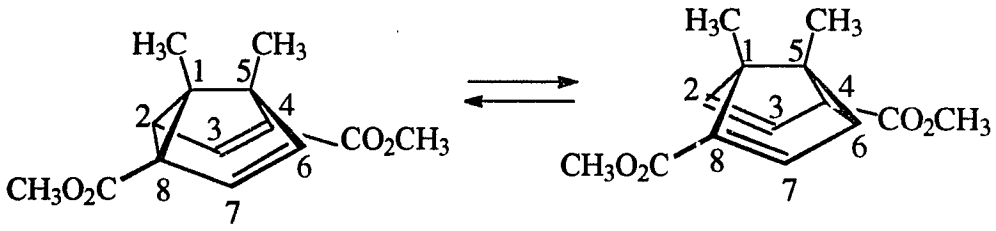


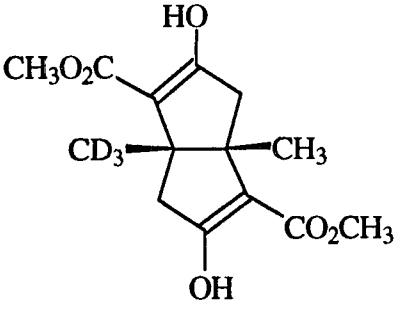
Figure 31:The Cope Rearrangement of Semibullvalene **4**.

Suggestions for Spectral Work

1) In order to obtain more information about the solution behavior of semibullvalene **4** a a series of low temperature ^{13}C spectra where the temperature will be varied from -70° to -160°C should be obtained and the pattern of line broadening studied as well as any changes in chemical shift.

2) Another method which can be used for the study of rapidly equilibrating species having small activation energies is variable temperature high resolution solid state ^{13}C-NMR.[89]

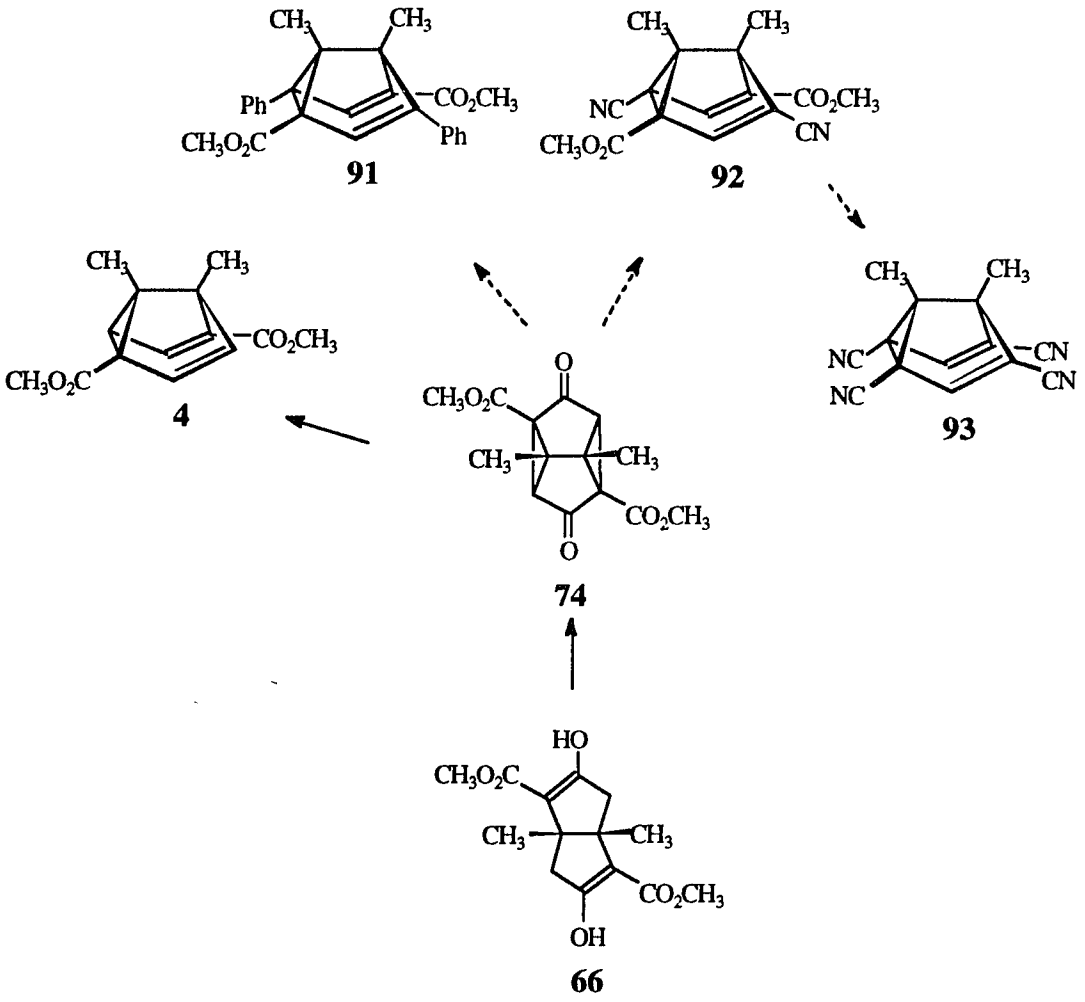
3)The isotopic perturbation of degenerate rearrangements brought about by the introduction of a deuterium atom into the rearranging system as studied by NMR has been useful for distinguishing between rapidly equilibrating and delocalized species. It may be possible to substitute deuterium into the semibullvalene and to study its effects using ^{13}C NMR. The most obvious place to substitute would be the methyl groups as in **66**.



66

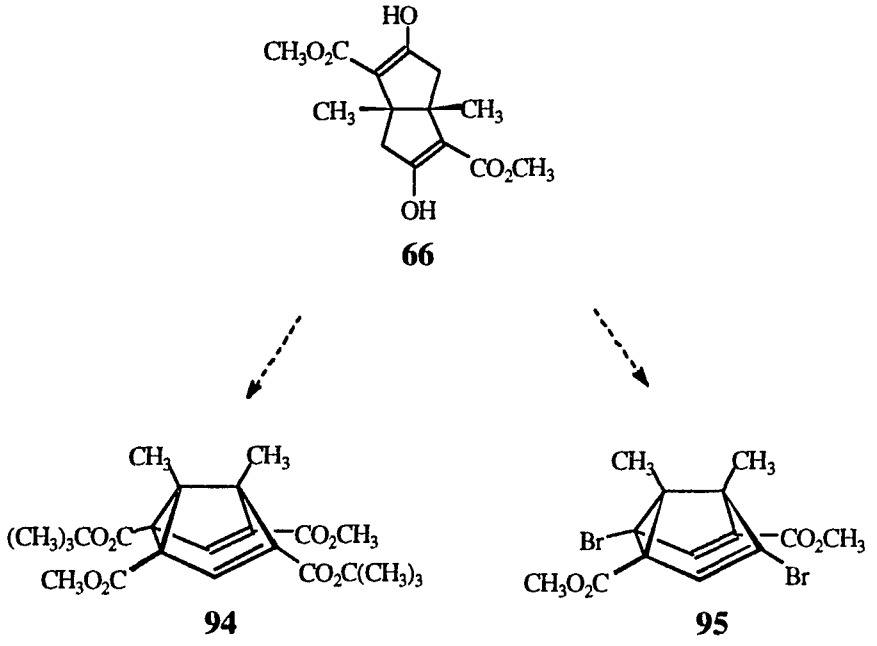
Suggestions for Experimental Work

Tetracyclic dione **74**, which is the key intermediate in the synthesis of 1,5-dimethyl-2,6-dicarbomethoxy semibullvalene **4** is also the key intermediate that can be used to approach semibullvalenes **91** and **92** (Scheme 36).



Scheme 36

Approaches Toward Symmetrical Diagonally Tetrasubstituted Semibullvalenes

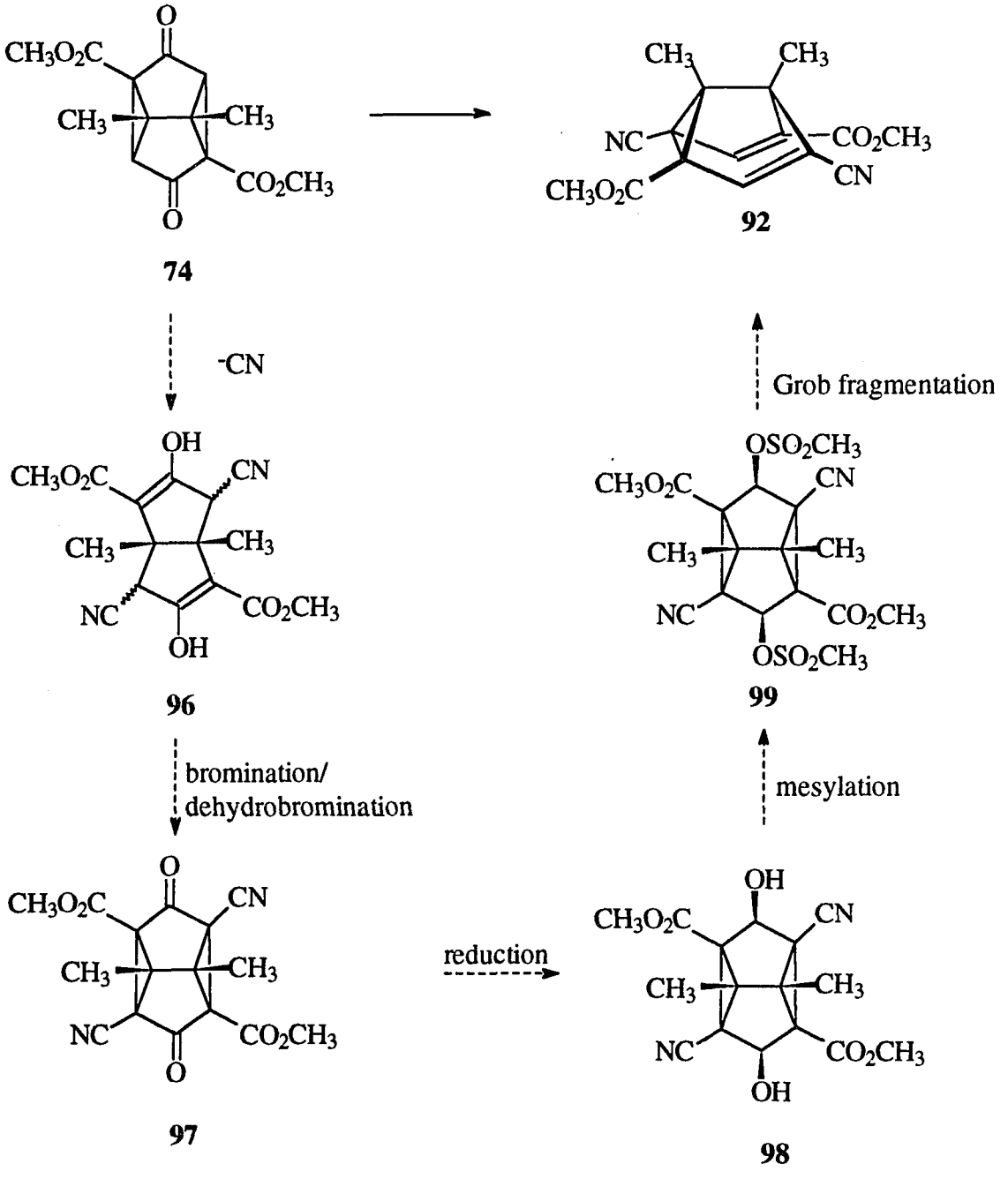


Scheme 37

Approaches Toward Symmetrical Diagonally Tetrasubstituted Semibullvalenes

Approach Toward 2,6-Dicyano-4,8-Dicarbomethoxy Semibullvalene

The proposed approach toward 2,6-dicyano-4,8-dicarbomethoxy-semibullvalene **92** involves nucleophilic opening of the cyclopropane ring[90,91] in tetracyclic ester **74** by a cyanide. Subsequent formation of the tetracyclic dicyano diester **96** is the key to this synthetic scheme. The dicyano diester tetracyclic intermediate **97** can then be converted to the corresponding semibullvalene through the use our general synthetic method (Scheme 38).

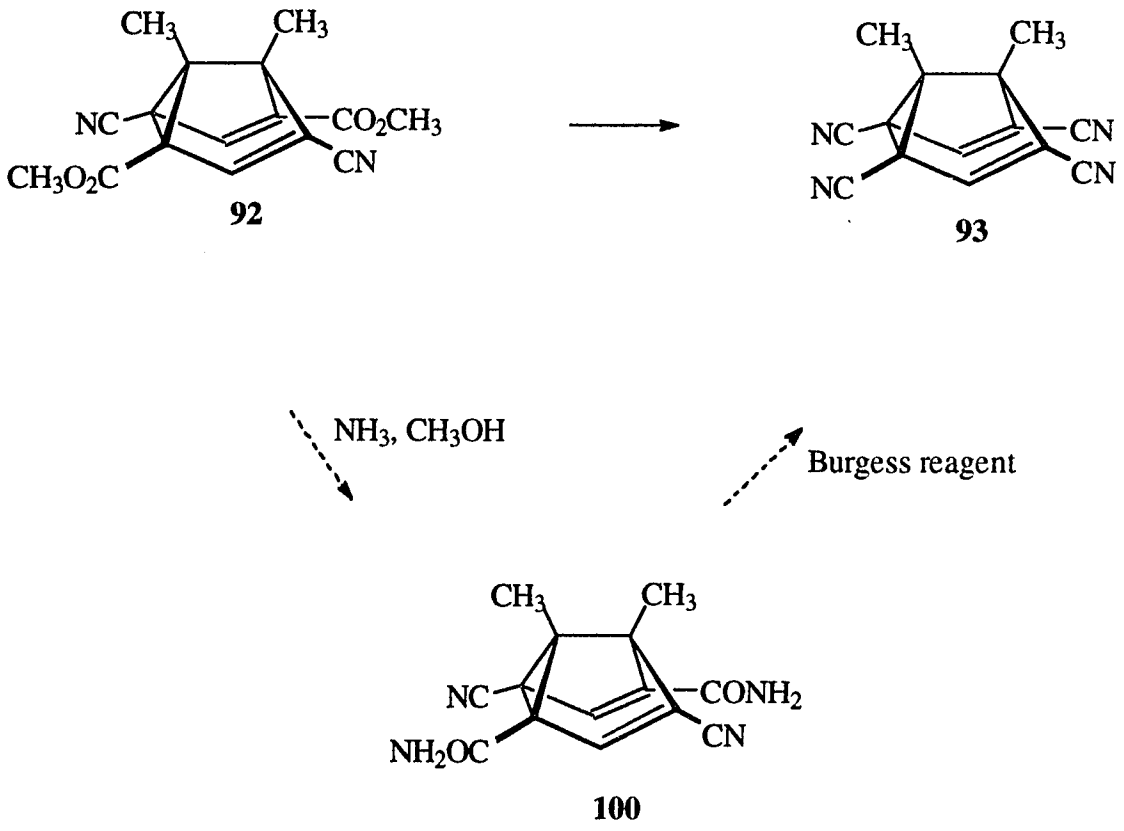


Scheme 38

Approach Toward 2,6-Dicyano-4,8-Dicarbomethoxy Semibullvalene

Approach Toward 2,6,4,8-Tetracyano Semibullvalene

2,4,6,8-Tetracarbomethoxy semibullvalene can be synthesized from the dicyano diester semibullvalene **92** by first making the dicyano diamide and then treating it with the Burgess reagent to yield **93** (Scheme 39).

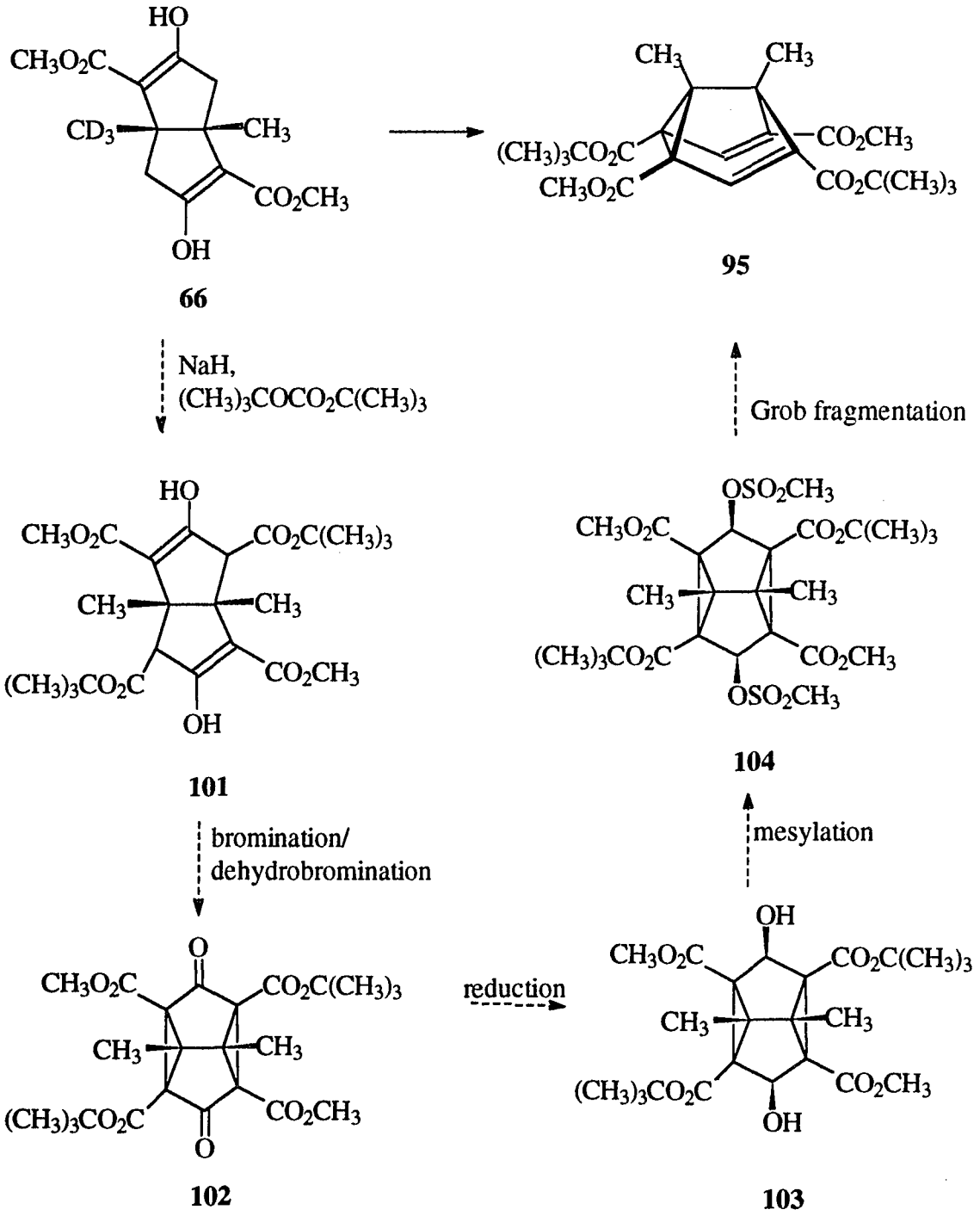


Scheme 39

Approach Toward 2,6,4,8-Tetracyano-Semibullvalene

Approach Toward 2,6-Dibromo-4,8-Dicarbomethoxy-Semibullvalene

The proposed approach toward 2,6-dibromo-4,8-dicarbomethoxy-semibullvalene involves the formation of tetrabromide intermediate **101** from the diester enol **66**. Subsequent cyclization of tetrabromide to the dibromo diester teracyclic **102** is the key to this synthetic scheme. The dibromo diester tetracyclic intermediate can then be converted to the corresponding semibullvalene **95** through the use our general synthetic scheme (Scheme 40).

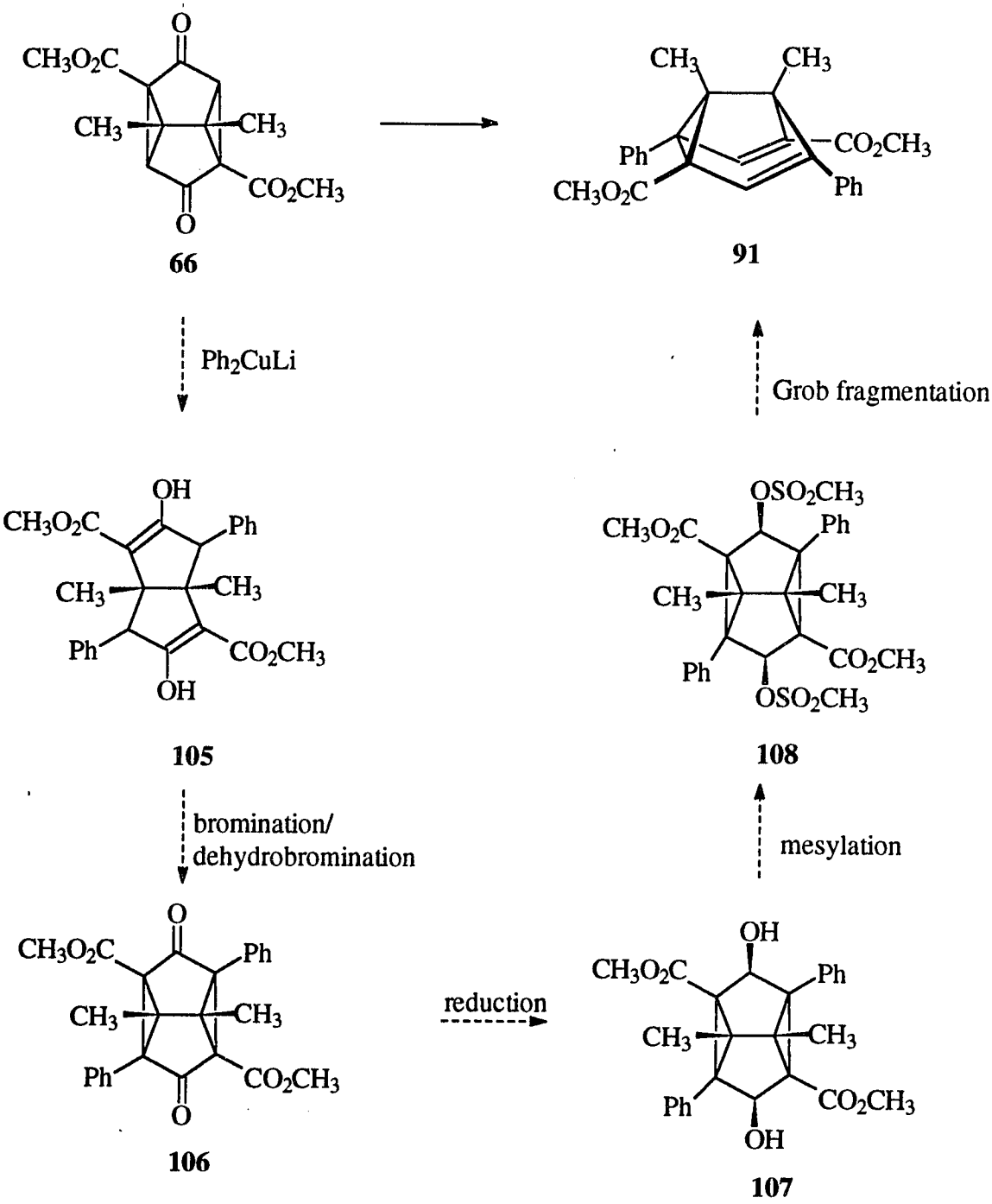


Scheme 40

Approach Toward 2,6-Dibromo-4,8-Dicarbomethoxy Semibullvalene

Approach Toward 2,6-Diphenyl-4,8-Dicarbomethoxy Semibullvalene

The proposed approach toward 2,6-diphenyl-4,8-dicarbomethoxy-semibullvalene **91** involves nucleophilic opening of the cyclopropane ring in tetracyclic **66** by a diphenyl copper lithium. Subsequent formation of the tetracyclic diphenyl diester **106** is the key to this synthetic scheme. The diphenyl diester tetracyclic intermediate **106** can then be converted to the corresponding semibullvalene **91** through the use our general synthetic scheme (Scheme 41).

