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AN EXPERIMENTAL AND THEORETICAL STUDY OF SEMIBULLVALENES - THE SEARCH FOR A NEUTRAL BISHOMOAROMATIC COMPOUND

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AN EXPERIMENTAL AND THEORETICAL STUDY OF SEMIBULLVALENES-
THE SEARCH FOR A NEUTRAL BISHOMOAROMATIC COMPOUND

by

Libby S. Miller

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

1982

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.

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Chairman of Examining Committee

28 September 1982
date

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Abstract

The synthesis of 1,5-dimethyl-2,4,6,8-tetrakis(carbomethoxy)semibullvalene is reported. This is the first semibullvalene substituted with pi-electron acceptors at positions predicted by theory to lower the E_{act} for the Cope rearrangement. A new synthetic route was utilzed which has been found applicable to the preparation of other substituted semibullvalenes. The compound was studied by x-ray crystallography and nmr spectroscopy. The x-ray structure indicates an unusual geometry; the cyclopropyl C2-C8 bond is very long (1.782 A) while the non-bonded distance (C4-C6) is shorter than in the unsubstituted compound. While the molecule does not exist in the delocalized form, it has undergone a substantial electronic rearrangement as manifested by the unusual crystal structure and the low temperature nmr results.

MNDO calculations on semibullvalene and some cyano-substituted analogs indicate that the 2,4,6,8-tetracyano and the 2,6-dicyano derivatives should have delocalized structures which are equal or lower in energy than the classical ground state. The Cl-C5 methylene annelated semibullvalene is also predicted to have a homoconjugated structure of lower energy than the classical ground state.

ACKNOWLEDGEMENTS

First and foremost I would like to thank my husband Alan and my two daughters, Elisa and Jennifer, for their encouragement, support and patience during this long and often trying undertaking. I am especially grateful to my research mentors, Dr. Klaus Grohmann and Dr. Joseph Dannenberg, for their guidance, time and enthusiasm. The other members of my thesis committee, Dr. Robert Lichter and Dr. Thomas Halgren, also provided valuable assistance.

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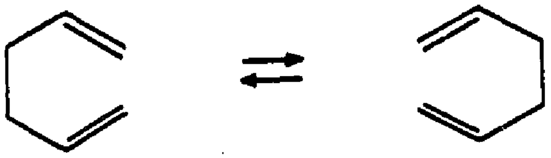
CHAPTER I

INTRODUCTION

A. Background

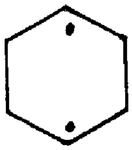
Molecules which can undergo (3,3) sigmatropic shifts (Cope rearrangements) have been of interest to experimental and theoretical organic chemists for a number of years. The rearrangement of 1,5-hexadiene is the classic example of this type of reaction (eqn 1) (1,2). The structure of the transition state for this rearrangement has been studied by many workers (2). Gajewski has utilized - secondary deuterium isotope effects to ascertain the transition state structure (3). He has concluded that the type of transition state depended upon the substituents and the geometric constraints on the molecule. Transition states can vary from the two nonconcerted extremes; two allyl radicals (a) or a cyclohexadiyl system (b) to the traditionally postulated concerted transition state (c). A study by Dewar and Wade (4) assessed the effects of substituents on the rate of Cope rearrangements in the 1,5-hexadiene system. They found a


(1)

large rate increase when phenyl groups were present at positions 2 and 5 and postulated a biradicaloid (type c) intermediate for this reaction. MINDO-3 calculations also supported this hypothesis (5).

a

b

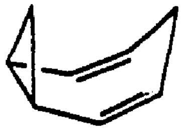
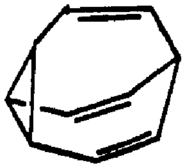
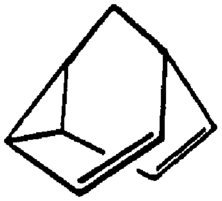
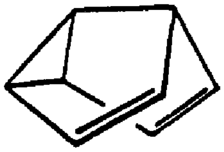


c

While the energy of activation (E_{act}) for the Cope rearrangement of 1,5-hexadiene has been reported to be 34.3 kcal/mole (6), there are many bridged compounds for which this energy is much smaller. In the series listed in Table 1, (7-10) semibullvalene has the lowest E_{act} for the Cope rearrangement and, in fact, the E_{act} for this molecule is the smallest known to date (10). In all the compounds listed in Table 1 the six carbons which undergo the rearrangement are bracketed by a carbon atom in a cyclopropyl ring and a methylene or methine carbon. In the tricyclic compounds the ring system is further constrained by the bridge. Therefore, any transition state for the Cope rearrangement must necessarily exist in a boat-like configuration for the cyclohexane part of the molecule.

Studies on the rate of rearrangement of substituted

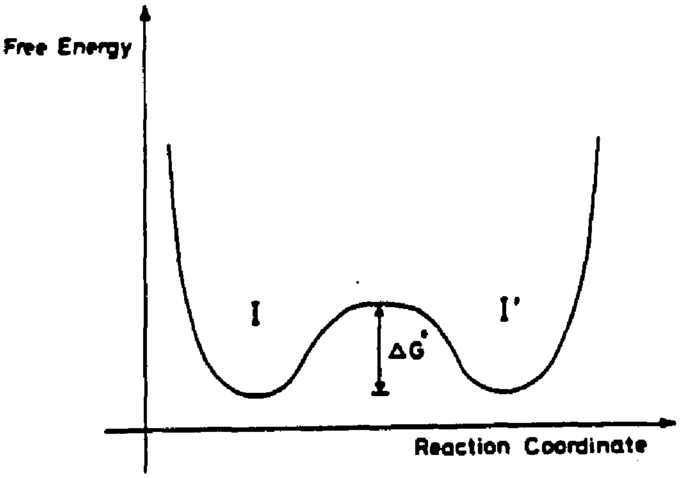
Table 1 $\Delta G^{\ddagger}$ for Cope Rearrangements

Compound	$\Delta G^{\ddagger}$ (kcal/mole)	ref.
 Homotropylidene	13.6	7
 Bullvalene	12.8	8
 Barbaralane	7.8	9
 Semibullvalene	5.5	10

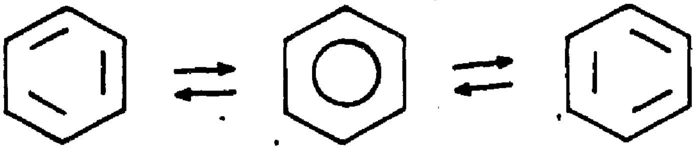
barbaralanes have discounted the 1,4-diyl transition state. The Cope rearrangement of 3,7-diphenylbarbaralane is slower than that of the parent molecule (11) while the 3-chloro- and 3-methoxy-6,8-dimethylbarbaralanes rearrange no faster than the unsubstituted compound (12). 3.7 diphenyl substitution in the barbaralane series would have stabilized a 1,4-diyl type transition state and the rate of Cope rearrangement should have increased upon introduction of this type of substituent. Gajewski has reasoned that the transition state for Cope rearrangement in the bridged polycyclic systems such as barbaralane and semibullvalene should involve more bond breaking than bond making since a bis allyl biradical would be more stable in these systems than the diyl alternative (23).

The degenerate Cope rearrangement of the molecules listed in Table 1 is characterized by a small E_{act}. A schematic representation of this reaction is shown on the next page using semibullvalene as an example.

I   I'

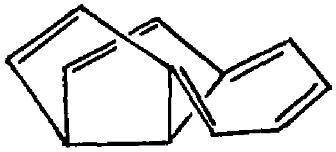


If one looks at the Kekule structures of benzene as the most extreme case of a rapidly rearranging cyclohexatriene system (eqn 2), then the proposed transition state, benzene itself, has a lower energy than either Kekule structure and thus , is the actual ground state of the molecule (14).

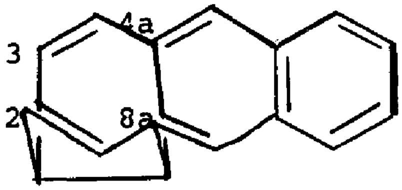
 (2)

Extension of this reasoning led workers to postulate methods of lowering the energy barrier to rearrangement in other systems. The idea of stabilizing a transition state to such an extent that it became the ground state of the molecle has fascinated many chemists (15). Prospects for success seemed likely if the semibullvalene nucleus was the target molecule. Since the E_{act} for the Cope rearrangement of the parent molecule is only 5.1 kcal/mole, it should not take a large perturbation to lower this value. It was thought that the transition state would exist in a homoaromatic form.

The concept of homoaromaticity was introduced into organic chemistry by Saul Winstein in 1967 (16). A homoaromatic molecule is defined as an aromatic system whose backbone has been interrupted by the interposition of one or more methylene groups and which still maintains its "aromatic" character. A cyclopropyl ring can be substituted for one of the double bonds in the aromatic structure. A bishomoaromatic molecule has two methylene groups interspersed in the aromatic ring system. To date, no one has realized the synthesis of a neutral bishomoaromatic molecule, however evidence for homoconjugative overlap has been found for the molecles listed below (17,18). In compound B overlap was found between C_{4a} and C_{8a} and even



A

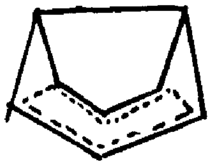


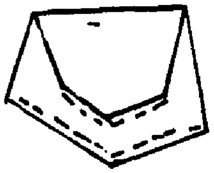
B

between C_2 and C_3. The overlap integral between these carbons was calculated from the X-ray data using a modification of the Mulliken procedure for determining pp-overlap integrals (18). The authors concluded that "mutually canted homoconjugated carbon atoms can still interact when separated by internuclear distances as large as 2.54A" (18).

There has been some controversy concerning these results (19).

The transition state for the Cope rearrangement of semibullvalene may exist as a bishomoaromatic molecule (14, 20). The six electrons involved in the rearrangement would be delocalized among the six carbons as shown. The amount of bond breaking at one end (C2-C8) would be approximately equal to the amount of bond making (C4-C6) at the other end of the molecule, i.e., C2-C8 should equal C4-C6. Other workers (21) have postulated a bis allyl type transition state for this rearrangement, reasoning that a large strain would be present if the two ends of the molecule were to get too close to each other as would happen in a diyl transition state. Some orbital overlap between the ends of the bis allyl system (C2-C8 and C4-C6) would still be possible.



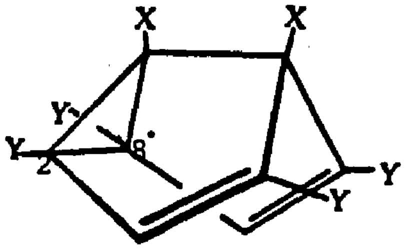


Whatever the precise nature of the transition state, many chemists have worked towards the goal of lowering the energy of this structure so that, ultimately, the transition state geometry would become the ground state structure.

Semibullvalene was first prepared in 1966 by Zimmerman (22) and its nmr spectrum showed only averaged signals for H1 and H5 and H2,4,6, and 8, even at temperatures as low as -110°C. At that time there was speculation that semibullvalene itself might exist as a "homoaromatic" molecule, but UV spectral data (22,23) and semiempirical calculations (20) did not support this view. As better low temperature nmr methodology became available, the Cope rearrangement was frozen out and the energy of activation for this reaction was determined from the nmr data (10).

In the early 1970's theoreticians utilized several different methods to calclate 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. Dewar and coworkers used MINDO-2 to study Cope rearrangements in the bullvalene-barbaralane-semibullvalene series (20,24). They obtained an activation energy of 2.3 kcal/mole (24) for the semibullvalene Cope rearrangement and calculated a transition state geometry where C2-C8 and C4-C6 bonds were 1.752 A apart. Since MINDO-2 is known to overestimate the stability of cyclic compounds, the calculated energies of activation were thought to be somewhat low. In a later study using MINDO-2, they calculated an E_{act} of 3.6kcal/mole (20).