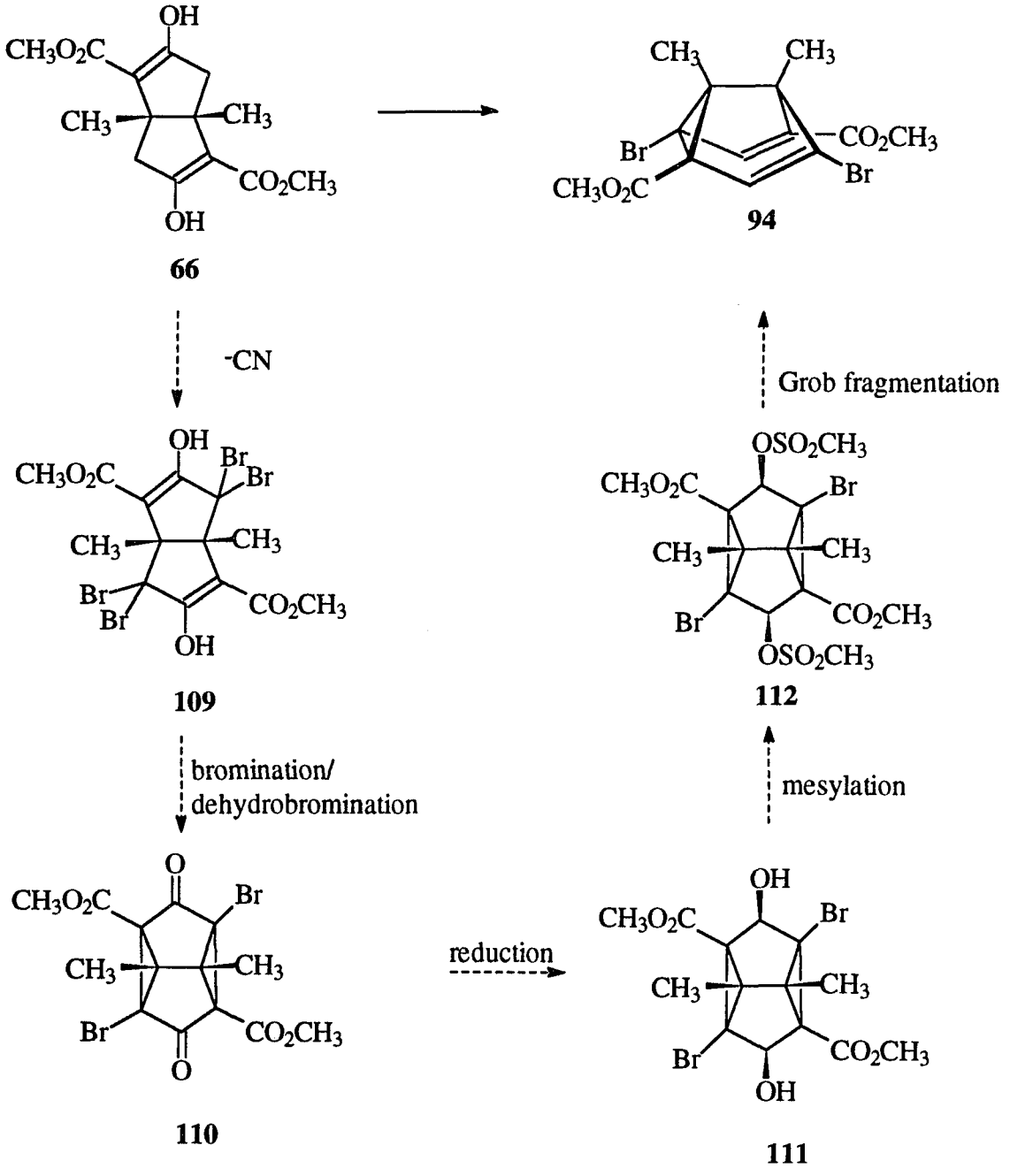


Scheme 41

Approach Toward 2,6-Diphenyl-4,8-Dicarbomethoxy Semibullvalene

2,6-Dicarbomethoxy-4,8-dicarbo(tert-butyl)-1,5-dimethyl semibullvalene

The approach toward 2,6-dicarbomethoxy-4,8-dicarbo(tert-butyl)-1,5-dimethyl-semibullvalene **94** involves the addition of di-tert-butyl carbonate in the presence of sodium hydride to form the tetraester enol **109**. Subsequent isolation of the corresponding semibullvallene should result by following our general method of synthesizing semibullvalenes. (Scheme 42)

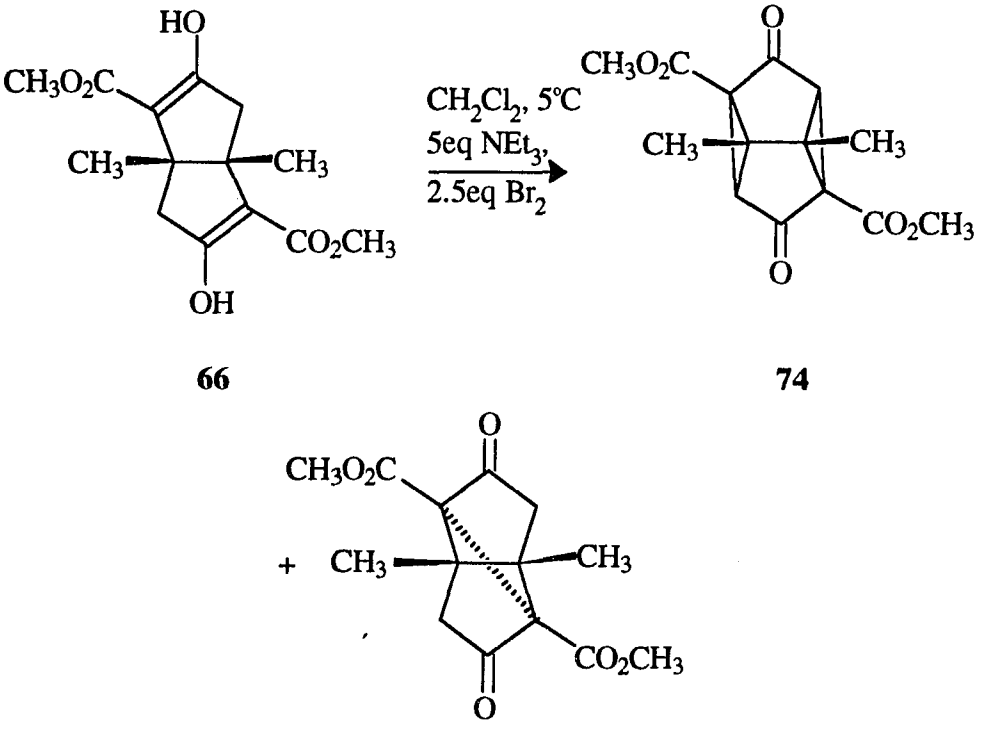


Scheme 42

Approach Toward 2,6-Dicarbomethoxy-4,8-Dicarbo(tert-butyl)-1,5-Dimethyl Semibullvalene

Approach Toward Unusual Semibullvalene

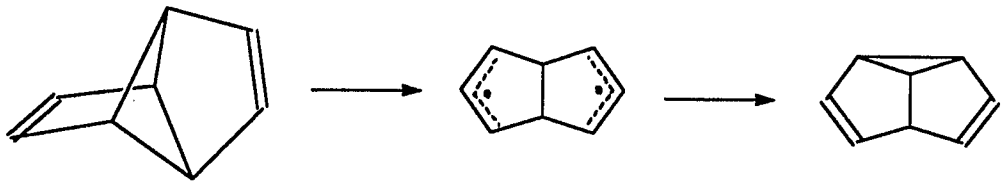
The bromination and dehydrobromination of diester enol **66** leads to the desired tetracyclic dione **74** and compound **75** (Scheme 43). Cyclobutane **75** could be converted to novel semibullvalenes **81** and/or **82** by first making the diol **113** and converting the corresponding dimesylate derivative **114** to a diene **115**. The diene **115** can then be heated mildly to the corresponding semibullvalene (Scheme 45). This procedure is based on known methodology in the literature (Scheme 44).



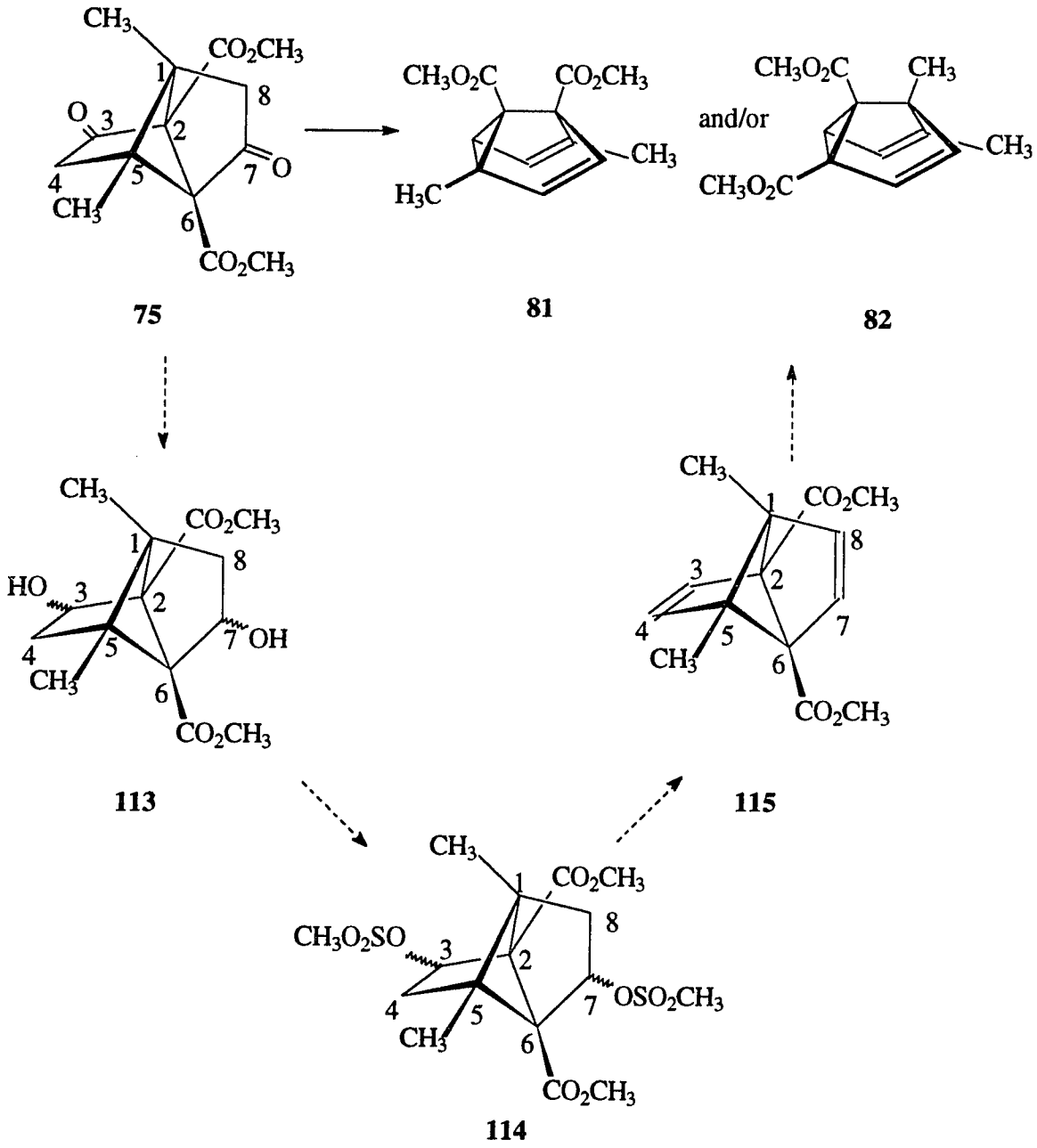
66 **74**

75

Scheme 43



Scheme 44



Scheme 45

Approach Toward Novel Semibullvalene

EXPERIMENTAL SECTION

CHAPTER 6

General procedure

Glassware used for an air or moisture sensitive reactions was dried in an oven at 120°C overnight, then flushed with nitrogen or argon before use. All non aqueous reactions were run under a blanket of either anhydrous nitrogen or argon. Usually a three neck round bottom flask was equipped with a pressure equilibrating dropping funnel, a magnetic stirrer, a rubber septum, and a reflux condenser. The top of the condenser was connected to a three-way stopcock with one branch connected to the nitrogen source and the other to a drying tube. Drying tubes were filled with anhydrous calcium chloride or potassium hydroxide as required. Reactions were followed by TLC whenever possible.

Spectroscopy

^{1}H and ^{13}C NMR were recorded on a 300-MHz General Electric QE-300 spectrometer. Samples were prepared in chloroform-d (99.8% D, 0.03% V/V TMS, Aldrich), unless where noted. Chemical shifts were measured in parts per million downfield from tetramethylsilane internal standard. Resonance splitting are described as s = singlet, t = triplet, m = multiplet, b = broad and AB = AB quartet. Coupling constants are reported in Hertz (J value). Labile protons were exchanged using deuterium oxide (99.8% D, Aldrich Gold Label).

Variable temperature solution 13C-NMR spectra were measured on the JEOL 400 spectrometer.

Infrared spectra were recorded on a Perkin-Elmer 1310 IR spectrometer during 12 minute scans, and calibrated with a polystyrene film. Bands and reported in wave numbers. Liquid samples were prepared as thin films deposited between sodium chloride cells (32x4mm). Solid samples were prepared as either melts or in solutions using sodium chloride cells and carbon tetrachloride or chloroform as the solvent or as KBr pellets.

X-Ray

The intensity data were measured on an Enraf-Nonius CAD4 diffractometer (graphite monochromated Cu Kα radiation, w-2Q scans). The structure was solved by using a multiple procedure solution and was refined by full matrix least squares. In the final refinement, the non hydrogen atoms were refined anisotropically. The hydrogens were included in the structure-factor calculations but their parameters were not refined.

Melting points

Melting points were recorded on a Buchi instrument in soft glass capillary tubes (1.5x90mm) and are uncorrected.

Chromatography

(a) Thin layer chromatography was performed using pre-coated plastic sheets of silica gel, with a thickness of 0.25 mm, supplied by Macherey-Nagel. UV active compounds were observed by 254 nm UV lamp. Non UV active compounds were either developed in iodine chambers or with phosphomolybdic acid in ethanol (230 g PMA/1 gal 95% ethanol). Ratio to front values (R_f) were measured from the center of the respective spot to its initial position divided by the distance traveled by the solvent.

(b) Flash and regular chromatography were performed according to published procedures using silica gel grade 60, available from Aldrich.

(c) Radial chromatography was used to separate 0.5g or less of samples. Chromatotron model 7924T made by Harrison research was used. The chromatotron plates were coated with silica gel 60 PF-254 containing calcium sulfate, available from EM Science or VWR Scientific, according to a recipe supplied by Harrison. The sample was introduced using the minimum amount of solvent, dried and eluted with hexane. The polarity of the eluent was increased only after a good separation was observed. Polarity changes were accomplished with 2.5 % increments of ethyl acetate. The plates were observed using a UV lamp.

(d) The eluents were distilled prior to use.

Solvents and reagents

Solvents were ACS reagent grade and available from Fisher Scientific or Aldrich. Commercially available reagents were obtained from Aldrich. Anhydrous diethyl ether and ethanol were obtained from other suppliers. All solvents were distilled as follows prior to use.

Tetrahydrofuran: distilled under nitrogen over potassium metal

Dimethyl sulfoxide: distilled under nitrogen over calcium hydride

Triethylamine: distilled over sodium metal

Methanol: distilled over magnesium metal

Methylene chloride: distilled over calcium hydride

Ethyl acetate: distilled over calcium hydride

Hexane: distilled over calcium hydride

Acetone: distilled over calcium chloride

Standard workup

When necessary, the reaction mixtures were first neutralized . In the case of reactions involving bromine, sodium bisulfite was added to the ice water in the separatory funnel. The desired compound was then extracted with the use of diethyl ether as the organic solvent. The aqueous layer was then extracted with 3 portions of diethyl ether. The combined organic layer was dried over magnesium sulfate, which was then removed by gravity filtration. The organic solvent was then distilled by a rotoevaporator. The crude material was then weighed and purification followed.

EXPERIMENTAL

Compound **41**

Tetramethyl-3,7-dihydroxy-1,5-(9,10-Phenanthra)-bicyclo-[3.3.0]-octa-2,6-diene-2,4,6,8-tetracarboxylate from the Weiss reaction.

Sodium hydroxide (7.6 g, 192 mmol) was dissolved in methanol (600 mL) in a 1 L, 2 neck, round bottom flask (rbf). 1,3-Dimethyl-acetonedicarboxylate (16.76 g, 96 mmol) was added dropwise through a dropping funnel. The solution was then heated to 60°C, and phenanthrenequinone (8.0 g, 38.0 mmol) was added slowly. The dark solution which is cloudy orange turned dark brown while it was stirred at about 68°C during the following 48 hours. At this point the reaction was then cooled to room temperature and the precipitate formed was collected through vacuum filtration and dissolved in 100-150 mL of ice water. The ensuing solution was acidified with 10% HCl to pH 3. An analytical sample was recrystallized out of chloroform and carbon tertrachloride. Compound **41** was used without further purification. Yields range from 10-60%. Melting point for pure compound 218-220°C.

^{1}H NMR δ; 2.9 (s, 6H, OCH_3), 4.0 (s, 6H, OCH_3), 4.7 (s, 2H, CH), 7.24-7.27 (t, 2H, aromatic), 11.30 (broad, 2H, enol).

^{13}C NMR δ; 51.88 (OCH_3), 52.20 (OCH_3), 58.53 (CH), 59.18 ($C_{1,5}$), 108.51 ($C_{3,7}$), 122.92 ($C_{2,6}$), 127.84 (aro), 128.14 (aro), 128.34 (aro), 131.40 (aro), 135.52 (aro), 167.96 (aro), 170.69 ($C_{4,8}$), 175.84.(C=O)

Compound **44**

Cis-1,5-(9.10-phenanthra)-bicyclo-[3.3.0]-octane-3,7-dione from compound **41.**

In a 250 mL flask a mixture of compound 14 (5.2 g, 10 mmol) in glacial acetic acid (108 mL) and 85% phosphoric acid (6 mL) was stirred and refluxed overnight. The mixture was stirred for 1/2 hour in a beaker containing 200 g of ice water, and neutralized slowly by adding 25% NaOH until pH is 9. A brownish precipitate formed and the whole mixture was transferred to a separatory funnel where the standard workup was used to extract the crude dione. Purification was done by column chromatography, 1:2 ethyl acetate to hexane. (mp: 229-230°C, 2.4 g, 8.3 mmol, R_f 0.46 , 69% yield).

^{1}H NMR δ; 2.6 and 2.9 (ab quartet, 8H, CH_2), 7.3-7.9 (m, 6H, aromatic), 7.9-7.9 (m, 2H, aromatic)

Compound **47**

Cis-1,5-(9.10-phenanthra)-bicyclo-[3.3.0]-octane-2,4,6,8-octadeutero-3,7-dione from compound **44.**

Dione **44** was dissolved in 5 mL of freshly distilled dioxane and added to a 20 mL solution of NaOD in D_2O in a 50 mL rbf. The reaction was stirred at room temperature for 2 days. Deutero analog **47** was neutralized with 1M HCl and extracted with methylene choride. Standard workup conditions followed.

^{1}H NMR δ; 7.3-7.9 (m, 6H, aromatic), 7.9-7.9 (m, 2H, aromatic)

Compound **49**

Tetramethyl-3,7-dihydroxy-1,5-(1,2-acenaphtha)-bicyclo-[3.3.0]-octa-2,6-diene-2,4,6,8-tetracarboxylate from the Weiss reaction.

In a 1 L solution containing a stirring solution of sodium hydroxide (8.4 g, 100 mmol) and methanol (300 mL), 1,3-dimethylacetone dicarboxylate (8.4 g, 48 mmol) was slowly added through a dropping funnel. The whitish solution was heated by oil bath to reflux and the acenaphthenequinone (3.6 g, 20 mmol) was added slowly. This orange solution turned brownish black after stirring at reflux for 48 hours. The resulting solution was allowed to cool to room temperature and the contents were added to a 1 L beaker containing ice water (300 g), while stirring rapidly the solution was acidified using 10% HCl, until pH 3. The precipitate formed was collected by vacuum and dried by air overnight. Purification was achieved by first digesting with methanol and then recrystallizing from ethyl acetate/hexanes. (mp: 209-211°C, 3.28 g, 6.6 mmol, yield 33%).

^{1}H NMR δ; 2.976 (s, 6H), 4.080 (s, 6H), 4.268 (s, 2H), 7.432, 7.484, 7.637 (m, 6H), 10.641 (broad enol, 2H)

^{13}C δ; 51.7 (OCH_3), 52.0 (OCH_3), 60.5 (CH), 67.8 ($C_{1,5}$), 106.7 ($C_{3,7}$), 120.9, 124.7, 127.5, 131.4, 138.3, 142.5 (aromatic), 168.3 (), 169.25 ($C_{2,6}$), 171.6 (C=O).

Compound **59**

Cis-1,5-(1,2-acenaphtha)-bicyclo-[3.3.0]-octane-3,7-dione from compound **49**.

In a 250 mL flask a mixture of compound 17 (4.94 g, 10 mmol) in glacial acetic acid (108 mL) and 85% phosphoric acid (6 mL) was stirred and refluxed for 3 hours. The

mixture was stirred for 1/2 hour in a beaker containing 200 g of ice water, neutralized slowly by adding 25% NaOH until pH is 9. A white precipitate formed and the whole mixture was transfered to a separatory funnel where the standard workup was used to extract the crude dione.. Recrystallization from ethyl acetate/hexanes white shiny crystals (1.98 g, 7.55 mmol, 75% yield).

^{1}H NMR δ; 2.8 and 2.9 (AB quartet, 8H), 7.3-7.7 (m, 6H, aromatic)

Compound **62**

Cis-1,5-(1,2-acenaphtha)-bicyclo-[3.3.0]-octane-2,4,6,8-octadeutero-3,7-dione from compound **59**.

Dione **59** was dissolved in 5 mL of freshly distilled dioxane and added to a 20 mL solution of NaOD in D_2O in a 50 mL rbf. The reaction was stirred at room temperature for 2 days. Deutero analog **59** was neutralized with 1M HCl and extracted with methylene choride. Standard work up conditions followed.

^{1}H NMR δ; 7.3-7.7 (m, 6H, aromatic)

Compound **51**

Tetramethyl-1,5-(1,2-acenaphtha)-tetracyclo[3.3.0^{2,8}.0^{4,6}]octane-3,7-dione-2,4,6,8-tertracarboxylate from compound **49**

In a 50 ml 2 neck rbf fitted with a spetum and a 10 ml dropping funnel a stirring solution of compound 17 (1.0 g, 2 mmol) and , methylene chloride (30 ml) was cooled to

ice bath temperature. 6 equivalents of triethylamine (.1.12 g, 0.65 ml, 12 mmol) were slowly syringed through the spetum .and after 10 minutes 2.2 equivalents of bromine (0.64 g, 4 mmol, 2 ml of a 2 M bromine/methylene chloride solution) were slowly added over a period of 1/2 hour. The cloudy whitish solution slowly turned reddish and back to white after each drop of the bromine solution was added. the reaction was stirred for about three hours and the temperature was allowed to come up to room temperature. A standard workup followed after the initial wash with ice water and sodium bisulfite to remove the excess bromine. Recrystallization from ethyl acetate/hexanes yielded white crystals (mp: 207-208°C, 0.58 g, 1.2 mmol, 60%).

^{1}H NMR δ; 3.9 (s, 12H, OCH_3), 7.5-7.9 (m, 6H, aromatic).

Compound **52**

Tetramethyl-1,5-(1,2-acenaphtha)-tetracyclo[3.3.0^{2,8}.0^{4,6}]octane-3,7-diol-2,4,6,8-tertracarboxylate from compound **51**

In a 50 ml 3 neck rbf, fitted with a 10 mL dropping funnel a thermometer and a gas adapter, dry and freshly distilled toluene (10 mL) was stirred under a blanket of argon. The stirring mixture was cooled to ice bath temperature and to it 6 eq of 1 M t-iso-butyl aluminum/toluene solution were added dropwise (10 mL, 10 mmole) over 0.5 hour. The stirring solution was kept at ice bath temperature for 3 hours in which time the creamy peach mixture turned clear. At this point the mixture is slowly acidified wiith 0.5 mL portions of 3 M HCl, while keeping the temperature below 10°C. The solid formed was removed by vacuum filtration and discarded. The mother liquor which contains compound 20 was extracted by a standard workup. White crystals were recovered after recrystallization in ethyl acetate/hexanes (mp: 260-262°C, 0.50 g, 1.0 mmol, 51% yield).

^{1}H NMR δ; 3.5 and 3.6 (d, 2H), 3.8 (s, 12H, OCH_3), 5.0 and 5.1 (d, 2H,), 7.5-7.7 (m, 6H, aromatic)

Compound **53**

Tetramethyl-1,5-(1,2-acenaphtha)-tetracyclo[3.3.0^{2,8}.0^{4,6}]octane-3,7-dimesylate-2,4,6,8-tertracarboxylate from compound **52**.

In a 250 mL rbf charged with a stirring bar, compound 20 (1.5 g, 3 mmol) was dissolved in dry metylene chloride (94 mL) and 2.9 eq. of triethylamine (1.2 mL, 9 mmol). The solution was cooled to 5°C while a solution of methane sulfonyl chloride (0.6 mL, 7.5 mmol) in methylene chloride (20 mL) was slowly added through a dropping funnel over 0.5 hour. The reaction was stirred for 3 hours while it reached room temperature. A standard workup followed after neutralization with 10% HCl. Shiny white crystals were collected by recrystallization from ethyl acetate/hexanes (1.1 g, 1.9 mmol, 57%).

^{1}H NMR δ; 2.952 (s, 6H), 3.814 (s, 12H), 6.077 (s, 2H), 7.582-7.862 (m, 6H)

Compound **3**

Tetramethyl-1,5-(1,2-acenaphtha)-2,4,6,8-tetracaboxylate-semibullvalene from compound **53**.

Dimesylate **53** (1 g, 1.5 mmol), NaI (3.7 g, 25 mmol) and K_2CO_3 (0.5 g) were stirred in 50 mL of dry acetone at room temperature under nitrogen. After stirring for 25

h, the red-brown colored reaction was quenched with 200 mL of ice water and dry ice. Reaction was washed with 90 mL of 10% aqueous Na_2SO_3 solution to remove excess I_2 and extracted with ether (4 x 200 mL). Standard workup followed. Only multicomponetent mixture was isolated.(0.5 g, 1.1mmol, 72%)

^1H NMR δ; multicomponent mixture NMR with a characteristic peak at 6.8 ppm. (See Appendix 1)

Compound **49a**

Tetramethyl-3,7-dihydroxy-1,5-(1,2-acenaphtha)-bicyclo-[3.3.0]-octa-2,6-diene-4,8-dibromide-2,4,6,8-tetracarboxylate from compound **49.**

In a 50 ml 2 neck rbf fitted with a spetum and a 10 ml dropping funnel a stirring solution of compound 17 (13.24 g, 27 mmol) and, methylene chloride (300 ml) was cooled to ice bath temperature 6 equivalents of triethylamine (13.6 g, 18.8 ml, 135 mmol) were slowly syringed through the spetum.and after 10 minutes 2.2 equivalents of bromine (30 mmol, 30 ml of a 1 M bromine/methylene chloride solution) were slowly added over a period of 1/2 hour. The cloudy whitish solution slowly turned reddish and back to white after each drop of the bromine solution was added. the reaction was stirred for about three hours and the temperature was allowed to come up to room temperature. A standard workup followed after the initial wash with ice water and sodium bisulfite to remove the excess bromine. Recrystallization from ethyl acetate/hexanes yielded white crystals (mp:211-213°C, 3.78 g, 5.6 mmol, 28.4% yield). For x-ray see Appendix 1.

^1H NMR δ; 3.287 (s, 6H), 4.041 (s, 6H), 7.480-7.512 (t, 2H), 7.603-7.627 (d, 2H), 7.725-7.752 (d, 2H)

Compound **65**

Tetramethyl-3,7-dihydroxyl-1,5-Dimethyl-bicyclo-[3.3.0]-octane-2,4,6,8-tetracarboxylate from the Weiss reaction.

In a 1 L Erlenmyer flask 800 mL of freshly prepared buffer at pH 9.2 (carbonate/bicarbonate) was rapidly stirred while 1,3-dimethyl-acetone-dicarboxylate was added (50 mL, 0.34 mol). The resulting cloudy white solution was stirred rapidly while butane dione was added in one shot (15 mL, 0.17 mol). The resulting yellow solution was stirred at room temperature for 2 days. The solid formed was collected by vacuum filtration and allowed to air dry overnight. Compound **65** was used without further purification (mp: 156-159°C, 65.38 g, 0.16 mol, 96% yield)

^{1}H NMR δ; 1.29 (s, 6H), 3.75 (s, 6H), 3.87 (s, 6H), 3.94 (s, 2H), 10.62 (broad enol, 2H)

^{13}C NMR δ; 43.7, 51.4, 52.3, 103.6, 168.7, 170.2, 170.5.

Compound **12**

1,5-Dimethyl-bicyclo-[3.3.0]-octane-3,7-dione from compound **65**.

In a 2 L rbf charged with a stirring bar compound 23 (40.0 g, 100 mmol) was dissolved in 6 M HCl (858 mL). This mixture was stirred and refluxed for 48 hours until the solid had completely dissolved in the acid to a clear peach solution. This solution was neutralized with the proper equivalent of 6 M NaOH and extracted in the standard workup. The beige powder that resulted was easily purified by recrystallization from carbon tetrachloride (mp: 188-190°C, 10.0 g, 60 mmol, 60% yield)

^{1}H NMR δ; 1.578 (s, 6H), 2.754 (s, 2H), 3.804 (s, 6H)

^{13}C NMR δ: 36.3, 43.5, 217.5.

Compound **66**

Dimethyl-3,7-dihydroxyl-1,5-dimethyl-bicyclo-[3.3.0]-octane-2,6-dicarboxylate

Method (a) from compound **12**

A 100 mL rbf was charged with a stirring suspension of sodium hydride (2.4 g, 0.1 mol) in 50 mL of freshly distilled and dry dioxane and dimethylcarbonate (9.0 g, 8.4 mL, 0.1 mol). To this mixture a solution of compound **12** (1.66 g, 0.01 mol) in 30 mL of dioxane was slowly added through a dropping funnel at room temperature. The mixture was stirred overnight at 60°C then at 85°C for the last 3 hours. The standard workup was used to extract the resulting compound 25. Digestion from methanol gave shiny white crystals (mp: 136-139, 10% yield).

Method (b) from compound **65**

Compound **12** (4 g, 10 mmol) was added to 300 mL of 50% KOH solution in a 500 mL rbf. After stirring over 24 hours the precipitate was collected and then dissolved in 1L of distilled ice water in a 2L Erlenmeyer flask. This cold solution was stirred for 2 hours after it was acidified to pH 3 slowly. The precipitate, diacid/diester **71**, was collected by vacuum and added to a 2L rbf containing 1.3L of carbonate/bicarbonate buffer pH 9.2. The suspension was stirred and gently refluxed for about 2-3 hours, it was then cooled down to ice bath temperature and carefully acidified to pH 3. The precipitate, diester **66**, formed was collected and air dried. Purification by digestion in methanol yielded white crystals (mp: 138-140°C, 2.2 g, 7.8 mmol, 78% yield).

^{1}H NMR δ; 1.155 (s, 6H), 2.334, 2.395, 2.842, 2.903 (q, 4H), 3.727 (s, 6H), 10.684 (broad enol, 2H)

Compound **71**

Dimethyl-3,7-dihydroxyl-1,5-dimethyl-bicyclo-[3.3.0]-octane-2,6-dicarboxylate-4,8-dicarboxylic acid from compound **12**.

Diacid/diester **71** was the result of selective decarboxylation in of compound **12** (4 g, 10 mmol) in a stirring 200mL solution of 50% KOH at room temperature, overnight. The salt of diacid **71** was collected by vacuum filtration and dissolved in 200 mL of water in a 2L erlenmyer flask. To this rapidly stirring mixture an 800 mL portion of 1M HCl solution was added, the resulting solution was allowed to stir for 3 hours and the resulting precipitate was collected by vacuum and air dried. (mp: 139-150°C, 2.9 g, 7.8 mmol, 78% yield). Spectral data in appendix 1.

Compound **74**

Tetramethyl-1,5-dimethyl-tetracyclo[3.3.0^{2,8}.0^{4,6}]octane-3,7-dione-2,4,6,8-tertracarboxylate from compound **66**.

In a 100 ml rbf fitted with a 10 ml dropping funnel a stirring solution of compound **66** (2.6 g, 9.3 mmol) and , methylene chloride (50 ml) was cooled to ice bath temperature and 6 equivalents of triethylamine (.5.6 g, 5.6 ml, 56 mmol) were slowly syringed through a spetum .and after 10 minutes 2.2 equivalents of bromine (21 mmol, 11 ml of a 2 M bromine/methylene chloride solution) were slowly added over a period of 1/2 hour. The cloudy whitish solution slowly turned reddish and back to white after each drop of the bromine solution was added. the reaction was stirred for about three hours

and the temperature was allowed to come up to room temperature. A standard workup followed after the initial wash with ice water and sodium bisulfite to remove the excess bromine. Initial digestion over methanol led separation of **74** (crystals) from a mixture of **74** and **75** (mother liqour). Recrystallization from carbon tetrachloride yielded white crystals (mp: 198-199°C, (1.78 g, 4.0 mmol, 44% yield).

^{1}H NMR δ; 1.525 (s, 6H), 3.860 (s, 6H), 5.090 (s, 2H), 10.620 (broad enol, 2H)

Cyclobutane **75**

Methanol mother liqour conataning mixture of **74** and **75** was recrystallyzed out of acetone/methanol 12-15 times to yeild pure **75**. (Mp: 90-91°C) For x-ray see appendix 1.

^{1}H NMR δ; 1.2 (s, 6H, CH_3), 2.2 and 2.5 (AB quartet, 4H, CH_2), 3.8 (s, 6H, OCH_3).

Compound **79**

Tetramethyl-1,5-dimethyl-tetracyclo[3.3.0^{2,8}.0^{4,6}]octane-3,7-diol-2,4,6,8-tertracarboxylate from compound **74**.

An ice cooled suspension of 13.2 g (47 mmol) of dione **74** in a 500 mL rbf in 230 mL of freshly distilled toluene was stirred under a blanket of argon, and 180 mL of tri-iso-butylaluminum (180 mmol, 1M solution in toluene) was added. The clear yellow solution was stirred overnight. After cooling the reaction with an ice-bath, 20 mL of ice cooled 6M HCl was added cautiously. The reaction mixture was poured into ice water containing 1.0M HCl (50 mL total volume), and 50 mL of ethyl acetate. The water layer

was extracted with 30 mL portions of ethyl acetate six times. The water layer was further extracted with methylene chloride (20 mL x 3). After stadard workup conditions 6.12 g (46% yield, 21 mmol) were collected. Recrystallyzation of diol from ethyl acetate/hexanes of this powder led to shiny white crystals coresponding to a mixture of exo-exo, endo-exo and endo-endo. The diol was used a mixture.

^{1}H NMR δ; 1.5 (s, 6H, CH_3), 2.0 (d, 2H, 5 Hz, CH), 4.0 (s, 6H, OCH_3), 4.2 (broad s, 2H diol), 5.2 (d, 2H, 5 Hz, CH).

Compound **80**

Tetramethyl-1,5-dimethyl-tetracyclo[3.3.0^{2,8}.0^{4,6}]octane-3,7-dimesylate-2,4,6,8-tertracarboxylate from compound **79**.

A solution of 1.1 g (3.9 mmol) of the diol **79** and of freshly distilled triethylamine 1.6mL (12 mmol) in 40 mL of freshly distilled methylene chloride was cooled in an ice bath. A solution of ethanesulfonyl cloride (0.72 mL, 94 mmol) in 10 mL of methylene chloride was slowly added through a dropping funnel. The solution was allowed to stir up to room temperature over 3 hours. The product was isolated by dilution with ice water acidification with 10% HCl and follwed by extraction with methylene chloride. After the standard workup mesylate **80** was collected as an oil in 97% yield, and used as is for the following procedure. For spectral data see appendix 1.

Compound **4**.

Dimethyl-1,5-dimethyl-2,6-dicarboxylate-semibullvalene from mesylate **80**.

Dimesylate **80** (1.3 g, 2.9 mmol), NaI (3.7 g, 25 mmol) and K_2CO_3 (0.5 g) were stirred in 50 mL of dry acetone at room temperature under nitrogen. After stirring for 12 h, the red-brown colored reaction was quenched with 200 mL of ice water and dry ice. Reaction was washed with 90 mL of 10% aqueous Na_2SO_3 solution to remove excess I_2 and extracted with ether (4 x 200 mL). Standard workup followed. The oil collected was chromatograghed by high pressure column chromatography, 6:1 hexanes to ethyl acetate. Semibullvalene **4** was isolated in 7% yield (17 mg, $R_f = 0.38$).

^{1}H NMR δ; 1.2 (s, 6H, CH_3), 3.7 (s, 6H, OCH_3), 4.7 (d, 2H, CH), 5.8 (d, 2H, CH).

^{13}C NMR THF-d_8 δ; 12.4 (CH_3), 52.9 (OCH_3), 66.9 ($C_{1,5}$), 100.3 ($C_{3,7}$)), 101.5 ($C_{6,8}$)), 126.5 ($C_{2,4}$)), 168.4 (C=O).

APPENDIX 1: SPECTRAL DATA

Figure 32: ^{1}H-NMR Spectrum of Crude Reaction Product.

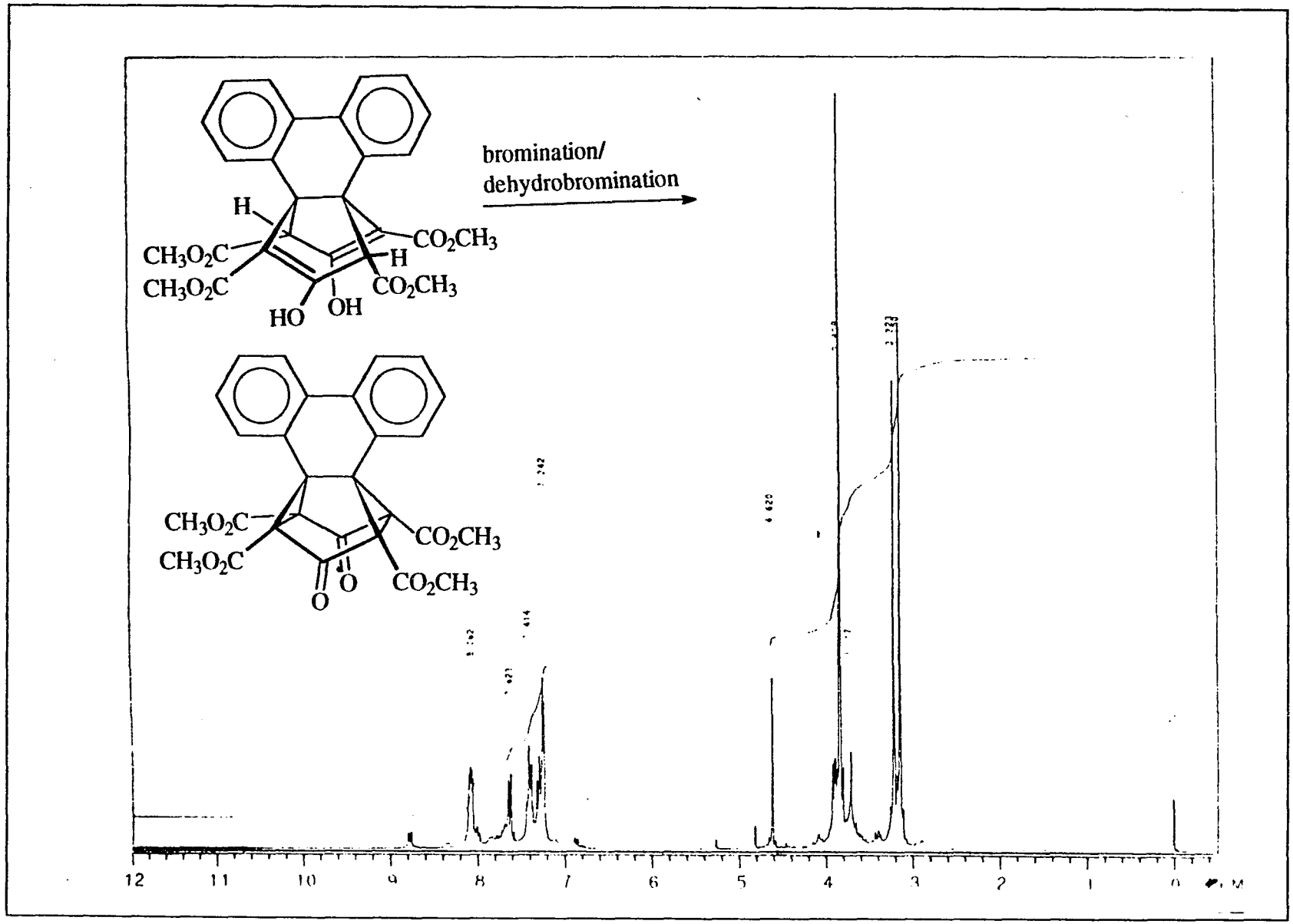
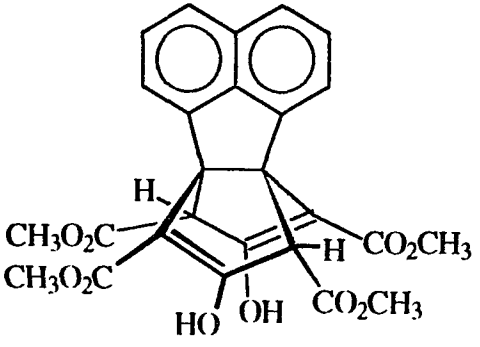

bromination/
dehydrobromination
H
CH3O2C
CH3O2C
CO2CH3
H
CO2CH3
HO
OH
CH3O2C
CH3O2C
CO2CH3
O
O
CO2CH3
12
11
10
9
8
7
6
5
4
3
2
1
0

Figure 33: ^{1}H-NMR Spectrum of **49**.


H
CH_3O_2C
CH_3O_2C
HO
OH
H
CO_2CH_3
CO_2CH_3

12
11
10
4

Figure 34: ^{1}H-NMR Spectrum of **53**.

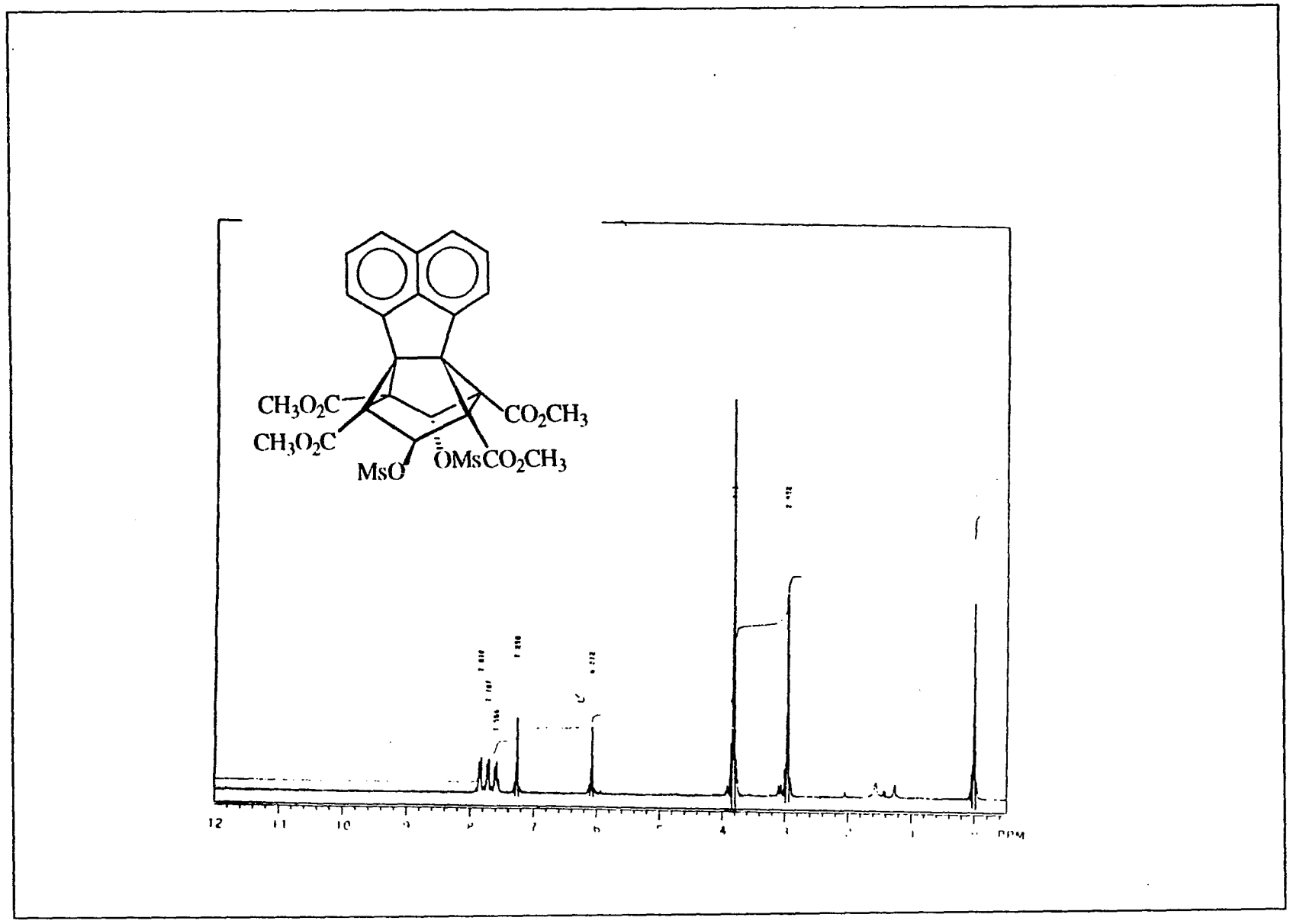

CH3O2C
CH3O2C
MsO
OMsCO2CH3
CO2CH3
12
11
10
PPM

Figure 35: ^{13}C-NMR Spectrum of **53**..

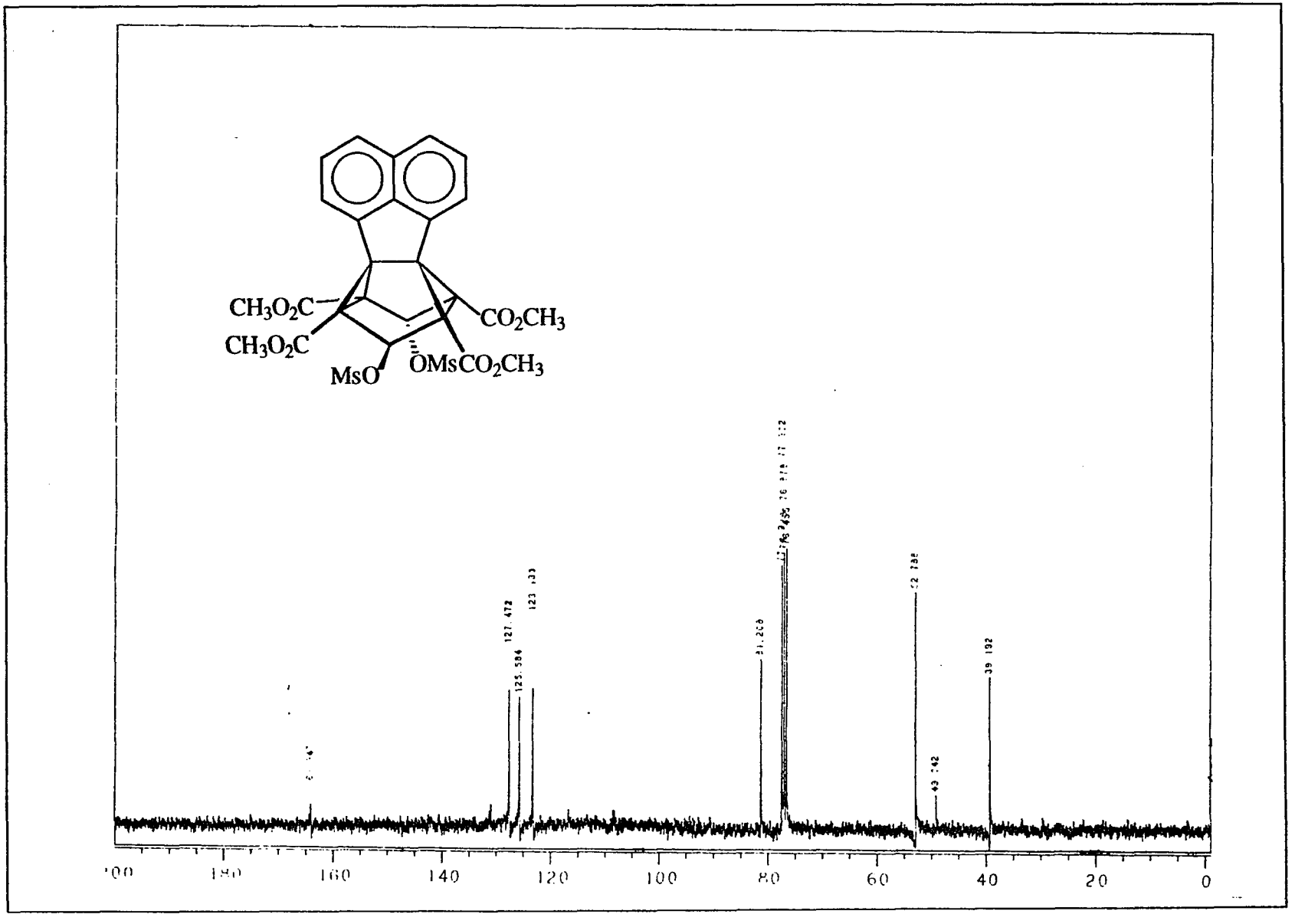

CH3O2C
CH3O2C
MsO
OMsCO2CH3
CO2CH3
127.472
125.584
123.133
81.269
52.138
49.542
39.192
200
180
160
140
120
100
80
60
40
20
0

Figure 36: ^{1}H-NMR Spectrum of **52**.

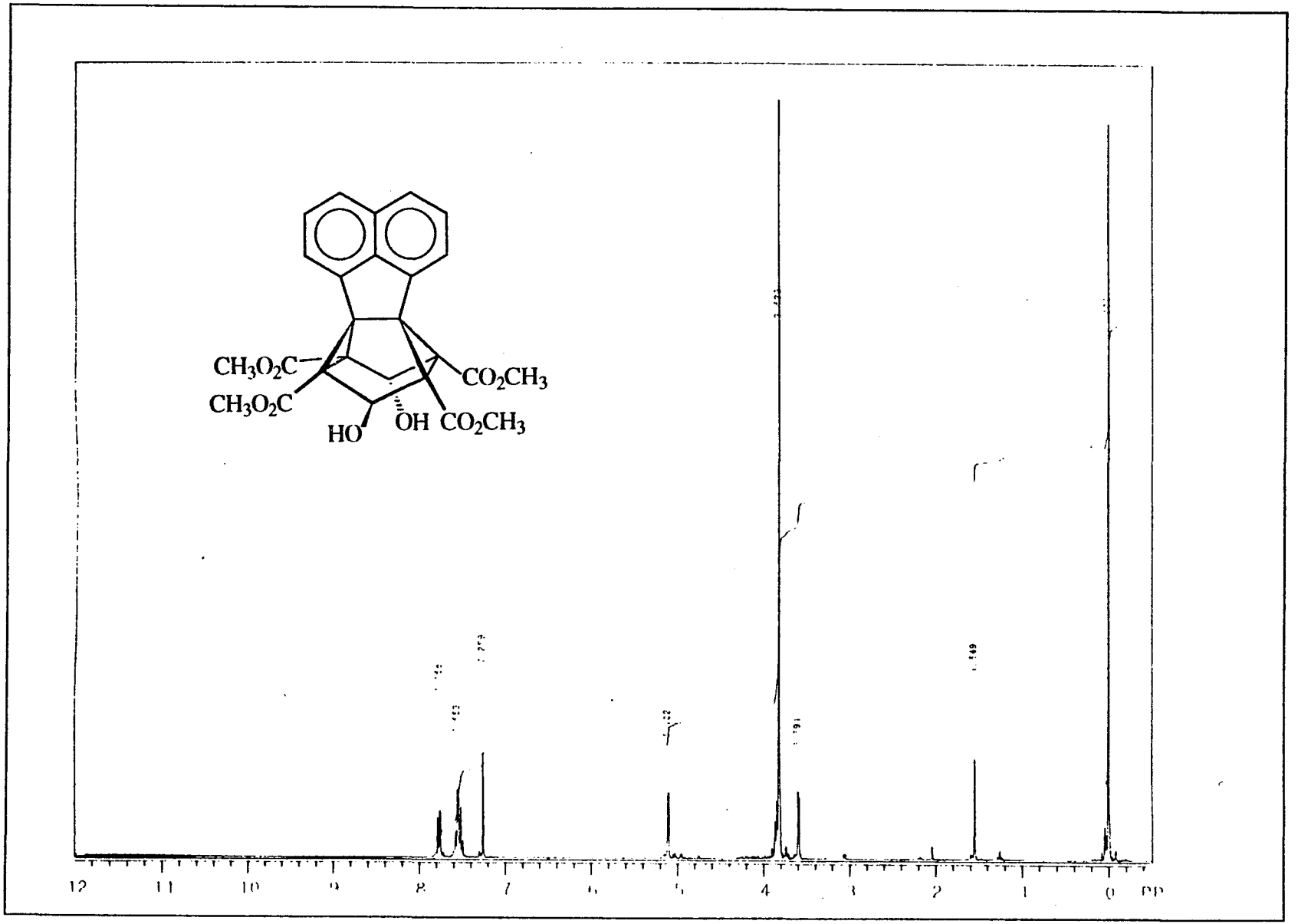

CH3O2C
CH3O2C
CO2CH3
HO
OH
CO2CH3
12
11
10
9
8
7
6
5
4
3
2
1
0
PP

Figure 37: ^{1}H-NMR Spectrum of **51**.