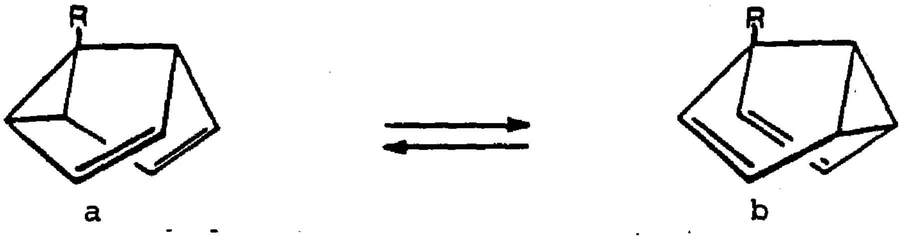
In a now classic study, Hoffmann and Stohrer used extended Huckel calculations to assess the effects of π-electron donating and withdrawing substituents on the ground state and transition state energies for the Cope rearrangement of semibullvalene (14). They constructed a set of orbitals for semibullvalene by combining the Walsh orbitals of cyclopropane and the orbitals of a penta-1,4-diene unit corresponding to the same geometry as the C3 to C7 portion of semibullvalene. The interaction of the orbitals of appropriate symmetry from π-electron donating and π-electron withdrawing substituents with the correct semibullvalene orbitals was then assessed. From these data, Hoffmann and Stohrer were able to calculate the relative stabilization or destabilization of the substituted ground state with respect to the unsubstituted semibullvalene. They concluded that the pattern of substitution shown below would maximally weaken the 2-8 bond in the reactant and product. When the same substituents interacted with the orbitals calculated for the transition state, the



X = π-electron donor
Y = π-electron acceptor

transition state was stabilized to a greater extent than the ground state. Hoffmann and Stohrer concluded that this pattern of substitution would be ideal for the stabilzation of a neutral "homoaromatic" geometry. They also calclated the activation energies of several model semibullvalenes with respect to the then unknown E_{act} for semibullvalene. Subsequently, Anet (10) calculated the activation energies for these products using the experimentally detemined value of 5.1 kcal/mole for the parent semibullvalene. He calculated $\Delta G^{\ddagger}$ = -2.8 kcal/mole for 2,4,6-8-tetracyanosemibullvalene and -8.7 kcal/mole for 1,5-difluoro-2,4,6,8-tetracyanosemibullvalene.

Until the present work, there were no reported syntheses of any semibullvalenes with the right type of substituents in the required positions. However, some early work did reinforce Hoffmann and Stohrer's predictions. Monosubstituted semibullvalenes which were substituted in position 1 (or 5) by a π-electron donating or withdrawing group had been prepared by Paquette and coworkers (25,26). Some of these compounds are listed below.



R=	Isomer Favored	(ref)
OCH_3	b	(25)
CN	a	(26)

Since the two Cope rearranging structures are not equivalent, these workers could use nmr data to determine which isomer was predominant. When the substitutent was OCH_3, a π-electron donor, isomer b was dominant. In the CN substituted case, isomer a was favored. These results are in accord with the theoretical predictions (14). A π-electron withdrawing substituent will strengthen the cyclopropyl bond opposite to it (the 2-8 bond) and thus, structure a should be favored when the substituent is CN. Conversely, π-electron donors will weaken the 2-8 bond. Since the Cope rearrangement is not degenerate in the monosubstituted cases, this type of substitution is not suitable for lowering the transition state energy as desired. The 1-CN compound was studied in depth by Christoph and Beno, (27) who determined the structure by X-ray crystallography (see Chapter 3).

Assuming one could synthesize the requisite molecule a method must be available for assessing the outcome. How can we determine if a molecule exists in a delocalized structure or if it is Cope rearranging so fast that we cannot freeze out the classical structure? At the present time low nmr temperature studies are the method of choice in determining the solution behavior of fluxional molecules; X-ray crystallography certainly will yield accurate information with respect to the crystal structure, although crystal packing effects cannot be ignored.

Another method which has been applied to the problem of differentiating between a delocalized structure and one that is undergoing a rapid degenerate rearrangement was developed by Saunders and coworkers (28) and recently applied to the semibullvalene system by Askani (29) and Klumpp (30). The technique involves introducing a deuterium atom in the molecule and studying the ^{13}C chemical shifts of a mixture of the deuterated and undeuterated compounds. In addition to an intrinsic change in the ^{13}C chemical shift which is due simply to 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 a delocalized structure. This new equilibrium constant can be determined from the change in chemical shift due to the equilibrium shift and from 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" (28). The ratio of the change in chemical shifts due to the deuterium, to the difference in chemical shifts for that particular carbon in the two frozen out states, is considered a measure of the delocalization.

The activation energy for the Cope rearrangement of unsubstituted and octamethylsemibullvalenes have been determined by low temperature nmr studies. Anet (10) found that at -133°C the average signals for protons 2,4,6 and 8 in the unsubstituted semibullvalene began to broaden and that the coalescence temperature was -143°C. At -167°C he was able to see the actual resonances for the frozen out semibullvalene structure. The exchange rate constants for the Cope rearrangements in semibullvalene were determined at several temperatures. These data were used to determine an activation energy (E_{act}) of 5.1 ± 0.2 kcal/mole. The free energy of activation ($\Delta G^{\ddagger}$) at -143° was 5.5 kcal/mole, while the enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation were 4.8 kcal/mole and -5.4±3 eu respectively.

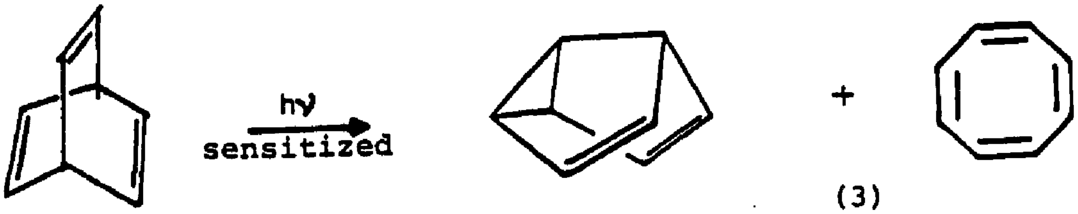
It is unclear whether one could obtain significant information from low temperature nmr studies if the energy of activation for the Cope rearrangement in question is much lower than 5.5 kcal/mole. Since it is not possible to run solution spectra at tempeatures lower than -160°, it might not be possible to freeze out a Cope rearrangement structure if the E_{act} is very small. This problem will be discussed further in Chapter 3.

Before discussing the work carried out in this study a review of previous synthetic methods is in order.

B. Previous Synthesis of Semibullvalenes

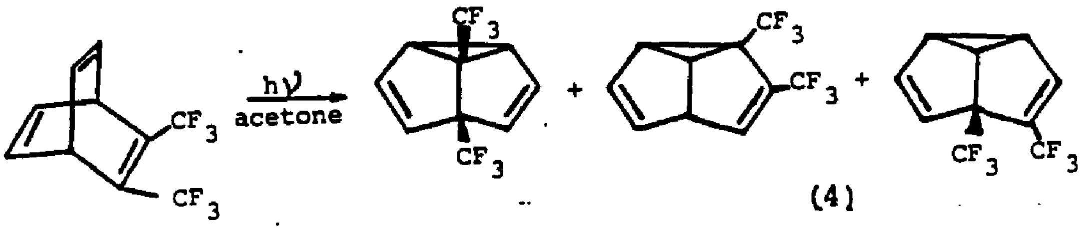
There have been three major precursor molecules used in synthesis of semibullvalenes, bicyclo(2.2.2)octatriene - (barrelene), cyclooctatetraene (COT) and bicyclo(3.3.0)-octane. Also, several reaction sequences have been followed in the preparation of specific semibullvalenes that are not applicable for the preparation of others (31).

Semibullvalene was first prepared by Zimmerman, (22,23) who utilized the sensitized irradiation of barrelene (eqn 3).



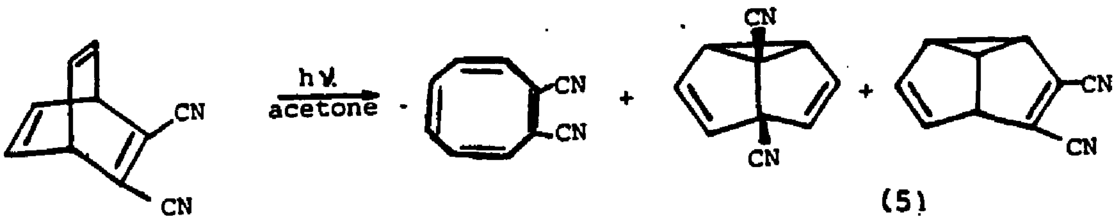
(3)

Barrelenes have been utilized as precursors for several substituted semibullvalenes. Liu and Krespan (32) photolyzed 1,2-bis(trifluoromethyl)barrelene and obtained a mixture of three semibullvalenes as shown in equation 4.



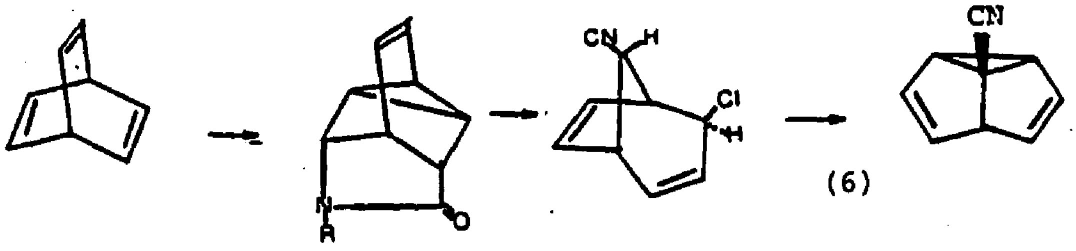
(4)

The same method was employed by Saita and Mukai (33) to prepare dicyanosemibullvalenes (eqn 5). In addition to 1,2-dicyanocyclooctatetraene only two isomers were formed. These authors demonstrated that irradiation of 1,2-dicyanocyclooctatetraene under the same conditions did not yield the semibullvalene products.



(5)

Barrelene itself, has been also utilzed in the preparation of 1-cyanosemibullvalene, via the addition of chlorosulfonylisocyanate (26) (eqn.6).

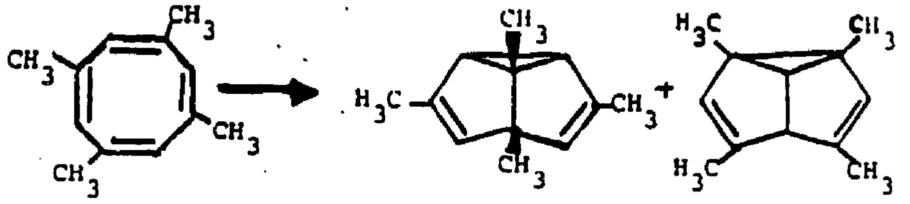


(6)

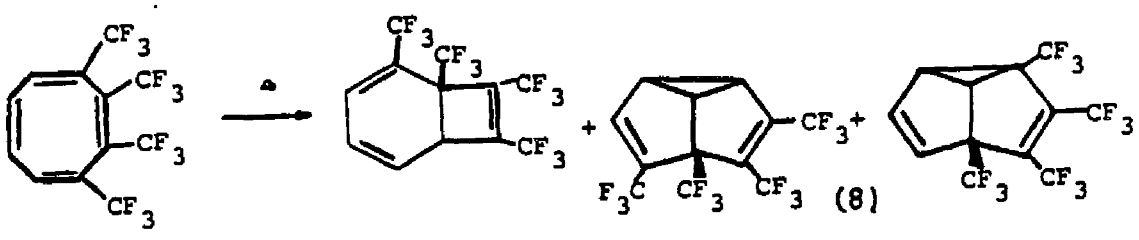
None of the methods utilizing the barrelene precursor has been applicable to the synthesis of the type of substituted semibullvalene that has been predicted to exist in the delocalized form.

The second major precursor to the semibullvalene system is cyclooctatetraene (COT) or its valence isomer bicyclo(4.2.0)octatriene. Although COT itself could be irradiated at -140^{o}C in acetone to yield a small amount of semibullvalene (34), substituted products could not be obtained from the corresponding reaction. Recently, semibullvalene has been prepared in quantitative yield by the vapor phase irradiation of COT, however, this method has not been applied to substituted derivatives (35).

Tetramethylsemibullvalenes have been prepared by heating 1,3,5,7-tetramethylcyclooctatetraene (eqn 7) (34) while two tetrakis(trifluoromethyl)semibullvalenes were prepared recently by the thermolysis of 1,2,3,4-tetrakis(trifluoromethyl)COT in pentane at 170-180°C for 6 days (eqn. 8) (36).



(7)

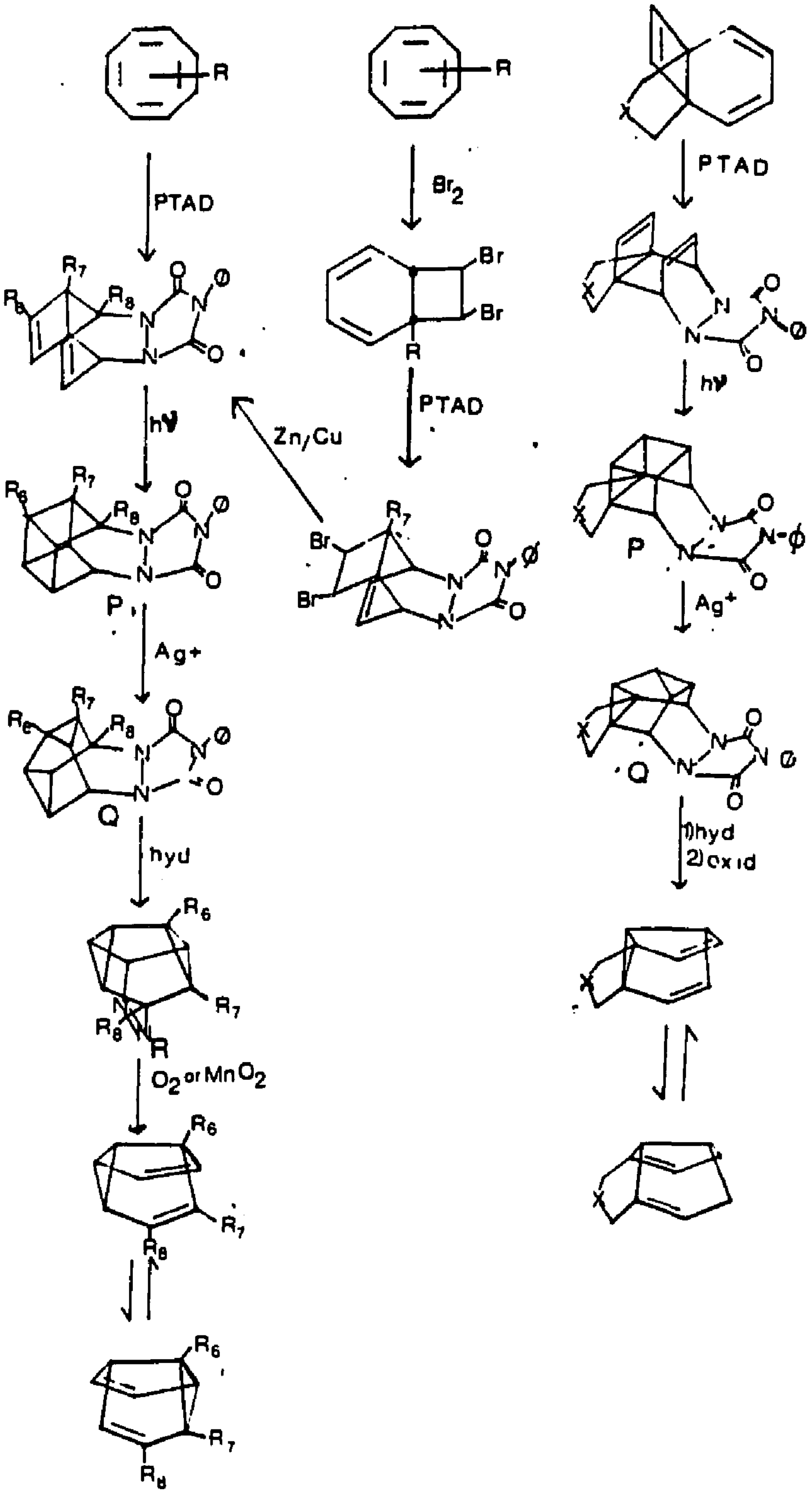


(8)

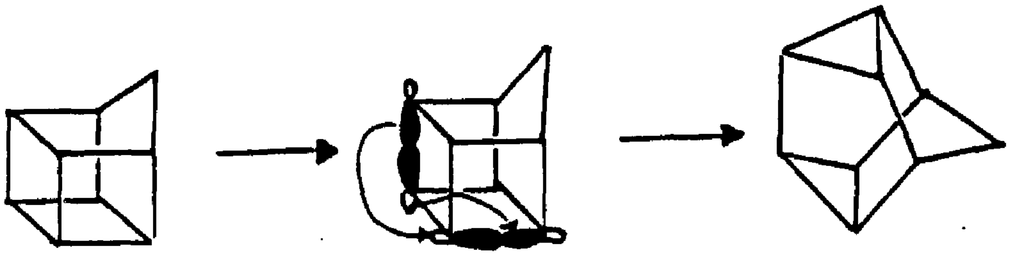
The major utilization of COT in the synthesis of semibullvalenes has been the method developed by Paquette and coworkers (37) outlined in Scheme 1. COT or its valence isomer bicyclo(4.2.0)octatriene reacts in a Diels Alder fashion with N-phenyltriazolidinedione as indicated in the scheme. Direct addition was utilized for some substituents while an indirect method (addition of Br_2 first to form the bicyclic system B of Scheme 1 was used for others. The substituents appeared in positions 6, 7 or 8 in the adduct. The same method was used for the preparation of the 2,8 (or 4,6) bridged semibullvalenes (scheme 1, part C). After the initial addition, a homocubyl system (P) was obtained by a 2+2 cycloaddition reaction (hν, acetone). The homocubyl

Scheme 1

SYNTHESIS OF SEMIBULLVALENES VIA COT OR BICYLCO(4.2.0)-OCTATRIENES AND N-PHENYLTRIAZOLIDENEDIONE (PTAD) (37)



system was then rearranged by Ag^+ to a 9,10 diazasnoutane (Q) derivative. The facile skeletal rearrangement of homocubanes (eqn.9) to pentacyclic systems had been described by Paquette in 1970 (38).


(9)

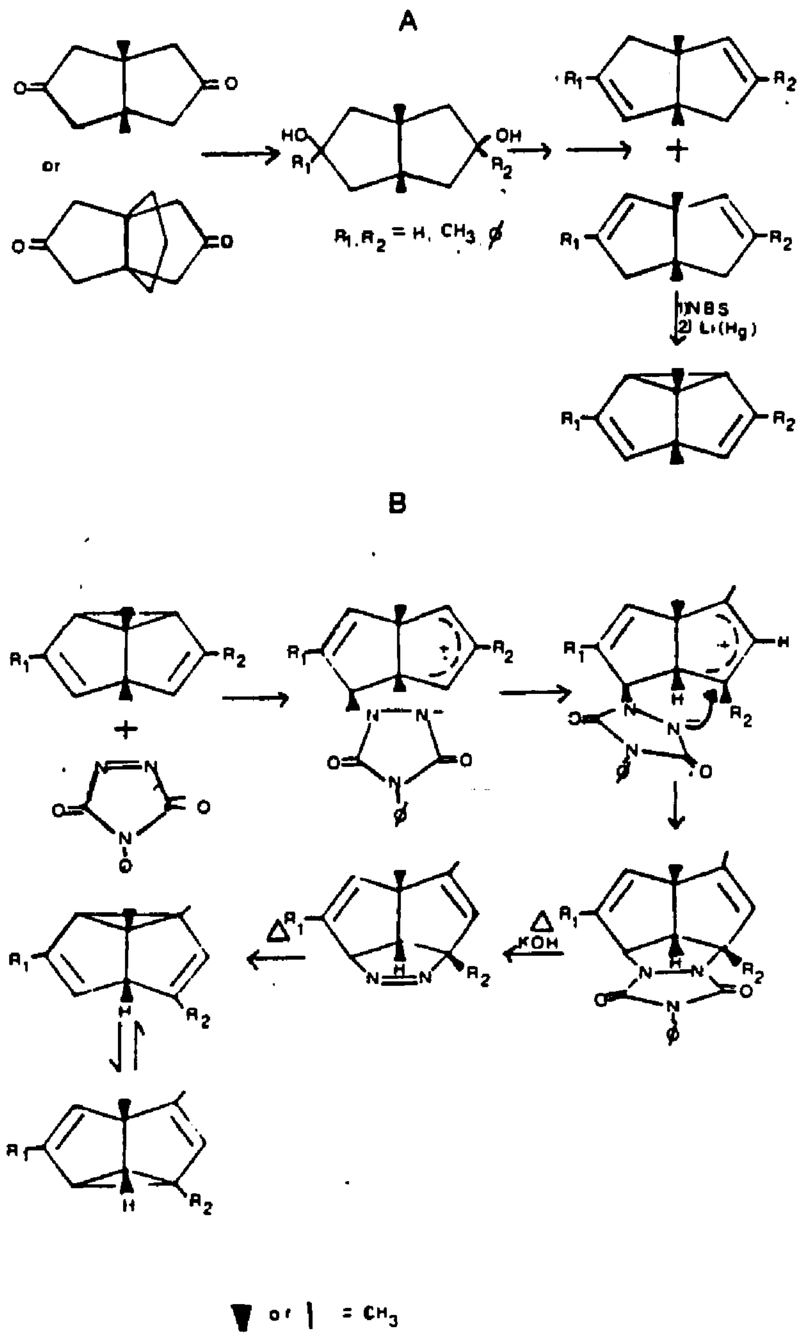
The rearranged product (Q) (Scheme 1) could be hydrolyzed to the azo derivative (R) and then oxidized in air or with MnO_2 to form the semibullvalene derivative. In this way a number of monosubstituted and 2,8 (4,6) bridged semibullvalenes have been synthesized. However, apart from the bridged compounds, only monosubstituted semibullvalenes have been synthesized following this route.

The other major pathway followed for the synthesis of substituted semibullvalenes was the conversion of bicyclo(3.3.0)octadiene derivatives to semibullvalenes. This is outlined in Scheme 2 (39). The bicyclo(3.3.0)octa-3,7-dione was reduced to the diol with various reagents, thus forming the secondary alcohol and the phenyl and methyl substituted

Scheme 2

SYNTHESIS OF SEMIBULLVALENES VIA BICYCLO(3.3.0)OCTANES

(39)



tertiary alcohols. The diol or the dimesylate was then dehydrated to a mixture of dienes. This mixture was not separated but brominated in the allylic positions with NBS and the resultant mixture of dibrominated compounds treated with Li(Hg) to yield the desired semibullvalenes.

Askani also treated the semibullvalenes prepared by the above route with N-phenyltriazolidindione. This reaction led to a rearrangement as shown in Scheme 2B (39,40). Hydrolysis and oxidation of this adduct yielded unsymmetrically substituted semibullvalenes.

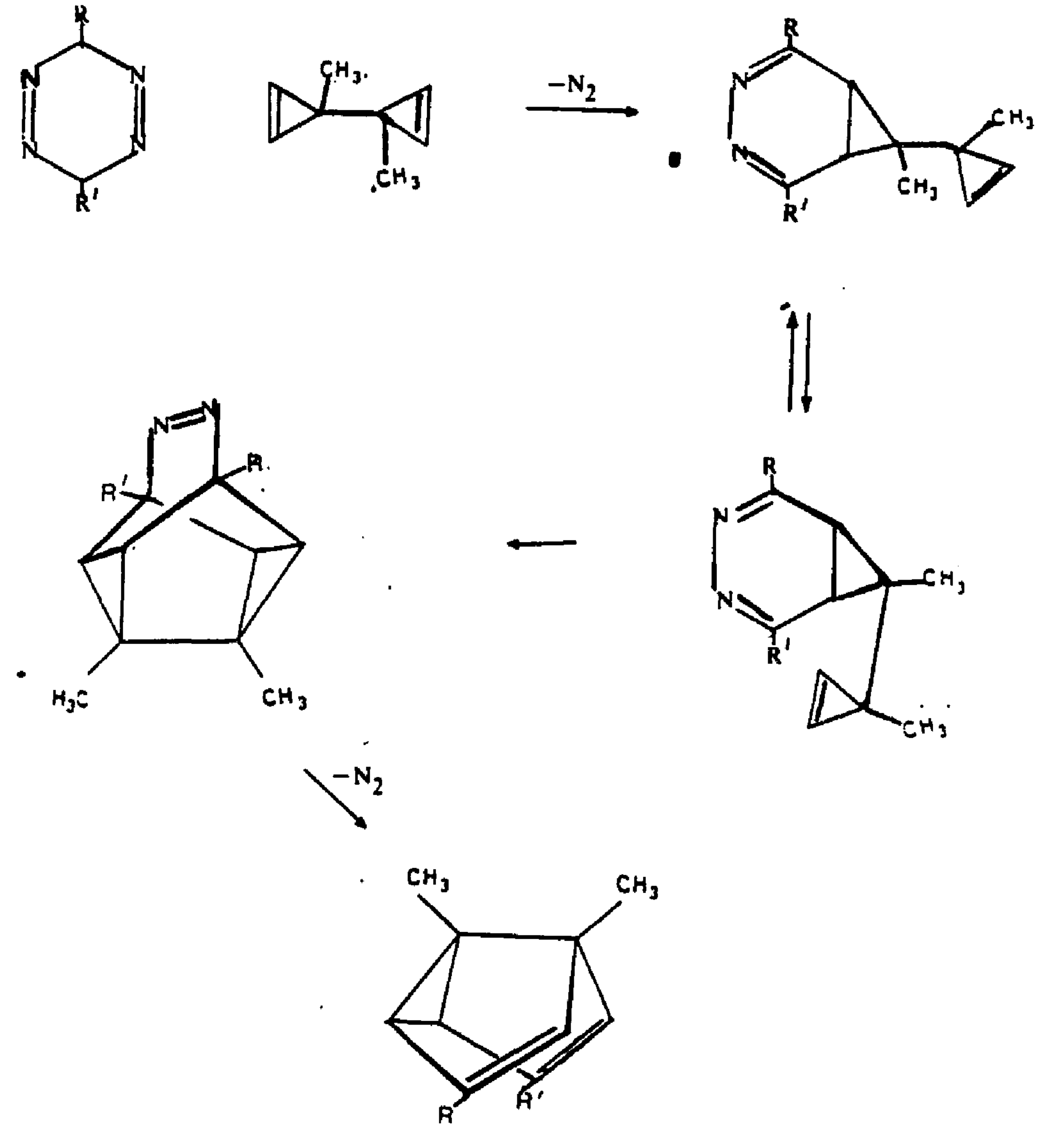
Another interesting route to 3,7-substituted semibullvalenes is outlined in Scheme 3 (41). Attempts at extending this reaction to the preparation of 2,4,6,8-tetrasubstituted semibullvalenes have not been successful. Reaction of the tetrazine with tetra-2,3,2',3' substituted dicyclopropenes led only to 1:2 adducts. Although this procedure is extremely useful for the synthesis of 3,7-substituted derivatives it is not yet applicable for the 2,4,6,8-substituted isomers.