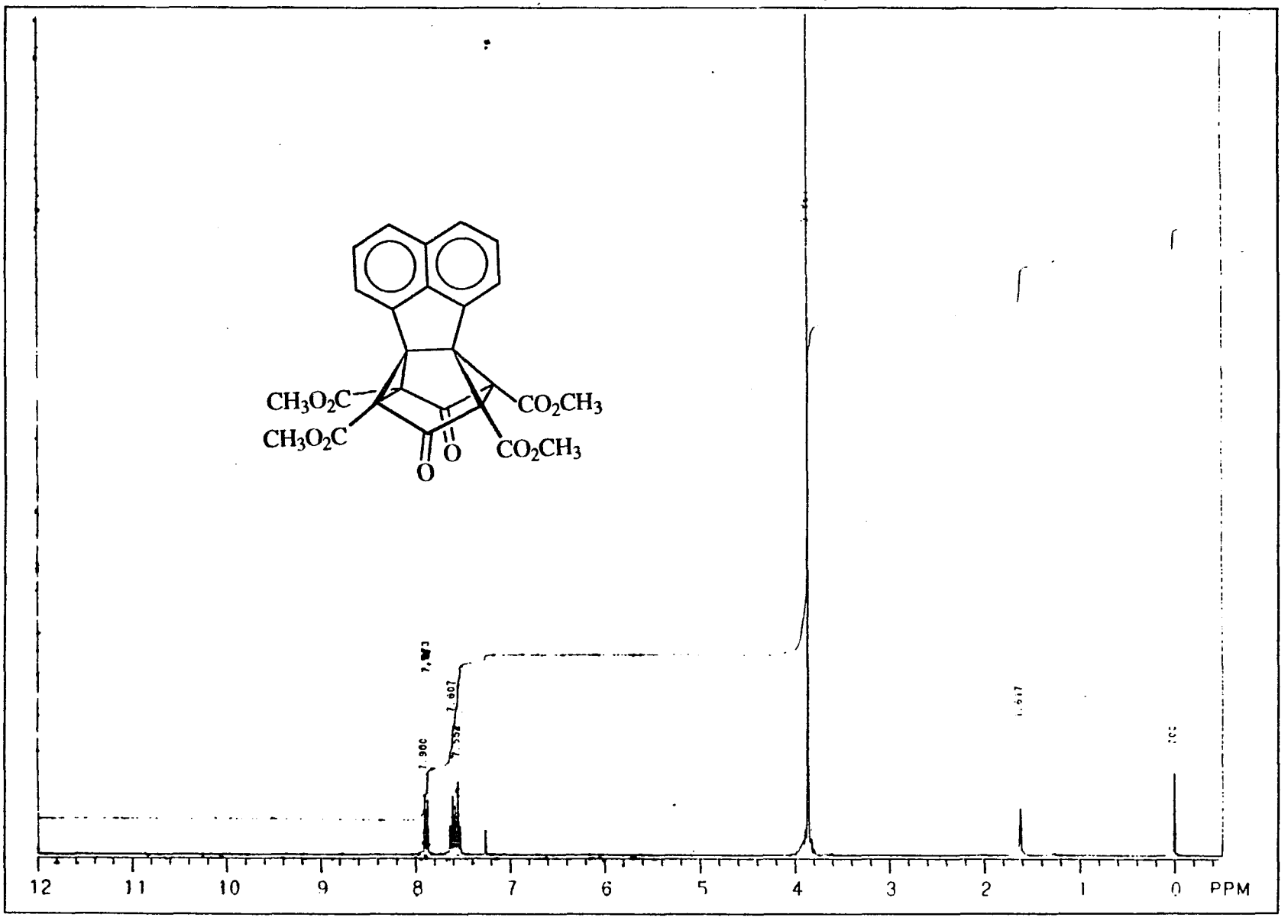

CH3O2C
CH3O2C
CO2CH3
CO2CH3
O
O
12
11
10
9
8
7
6
5
4
3
2
1
0
PPM

Figure 38: ^{13}C-NMR Spectrum of **51**.

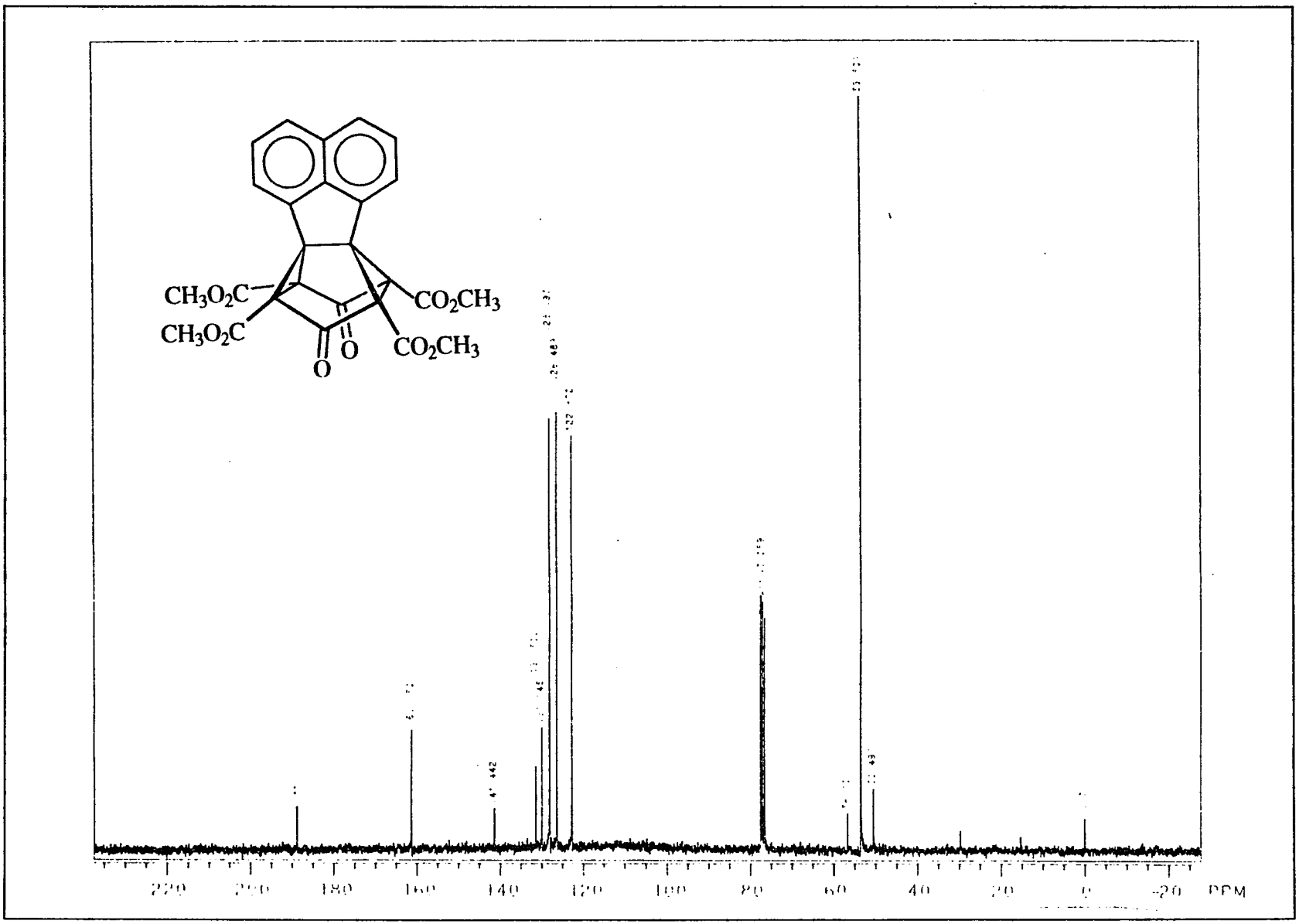

CH3O2C
CH3O2C
CO2CH3
CO2CH3
O
O
220
200
180
160
140
120
100
80
60
40
20
0
-20
PPM

Figure 39: ^{1}H-NMR Spectrum of **3**.

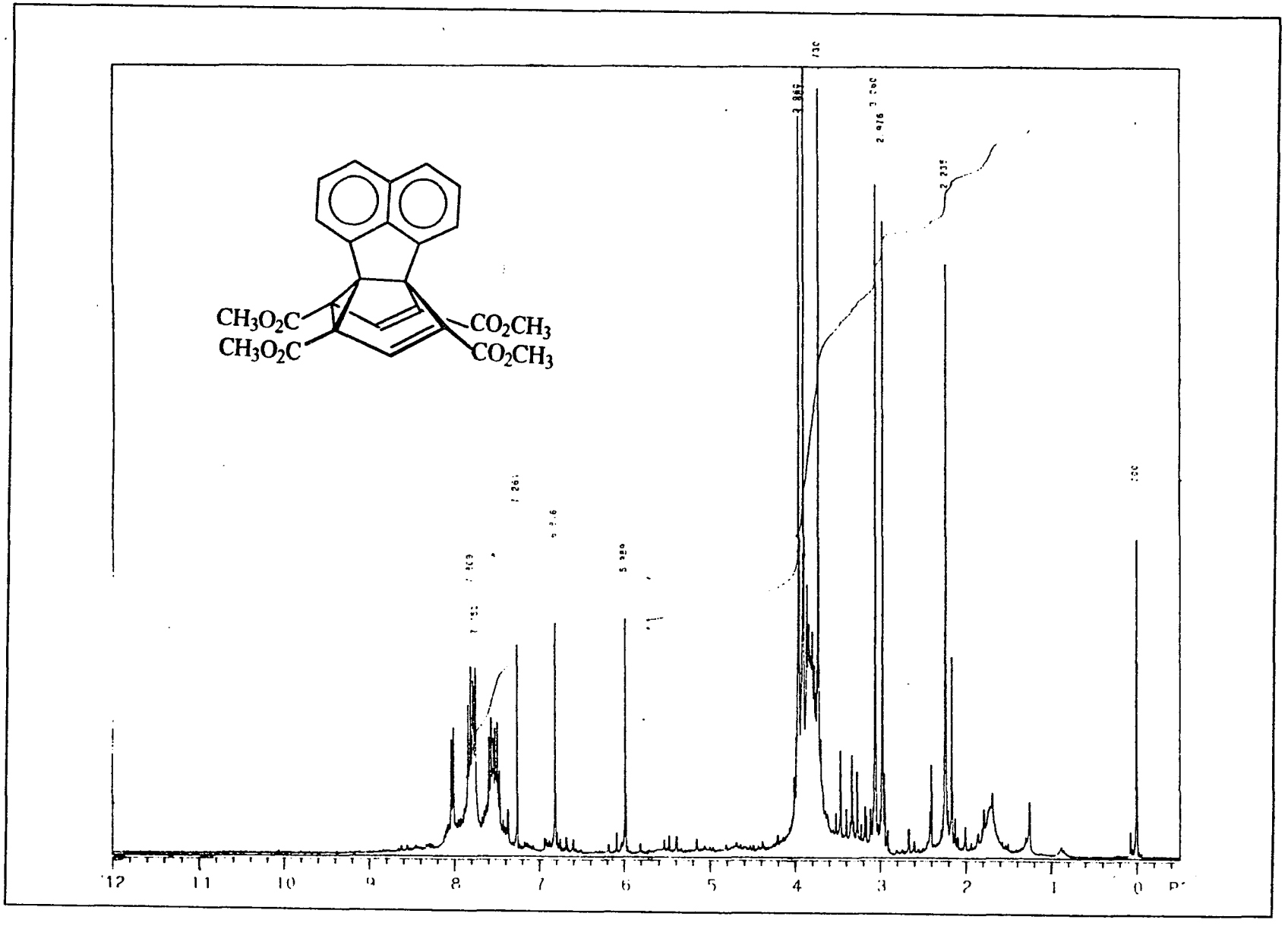

CH3O2C
CH3O2C
CO2CH3
CO2CH3
12
11
10
9
8
7
6
5
4
3
2
1
0

Figure 40: ^{1}H-NMR Spectrum of **71**.

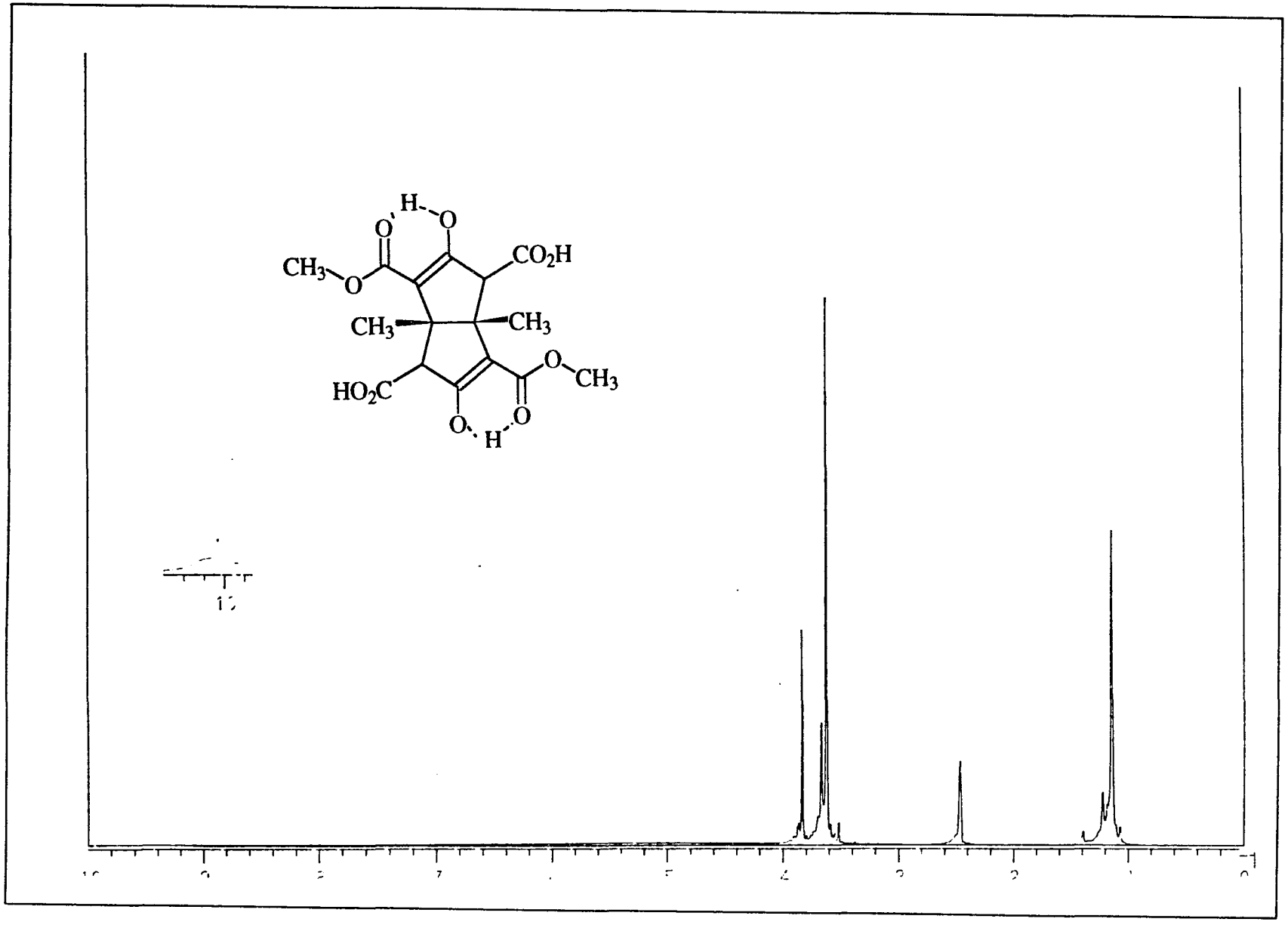

H
O
O
CH3
O
CO2H
CH3
CH3
HO2C
O
O
CH3
O
H

Figure 41: ^{13}C-NMR Spectrum of **71**.

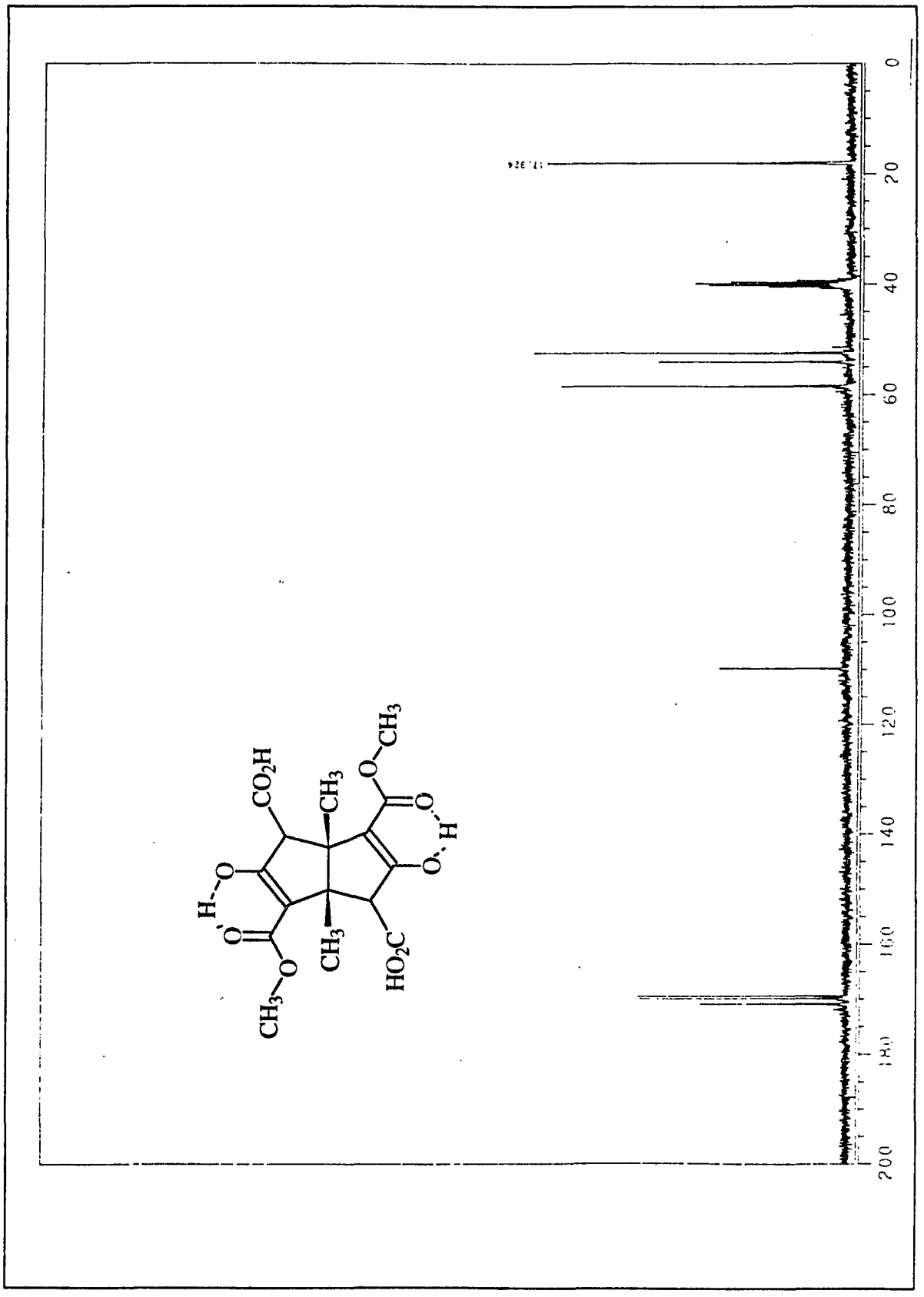

CO2H
CH3
O
CH3
O
H
O
O
H
O
CH3
O
CH3
HO2C
0
20
40
60
80
100
120
140
160
180
200

Figure 42: ^{1}H-NMR Spectrum of **66**.

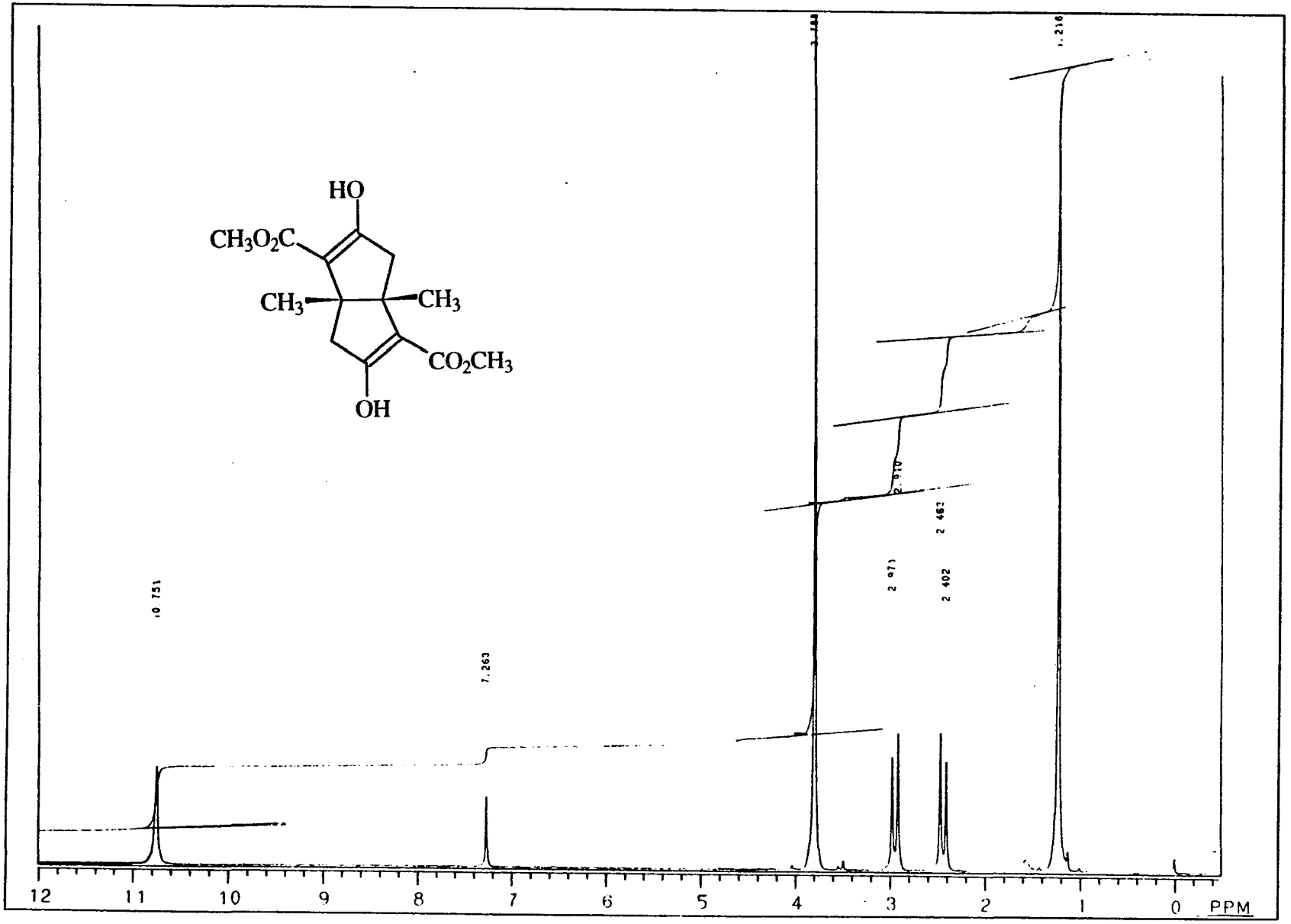

HO
CH3O2C
CH3
CH3
CO2CH3
OH
10.751
7.263
3.000
2.971
2.910
2.463
2.402
1.216
12
11
10
9
8
7
6
5
4
3
2
1
0
PPM

Figure 43: ^{13}C-NMR Spectrum of **66**.

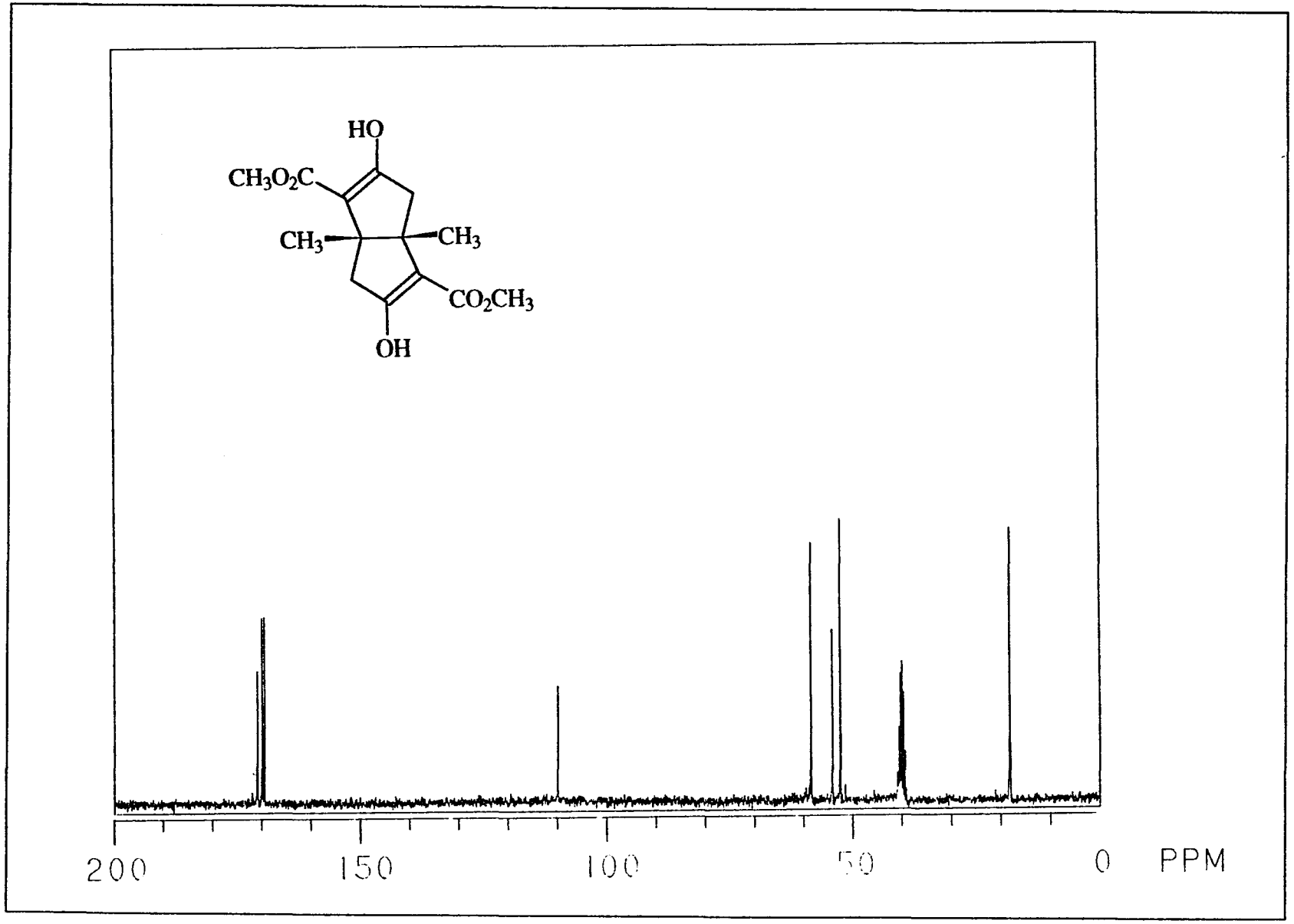

HO
CH3O2C
CH3
CH3
CO2CH3
OH
200
150
100
50
0
PPM

Figure 44: ^{1}H-NMR Spectrum of **74**.