C. OUTLINE OF WORK PROPOSED FOR THIS STUDY

Our approach to the semibullvalene problem was twofold. We wanted to devise a synthesis which would lead to 1,5-dimethyl-2,4,6,8-tetrakis(carbomethoxy)semibullvalene. This compound could then be studied by available techniques to determine its crystal and solution behavior. Since none of the previously used methods were easily adaptable to our

Scheme 3

SYNTHESIS OF SEMIBULLVALENES VIA 1,1'-SUBSTITUTED-DICYCLOPROPENYLS (41)



need, we had to look for a new preparative route. We then hoped to apply this route to the synthesis of other substituted semibullvalenes.

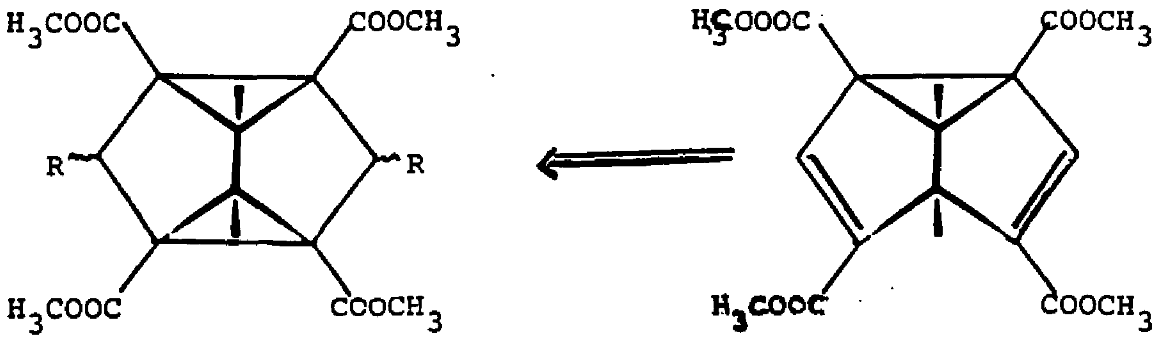
The second method of attack was through the use of theory. We wanted to use the MNDO semiempirical method to study the ground states, transition states and reaction paths for the Cope rearrangement of several substituted semibullvalenes. It had to be found that calculations using the MNDO approximation led to geometries and energies which correlated well with experimental data in other systems. Also, 2x2 CI could be included for "diradical like" transition states. We hoped that the results of these studies would guide us in our synthetic designs as well as shed some light on the mechanism involved in the Cope rearrangement of semibullvalenes.

CHAPTER 2

SYNTHESIS - RESULTS AND DISCUSSION

A. Retrosynthetic Analysis:

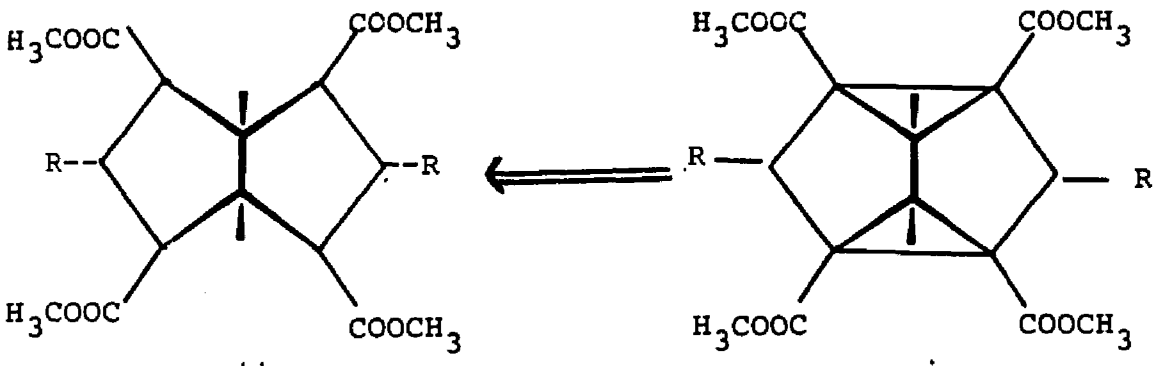
The successful synthesis of the desired semibullvalene Ib required the preparation of several polycyclic precurser molecules. Our goal was a synthesis of 1,5-dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene (Ib) which would be general enough to be applicable to other molecules and which would have as its last step, a 1,4-Grob type elimination (42,43). One target molecule was a suitably substituted tetracyclo(3.3.0.$0^{2.8}$.0.$^{4.6}$)octane, i.



i.

Ib

Several methods leading to the synthesis of the tetracyclic system i have been reported (44,45,46). However, none of the methods previously employed were appropriate for the synthesis of i with the particular substitution pattern that we needed. We felt that we could synthesize the tetracyclic precursor i from an appropriately substituted bicyclo(3.3.0)octane, ii.



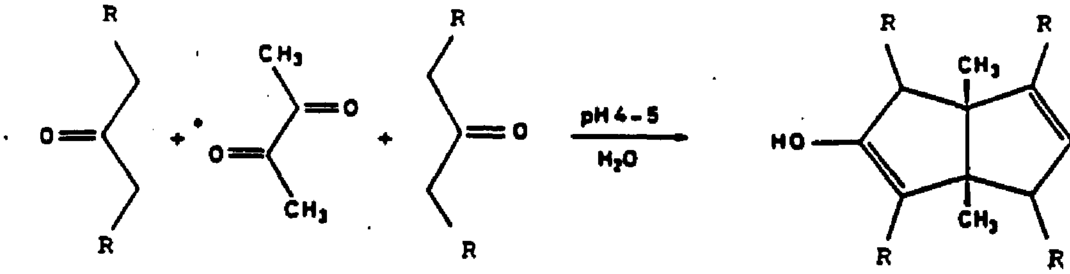
ii. i.

Tetrabromo derivatives of ii could be cyclized using NaI in acetone (47). The ring closure of dibromo derivatives of ii could be accomplished by dehydrohalogenation across C_2 - C_8 and C_4 - C_6 using triethylamine. Dreiding and coworkers had performed similar reactions in the bishomoquinone and triasterane systems (48,49). The target molecule ii could be obtained by bromination of the known 1,5-dimethyl-2,4,6,8-tetracarbomethoxybicyclo(3.3.0)octane-

3,7-dione, 1. Even if the proposed conversion of i to the desired semibullvalene Ib was unsuccessful, we felt that the precursor molecules could be manipulated in other ways to eventually yield the desired compound.

B. Synthesis of 1,5-dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene - Ib.

The synthetic route successfully employed in the preparation of 2,5-dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene Ib is outlined in Scheme 4. The cis fused bicyclo(3.3.0)octane system was prepared by condensation of two moles of dimethyl acetone-1,3-dicarboxylate and one mole of butane-2,3-dione in an aqueous acetate buffer at pH=5 according to the procedure reported by Weiss (50) (eqn 10).

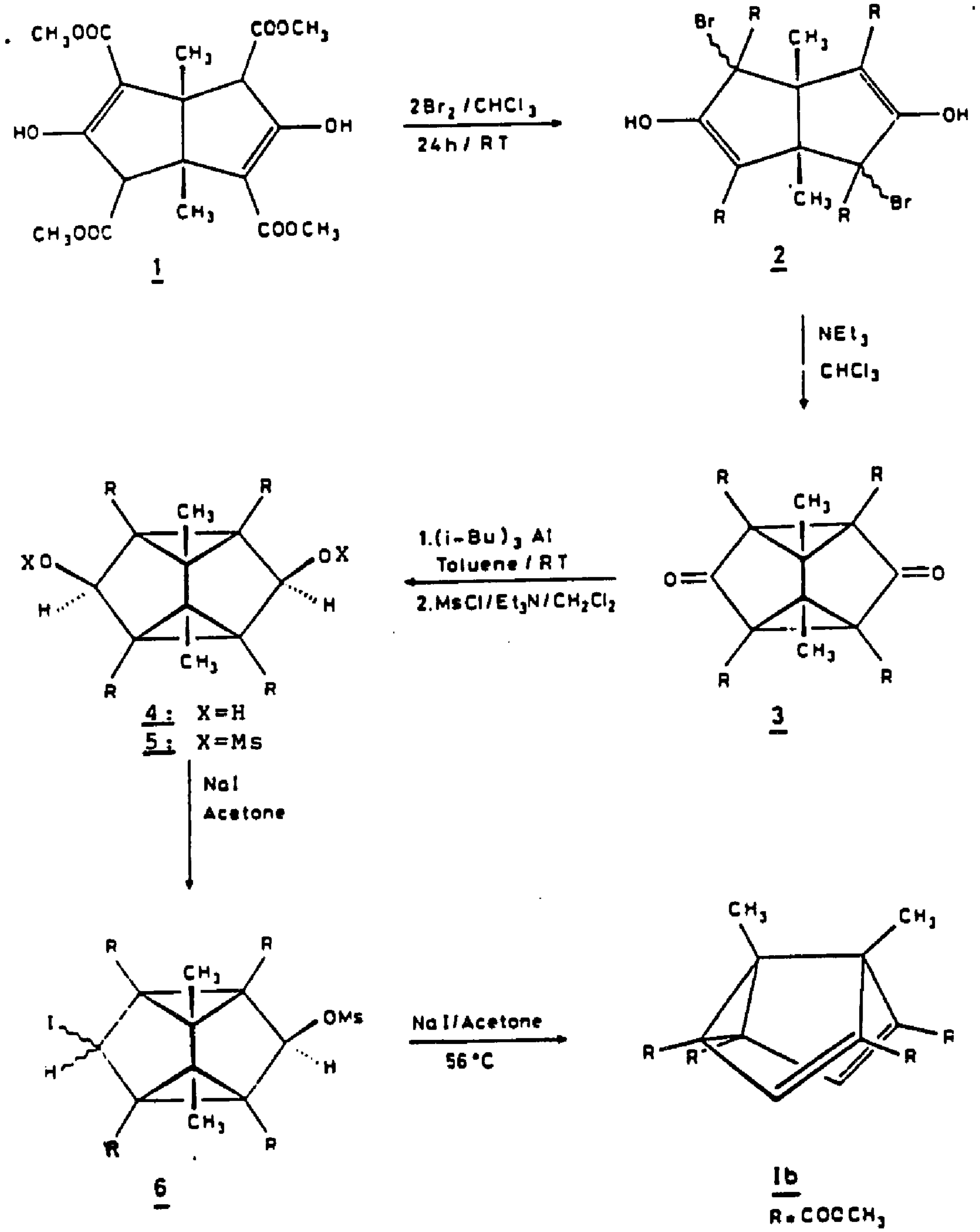


(10)

The mechanism proposed for this reaction is a combination of aldol and Michael additions as outlined in Scheme 5 (51). Initial 1:1 aldol condensation leads to species a which can undergo a second intramolecular aldol condensation to form b. This molecule will easily lose one mole of water forming