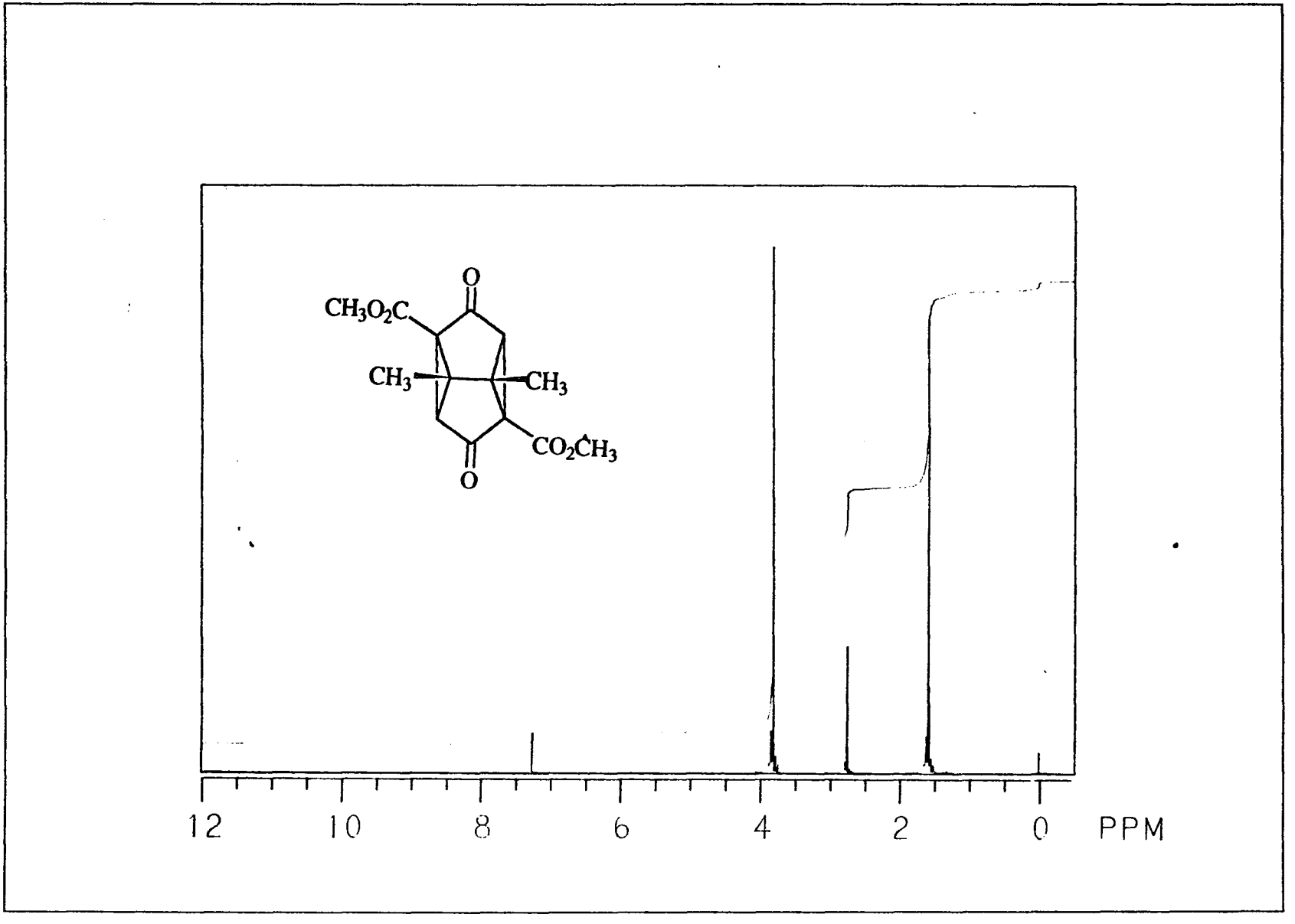

O
CH3O2C
CH3
CH3
CO2CH3
O
12
10
8
6
4
2
0
PPM

Figure 45: ^{13}C-NMR Spectrum of **74**.

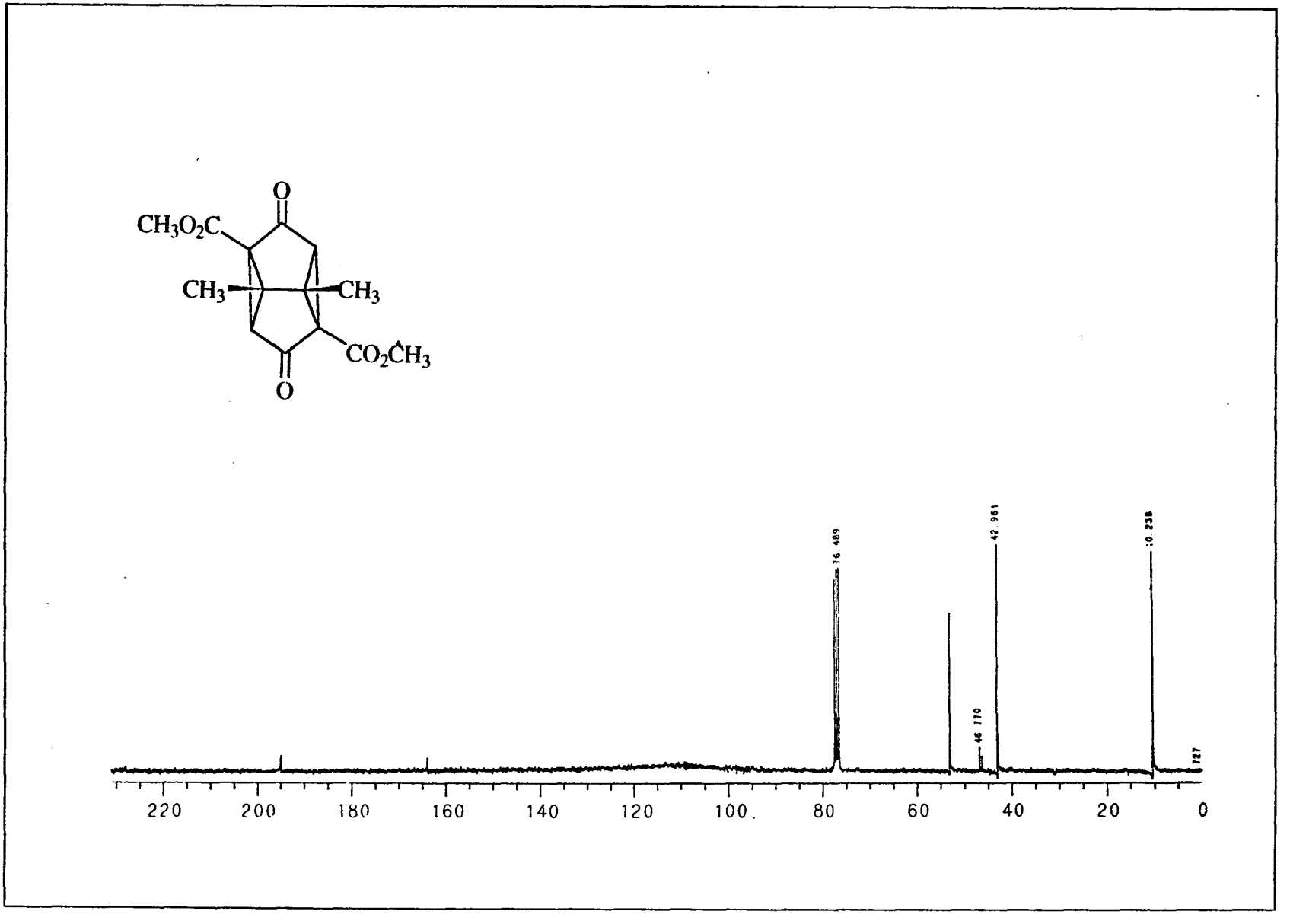

O
CH3O2C
CH3
CH3
CO2CH3
O
16.489
42.961
10.238
46.170
.727
220
200
180
160
140
120
100
80
60
40
20
0

Figure 46: ^{1}H-NMR Spectrum of **75**.

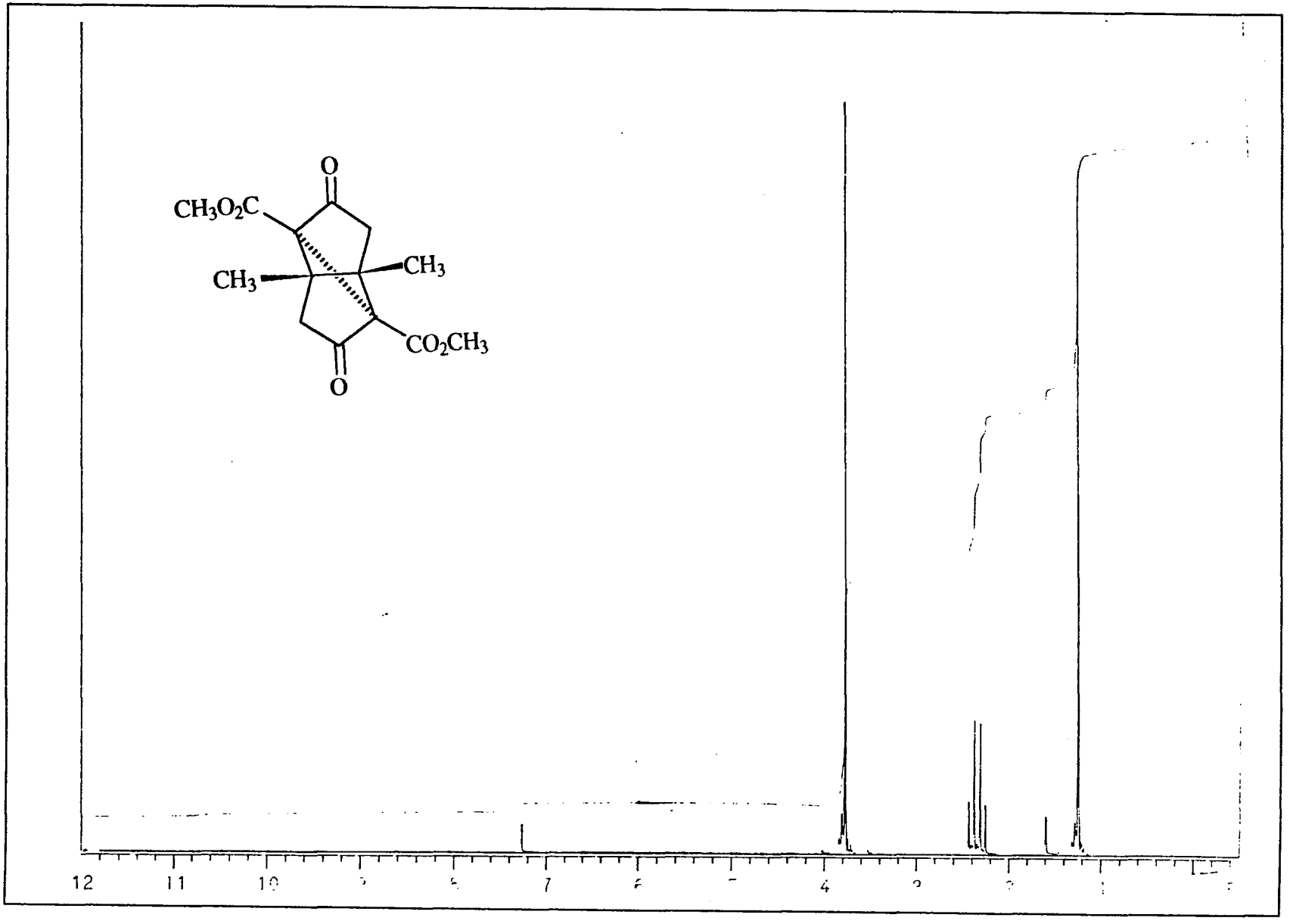

O
CH3O2C
CH3
CH3
CO2CH3
O
12
11

Figure 47: ^{13}C-NMR Spectrum of **75**.

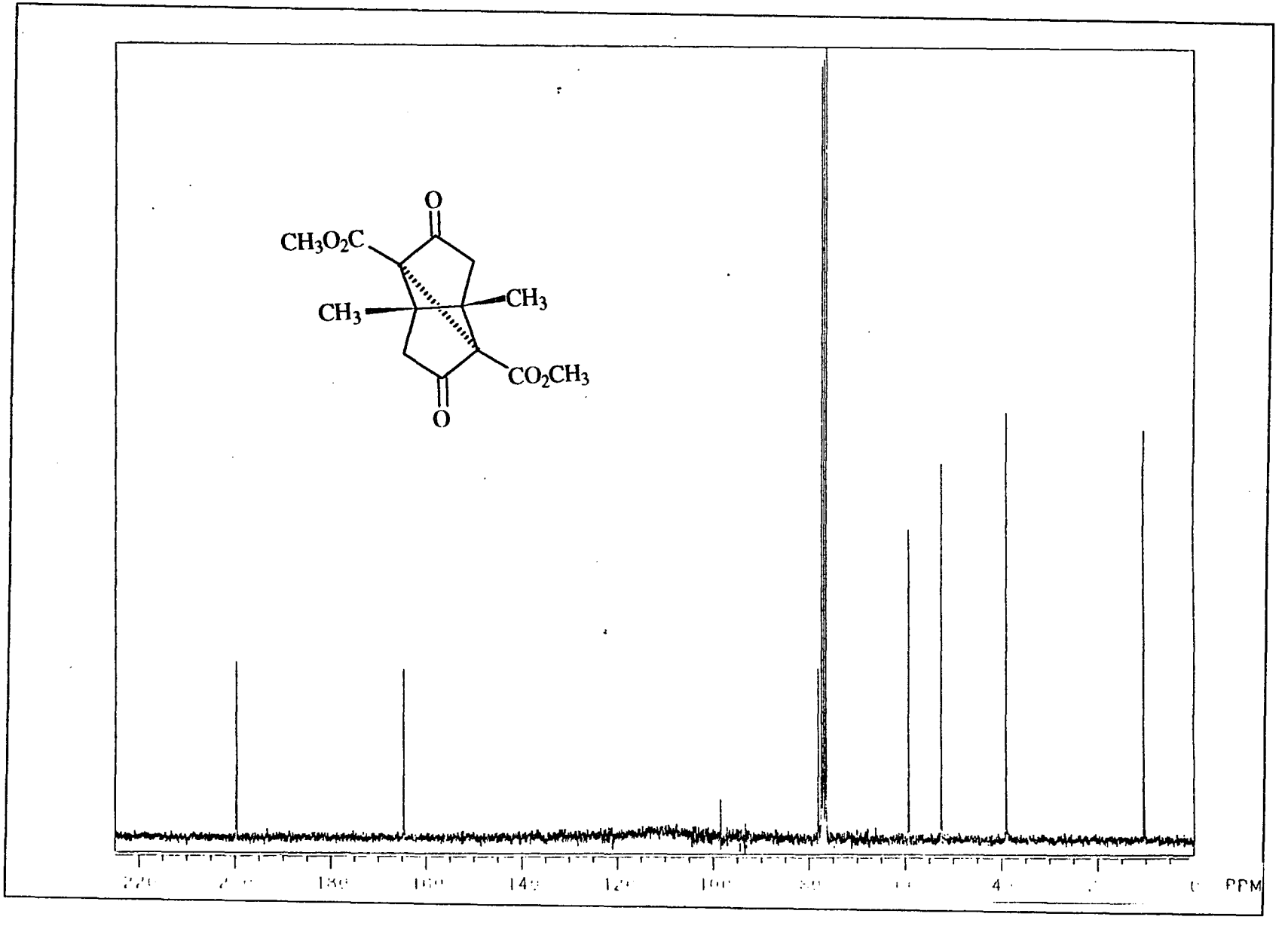
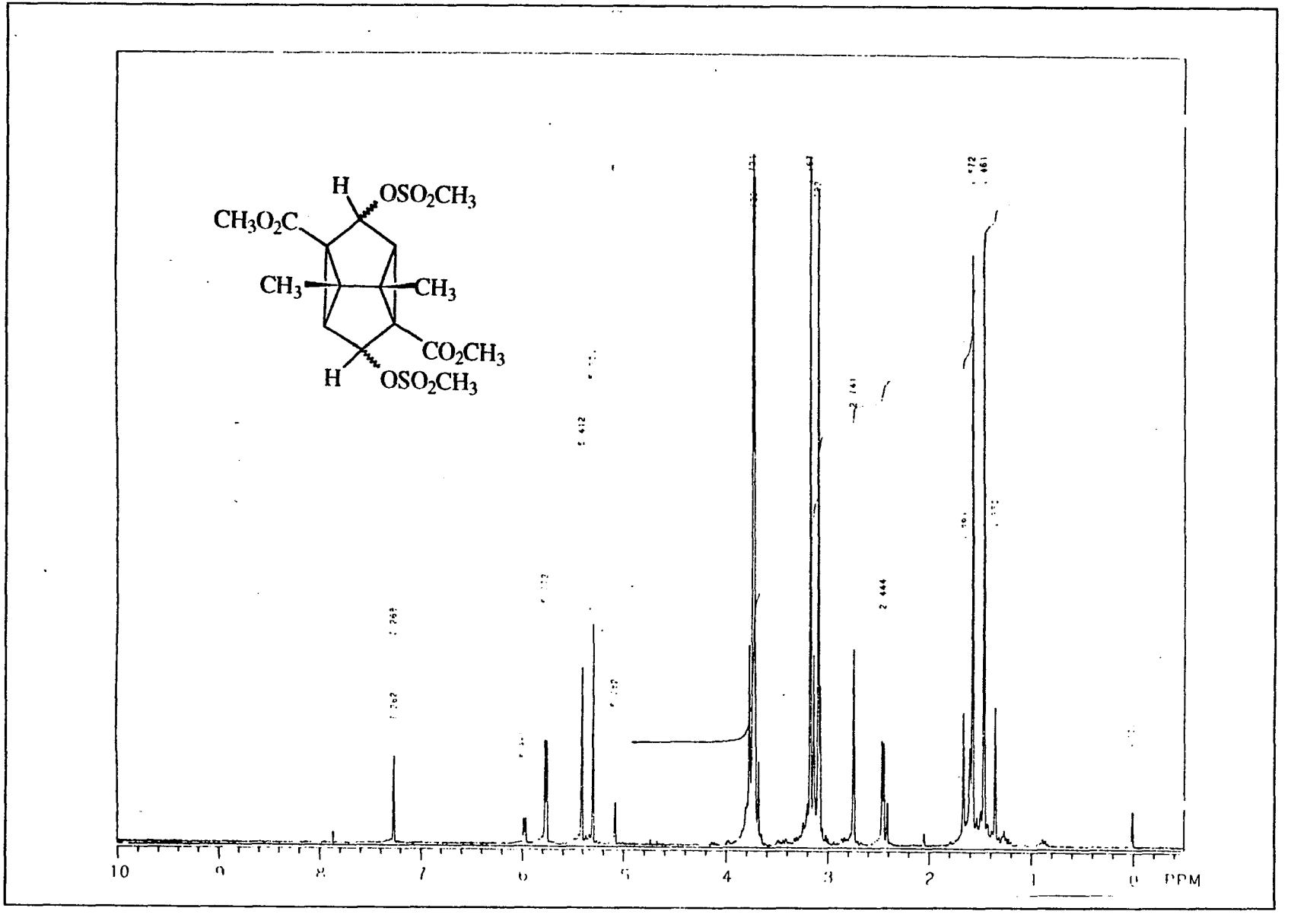
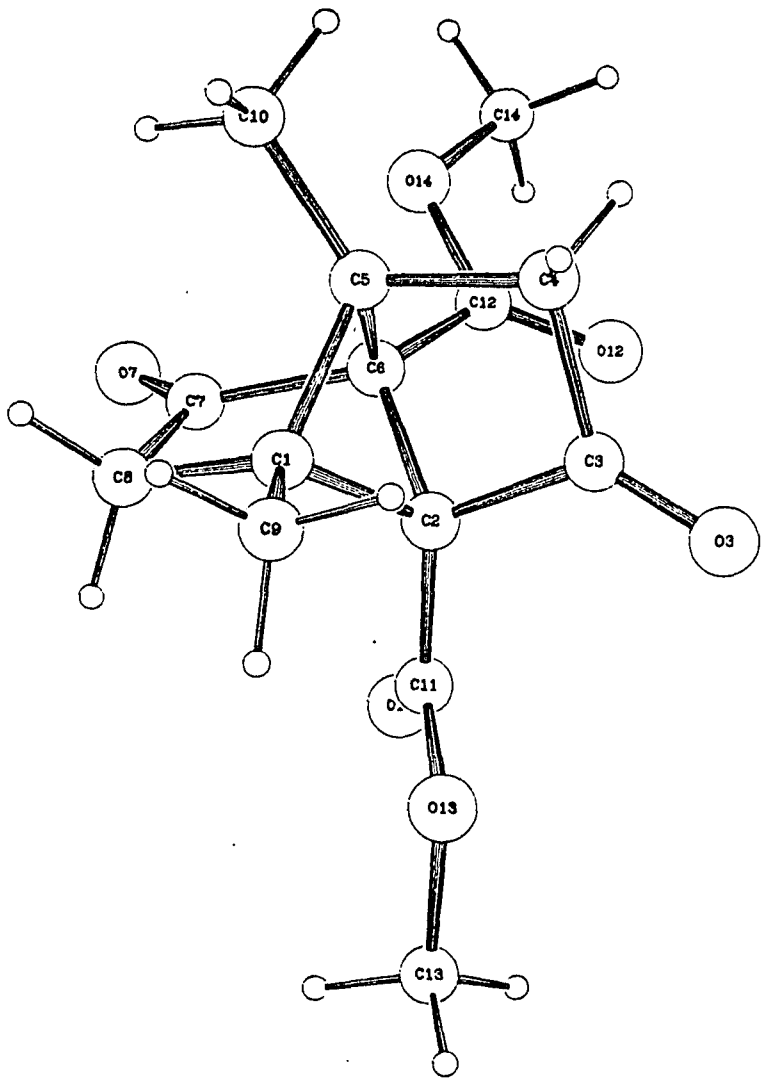
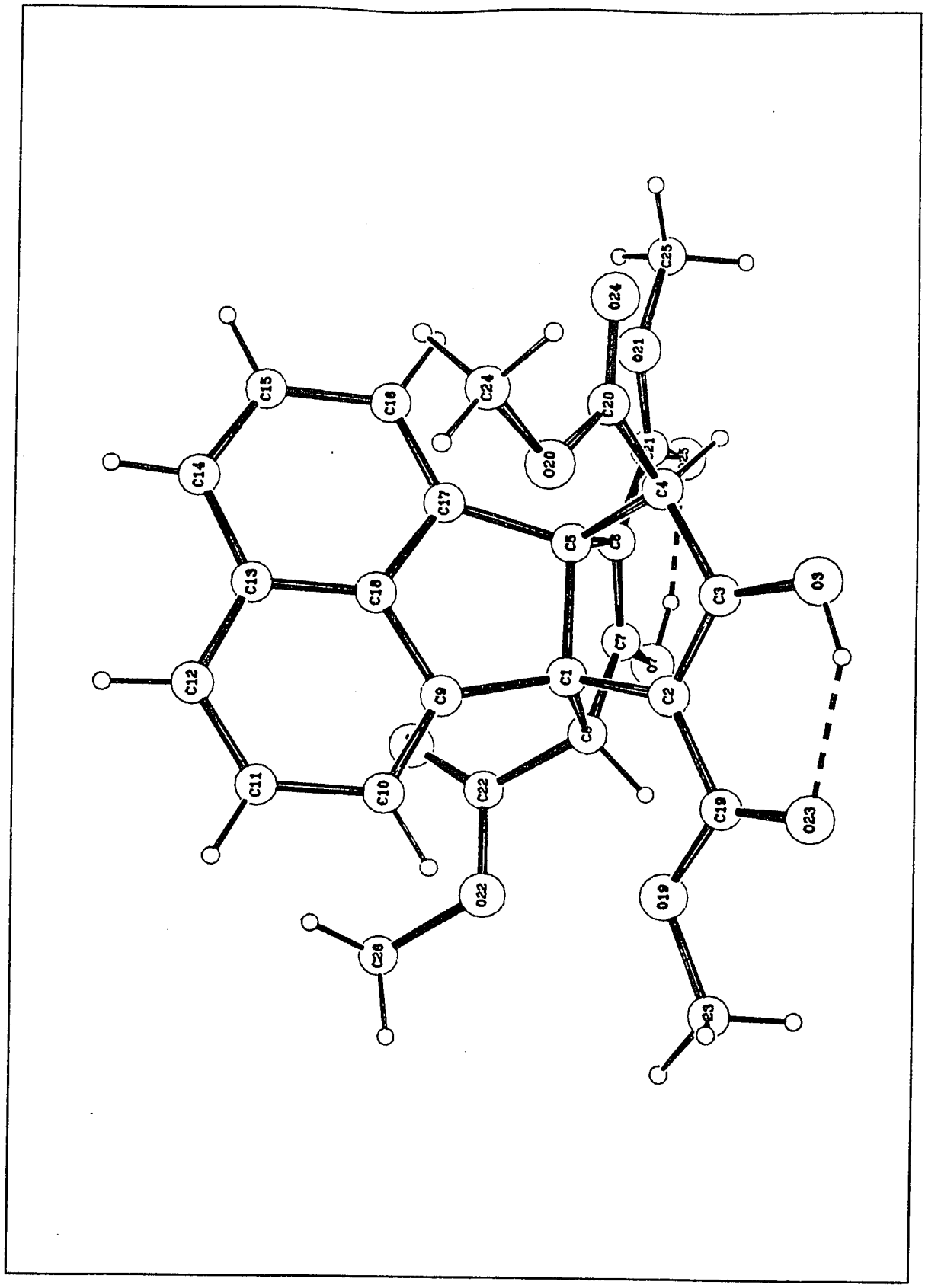

O
CH3O2C
CH3
CH3
CO2CH3
O
PPM

Figure 48: ^{1}H-NMR Spectrum of **80**.