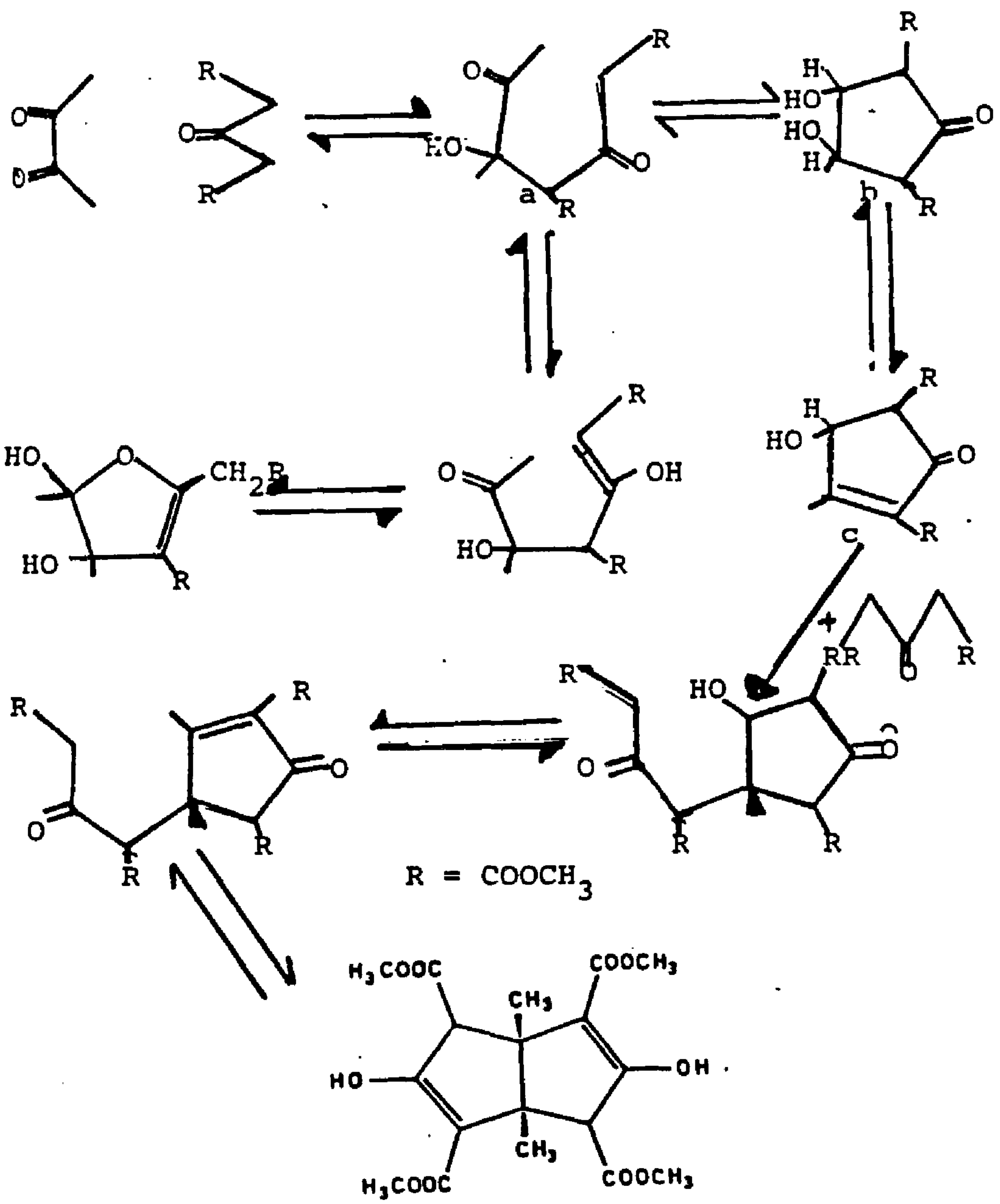
Scheme 4

SYNTHETIC ROUTE FOR THE PREPARATION OF 1,5-DIMETHYL-2,4,6,8-TETRAKIS(CARBOMETHOXY)SEMIBULLVALENE



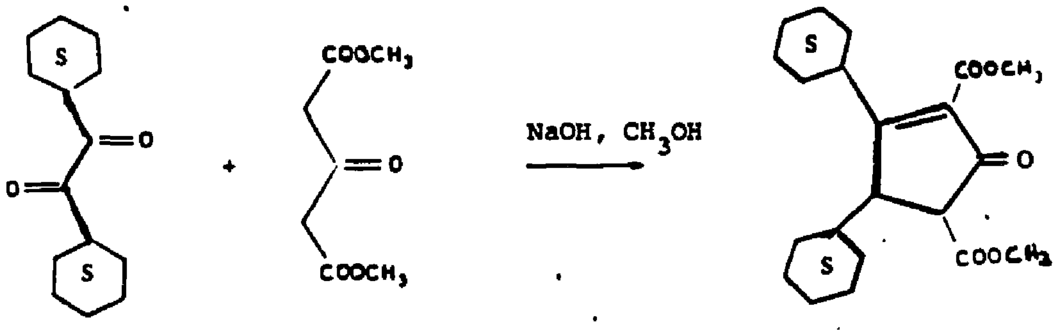
Scheme 5

PROPOSED MECHANISM FOR THE REACTION DIMETHYL ACETONE-1,3-DICARBOXYLATE AND 2,3-BUTANEDIONE



$R = COOCH_3$

the key intermediate c, which can then add aother molecule of dimethyl acetonedicarboxylate via an intramolecular Michael reaction followed by an intramolecular Michael addition. Many attempts have been made to isolate the intermediate c from this reaction. Recently, Weiss and coworkers (52) have isolated a 1:1 intermediate analogous to c from the reaction of biscyclohexyldiketone and dimethyl acetone-1,3-dicarboxylate in alkaline solution (eqn 11). In this case the intermediate is too hindered to react with another mole of dimethyl acetone-1,3-dicarboxylate.

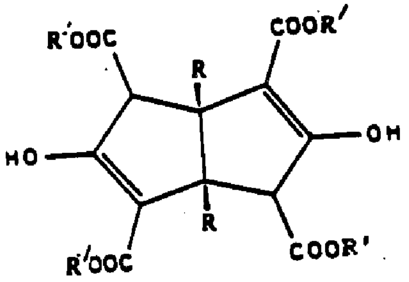


(11)

By optimization of the experimental conditions (pH = 5, acetate buffer, room temperature, 24 hours, trituration of the crude product with methanol) we were able to isolate pure product 1 in consistent yields of 85-90%. The melting point of 1, was 158-162^{o}, well above the reported values of 144-146 (50) and 153-5 (53). The compound exists as the bisenol, a fact that has been noted for the corresponding molecules with protons instead of methyl groups at C1 and C5 (see Table 2). Using ^{1}H NMR, Camps (54) demonstrated that 2,4,6,8-tetracarboethoxybicyclo(3.3.0)octane-3,7-dione was

Table 2

^{1}H and ^{13}C NMR DATA FOR ENOL ESTERS



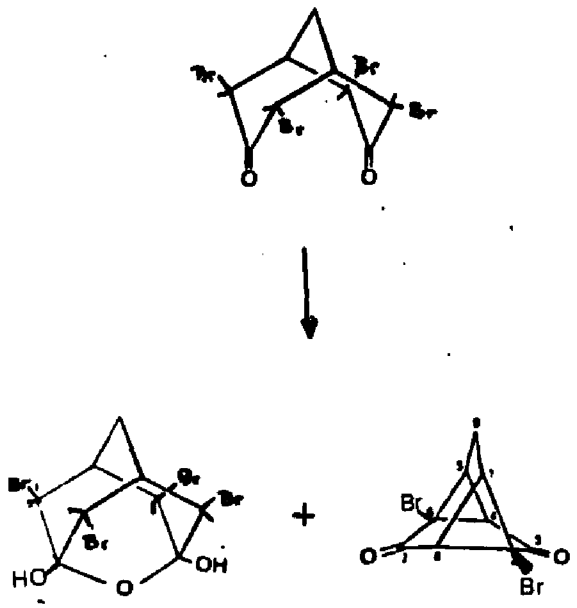
1a. R=H, R'=CH_2CH_3 (54)
1b: R=H R'=CH_3 (55)
1. R=CH_3, R'=CH_3 (this work & 56)

Cpd	1a	1b	1
^{1}H			1.30 (s,6H, CH_3)
	3.60 (t, 2H, J=2.7Hz)	3.64 (t, 2H, J=2.5Hz)	
		3.78 (s, 6H)	3.75 (s,6H, OCH_3)
		3.80 (s 6H)	3.88 (s, 6H, OCH_3)
	3.87 (t,2H J=2.7Hz)	3.88 (t, 2H, J=2.5Hz)	3.92 (s, 2H, H4,8)
	10.35 (br s, 2H, OH)	10.30 (br s, 2H, OH)	10.80 (br s, 2H, OH)
^{13}C			18.0 (CH_3)
		43.7	51.7 (OCH_3)
		51.4	52.2 (OCH_3)
		52.3	54.2 (C1,5)
		55.2	58.2 (C4,8)
		103.6	109.4 (C2,6)
		168.7	169.3 (C3,7)
		170.2	170.6 (C=0)
		170.5	170.9 (C=0)

totally enolized. He concluded from the size of the vicinal coupling constant (J_{AB}=2.7 Hz) that the ester groups on the sp^3 carbon were in the exo orientation. Recently Bertz (55) has confirmed the enol structure for the tetracarbomethoxy ester. Spectral data for 1 were also reported while this manuscript was being prepared (56) (see Table 2).

Our data are consistent with a bisenol structure and correlate well with the reported spectral data (Table 2). The proton nmr shows a broad singlet (2H) at 10.8 ppm for the enol hydroxy hydrogens, which disappears upon the addition of D_2O. The ^{13}C spectrum shows a resonance at 169.3 ppm for the enol carbon and does not have any ketone carbonyl resonance. Additional confirmation of the structure was obtained by the quantitative conversion of the enol 1 to its methyl ether 13, using diazomethane in ether without catalyst.

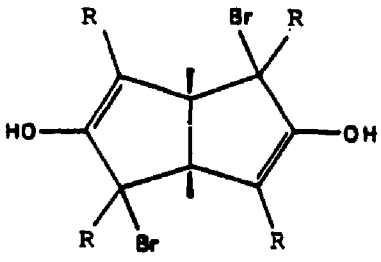
The next step involved the bromination of 1. When this was attempted using bromine in several different solvents variable results were obtained. In related work Dreiding (48) had found that bromination of cyclooctane-1,5-dione with 4 equivalents of phenyltrimethylammonium tribromide in CH_2Cl_2 led to a mixture of stereoisomers of tetrabrominated products in 53% yield. Applying the same reaction conditions to bicyclo(3.3.1)nonane-3,7-dione, Dreiding isolated a tetrabromosubstituted 1,3-dihydroxy-2-oxa-adamantane in 23% yield along with 10% of a tetracyclic product (49) (eqn 12).



(12)

When bromine in acetic acid was used, a 40% yield of a different tetrabromo stereoisomer was obtained. In both cases the products existed as hydrates of the diketones (49).

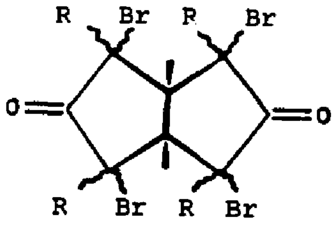
In our case, addition of 4 moles of bromine in acetic acid to 1 produced the tetrabromo and the dibromo adducts (2 and 2a) in varying proportions.