H
OSO2CH3
CH3O2C
CH3
CH3
CO2CH3
H
OSO2CH3
10
9
8
7
6
5
4
3
2
1
0
PPM

X-RAY DATA FOR SELECTED COMPOUNDS


C10
C14
O14
C5
C4
C12
O12
O7
C7
C6
C8
C1
C3
C9
C2
O3
C11
O13
C13


C25
O24
O21
C24
C20
C15
C16
O20
C14
C17
C5
C13
C18
C3
O3
C12
C9
C1
C2
C11
C10
C22
C19
O23
O19
O22
C26
C23

Crystal Data for Acenaphtha-Weiss

Formula	$C_{26}H_{22}O_{10}$
Formula weight	494.46
Crystal system	monoclinic
Space group	$P2_1/n$
a	11.283(4) Å
b	12.218(3) Å
c	17.217(3) Å
β	95.79(2)°
Z	4
d_{calc}	1.391 g cm^{-3}
μ(Cu Kα)	8.7 cm^{-1}

Final Atomic Parameters for Acenaphtha-Weiss

Atom	x	y	z	B(A2)
O3	-0.0125(2)	0.1343(2)	0.4749(1)	4.21(5)
O7	0.1037(2)	0.5972(2)	0.5739(1)	3.44(4)
O19	0.0375(2)	0.2297(2)	0.7092(1)	3.62(5)
O20	0.2677(2)	0.0924(2)	0.4698(1)	4.26(5)
O21	0.2172(2)	0.4676(2)	0.3685(1)	3.71(5)
O22	0.2106(2)	0.4286(2)	0.7674(1)	4.86(6)
O23	-0.0709(2)	0.1271(2)	0.6200(1)	4.54(5)
O24	0.2541(2)	0.1733(2)	0.3529(1)	5.06(6)
O25	0.1350(2)	0.6111(2)	0.4249(1)	3.39(4)
O26	0.3287(2)	0.5154(2)	0.6904(2)	5.20(6)
C1	0.1930(2)	0.3092(2)	0.5981(1)	2.10(5)
C2	0.0902(2)	0.2307(2)	0.5826(2)	2.41(5)
C3	0.0718(2)	0.2026(2)	0.5076(2)	2.70(5)
C4	0.1548(2)	0.2539(2)	0.4557(2)	2.53(5)
C5	0.2273(2)	0.3373(2)	0.5121(1)	2.14(5)
C6	0.1825(2)	0.4529(2)	0.4997(2)	2.30(5)
C7	0.1464(2)	0.4960(2)	0.5648(2)	2.51(5)
C8	0.1542(2)	0.4207(2)	0.6329(2)	2.47(5)
C9	0.3074(2)	0.2622(2)	0.6395(2)	2.33(5)
C10	0.3331(3)	0.2170(2)	0.7119(2)	3.05(6)
C11	0.4536(3)	0.1886(3)	0.7360(2)	3.82(7)
C12	0.5436(3)	0.2070(3)	0.6902(2)	3.84(7)
C13	0.5193(3)	0.2523(2)	0.6148(2)	3.01(6)
C14	0.6023(3)	0.2771(3)	0.5612(2)	3.80(7)
C15	0.5667(3)	0.3257(3)	0.4909(2)	3.84(7)
C16	0.4439(3)	0.3501(3)	0.4683(2)	3.14(6)
C17	0.3619(2)	0.3248(2)	0.5183(2)	2.44(5)
C18	0.3998(2)	0.2779(2)	0.5912(2)	2.49(5)
C19	0.0109(3)	0.1900(2)	0.6378(2)	3.11(6)
C20	0.2305(3)	0.1703(3)	0.4185(2)	3.15(6)
C21	0.1759(2)	0.5176(2)	0.4289(2)	2.71(5)
C22	0.2417(3)	0.4621(2)	0.6989(2)	3.38(6)
C23	-0.0372(3)	0.1952(4)	0.7683(2)	5.46(9)
C24	0.3421(4)	0.0091(3)	0.4407(3)	7.0(1)
C25	0.2164(4)	0.5307(3)	0.2969(2)	4.87(9)
C26	0.2959(5)	0.4494(4)	0.8358(3)	7.6(1)

Final Atomic Parameters for Acenaphtha-Weiss

Atom	x	y	z	B(A2)
H03	-0.054	0.114	0.515	4.9
H07	0.103	0.628	0.526	4.0
H4	0.114	0.291	0.409	3.0
H8	0.078	0.414	0.657	2.9
H10	0.269	0.204	0.747	3.6
H11	0.473	0.154	0.788	4.5
H12	0.627	0.188	0.710	4.5
H14	0.688	0.259	0.575	4.5
H15	0.628	0.345	0.455	4.5
H16	0.419	0.385	0.417	3.7
H23A	-0.009	0.230	0.819	6.5
H23B	-0.122	0.218	0.752	6.5
H23C	-0.033	0.114	0.774	6.5
H24A	0.365	-0.045	0.483	8.3
H24B	0.297	-0.029	0.395	8.3
H24C	0.415	0.044	0.423	8.3
H25A	0.249	0.485	0.256	5.8
H25B	0.133	0.553	0.279	5.8
H25C	0.266	0.598	0.307	5.8
H26A	0.264	0.421	0.884	9.0
H26B	0.373	0.411	0.829	9.0
H26C	0.311	0.530	0.841	9.0

The parameters of the hydrogen atoms were not refined.

Standard deviations are in parentheses.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

Final Anisotropic Thermal Parameters (U's) for Acenaphtha-Weiss

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O3	0.049(1)	0.061(1)	0.049(1)	-0.023(1)	-0.002(1)	-0.013(1)
O7	0.050(1)	0.033(1)	0.048(1)	0.0142(9)	0.006(1)	-0.0011(9)
O19	0.047(1)	0.057(1)	0.035(1)	-0.003(1)	0.0160(8)	0.004(1)
O20	0.062(1)	0.043(1)	0.056(1)	0.017(1)	0.004(1)	-0.007(1)
O21	0.067(1)	0.042(1)	0.033(1)	0.004(1)	0.0107(9)	0.0089(9)
O22	0.098(2)	0.056(1)	0.027(1)	0.001(1)	-0.011(1)	-0.004(1)
O23	0.046(1)	0.057(1)	0.071(1)	-0.021(1)	0.014(1)	-0.001(1)
O24	0.081(2)	0.073(2)	0.042(1)	-0.000(1)	0.026(1)	-0.014(1)
O25	0.039(1)	0.037(1)	0.053(1)	0.0077(9)	0.0033(9)	0.0142(9)
O26	0.060(1)	0.060(1)	0.073(2)	-0.016(1)	-0.015(1)	-0.009(1)
C1	0.027(1)	0.028(1)	0.025(1)	0.001(1)	0.0027(9)	0.001(1)
C2	0.031(1)	0.028(1)	0.033(1)	-0.001(1)	0.005(1)	0.002(1)
C3	0.031(1)	0.035(1)	0.036(1)	-0.001(1)	-0.000(1)	-0.002(1)
C4	0.036(1)	0.034(1)	0.026(1)	-0.000(1)	0.000(1)	-0.001(1)
C5	0.028(1)	0.028(1)	0.025(1)	0.002(1)	0.000(1)	0.000(1)
C6	0.024(1)	0.031(1)	0.032(1)	0.001(1)	0.001(1)	0.004(1)
C7	0.030(1)	0.028(1)	0.037(1)	0.004(1)	0.000(1)	0.001(1)
C8	0.032(1)	0.034(1)	0.028(1)	0.001(1)	0.002(1)	-0.003(1)
C9	0.030(1)	0.029(1)	0.028(1)	0.001(1)	-0.002(1)	0.001(1)
C10	0.041(1)	0.039(1)	0.036(1)	0.002(1)	-0.001(1)	0.006(1)
C11	0.051(2)	0.048(2)	0.044(2)	0.005(2)	-0.011(1)	0.013(1)
C12	0.039(2)	0.047(2)	0.057(2)	0.004(1)	-0.011(1)	0.008(2)
C13	0.030(1)	0.034(1)	0.049(2)	0.001(1)	-0.003(1)	-0.000(1)
C14	0.028(1)	0.049(2)	0.068(2)	0.000(1)	0.006(1)	-0.002(2)
C15	0.036(1)	0.052(2)	0.060(2)	-0.001(1)	0.017(1)	-0.001(2)
C16	0.035(1)	0.046(2)	0.040(1)	-0.001(1)	0.010(1)	-0.001(1)
C17	0.030(1)	0.029(1)	0.034(1)	0.003(1)	0.003(1)	-0.002(1)
C18	0.030(1)	0.030(1)	0.034(1)	0.001(1)	0.001(1)	-0.000(1)
C19	0.037(1)	0.039(1)	0.043(1)	0.000(1)	0.007(1)	0.002(1)
C20	0.041(2)	0.043(2)	0.035(1)	-0.005(1)	0.004(1)	-0.011(1)
C21	0.030(1)	0.035(1)	0.038(1)	-0.004(1)	0.001(1)	0.003(1)
C22	0.053(2)	0.034(1)	0.039(1)	0.006(1)	-0.007(1)	-0.006(1)
C23	0.072(2)	0.087(3)	0.054(2)	0.001(2)	0.038(1)	0.017(2)
C24	0.081(3)	0.066(2)	0.118(3)	0.039(2)	0.006(2)	-0.024(2)
C25	0.096(3)	0.054(2)	0.035(2)	-0.002(2)	0.011(2)	0.016(2)
C26	0.158(4)	0.076(3)	0.043(2)	-0.001(3)	-0.050(2)	-0.005(2)

The form of the anisotropic displacement parameter is:
exp[-2PI2(h2a2U(1,1) + k2b2U(2,2) + l2c2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3))] where a,b, and c are reciprocal lattice constants.

Bond Distances (Å) for Acenaphtha-Weiss

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
03	C3	1.345(3)	C3	C4	1.495(4)
07	C7	1.342(3)	C4	C5	1.579(4)
019	C19	1.327(3)	C4	C20	1.514(4)
019	C23	1.448(4)	C5	C6	1.509(4)
020	C20	1.337(4)	C5	C17	1.520(4)
020	C24	1.441(5)	C6	C7	1.338(4)
021	C21	1.329(4)	C6	C21	1.449(4)
021	C25	1.453(4)	C7	C8	1.485(4)
022	C22	1.330(4)	C8	C22	1.515(4)
022	C26	1.466(5)	C9	C10	1.367(4)
023	C19	1.216(4)	C9	C18	1.410(4)
024	C20	1.188(4)	C10	C11	1.424(4)
025	C21	1.232(3)	C11	C12	1.366(5)
026	C22	1.199(4)	C12	C13	1.411(4)
C1	C2	1.508(4)	C13	C14	1.413(4)
C1	C5	1.604(4)	C13	C18	1.404(4)
C1	C8	1.568(4)	C14	C15	1.372(5)
C1	C9	1.523(3)	C15	C16	1.432(4)
C2	C3	1.333(4)	C16	C17	1.361(4)
C2	C19	1.458(4)	C17	C18	1.406(4)

Standard deviations are in parentheses.

Bond Angles (°) for Acenaphtha-Weiss

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C19	019	C23	116.8(2)	C1	C8	C22	113.0(2)
C20	020	C24	115.4(3)	C7	C8	C22	111.5(2)
C21	021	C25	116.6(2)	C1	C9	C10	132.1(2)
C22	022	C26	116.6(3)	C1	C9	C18	108.3(2)
C2	C1	C5	103.0(2)	C10	C9	C18	119.4(2)
C2	C1	C8	112.4(2)	C9	C10	C11	118.2(3)
C2	C1	C9	116.3(2)	C10	C11	C12	122.3(3)
C5	C1	C8	105.6(2)	C11	C12	C13	120.6(3)
C5	C1	C9	103.9(2)	C12	C13	C14	127.2(3)
C8	C1	C9	113.9(2)	C12	C13	C18	116.4(3)
C1	C2	C3	112.2(2)	C14	C13	C18	116.3(3)
C1	C2	C19	127.9(2)	C13	C14	C15	121.0(3)
C3	C2	C19	119.9(2)	020	C20	C4	110.7(2)
03	C3	C2	126.8(3)	024	C20	C4	124.9(3)
03	C3	C4	118.0(2)	021	C21	025	122.8(3)
C2	C3	C4	115.2(2)	021	C21	C6	114.6(2)
C3	C4	C5	102.7(2)	025	C21	C6	122.6(3)
C3	C4	C20	112.6(2)	022	C22	026	124.7(3)
C5	C4	C20	114.6(2)	022	C22	C8	110.6(3)
C1	C5	C4	105.8(2)	026	C22	C8	124.7(3)
C1	C5	C6	102.8(2)	C14	C15	C16	121.2(3)
C1	C5	C17	104.3(2)	C15	C16	C17	118.8(3)
C4	C5	C6	111.8(2)	C5	C17	C16	132.1(2)
C4	C5	C17	115.5(2)	C5	C17	C18	108.3(2)
C6	C5	C17	115.0(2)	C16	C17	C18	119.5(2)
C5	C6	C7	112.1(2)	C9	C18	C13	122.9(2)
C5	C6	C21	128.1(2)	C9	C18	C17	114.0(2)
C7	C6	C21	119.8(2)	C13	C18	C17	123.1(3)
07	C7	C6	127.1(2)	019	C19	023	124.1(3)
07	C7	C8	118.1(2)	019	C19	C2	112.5(2)
C6	C7	C8	114.8(2)	023	C19	C2	123.4(3)
C1	C8	C7	103.5(2)	020	C20	024	124.4(3)

Standard deviations are in parentheses.

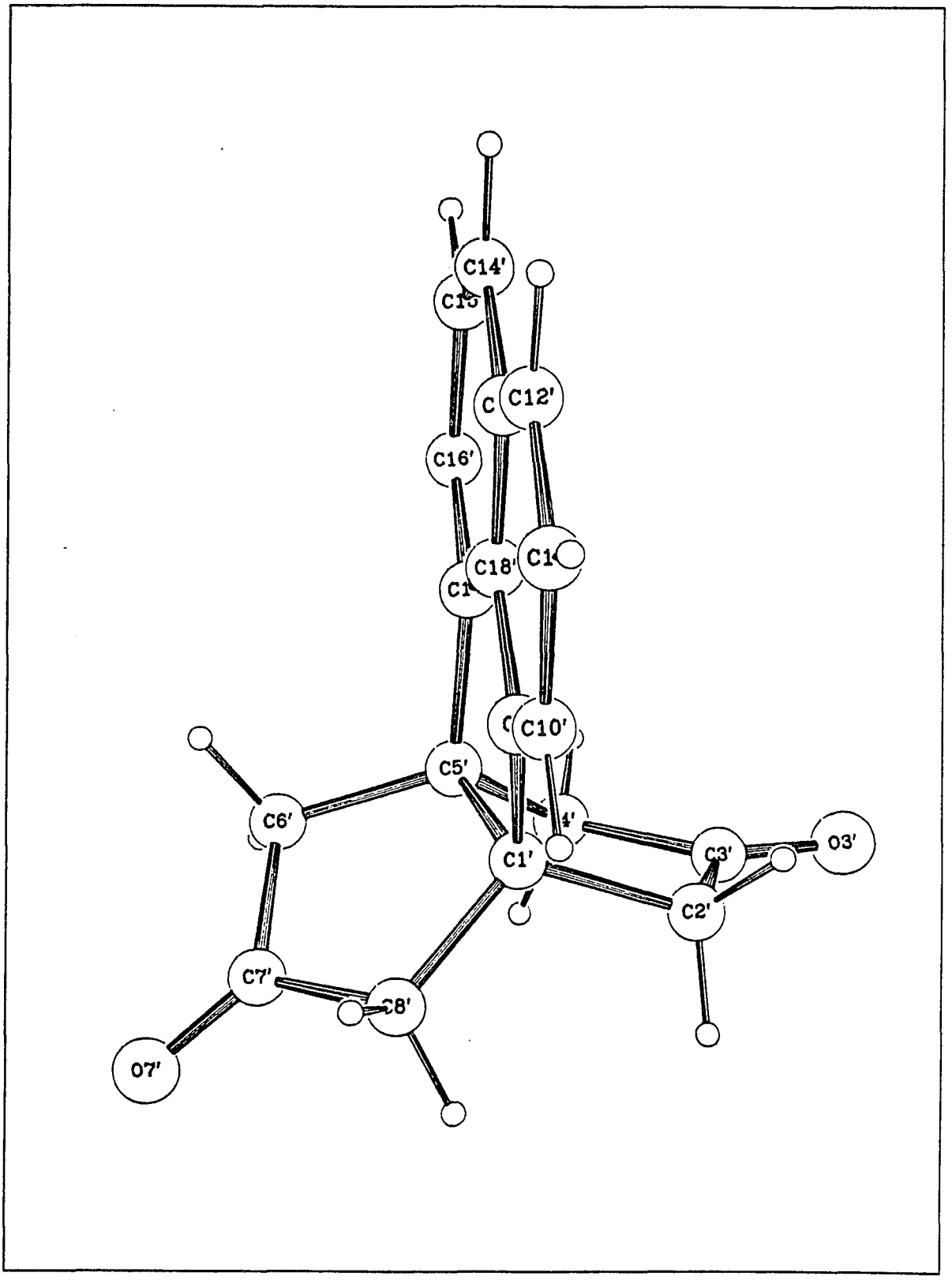

C14'
C12'
C16'
C18'
C10'
C5'
C6'
C1'
C3'
O3'
C2'
C7'
O7'

Table I. Crystal Data for Acenaphtho Diketone

Formula	$C_{18}H_{14}O_2$
Formula weight	262.31
Crystal system	monoclinic
Space group	C2/c
a	22.703(1) Å
b	8.165(3) Å
c	29.114(2) Å
β	101.62(1)°
Z	16
d_{calc}	1.318 g cm^{-3}
μ(Cu Kα)	6.4 cm^{-1}

Final Atomic Parameters for Acenaphtho Diketone

Atom	x	y	z	B(A2)
O3	0.2435(1)	0.1465(4)	0.21057(8)	7.68(7)
O7	0.50770(9)	0.4052(4)	0.19167(8)	6.58(7)
C1	0.3529(1)	0.2966(3)	0.14698(8)	2.73(5)
C2	0.3113(1)	0.1566(4)	0.1570(1)	3.68(6)
C3	0.2871(1)	0.2067(4)	0.1992(1)	4.26(7)
C4	0.3237(1)	0.3469(4)	0.22392(9)	4.08(7)
C5	0.3475(1)	0.4354(3)	0.18487(8)	2.93(6)
C6	0.4111(1)	0.5067(4)	0.2000(1)	4.29(7)
C7	0.4534(1)	0.3902(4)	0.18315(9)	3.94(7)
C8	0.4199(1)	0.2541(4)	0.1548(1)	3.71(7)
C9	0.3265(1)	0.3778(3)	0.10068(8)	2.74(5)
C10	0.3238(1)	0.3285(4)	0.05530(9)	3.37(6)
C11	0.2889(1)	0.4225(4)	0.01895(9)	3.75(7)
C12	0.2566(1)	0.5563(4)	0.02723(9)	3.42(6)
C13	0.2593(1)	0.6116(3)	0.07381(9)	2.92(6)
C14	0.2287(1)	0.7459(4)	0.0888(1)	3.69(6)
C15	0.2353(1)	0.7806(4)	0.1355(1)	3.98(7)
C16	0.2731(1)	0.6868(4)	0.17088(9)	3.63(6)
C17	0.3033(1)	0.5560(3)	0.15731(8)	2.79(5)
C18	0.2958(1)	0.5192(3)	0.10929(8)	2.50(5)
O3′	0.6530(1)	0.6092(3)	0.08477(8)	6.33(6)
O7′	0.5882(1)	0.9783(4)	0.25679(7)	9.62(8)
C1′	0.5929(1)	0.9597(3)	0.13425(9)	3.03(6)
C2′	0.6432(1)	0.8841(4)	0.1125(1)	3.86(7)
C3′	0.6314(1)	0.7020(4)	0.10874(9)	3.72(6)
C4′	0.5887(1)	0.6560(4)	0.1401(1)	3.71(6)
C5′	0.5507(1)	0.8095(3)	0.14151(9)	2.92(6)
C6′	0.5331(1)	0.8400(4)	0.18926(9)	3.55(6)
C7′	0.5795(1)	0.9542(4)	0.2152(1)	4.54(7)
C8′	0.6148(1)	1.0347(4)	0.1831(1)	4.61(8)
C9′	0.5523(1)	1.0683(3)	0.09951(8)	2.92(6)
C10′	0.5599(1)	1.2238(4)	0.0837(1)	3.94(7)
C11′	0.5148(1)	1.2887(4)	0.0475(1)	4.58(7)
C12′	0.4647(1)	1.2020(4)	0.0275(1)	4.42(7)
C13′	0.4556(1)	1.0409(4)	0.04333(9)	3.66(6)
C14′	0.4070(1)	0.9346(5)	0.0266(1)	4.73(8)
C15′	0.4051(1)	0.7821(5)	0.0460(1)	5.13(8)
C16′	0.4505(1)	0.7245(4)	0.0834(1)	4.38(7)
C17′	0.4976(1)	0.8261(4)	0.10050(8)	3.04(6)
C18′	0.5002(1)	0.9809(4)	0.07996(8)	2.88(6)

Final Atomic Parameters for Acenaphtho Diketone

Atom	x	y	z	B(A2)
H2A	0.335	0.052	0.163	4.3
H2B	0.278	0.141	0.129	4.3
H4A	0.358	0.305	0.248	4.8
H4B	0.298	0.422	0.239	4.8
H6A	0.422	0.516	0.235	5.1
H6B	0.413	0.617	0.186	5.1
H8A	0.433	0.245	0.124	4.3
H8B	0.428	0.148	0.172	4.3
H10	0.346	0.229	0.048	3.9
H11	0.288	0.389	-0.014	4.5
H12	0.231	0.616	0.000	4.0
H14	0.202	0.816	0.065	4.4
H15	0.213	0.876	0.145	4.7
H16	0.277	0.716	0.205	4.3
H2A'	0.683	0.906	0.133	4.5
H2B'	0.642	0.932	0.081	4.5
H4A'	0.611	0.627	0.172	4.4
H4B'	0.563	0.561	0.127	4.4
H6A'	0.533	0.735	0.207	4.2
H6B'	0.492	0.891	0.184	4.2
H8A'	0.608	1.155	0.182	5.4
H8B'	0.659	1.013	0.194	5.4
H10'	0.596	1.290	0.098	4.6
H11'	0.520	1.402	0.036	5.5
H12'	0.434	1.252	0.001	5.2
H14'	0.374	0.970	0.001	5.6
H15'	0.370	0.708	0.034	6.1
H16'	0.448	0.612	0.097	5.1

The parameters of the hydrogen atoms were not refined.

Standard deviations are in parentheses.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

Bond Distances (Å) for Acenaphtho Diketone

		Unprimed	Primed
O3	C3	1.208(4)	1.201(4)
O7	C7	1.214(3)	1.202(4)
C1	C2	1.547(4)	1.543(4)
C1	C5	1.604(4)	1.596(4)
C1	C8	1.531(4)	1.537(4)
C1	C9	1.514(3)	1.510(3)
C2	C3	1.501(4)	1.511(4)
C3	C4	1.509(4)	1.507(4)
C4	C5	1.533(4)	1.527(4)
C5	C6	1.538(4)	1.542(4)
C5	C17	1.515(3)	1.522(3)
C6	C7	1.501(5)	1.494(4)
C7	C8	1.497(4)	1.499(5)
C9	C10	1.370(4)	1.374(4)
C9	C18	1.398(4)	1.400(3)
C10	C11	1.415(4)	1.416(4)
C11	C12	1.363(4)	1.367(4)
C12	C13	1.419(4)	1.422(5)
C13	C14	1.413(4)	1.412(4)
C13	C18	1.407(3)	1.404(3)
C14	C15	1.368(4)	1.372(5)
C15	C16	1.424(4)	1.419(4)
C16	C17	1.369(4)	1.366(4)
C17	C18	1.406(3)	1.404(4)

Standard deviations are in parentheses.

Final Atomic Parameters for Acenaphtho Diketone

Atom	x	y	z	B(A2)
O3	0.55651(6)	0.2371(1)	0.43893(9)	3.14(2)
O5	0.37918(6)	0.2557(1)	0.3706(1)	3.41(2)
O6	0.69772(6)	0.3799(1)	0.49096(9)	3.02(2)
O7	0.41229(6)	0.4426(1)	0.47417(9)	3.37(2)
O8	0.70709(6)	0.4504(1)	0.3234(1)	3.74(3)
C1	0.53840(6)	0.5119(1)	0.2432(1)	2.03(2)
C2	0.45823(7)	0.3931(1)	0.3239(1)	2.09(2)
C3	0.53745(7)	0.3280(1)	0.3719(1)	2.19(2)
C4	0.58424(7)	0.3959(1)	0.3156(1)	2.13(2)
C5	0.41313(7)	0.3711(1)	0.3980(1)	2.38(3)
C6	0.66974(7)	0.4098(1)	0.3748(1)	2.49(3)
C7	0.3367(1)	0.2168(2)	0.4395(2)	5.03(4)
C8	0.7773(1)	0.4160(2)	0.5632(2)	4.04(4)
C9	0.55817(7)	0.6500(1)	0.2362(1)	2.33(3)
C10	0.61532(8)	0.7114(2)	0.2161(1)	2.90(3)
C11	0.61473(9)	0.8494(2)	0.2125(1)	3.48(3)
C12	0.5600(1)	0.9215(2)	0.2288(2)	3.63(4)
C13	0.500	0.8602(2)	0.250	2.99(4)
C14	0.500	0.7243(2)	0.250	2.45(4)
H7A	0.3135	0.1292	0.4122	6
H7B	0.3725	0.2134	0.5273	6
H7C	0.2947	0.2810	0.4267	6
H8A	0.7924	0.3890	0.6489	4
H8B	0.8113	0.3717	0.5310	4
H8C	0.7830	0.5120	0.5595	4
H10	0.6562	0.6607	0.2041	3
H11	0.6561	0.8950	0.1974	4
H12	0.5620	1.0182	0.2260	4

The parameters of the hydrogen atoms were not refined.