2

and

R = $COOCH_3$

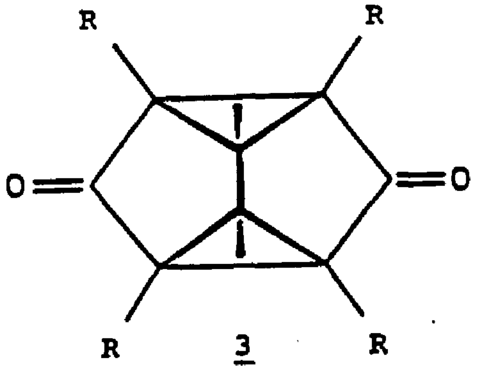


2a

When the tetrabromoadduct was isolated, it was extremely insoluble in organic solvents and decomposed easily. Th tetrabromo compound reacted readily with NaI in acetone at room temperature liberating a yellow solid (IBr) and yielding the desired tetracyclic ketone 3 in 78% yield. The major problem associated with this reaction was the nonreproducibility of the bromination step. Although the same reaction conditions were repeated, it became impossible to predict whether the tetrabromo, the dibromo or mixtures of the two compounds would be formed. Reducing the molar ratio of bromine to 2 equivalents also led to mixtures of the two products although the dibromo product could be isolated as a solid in low yield. Changing the solvent to $CHCl_3$ or CH_2Cl_2 while using 4 equivalents of bromine yielded no better results. A small amount of a non halogenated product was isolated from the reaction mixture. The mp and spectral properties were identical to those of the desired ketone 3. Apparently 3 was formed either during the reaction or, more likely, during the aqueous work-up of the reaction mixture. This result, taken into account with the results obtained by Dreiding (eqn 12) led us to devise a "one-pot" reaction for the transformation of 1 to 3 without the isolation of 2, as follows: The bisenol tetraester 1, was treated with 2 equivalents of bromine in $CHCl_3$ overnight at room temperature. The excess bromine was removed by washing the chloroform solution with aqueous $NaHSO_3$. The solution of dibromo-bisenol-tetraester 2 was then dehydrobrominated by the addition of a solution of triethylamine in

$CHCl_3$. The tetracyclic ketone 3, was isolated in consistent yields of 50% for the two step process.

Although tetracyclo(3.3.0.0$^{2.8}$.0$^{4.6}$) octane systems are known (44,45,46), there are not too many spectral data available. The proton and ^{13}C NMR data for compound 3 verified its structure and symmetry. The proton nmr consisted of only 2 singlets, one at 1.8 ppm for the 6 CH_3 protons and one at 3.8 ppm which corresponded to the OCH_3 protons. The carbon spectrum consisted of 6 peaks at 8.5, 48.1, 49.8, 53.2, 162, 0 and 189.6 ppm. The appearance of the methyl carbon resonance at 8.5 ppm is indicative of its being situated on a cyclopropyl ring. Only the symmetrical structure 3, below satisfies these spectral data. All of the spectral data agree with those reported recently by Gomppers for the same compound (56).

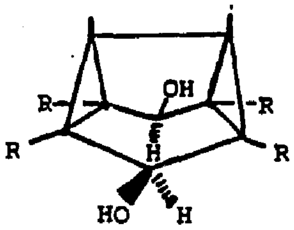


3

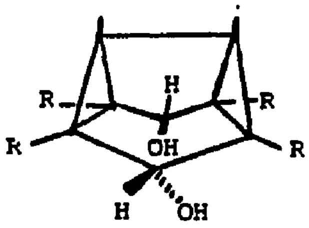
R = $COOCH_3$

Ultimately, this ring structure was verified by the conversion of 3 to the desired tricyclic semibullvalene Ib.

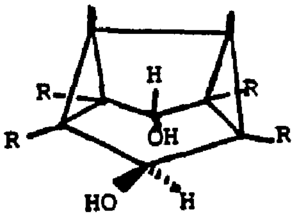
The next step in the synthetic scheme involved the reduction of the ketone groups to alcohols. Clearly, there are a number of reagents which would accomplish the reduction while still leaving the carbomethoxy groups and the ring system intact. However, stereochemistry of the product diol became an important factor. It is apparent that three different diols could form in the reduction reaction.



4a



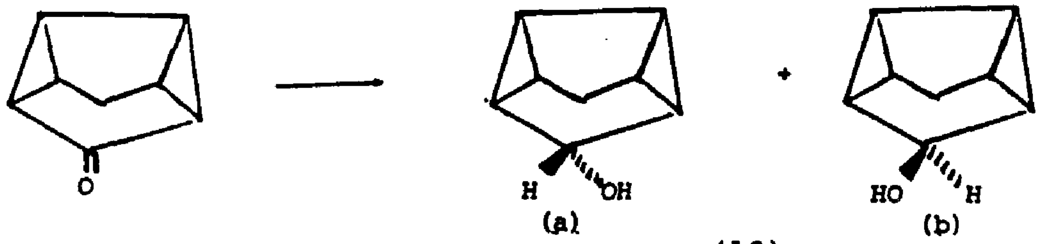
4b



4c

R = $COOCH_3$

LeBel and coworkers had reduced the unsubstituted monoketone with $NABH_4$ and diisobutylaluminum hydride (DIBAL) (44) (eqn 13).



(13)

NaBH$_4$: 70%a:; 30%b
DIBAL : 55%a . 45%b

He reasoned that the hydride would encounter less hindrance approaching from the top of the ring system. While he did not comment on the different ratios of products obtained when DIBAL was used, it seems clear that since DIBAL is a hindered reducing agent itself, it would prefer to complex with the carbonyl oxygen from the top side of the ring system and, therefore, the ratio of products reflects a competition between the hydride and the bulky reagent.

In a related system, Paquette and Winstein (43) found that LAH reduction of the bishomoquinine M, produced a mixture of diols whose major component was the exo/endo diol (eqn 14). When these workers used NaBH$_4$, they obtained a different mixture of diols in which the di-exo isomer predominated.

M

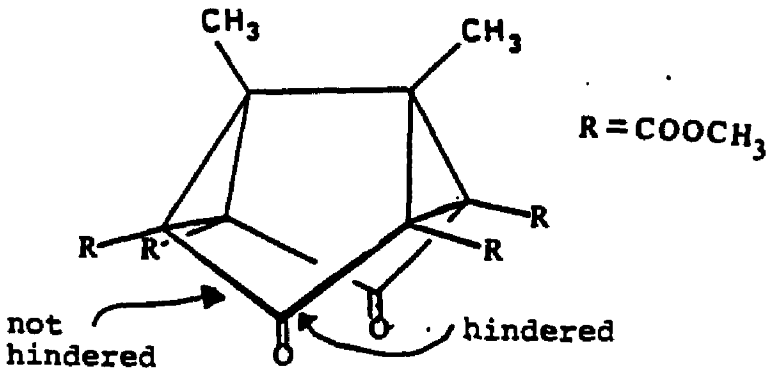
(14)

LAH : R_1 = OH, R_2 = H

$NaBH_4$:R_1 = H, R_2 = OH

The first reducing agents we tried were $NaBH_4$ and $NaBH_3CN$. Both reagents gave the same product, to which we have assigned the di-endo diol configuration, 4b. Neither PBr_3 nor Ph_3P and bromine (a reagent known to convert endo-2-norbornanol to exo-2norbornylbromide (57)) reacted with the diol to form the dibromide. The product from the PBr_3 reaction did not contain any halogen ,its proton nmr spectrum showed doublets for the CH_3 and $COOCH_3$ groups, although ^{13}C nmr indicated that the methyl groups were still attached to cyclopropyl rings (δ = 8.3, 8.7 ppm). The Ph_3P and bromine reaction did not yield any identifiable product. When the diol was allowed to react with 2 equivalents of methanesulfonyl chloride, a new product was isolated from the reaction mixture. Proton nmr indicated the presence of only one CH_3SO_2 group (see Table 3). The compound has been assigned the monomesyl-monohydroxy structure, 5b. Increasing the reaction time or the amount of CH_3SO_2Cl used did not change the product's structure or yield. Refluxing the diol in CH_3ONa and CH_3OH did not cause isomerization of the OH groups.

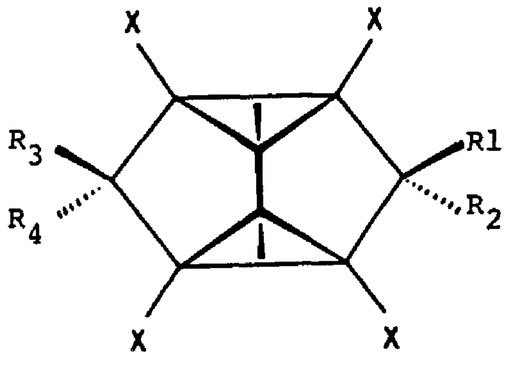
After studying molecular models of the tetracyclic ketone 3 we realized that the approach of any hydride reducing agent from the bottom of 3 would be hindered by the concavity of the ring system, just as Lebel had suggested (44). Therefore, it was logical that the $NaBH_4$, and, in fact, any unhindered reducing agent would deliver its hydride anion in an exo manner, thus forming the di-endo diol.



We needed a reducing agent which was bulky enough to complex with the ketone in such a way as to force delivery of the hydride solely from the bottom of the ring system. It was known that $Al(iOPr)_3$ in isopropanol can reduceketones in a stereospecific way depending upon the reaction conditions (58). Triisobutylaluminum was another mild reducing agent which was known to reduce hindered ketones to the less thermodynamically favored isomer (59,60).

Table 3

NMR DATA FOR TETRACYCLIC TETRACARBOMETHOXYDIOLS AND THEIR DERIVATIVES (4,5,6)



X = COOCH$_3$

Cpd	R1=	R2=	R3=	R4=
4a	OH	H	OH	H
4a'	(isopropyl ester of 4a)			
4b	H	OH	H	OH
5a	OMs	H	OMs	H
5b	H	OMs	H	OH
6	OMs	H	I(H)	H(I)

OMs = OSO$_2$CH$_3$

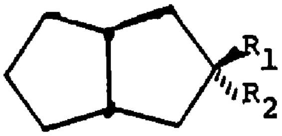
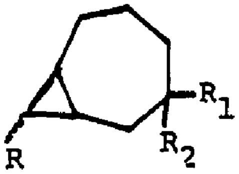
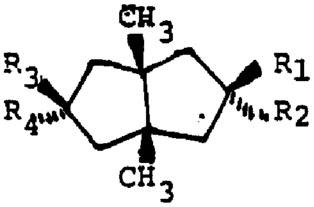
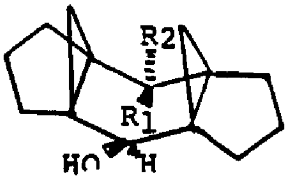
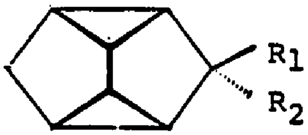
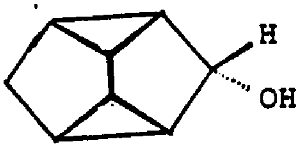
^{1}H NMR					
4a	4a'	4b	5a	5b	6
	1.30 (d, J=6Hz, 24H)				1.53 (s, 6H, CH$_3$,
1.70 (s, 6H, CH$_3$)	1.78 (s, 6H CH$_3$)	1.49 (s, 6H, CH$_3$)	1.80 (s, 6H, CH$_3$)	1.47 (s, 6H, CH$_3$)	2.91 (s, 3H CH$_3$S)
3.72 (s 12H, OCH$_3$)	3.95 (d J=2Hz, OH)	3.78 (s 12H, OCH$_3$)	3.08 (s, 6H, CH$_3$S)	3.21 (s, 3H, CH$_3$S)	3.63 (s, 6H, OCH$_3$)
3.80 (d, J=3Hz, OH)		4.38 (d J=7Hz, OH)	3.75 (s, 12H, OCH$_3$)	3.75 (s, 12H, OCH$_3$)	3.65 (s, 6H, OCH$_3$)
4.60 (d, J=3Hz, H3,7)	4.70 (d J=2Hz H3,7)	5.35 (d, J=7Hz H3,7)	5.73 (s, 2H, H3,7)	5.32 (s, 1H, H7)	5.38 (s, 1H, H7)
	5.10 (m, 4H)			6.20 (s, 1H, H3)	6.06 (s, 1H, H7)
^{13}C NMR					
9.6		8.9	9.2		8.8
					39.1
47.6		45.3	39.3		49.1
					49.4
49.4		48.4	47.9		50.0
					50.4
52.3		52.4	52.7		52.6
					53.6
71.6		72.1	79.5		74.8
					80.6
167.4		167.7	164.8		164.8
					165.0

Reduction of 3 with Al(OiPr)$_3$ in iPrOH for three hours at reflux followed by the distillation of iPrOH and acetone, produced a single product which, in addition to having been reduced, was also transesterfied. Proton nmr data are reported in Table 3 and are consistent with the tetraisopropyl ester of the desired di-exo diol. In order to circumvent the transterification problem, (iBu)$_3$Al in toluene was used as the reducing agent. When 3 reacted with this reagent only one product was isolated (in 50% yield). This proved to be a different diol from that formed in the NaBH$_4$ reaction. Spectral data (see Table 3) and chemical reactivity led us to assign the di-exo diol (4a) structure to this compound.

Diol 4a reacted readily with 2 equivalents of methanesulfonyl chloride yielding the dimesylate, 5a, in good yield. At times the dimesylate was contaminated with a product which contained only one CH$_3$SO$_2$ group, but use of recrystallized diol led to the dimesylate consistently.

Proton and ^{13}C NMR data for the di-endo and di-exo alcohols and mesylates are presented in Table 3 while relevant literature data are presented in Table 4. There are several striking differences in the spectra. In the proton spectra, the methyl resonances for the di-exol diols and mesylates (4a - 1.70 ppm, 4a' - 1.78 ppm, 5a - 1.80 ppm) appear further downfield than the signal for the same group in the di-endo compounds (4b - 1.49 ppm and 5b - 1.47 ppm). The same trend is evident when one examines entries c (39b)

Table 4
^1H and ^{13}C NMR DATA FROM THE LITERATURE

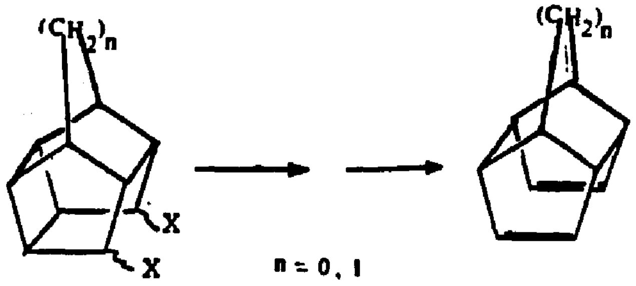
Cpd	Ref	Structure	Chemicl Shift (ppm from TMS)		
a	63		R_1=OH, R_2=H	74.8	^{13}C
			R_1=H, R_2=OH	76.1	
b	61	 R=CH_3,H	R_1=OH R_2=H	3.3-3.4	^1H
			R_1=H R_2=OH	4.2-4.6	
c	39		$R_{1,3}$=H, $R_{2,4}$=OH	0.95 (CH_3)	
			$R_{1,4}$=H $R_{2,3}$=OH	1.03 (CH_3)	
			$R_{2,4}$=H, $R_{1,3}$=OH	1.14 (CH_3)	
d	39b		$R_{1,3}$=H, $R_{2,4}$=OH	1.32 (4C bridge)	
			$R_{1,4}$=H, $R_{2,3}$=OH	1.40 "	
			$R_{2,4}$=H, $R_{1,3}$=OH	1.53 "	
e	43		R_1=H, R_2=OH	3.19 (H3)	
			R_1=OH, R_2=H	4.33 (H3)	
f	45		R_1=OCH_3, R_2=H	3.32 (s)	
			R_1=H, R_2=OCH_3	4.00 (m)	
g	44			4.64 (br s)	

and d (39b)in Table 4. In both the bicyclo(3.3.0)octane series (c) and the propellanes (d), the methyl or methylene group at the bridgehead positions is more shielded when the OH group is in the endo configuration. Apparently, the exo-OH (or OMs) groups exert a deshielding effect upon the methyl groups at the bridgehead position.

Another interesting feature of the proton nmr is the chemical shift of the proton attached to the carbonyl carbon. Here we see that this proton resonates further upfield when it is in the endo position; i.e., in the exo diols the carbinyl H resonates at 4.60 ppm (4a), 5.1 ppm (4a') and 5.73 ppm (5a) as compared to the comparable protons in the di-endo diols, 5.35 ppm (4b) and 5.32 and 6.20 ppm (5b). Some relevant examples from the literature are listed in entries b (61), e (43) and f (45) in Table 4. The closest comparison can be made between the methyl ethers reported in entry f (45) and the compounds prepared by us. In this case, the ring system is exactly the same and the proton on the carbinyl carbon is also shifted downfield when it is exo to the ring system as drawn. In all of the examples this is true even when the ring system is only bicyclic (b and e). It is hard to find many literature examples to study because reduction of ketones in systems such as these tend to produce mixtures of diols which are hard to separate and nmr data are not available for both isomers. It does appear that protons on carbinyl carbons in ring systems such as these are more shielded when they are pointing towards the bottom of the ring system. The compounds synthesized in this study also have carbomethoxy groups attached to all the carbons adjacent to the carbinyl carbons. When the carbinyl proton is in the exo position it should be more affected by these electron withdrawing groups and thus it should appear further downfield. It is hard to assess the effect of the cyclopropyl group on the chemical shifts of the protons attached to the carbinyl carbon. It is known that when a proton is in the plane of a cyclopropyl ring it is shielded (62). In our case this would lead one to predict a more shielded resonance for the exo protons, i.e. 4b and 5b. But, this is not the case. The ^{13}C nmr chemical shifts show smaller differences. The methyl group resonates at slightly higher field in 4b than in 4a and the ring quaternary carbons are both shifted slightly. The carbinyl carbons do show a 2.5 ppm difference in chemical shift with the carbon for the endo diol resonating at lower field (74.1 ppm) than the corresponding carbon in the exo diol (71.6 ppm). Whitesell's data (63) for the bicylo(3.3.0)octane-3-ols (Table 4, entry a) show the same trend for the carbinyl carbons. The nmr data are also consistent with those obtained for the 2,6-dibromo series which is discussed later in this chapter.

It is interesting to note that while other workers often obtained endo/exo mixtures when they reduced diketones (43) in our case no trace of endo-exo products was seen. Furthermore, 4a was never isolated from the $NaBH_4$ reduction nor was 4b recovered from the $(iBu)_3Al$ reaction although the isolated yields were only in the 50% range. We can assume that in the case of the tetracarbomethoxy substituted compounds these reagents are reacting stereospecifically.

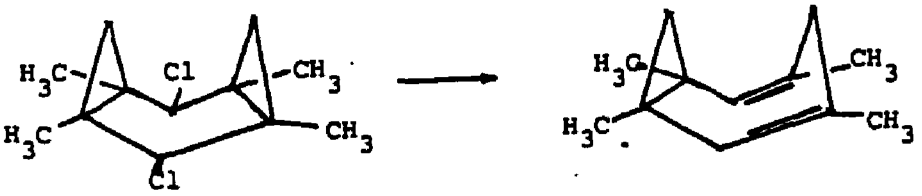
After characterization of the dimesylate 5a, it was then essential to find appropriate reaction conditions in order to effect a 1,4-Grob type elimination which would yield the desired product, Ib in one or two steps. There is precedence in the literature for this type of reaction. Substituted polycyclic hydrocarbons have been converted into homohypostrophene and hypostrophene (eqn 15) by the use of KI in polyhydrogen fluoride (64), NaI in HMPA (65), t-BuLi (66), NaK alloy (66) in THF and Na in liq NH_3 (66). When ditosylate or the diol was the precursor molecule, the diiodo substituted product was always isolated along with the desired diene.



(15)

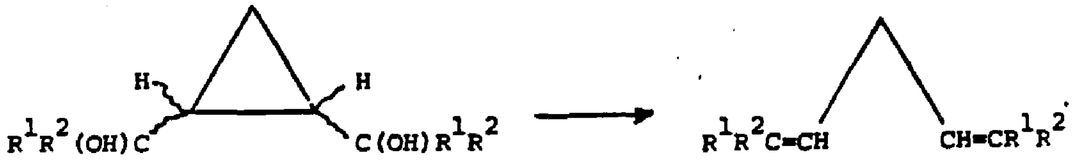
X = OTs, OH, I

Winstein and coworkers had utilized Li(Hg) or Na in liquid NH_3 to effect a homoconjugative elimination in the synthesis of a homotropylidine (eqn 16) (43). This reaction did not work, however, in a related system (44).



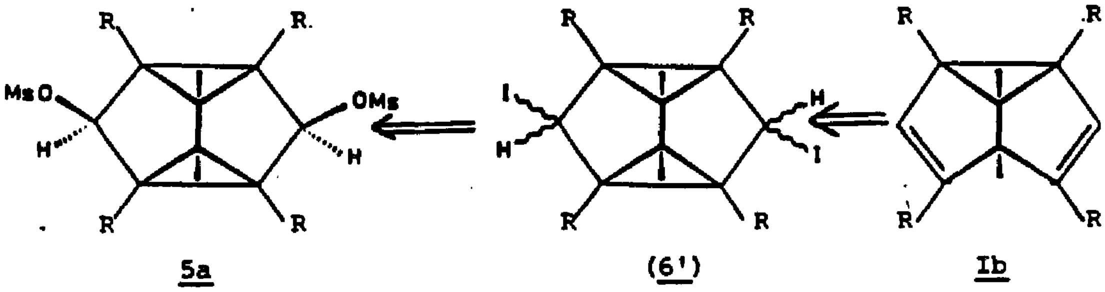
(16)

It was also known that P_2I_4 could convert substituted dihydroxycyclopropanes to 1,4-dienes (67) (eqn 17).



(17)

The expected pathway for the conversion of the dimesylate 5a, to the semibullvalene Ib would be via the diiodide derivative 6' (eqn 18). We felt that conversion of the dimesylate to the diiodide could be accomplished using

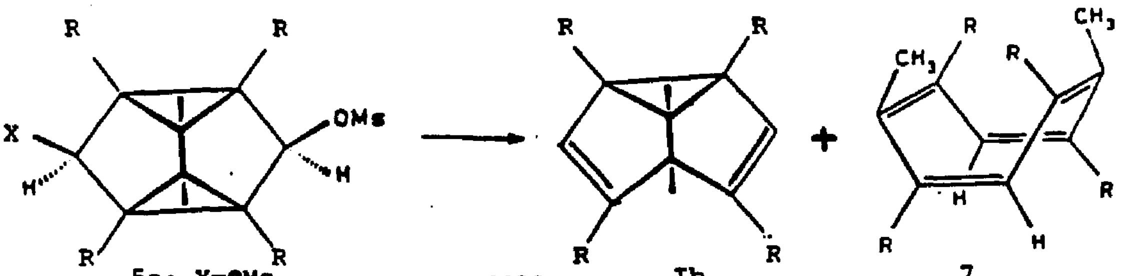


(18)

NaI in acetone and that this reagent possibly would react further to facilitate the 1,4 elimination reaction. Even if this latter step did not occur with NaI in acetone, the diiodide could be treated with some other reagent to effect this transformation. We could not utilize many of the literature procedures as the reagents employed would have reacted with the carbomethoxy groups. NaI in acetone proved to be the reagent of choice for the entire sequence (5a to Ib); however, the intermediate isolated during the reaction was somewhat of a surprise.

Refluxing the dimesylate 5a in acetone and an excess of NaI produced a mixture of component from one compound of which was easily isolated by crystallization. The monomesyl-monoiodo structure 6 was postulated based on spectral and chemical data (see Table 3). The proton spectrum showed a peak for the methyl groups at 1.53 ppm, a singlet (3H) for the CH_3S group at 2.92 ppm and two singlets for the OCH_3 protons at 3.63 and 3.65 ppm. There were two other singlets (1H each) at 5.38 and 6.06 ppm which have been assigned to the H-C-I and the H-C-OMs resonances. The ^{13}C nmr spectrum also had two resonances for C_3 and C_7 at 74.8 and 80.6 ppm. In no case was the di-iodo compound ever isolated.

Two additional products were seen on tlc. ^1H nmr of this mixture indicated that the desired semibullvalene was being formed along with the dimesylate 6 and at least one other product. Varying the reflux time resulted in changing the proportion of the products isolated; at short reflux times more of the intermediate 6 was isolated; however, longer reflux times increased the yield of the undesired compound, apparently at the expense of the desired semibullvalene (eqn 19). Several variations of solvent and reaction temperature were tried. The iodimesylate 6 was reacted with NaI in DMF at reflux resulting in an intractable gum; treatment of 6 with Zn in DMF at 145°C yielded no product. The dimesylate was also treated with NaI in HMPA, diethyl ketone and methyl ethyl ketone at reflux. The higher reflux temperature of these solvents, even for short times, increased the yield of the undesired product 7, once again at the expense of Ib. Equation 19 outlines the probable sequence of events from 6 to Ib and 7.