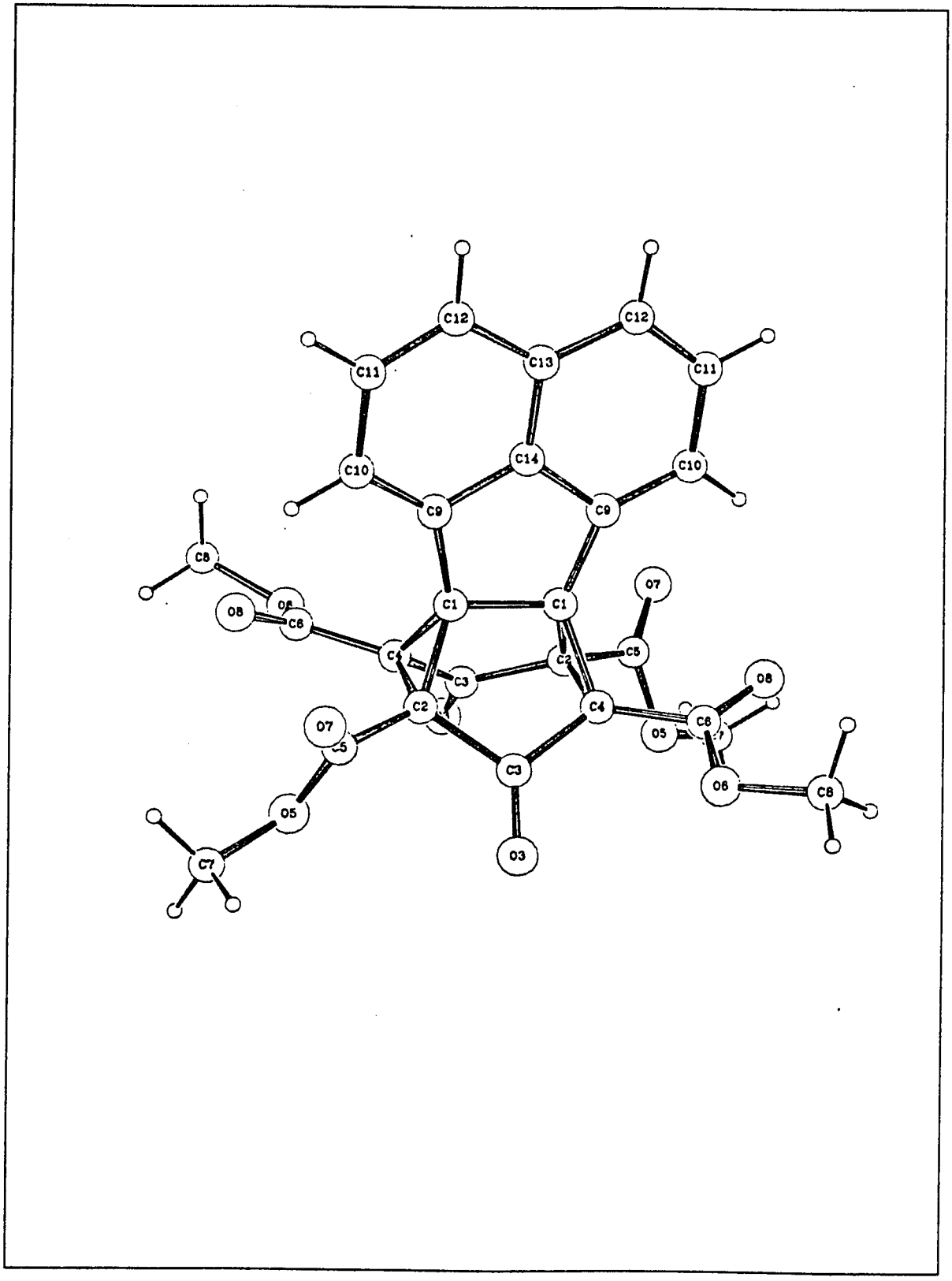
Standard deviations are in parentheses.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

Bond Angles (°) for Acenaphtho Diketone

			Unprimed	Primed
C2	C1	C5	104.9(2)	105.1(2)
C2	C1	C8	115.5(2)	114.3(2)
C2	C1	C9	110.2(2)	111.2(2)
C5	C1	C8	105.6(2)	105.9(2)
C5	C1	C9	103.4(2)	103.8(2)
C8	C1	C9	115.8(2)	115.2(2)
C1	C2	C3	106.9(2)	106.7(2)
O3	C3	C2	124.6(3)	125.1(3)
O3	C3	C4	125.6(3)	125.7(3)
C2	C3	C4	109.8(3)	109.2(2)
C3	C4	C5	104.3(2)	104.3(2)
C1	C5	C4	105.3(2)	105.7(2)
C1	C5	C6	105.4(2)	105.5(2)
C1	C5	C17	103.3(2)	103.2(2)
C4	C5	C6	114.6(2)	114.0(2)
C4	C5	C17	113.9(2)	114.5(2)
C6	C5	C17	112.9(2)	112.6(2)
C5	C6	C7	107.0(2)	105.8(2)
O7	C7	C6	124.0(3)	124.6(3)
O7	C7	C8	124.7(3)	123.8(3)
C6	C7	C8	111.3(2)	111.7(2)
C1	C8	C7	107.0(2)	106.8(2)
C1	C9	C10	131.5(3)	131.8(2)
C1	C9	C18	109.0(2)	108.9(2)
C10	C9	C18	119.2(2)	119.2(2)
C9	C10	C11	118.1(3)	118.3(3)
C10	C11	C12	122.9(2)	122.6(3)
C11	C12	C13	120.2(2)	120.2(3)
C12	C13	C14	127.8(2)	127.7(2)
C12	C13	C18	115.9(2)	116.1(2)
C14	C13	C18	116.3(2)	116.2(3)
C13	C14	C15	120.4(2)	120.2(3)
C14	C15	C16	122.5(3)	122.6(3)
C15	C16	C17	118.3(3)	118.2(3)
C16	C17	C5	132.1(2)	132.0(3)
C16	C17	C18	119.1(2)	119.3(2)
C5	C17	C18	108.8(2)	108.6(2)
C9	C18	C13	123.6(2)	123.5(3)
C9	C18	C17	112.9(2)	113.0(2)
C13	C18	C17	123.4(2)	123.5(2)

Standard deviations are in parentheses.


C12
C12
C11
C13
C11
C10
C14
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C9
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O7
O8
C1
C1
C6
C5
C4
C2
C3
O8
C2
C4
O7
O5
C6
C3
O6
C8
O5
C7
O3

Crystal Data for acenaphtho-tetracyclic ester

Formula	$C_{26}H_{18}O_{10}$
Formula weight	490.43
Crystal system	monoclinic
Space group	C2/c
a	19.099(2) Å
b	10.319(1) Å
c	12.193(2) Å
β	114.83(1)°
Z	4
d_{calc}	1.494 g cm^{-3}
μ(Cu Kα)	9.4 cm^{-1}

Bond Distances (Å) for Acenaphtho Diketone

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O3	C3	1.196(2)	C2	C5	1.505(2)
O5	C5	1.330(2)	C3	C4	1.509(2)
O5	C7	1.449(3)	C4	C6	1.489(2)
O6	C6	1.324(2)	C9	C10	1.370(2)
O6	C8	1.450(2)	C9	C14	1.417(2)
O7	C5	1.191(2)	C10	C11	1.425(2)
O8	C6	1.205(2)	C11	C12	1.364(3)
C1	C4	1.526(2)	C12	C13	1.424(2)
C1	C9	1.485(2)	C13	C14	1.402(3)
C2	C3	1.529(2)			

Table V. Bond Angles (°) for Acenaphtho Diketone

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C5	O5	C7	115.7(1)	O7	C5	C2	125.0(1)
C6	O6	C8	116.1(1)	O6	C6	O8	125.2(1)
C4	C1	C9	133.42(9)	O6	C6	C4	111.4(1)
C3	C2	C5	115.3(1)	O8	C6	C4	123.3(1)
O3	C3	C2	125.1(1)	C1	C9	C10	134.0(1)
O3	C3	C4	127.3(1)	C1	C9	C14	106.3(1)
C2	C3	C4	107.6(1)	C10	C9	C14	119.6(1)
C1	C4	C3	108.8(1)	C9	C10	C11	118.1(2)
C1	C4	C6	116.8(1)	C10	C11	C12	122.5(2)
C3	C4	C6	124.2(1)	C11	C12	C13	120.6(2)
O5	C5	O7	125.9(2)	C12	C13	C14	116.4(1)
O5	C5	C2	109.0(1)	C9	C14	C13	122.76(9)

Standard deviations are in parentheses.

Final Anisotropic Thermal Parameters (U's) for Acenaphtho Diketone

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O3	0.114(1)	0.101(2)	0.094(1)	-0.038(1)	0.064(1)	-0.002(1)
O7	0.043(1)	0.121(2)	0.085(1)	-0.014(1)	0.010(1)	-0.018(2)
C1	0.038(1)	0.029(1)	0.036(1)	0.002(1)	0.006(1)	0.001(1)
C2	0.053(1)	0.037(2)	0.051(1)	-0.004(1)	0.015(1)	0.005(1)
C3	0.065(2)	0.052(2)	0.049(1)	-0.001(2)	0.021(1)	0.015(2)
C4	0.073(2)	0.049(2)	0.035(1)	0.005(2)	0.016(1)	0.006(1)
C5	0.042(1)	0.036(2)	0.033(1)	0.002(1)	0.006(1)	0.000(1)
C6	0.048(2)	0.057(2)	0.054(2)	-0.004(2)	0.001(1)	-0.005(2)
C7	0.042(1)	0.064(2)	0.041(1)	-0.003(2)	0.002(1)	0.008(2)
C8	0.040(1)	0.047(2)	0.053(2)	0.007(1)	0.006(1)	0.005(2)
C9	0.033(1)	0.035(2)	0.037(1)	-0.000(1)	0.010(1)	0.002(1)
C10	0.046(1)	0.044(2)	0.040(1)	-0.000(1)	0.012(1)	-0.003(1)
C11	0.052(1)	0.053(2)	0.036(1)	-0.013(2)	0.008(1)	-0.000(1)
C12	0.041(1)	0.047(2)	0.040(1)	-0.008(1)	0.003(1)	0.009(1)
C13	0.033(1)	0.034(2)	0.045(1)	-0.005(1)	0.012(1)	0.008(1)
C14	0.045(1)	0.037(2)	0.060(2)	0.001(1)	0.015(1)	0.012(1)
C15	0.052(1)	0.033(2)	0.071(2)	0.007(1)	0.023(1)	0.006(2)
C16	0.054(1)	0.035(2)	0.053(1)	-0.002(1)	0.021(1)	-0.005(1)
C17	0.039(1)	0.030(1)	0.039(1)	-0.003(1)	0.014(1)	-0.003(1)
C18	0.032(1)	0.028(1)	0.036(1)	-0.003(1)	0.009(1)	0.003(1)
O3'	0.096(1)	0.067(2)	0.092(1)	0.016(1)	0.052(1)	-0.013(1)
O7'	0.151(2)	0.171(3)	0.049(1)	-0.084(2)	0.034(1)	-0.044(2)
C1'	0.038(1)	0.035(2)	0.041(1)	-0.005(1)	0.007(1)	-0.004(1)
C2'	0.041(1)	0.046(2)	0.062(2)	0.001(1)	0.016(1)	0.008(2)
C3'	0.044(1)	0.049(2)	0.049(1)	0.010(1)	0.010(1)	0.002(2)
C4'	0.053(1)	0.035(2)	0.056(2)	0.002(1)	0.019(1)	0.002(1)
C5'	0.038(1)	0.033(2)	0.042(1)	-0.001(1)	0.013(1)	0.000(1)
C6'	0.046(1)	0.048(2)	0.043(1)	-0.004(1)	0.013(1)	-0.002(1)
C7'	0.063(2)	0.068(2)	0.042(1)	-0.006(2)	0.012(1)	-0.012(2)
C8'	0.068(2)	0.061(2)	0.044(2)	-0.019(2)	0.005(1)	-0.004(2)
C9'	0.040(1)	0.036(2)	0.038(1)	0.001(1)	0.014(1)	-0.004(1)
C10'	0.056(2)	0.036(2)	0.060(2)	0.003(1)	0.019(1)	0.000(2)
C11'	0.069(2)	0.043(2)	0.067(2)	0.013(2)	0.026(1)	0.010(2)
C12'	0.056(2)	0.067(2)	0.049(2)	0.020(2)	0.018(1)	0.012(2)
C13'	0.039(1)	0.060(2)	0.042(1)	0.008(1)	0.012(1)	-0.005(2)
C14'	0.046(1)	0.088(3)	0.046(2)	0.001(2)	0.009(1)	-0.003(2)
C15'	0.044(2)	0.091(3)	0.058(2)	-0.019(2)	0.004(1)	-0.007(2)
C16'	0.050(2)	0.062(2)	0.054(2)	-0.019(2)	0.009(1)	-0.007(2)
C17'	0.037(1)	0.041(2)	0.039(1)	-0.005(1)	0.014(1)	-0.005(1)
C18'	0.036(1)	0.039(2)	0.037(1)	0.003(1)	0.012(1)	-0.004(1)

The form of the anisotropic displacement parameter is:
exp[-2PI2(h2a2U(1,1) + k2b2U(2,2) + l2c2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3))] where a,b, and c are reciprocal lattice constants.

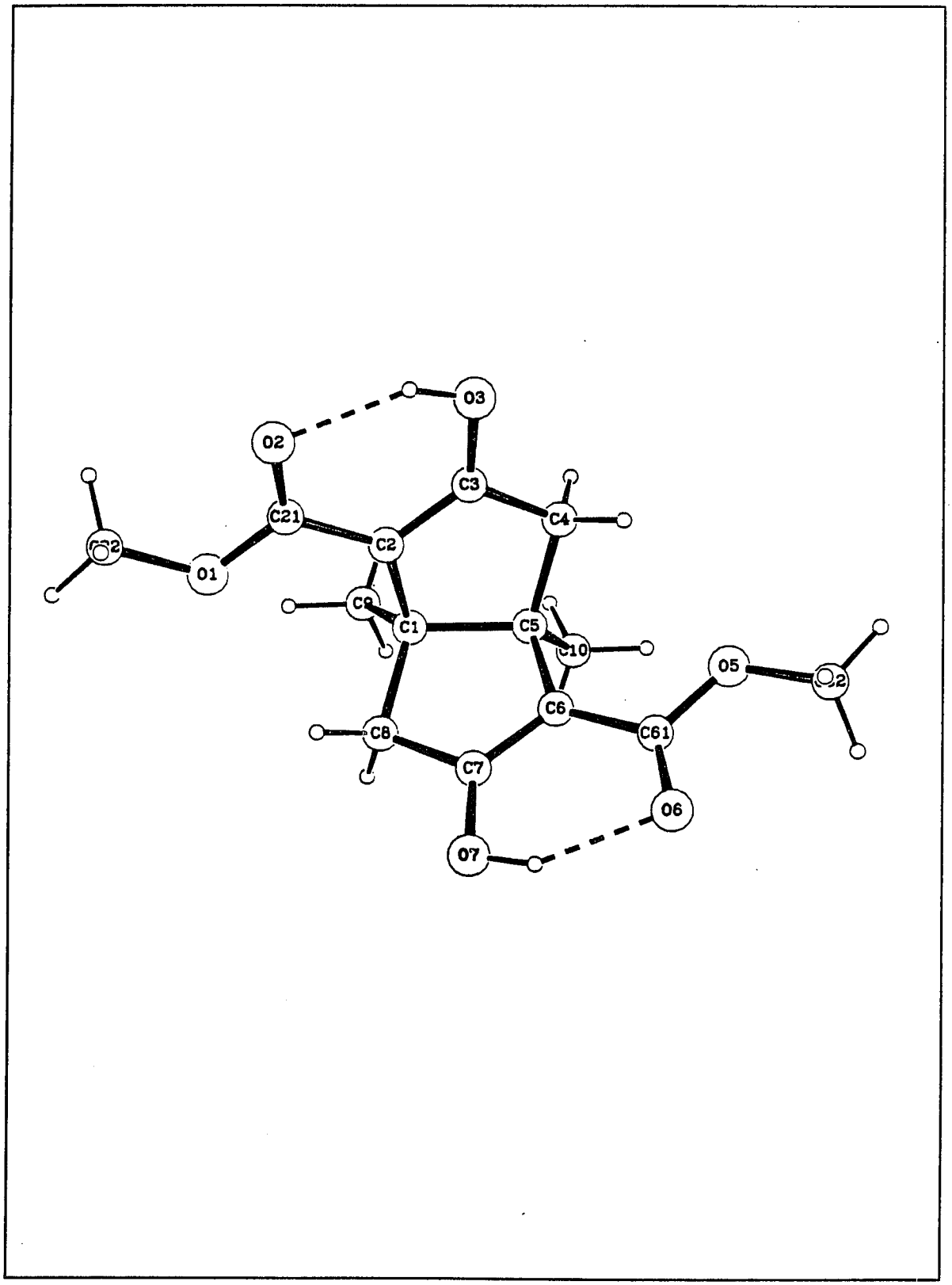

O3
O2
C3
C21
C4
C2
O1
C1
C5
C10
O5
C6
C61
C8
C7
O6
O7

Table I. Crystal Data for Diester Weiss

Formula	$C_{14}H_{18}O_6$
Formula weight	282.30
Temperature	110 K
Crystal system	monoclinic
Space group	$P2_1/c$
a	17.936(2) Å
b	7.079(2) Å
c	10.734(2) Å
β	95.84(1)°
Z	4
d_{calc}	1.383 g cm^{-3}
μ(Cu Kα)	8.7 cm^{-1}

Table II. Final Atomic Parameters for Diester Weiss

Atom	x	y	z	B(A2)
O1	0.09282(6)	0.5771(2)	0.4263(1)	1.61(2)
O2	0.07112(7)	0.2656(2)	0.3986(1)	2.00(2)
O3	0.14573(7)	0.0287(2)	0.5532(1)	1.95(2)
O5	0.40901(7)	0.1219(2)	0.6825(1)	1.77(2)
O6	0.45360(7)	0.2954(2)	0.5307(1)	1.74(2)
O7	0.37288(6)	0.5902(2)	0.4412(1)	1.84(2)
C1	0.21646(8)	0.5080(2)	0.6254(1)	1.13(2)
C2	0.16790(9)	0.3640(2)	0.5499(1)	1.25(3)
C3	0.18131(9)	0.1867(2)	0.5935(2)	1.42(3)
C4	0.24154(9)	0.1785(2)	0.6992(2)	1.44(3)
C5	0.27890(8)	0.3752(2)	0.6952(1)	1.14(3)
C6	0.33958(8)	0.3846(2)	0.6058(1)	1.20(3)
C7	0.32860(8)	0.5325(2)	0.5266(1)	1.27(3)
C8	0.25907(9)	0.6402(2)	0.5428(2)	1.33(3)
C9	0.17009(9)	0.6178(2)	0.7123(2)	1.47(3)
C10	0.30970(9)	0.4428(3)	0.8254(2)	1.57(3)
C21	0.10732(9)	0.3953(2)	0.4526(2)	1.40(3)
C22	0.0316(1)	0.6130(3)	0.3305(2)	2.03(3)
C61	0.40522(9)	0.2671(2)	0.6019(1)	1.37(3)
C62	0.4700(1)	-0.0106(3)	0.6732(2)	2.42(3)
H03	0.112	0.067	0.491	2.3
H07	0.411	0.508	0.448	2.2
H4A	0.278	0.076	0.686	1.7
H4B	0.220	0.158	0.781	1.7
H8A	0.271	0.763	0.586	1.6
H8B	0.229	0.664	0.460	1.6
H9A	0.132	0.697	0.661	1.8
H9B	0.144	0.527	0.764	1.8
H9C	0.204	0.701	0.768	1.8
H10A	0.348	0.352	0.862	1.9
H10B	0.333	0.570	0.819	1.9
H10C	0.268	0.451	0.880	1.9
H22A	0.025	0.752	0.318	2.4
H22B	0.043	0.553	0.250	2.4
H22C	-0.016	0.559	0.357	2.4
H62A	0.468	-0.113	0.737	2.9
H62B	0.465	-0.068	0.588	2.9
H62C	0.519	0.057	0.689	2.9

The parameters of the hydrogen atoms were not refined.

Standard deviations are in parentheses.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
$(4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(\cos\gamma)*B(1,2) + ac(\cos\beta)*B(1,3) + bc(\cos\alpha)*B(2,3)]$

Table III. Final Anisotropic Thermal Parameters (U's) for Diester Weiss

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.0164(5)	0.0208(5)	0.0235(5)	0.0009(5)	-0.0013(4)	0.0044(5)
O2	0.0244(6)	0.0244(6)	0.0261(6)	-0.0045(5)	-0.0019(5)	-0.0025(5)
O3	0.0270(6)	0.0149(5)	0.0318(6)	-0.0055(5)	0.0015(5)	-0.0012(5)
O5	0.0218(5)	0.0226(6)	0.0234(5)	0.0105(5)	0.0054(4)	0.0046(5)
O6	0.0177(5)	0.0249(6)	0.0247(5)	0.0027(5)	0.0083(4)	-0.0003(5)
O7	0.0203(5)	0.0237(6)	0.0277(5)	0.0018(5)	0.0116(4)	0.0071(5)
C1	0.0135(6)	0.0132(6)	0.0165(6)	0.0010(5)	0.0032(5)	0.0005(5)
C2	0.0146(6)	0.0162(7)	0.0173(6)	-0.0002(6)	0.0042(5)	-0.0009(6)
C3	0.0176(7)	0.0152(7)	0.0219(7)	-0.0018(6)	0.0063(6)	-0.0015(6)
C4	0.0185(7)	0.0142(7)	0.0225(7)	0.0008(6)	0.0041(6)	0.0037(6)
C5	0.0148(6)	0.0129(6)	0.0163(6)	0.0025(6)	0.0039(5)	0.0013(5)
C6	0.0137(6)	0.0150(7)	0.0173(6)	0.0002(6)	0.0035(5)	-0.0010(6)
C7	0.0147(6)	0.0162(7)	0.0181(6)	-0.0015(6)	0.0046(5)	-0.0008(6)
C8	0.0160(6)	0.0141(7)	0.0211(7)	0.0012(6)	0.0054(5)	0.0030(6)
C9	0.0188(7)	0.0181(7)	0.0197(7)	0.0047(6)	0.0052(5)	-0.0023(6)
C10	0.0199(7)	0.0225(8)	0.0174(7)	0.0031(6)	0.0023(6)	0.0004(6)
C21	0.0153(6)	0.0194(7)	0.0193(7)	-0.0002(6)	0.0046(5)	0.0002(6)
C22	0.0172(7)	0.0312(9)	0.0274(8)	-0.0005(7)	-0.0033(6)	0.0089(7)
C61	0.0174(7)	0.0170(7)	0.0177(7)	0.0011(6)	0.0016(6)	-0.0020(6)
C62	0.0274(8)	0.0312(9)	0.0343(9)	0.0168(7)	0.0078(7)	0.0059(8)

The form of the anisotropic displacement parameter is:
$\exp[-2\pi^2\{h^2a^2U(1,1) + k^2b^2U(2,2) + l^2c^2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)\}]$ where a,b, and c are reciprocal lattice constants.

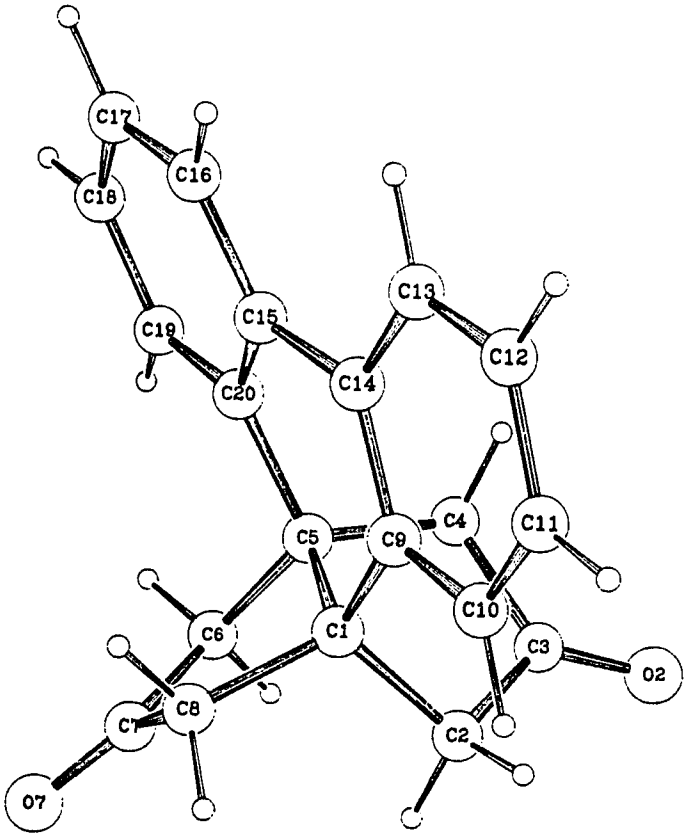
Table IV. Bond Distances (Å) for Diester Weiss

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O1	C21	1.337(2)	C1	C9	1.524(2)
O1	C22	1.449(2)	C2	C3	1.352(2)
O2	C21	1.234(2)	C2	C21	1.446(2)
O3	C3	1.337(2)	C3	C4	1.486(2)
O5	C61	1.341(2)	C4	C5	1.547(2)
O5	C62	1.451(2)	C5	C6	1.524(2)
O6	C61	1.229(2)	C5	C10	1.526(2)
O7	C7	1.336(2)	C6	C7	1.351(2)
C1	C2	1.520(2)	C6	C61	1.446(2)
C1	C5	1.590(2)	C7	C8	1.487(2)
C1	C8	1.544(2)			

Table V. Bond Angles (°) for Diester Weiss

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C21	O1	C22	115.8(1)	C1	C5	C10	114.7(1)
C61	O5	C62	116.1(1)	C4	C5	C6	113.3(1)
C2	C1	C5	101.1(1)	C4	C5	C10	112.0(1)
C2	C1	C8	113.0(1)	C6	C5	C10	110.3(1)
C2	C1	C9	110.4(1)	C5	C6	C7	111.3(1)
C5	C1	C8	105.3(1)	C5	C6	C61	129.0(1)
C5	C1	C9	114.5(1)	C7	C6	C61	119.6(1)
C8	C1	C9	112.0(1)	O7	C7	C6	127.6(1)
C1	C2	C3	111.5(1)	O7	C7	C8	119.2(1)
C1	C2	C21	129.1(1)	C6	C7	C8	113.2(1)
C3	C2	C21	119.1(1)	C1	C8	C7	103.1(1)
O3	C3	C2	127.0(1)	O1	C21	O2	122.3(1)
O3	C3	C4	120.0(1)	O1	C21	C2	114.6(1)
C2	C3	C4	112.9(1)	O2	C21	C2	123.1(2)
C3	C4	C5	103.1(1)	O5	C61	O6	122.2(1)
C1	C5	C4	105.0(1)	O5	C61	C6	114.2(1)
C1	C5	C6	101.0(1)	O6	C61	C6	123.6(1)

Standard deviations are in parentheses.


C17
C16
C18
C13
C15
C19
C12
C20
C14
C4
C11
C5
C9
C10
C6
C1
C3
O2
C8
C7
C2
O7

Crystal Data for Phenanthro Diketone

Formula	$C_{20}H_{26}O_2$
Formula weight	298.43
Crystal system	monoclinic
Space group	$P2_1/a$
a	14.250(2) Å
b	7.142(5) Å
c	15.303(3) Å
β	110.75(1)°
Z	4
d_{calc}	1.361 g cm^{-3}
μ(Cu Kα)	6.3 cm^{-1}

Final Atomic Parameters for Phenanthro Diketone

Atom	x	y	z	B(A2)
O2	0.5199(1)	0.5323(2)	0.3554(1)	5.58(4)
O7	0.3585(1)	-0.1552(2)	0.48114(9)	5.69(4)
C1	0.3063(1)	0.2548(3)	0.3400(1)	2.96(4)
C2	0.3939(1)	0.3780(3)	0.4013(1)	3.64(4)
C3	0.4586(1)	0.4083(3)	0.3435(1)	3.75(4)
C4	0.4347(1)	0.2631(3)	0.2679(1)	3.92(4)
C5	0.3597(1)	0.1294(3)	0.2875(1)	3.22(4)
C6	0.4113(1)	-0.0189(3)	0.3622(1)	4.26(5)
C7	0.3474(1)	-0.0368(3)	0.4220(1)	3.92(4)
C8	0.2699(1)	0.1154(3)	0.3974(1)	3.66(4)
C9	0.2215(1)	0.3714(3)	0.2749(1)	3.04(4)
C10	0.1897(1)	0.5331(3)	0.3073(1)	3.90(4)
C11	0.1123(1)	0.6417(3)	0.2494(1)	4.62(5)
C12	0.0660(1)	0.5898(3)	0.1574(1)	4.98(5)
C13	0.0948(1)	0.4287(3)	0.1247(1)	4.54(5)
C14	0.1713(1)	0.3147(3)	0.1824(1)	3.29(4)
C15	0.1976(1)	0.1360(3)	0.1481(1)	3.49(4)
C16	0.1336(2)	0.0557(3)	0.0648(1)	4.80(5)
C17	0.1591(2)	-0.1081(4)	0.0304(1)	5.86(6)
C18	0.2484(2)	-0.1959(4)	0.0791(2)	6.09(5)
C19	0.3116(1)	-0.1211(3)	0.1624(1)	5.05(5)
C20	0.2875(1)	0.0445(3)	0.1982(1)	3.57(4)
H2A	0.432	0.312	0.461	4.3
H2B	0.368	0.500	0.416	4.3
H4A	0.497	0.194	0.271	4.7
H4B	0.404	0.323	0.205	4.7
H6A	0.481	0.023	0.401	5.1
H6B	0.415	-0.142	0.332	5.1
H8A	0.202	0.065	0.359	4.3
H8B	0.267	0.176	0.455	4.3
H10	0.224	0.571	0.374	4.6
H11	0.090	0.757	0.274	5.5
H12	0.011	0.669	0.114	5.9
H13	0.060	0.392	0.058	5.4
H16	0.068	0.118	0.029	5.7
H17	0.113	-0.163	-0.030	7.0
H18	0.267	-0.314	0.054	7.3
H19	0.376	-0.187	0.198	6.0

The parameters of the hydrogen atoms were not refined.

Standard deviations are in parentheses.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

Final Anisotropic Thermal Parameters (U's) for Phenanthro Diketone

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O2	0.0657(7)	0.0531(9)	0.0984(9)	-0.0216(7)	0.0354(6)	-0.0041(8)
O7	0.0840(9)	0.0603(9)	0.0717(8)	0.0029(8)	0.0272(6)	0.0259(7)
C1	0.0393(7)	0.037(1)	0.0397(8)	-0.0004(7)	0.0175(6)	-0.0017(8)
C2	0.0421(8)	0.047(1)	0.0476(9)	-0.0037(9)	0.0141(7)	-0.0044(9)
C3	0.0388(8)	0.041(1)	0.061(1)	-0.0002(8)	0.0146(7)	0.0059(9)
C4	0.0449(8)	0.051(1)	0.0608(9)	-0.0052(8)	0.0280(6)	-0.0031(9)
C5	0.0394(7)	0.036(1)	0.0524(8)	0.0013(7)	0.0235(6)	-0.0008(8)
C6	0.0522(9)	0.045(1)	0.068(1)	0.0094(9)	0.0253(7)	0.008(1)
C7	0.0527(9)	0.042(1)	0.0505(9)	-0.0067(9)	0.0137(7)	0.0029(9)
C8	0.0486(8)	0.048(1)	0.0481(8)	0.0000(9)	0.0241(6)	0.0056(9)
C9	0.0378(7)	0.037(1)	0.0453(8)	-0.0010(7)	0.0204(6)	0.0008(8)
C10	0.0480(8)	0.045(1)	0.0625(9)	0.0032(9)	0.0285(6)	-0.0036(9)
C11	0.0561(9)	0.046(1)	0.084(1)	0.0103(9)	0.0383(7)	0.008(1)
C12	0.057(1)	0.060(1)	0.077(1)	0.017(1)	0.0299(8)	0.024(1)
C13	0.055(1)	0.063(1)	0.0510(9)	0.004(1)	0.0154(8)	0.014(1)
C14	0.0431(8)	0.043(1)	0.0425(8)	-0.0024(8)	0.0191(6)	0.0044(8)
C15	0.0505(8)	0.047(1)	0.0401(7)	-0.0105(8)	0.0223(6)	-0.0025(8)
C16	0.072(1)	0.064(1)	0.0485(9)	-0.022(1)	0.0240(8)	-0.008(1)
C17	0.093(1)	0.078(2)	0.064(1)	-0.038(1)	0.0436(8)	-0.029(1)
C18	0.093(1)	0.069(1)	0.094(1)	-0.028(1)	0.0626(8)	-0.041(1)
C19	0.0670(9)	0.052(1)	0.089(1)	-0.009(1)	0.0478(7)	-0.024(1)
C20	0.0504(8)	0.041(1)	0.0546(8)	-0.0090(8)	0.0316(6)	-0.0088(8)

The form of the anisotropic displacement parameter is:
exp[-2PI2{h2a2U(1,1) + k2b2U(2,2) + l2c2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3)+ 2klbcU(2,3)}] where a,b, and c are reciprocal lattice constants.

Bond Distances (Å) for Phenanthro Diketone

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O2	C3	1.212(2)	C9	C10	1.394(3)
O7	C7	1.207(3)	C9	C14	1.400(2)
C1	C2	1.544(2)	C10	C11	1.382(2)
C1	C5	1.569(3)	C11	C12	1.378(3)
C1	C8	1.534(3)	C12	C13	1.374(3)
C1	C9	1.514(2)	C13	C14	1.396(2)
C2	C3	1.502(3)	C14	C15	1.478(3)
C3	C4	1.500(3)	C15	C16	1.401(2)
C4	C5	1.539(3)	C15	C20	1.400(2)
C5	C6	1.541(3)	C16	C17	1.383(3)
C5	C20	1.517(2)	C17	C18	1.376(3)
C6	C7	1.508(3)	C18	C19	1.381(3)
C7	C8	1.499(3)	C19	C20	1.396(3)

Table V. Bond Angles (°) for Phenanthro Diketone

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C2	C1	C5	101.6(1)	C1	C8	C7	104.3(2)
C2	C1	C8	112.7(1)	C1	C9	C10	120.4(1)
C2	C1	C9	111.8(1)	C1	C9	C14	120.6(2)
C5	C1	C8	104.2(1)	C10	C9	C14	119.0(1)
C5	C1	C9	113.3(1)	C9	C10	C11	121.5(2)
C8	C1	C9	112.4(1)	C10	C11	C12	119.3(2)
C1	C2	C3	104.9(1)	C11	C12	C13	120.0(2)
O2	C3	C2	125.2(2)	C12	C13	C14	121.6(2)
O2	C3	C4	125.1(2)	C9	C14	C13	118.4(2)
C2	C3	C4	109.6(2)	C9	C14	C15	120.4(1)
C3	C4	C5	105.2(2)	C13	C14	C15	121.2(1)
C1	C5	C4	104.0(1)	C14	C15	C16	120.8(2)
C1	C5	C6	101.7(1)	C14	C15	C20	120.4(1)
C1	C5	C20	113.1(1)	C16	C15	C20	118.8(2)
C4	C5	C6	112.9(1)	C15	C16	C17	121.2(2)
C4	C5	C20	111.7(2)	C16	C17	C18	119.8(2)
C6	C5	C20	112.8(1)	C17	C18	C19	119.9(2)
C5	C6	C7	106.0(2)	C18	C19	C20	121.3(2)
O7	C7	C6	124.6(2)	C5	C20	C15	120.3(2)
O7	C7	C8	125.8(2)	C5	C20	C19	120.6(1)
C6	C7	C8	109.6(2)	C15	C20	C19	119.0(1)

Standard deviations are in parentheses.

APPENDIX 2: NSF PROPOSAL

PERSONAL STATEMENT

I was born in El Salvador, Central America, in 1965. I received a B.S. degree in 1986 at St. Joseph's College, in New York, where I majored in chemistry. In 1988 I began my graduate studies at Hunter College, under the supervision of Professor Klaus Grohmann. Currently I am in the process of writing my thesis in the area of dynamic rearrangements of constrained systems such as the Cope rearrangement in semibullvalenes.

My future goals are to teach and carry out research. In graduate school I taught laboratory and recitation, and supervised the research of three undergraduate students. The latter activity was particularly rewarding and is one of the reasons I want to teach. In addition, I want to continue to encourage and foster an interest in chemistry as a career option in other women.

My long term research goals involve the development and subsequent application of new synthetic methods, involving free radical reactions, toward the synthesis of natural products. Radical reactions have a number of advantages over non-radical pathways. First, carbon centered radicals are very reactive, thereby allowing conformationally restricted cyclizations, which are normally difficult to obtain, to take place under relatively mild conditions. Second, the addition of radicals to carbon-carbon double bonds often lead to unusual products that are not easily accessible through non-radical pathways.

In short, my interests involve methodology towards the formation of carbon-carbon bonds, specifically those leading to complex ring systems, such as those found in sequiterpenes. Initially, I plan to further develop existing methodology in the area of

sequiterpenes. Initially, I plan to further develop existing methodology in the area of [3+2] photocycloadditions of the type developed by Professor Agosta, at Rockefeller University. Ultimately I want to develop new methodologies from my work in the field of organic photochemistry and to apply them to organic synthesis.

As a Post-Doctoral Fellow I will work on further developing [3+2] photocycloadditions by studying the role that alkenes have on the rate of these types of reactions. Two aspects of this study will involve the role of steric hindrance and electronic properties of the alkene on the fate of these reactions. Professor Agosta and I have overlapping research interests in developing new synthetic methods and the study of reactive intermediates. Therefore, as a Post-Doctoral Fellow working with Professor Agosta I will have the opportunity to learn about developing new and independent synthetic methodology in organic photochemistry.

ABSTRACT

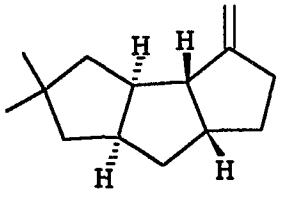
On Developing New Synthetic Methodologies

by

Mercedes B. Connelly

Fused cyclopentaniod natural and non-natural products represent an important class of compounds, and have been the target of many synthetic approaches. Among the tricyclic cyclopetanoid class of compounds, which are of wide interest, 1-3 are represented. Approaches towards the cyclopentanoid skeleton involving photocycloadditions have been widely used in the multistep synthesis of molecules 1-3.[92]

This proposal will explore the further development of [3+2] photocycloadditions and possible applications towards the synthesis of cyclopentanoids skeletons 1-7.



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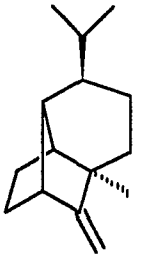
hirsutene



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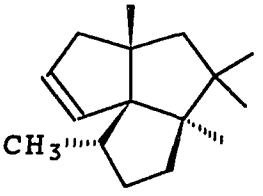
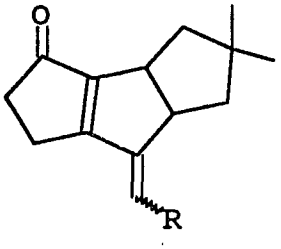
sativene



3

silphinene



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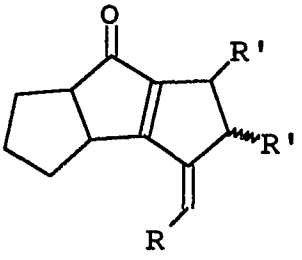

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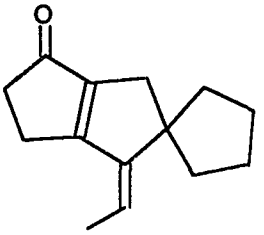

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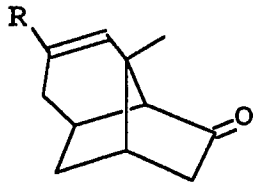


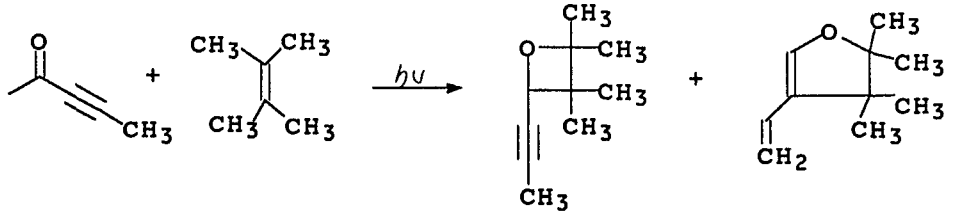
7

Training and Research Plan

Background

Professor Agosta, at Rockefeller University, works in the field of developing new synthetic methods. Professor Agosta is a pioneer in the area of [3+2] photocycloadditions. He first observed [3+2] photocycloadditions competing with [2+2] photocycloadditions of alkynones to alkenes in 1981, (fig. 1).[93]

Figure 1

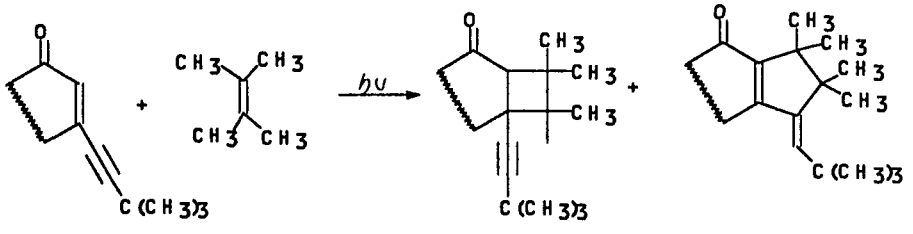


8 9 10 11

7% 77%

Over the past decade, Professor Agosta's research into [3+2] photocycloadditions has involved the use of 3-alkynyl-cyclopentenone and 3-alkynyl-cyclohexenone in the presence of simple alkenes, (fig. 2).[94]

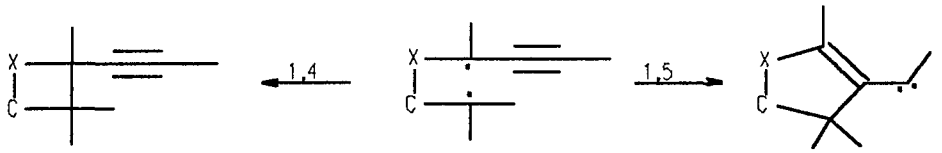
Figure 2



cyclohexenone 17% +34% + isomers

Professor Agosta and his coworkers have demonstrated that alkyl propargyl 1,4-biradicals of the general structure 12 can either close 1,4 to form four-membered ring 13a or close 1,5 to form vinyl carbenes 13b, (fig. 3).[2] He also notes that there is evidence that suggests that 1,5 closure occurs specifically from the triplet 12. The carbene resulting from 1,5 cyclization of 12 is traped by an either an internal or exteranal trapping agent to yield a mixture of products.

Figure 3

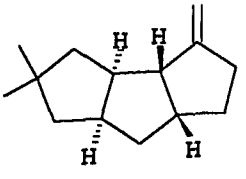


13a 12 13b

Research Plan

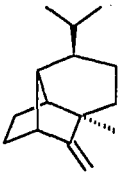
I plan to develop new methodologies, especially those involving free radical chemistry, to synthesize natural and non-natural products as well as heterocyclic compounds. The focus of this approach will be to use free radical chemistry in the formation of carbon-carbon bonds and carbon-heteroatom bonds, especially those leading to a series of five-membered ring systems (cyclopentanoid). Molecules containing fused cyclopentanoids are of wide interest and utility. Examples of fused cyclopentanoids include, hirsutene, sativene, and silphinene. Molecules containing a cyclopentanoid backbone have been the subject of other approaches including photochemical as well as ionic reactions.[1] However, the success of a transformation and functionality contained in the product depends heavily on the approach chosen. Therefore, it is always advantageous to have a variety of methods available to conform to the specificity of the desired molecule. Figure 4 shows examples of target compounds that can be approached by application of [3+2] photocycloaddition methodology.

Figure 4



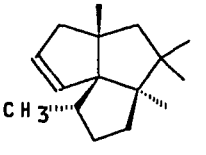
1

hirsutene



2

sativene



3

silphinene

Scope and Limitations

Problems associated with [3+2] photocycloadditions will be addressed in the preliminary stage of research. The problems are as follows: 1) there is competition with [2+2] photocycloadditions; 2) the reactive intermediate involved in [3+2] photocycloadditions is the source of many products including the desired five-membered ring system; 3) there has been very little work done involving the reactivity, regioselectivity and stereoselectivity resulting from the choice of alkene. However, based on what is known, it is realistic to further develop this methodology and thereby successfully apply it to organic synthesis in the near future.

The initial efforts of my laboratory will be directed towards the further understanding of how to increase the rate of 1,5-ring closure of the 1,4-diradical versus 1,4-ring closure. It is known that the 1,4-diradical is in the triplet state and 1,5-ring closure occurs in the triplet state. On the other hand, the 1,4-diradical must undergo intersystem crossing to the singlet state in order close in a 1,4-ring closure. Therefore, 1,5-ring closures compete with this intersystem crossing. One simple approach involves taking advantage of the fact that 1,5-ring closures are temperature dependent, while 1,4-ring closures are not. Therefore, one can increase the rate of 1,5-ring closures while keeping the rate of 1,4-ring closures constant. However, it will be necessary to further investigate what conditions can help to prevent [2+2] cycloadditions altogether.

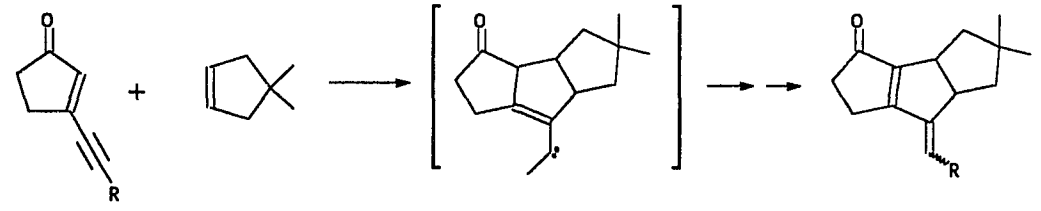
In addition, there are examples in the literature where carbenes have been successfully directed to form desired compounds. I anticipate my coworkers and I will spend some time researching how to focus the reactivity of these carbenes. One approach to this problem is to provide methoxy groups on neighboring carbons to the carbene since they have been known to form furans fused to the carbocyclic skeletons. Another

approach could be to trap the carbene with either an external or internal trapping agent such an alcohol or alkene.

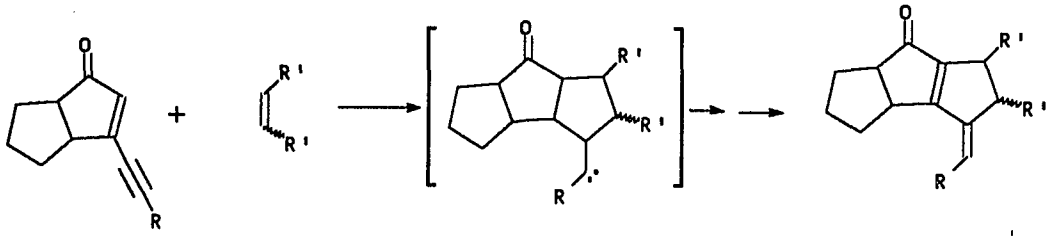
Lastly, there will be a systematic study of the effect that different electron withdrawing and electron donating groups have on the rate of [3+2] photocycloadditions. This study will include the regio- and stereoselectivities that these different groups have on the product. Some of the groups that will be included in this study are nitriles, esters, alkyl groups other than methyl groups and phenyl groups. The reaction products in these studies will be purified by HPLC and identified by IR, GC-MS in addition to 1D and 2D ^{1}H and ^{13}C NMR. In cases that involve the identification of a crystalline compound x-ray crystallography may be employed to confirm the stereochemistry of the molecule. This phase of the work could be further developed through collaboration with students and additional coworkers. I anticipate this first phase of research to take about 1 to 2 years.

Applications

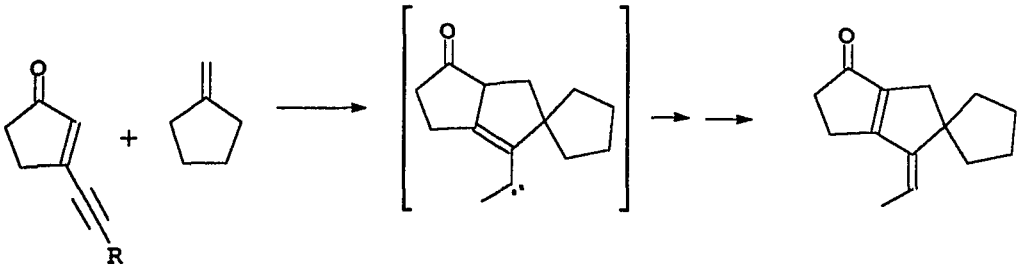
The successful completion of the fundamental studies mentioned above will allow my laboratory to apply this methodology to the synthesis of cyclopentanoid containing molecules 1-7. I anticipate dedicating 8 to 10 years to this phase of the research. The target cyclopentanoid natural products in this proposal are important because they have shown biological activity and as such have stimulated further interest in this area of research. A notable approach applied by Trost[95] involves palladium mediated cycloaddition as a key reaction. Curran's[96] methodology towards the synthesis of molecules that contain fused cyclopentanoid involves tin hydride promoted radical cyclizations. Spiro compounds have been synthesized by three types of photochemical reactions: (i) photorearrangement of cross conjugated dienones; (ii) photocyloadditions; (iii) combination of two photocycloadditions,[97] however, the photochemistry involved is one of many steps required to reach the desired skeleton.



14 15 16 4

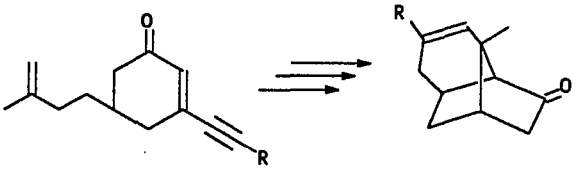


17 18 19 5



20 21 22 6

Unlike [2+2] photocycloaddition the use of tethers in the [3+2] photocycloaddition of alkenes to 3-alkynyl-α, β–unsaturated cyclic ketones has not yet been studied. It could lead to unusual molecules containing tricyclic skeletons 7, such as sativene 2, in one simple step from relatively simple starting materials. Sesquiterpene sativene was first synthesized by McMurry in 1968, in this multistep synthesis. The key step in this synthesis involves intramolecular alkylation to form the tricyclic skeleton.[98] Intramolecular [2+2] photocycloadditions have been widely used in the synthesis of many interesting natural products and non-natural products.[99] Therefore, the use of tethers in [3+2] photocycloadditions, is anticipated to become useful methodology in the synthesis of the following general type of compounds.



26 7

Conclusion

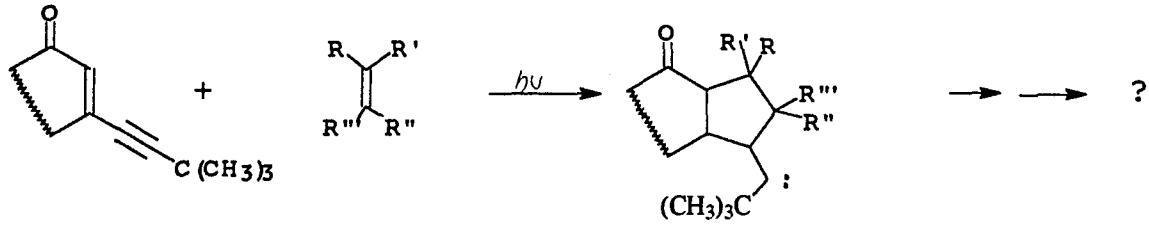
In conclusion, there always is a need to find simple useful methodology that will allow one to begin with simple starting materials and end up with sophisticated molecules. This proposal approaches useful and otherwise difficult to make molecules by using the novel [3+2] photocycloaddition as a key step. The use of photochemistry as a way to provide new methodology will be studied, as well as the reactive intermediates which result in this type of chemistry.

Post-Doctoral Research

Professor Agosta and his group have studied [3+2] photocycloaddition of 3-alkynyl-substituted α, β-unsaturated ketones and simple alkenes leading to cyclopentane derivatives. He and his group have also studied the consequent rearrangement of carbenes, which are the reactive intermediates in this type of photocycloadditions. As a Post-Doctoral Fellow I will be studying the competition between [2+2] photocycloaddition and [3+2] photocycloaddition as a result of placing electron donating and electron withdrawing groups on the alkenes, such nitriles, different esters (carbomethoxy, carboethoxy, etc.), A range of alkyl groups and phenyl groups. Also, we will be investigating whether the sizes of the groups on the alkene exhibit any effect on the competition between these two reactions, and whether the stereochemistry of disubstituted alkenes will make any difference on the outcome of the reaction. In addition, in the case of cyclic alkenes we are interested in observing reactivity effects due to ring size.

One problem anticipated with this project is that there will be many products along with the desired five-membered rings due to the carbene formed as a result of 1,5-ring closure. We plan to explore methods in which to focus the reactivity of theses carbenes. We do not know whether we will see any regio- and stereocontrol in these reactions.[100] However, products formed will be isolated and purified by HPLC. Furthermore, identification of structures will be done by use of IR, GCMS, 1D and 2D ^{1}H and ^{13}C NMR.

Figure 1



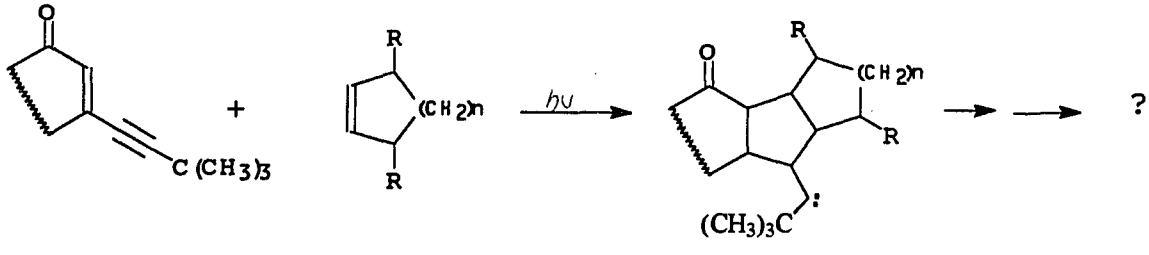
Where R' and R"' = -CN or

$-CO_2CH_3$ or

-CHO or

$-CH_2(CH_2)nCH_3$

Figure 2



The work done as a Post-Doctoral Fellow will provide the training in two of the research areas I will be involved with in the future; practical photochemistry and the study of reactive intermediates. Professor Agosta is a pioneer in the area of [3+2]

photocycloaddition, while Rockefeller University is a first class research facility that will provide the kind environment necessary to further develop scientifically.

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[1] Winstein, s., *J. Chem. Soc.*, **1959**, *81*, 6524.: *Chem Soc. Special Publication*, **1967**, No. 21, 5.

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