5a: X=OMs

6: X=I

R = COOCH$_3$ Ib 7 (19)

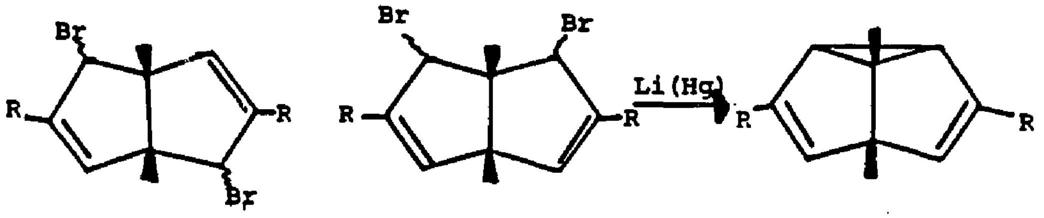
We found that we were able to isolate 6 after reaction of 5a in NaI and acetone at room temperature for one to two days. There was often a small amount of semibullvalene formed but it was easily separable from 6 by fractional precipitation. The intermediate 6 was insoluble in CCl$_4$ while all other products formed were soluble. This was a fast and efficient way of separating any product formed from the intermediate and was used routinely in this synthesis since the semibullvalene Ib would react further yielding 7 if left in the reaction mixture. The isolated intermediate 6 was treated again with NaI in acetone for short times at reflux or for a long time (overnight) at room temperature and modest yields of Ib were isolated. If very short reaction times were used little or no 7 was formed. After longer reaction time mixtures of Ib and 7 were isolated. The compounds could be separated on a silica column using CH_2Cl_2 as eluent. The undesired compound 7 eluted first and was obtained as a white crystalline solid, mp 104-6°C. Semibullvalene Ib was eluted next and crystallized as bright yellow prisms, mp 102.5 - 103°C. After much trial and error the best preparative method appeared to be an initial long (2 days) room temperature reaction of 5a with NaI acetone followed by isolation of 6 and separation of any semibullvalene formed. The intermediate 6 was then allowed to react with fresh NaI in acetone at reflux for 1-2 hours; unchanged 6 was isolated and treated again with fresh NaI in acetone. This procedure could be repeated two to three times. After each short reaction, Ib was isolated (usually without a column) and crystallized in a small volume of methanol. Even with this method only ca.10:15% of Ib was collected. There was always a small amount of 6 left after reaction; however, the main problem was the ease with which Ib isomerized to 7 and even to another isomer 8 (vide infra). All other attempts at increasing the yield of Ib led to increasing the amount of 7 formed at the expense of Ib.

It was found that Ib isomerized to 7 while dissolved in CH_3OH or $CHCl_3$ even in the refrigerator! Complete analysis, spectral data and discussion of Ib and 7 will be presented in Chapter 3.

C. Other Approaches to the Synthesis of Ib

Several other methods of synthesis were attempted in the preparation of Ib. Reaction of the di-exo diol 4a with P_2I_4 in pyridine and benzene at reflux yielded a thick oil whose nmr spectrum did not show any of the desired semibullvalene; however there was clear evidence in the spectrum for the formation of the undesired side product 7. This approach was abandoned as the reaction conditions seemed too extreme for isolation of Ib.

Another possible route to Ib is to utilize the bicyclo(3.3.0)octa(2,6 or 2,7)diene system directly. Askani (39b) has synthesized several 3,7-substituted - 1,5 dimethyl semibullvalenes in 30-50% yield by the reaction



(20)

depicted in equation 20. While we could not utilize the

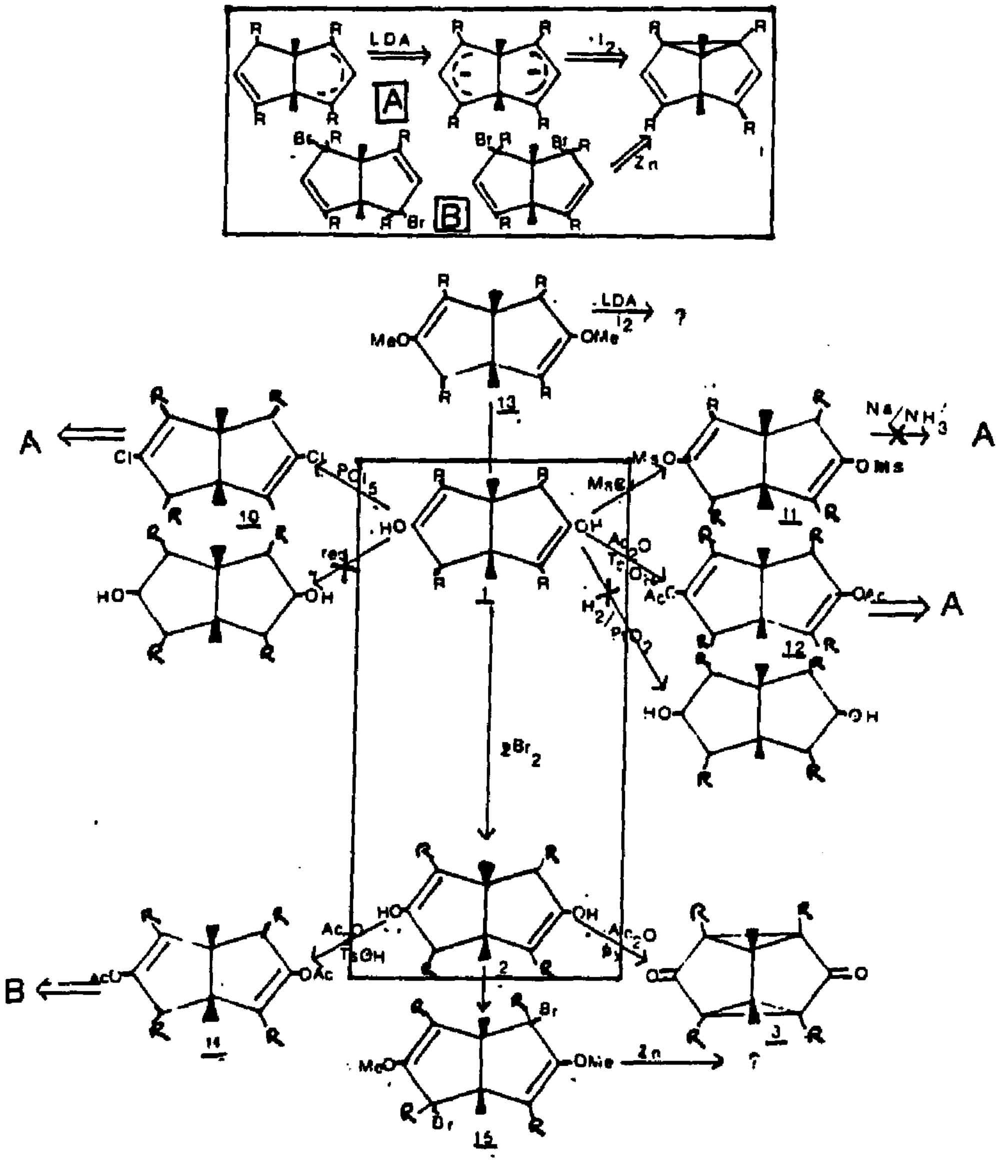
Li(Hg) system as it would be too reactive, we felt that we could effect ring closure by different means.

Scheme 6 outlines the possible alternative pathways we explored utilizing the bicyclo(3.3.0)octadiene system. Our goal was the synthesis of A or B which could then be converted into Ib or a close derivative, as shown in the insert to Scheme 6. The starting material for the route utilized the bicyclic tetracarbomethoxybisenol 1 which possessed the necessary prerequisites for conversion into one of the desired intermediates. Our first attempts were to stabilize the enol in the diene form; i.e. to form intermediate A.

Schlessinger (68) had reported the reduction of an enol using $NaBH_4$ and $NaBH_3CN$ in acidic solution. However, we were unable to obtain anything but starting material when 1 was treated with either reducing agent. Substitution of the OH by Cl, which then could be removed by dehydrohalogenation to yield the desired diene mixture A, was attempted using PCl_5 as chlorinating agent (69). A chlorine containing product (10) was isolated (see Table 5), however, the yield was extremely low. Direct hydrogenation of the enol was also attempted using H_2 and Pt_2O in acetic acid (70). Only starting material was recovered from several attempts both at atmospheric pressure and in a pressure bottle. Enol 1 reacted smoothly with methanesulfonyl chloride, acetic anhydride and diazomethane to yield the dimesyl derivative 11, the diacetate 12 and the dimethyl ether 13 respectively. Spectral data are recorded in Table 5 and are consistent

Scheme 6

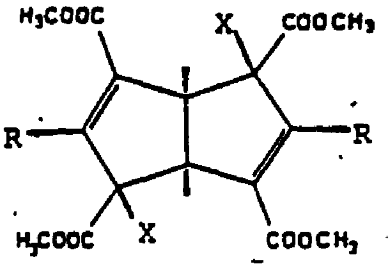
OTHER APPROACHES TO THE SYNTHESIS OF 1,5-DIMETHYL-2,4,6,8-TETRAKIS(CARBOMETHOXY)SEMIBULLVALENE (Ib)



R = COOCH$_3$

Table 5

^{1}H and ^{13}C NMR DATA FOR DIMETHYLBICYCLO(3.3.0)OCTA-2,6-DIENES



^{1}H NMR

1 X=H R=OH	10 X=H R=Cl	11 X=H R=OMs	12 X=H R=OAc	13 X=H R=OCH$_3$
1.30 (s,6H)	1.35 (s,6H)	1.38 (s,6H)	1.40 (s,6H)	1.30 (s,6H)
3.75 (s,6H)	3.65 (s,6H)	3.12 (s,6H)	2.15 (s,6H)	3.65 (s,6H)
3.88 (s,6H)	3.72 (s,6H)	3.72 (s,6H)	3.72 (s,12H)	3.75 (s,12H)
3.92 (s,2H)	4.12 (s,2H)	3.78 (s,2H)	4.15 (s,2H)	4.30 (s,2H)
10.80 (s,2H)				

2 X=Br R=OH	14 X=Br R=OAc	15 X=Br R=OCH$_3$
1.85 (s, 6H)	1.92 (s, 6H)	1.88 (s, 6H)
3.75 (s, 6H)	2.15 (s, 6H)	3.68 (s, 12H)
3.80 (s, 6H)	3.62 (s, 6H)	3.82 (s, 6H)
11.0 (s, 2H)	3.70 (s, 6H)	

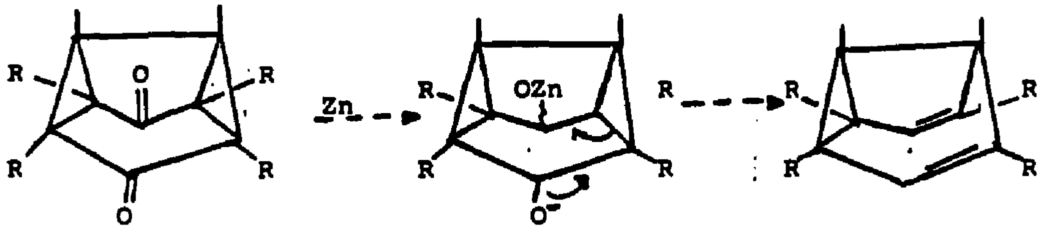
^{13}C NMR

1 X=H R=OH	13 X=H R=OCH$_3$	2 X=Br R=OH
18.0	18.4	20.3
51.7	51.1	52.0
52.2	52.4	53.7
54.2	55.4	59.4
58.2	56.5	74.3
109.4	57.7	105.3
169.3	113.0	165.8
170.6	165.1	168.9
170.9	171.2	

with the proposed structure. The dimesylate could not be converted into A using Na in liquid NH_3 as the conjugated double bonds were reduced immediately. We had hoped to hydrogenate the double bonds in the diacetate and then dehydroacetylate the product to form A. This method was not explored further after the proposed ring closure of 13 did not work. The dimethylether 13 was prepared as a model in order to investigate methods of ring closure to the semibullvalene ring system. Compound 13 was treated with LDA in THF at -78°C. Iodine was added and the reaction was allowed to warm up to room temperature. After work-up an oil was isolated which showed at least three spots on tlc and whose nmr spectrum no longer had any methyl singlets. Chromatography of the oil on silica resulted in a very small yield of only one compound (pure by tlc). The proton nmr spectrum showed four peaks between 0.95 and 2.5 ppm (two doublets?) (6H) and a broad singlet at 3.8 ppm (18H). The ^{13}C nmr consisted of approximately 40 peaks. Apparently the ring system was no longer intact and some sort of rearrangement or degradation had occurred. This method was not pursued further.

Attempts to convert the dibromo compound 2 into the precursor B and then Ib were not successful, although all aspects were not thoroughly investigated. The dibromo enol 2 was synthesized by reaction of 1 with two moles of bromine in acetic acid (see previous discussion of bromination). It was then treated with acetic anhydride or diazomethane to form the diacetate 14 and the dimethyl ether 15 respectively (see Table 5). Once again spectral are data consistent with proposed structures. The dimethyl ether 15 was used as a model for ring manipulation. Reaction of 15 with Mg in THF at reflux yielded only starting material. Use of Zn in ether, DMF, or a mixture of CH_3OH and THF with a trace of disodium EDTA, appeared to give the same product; a thick oil whose nmr spectrum was very similar to that obtained from the LDA-I_2 reaction with 13. In no instance was even a trace of the desired semibullvalene ring structure seen by nmr.

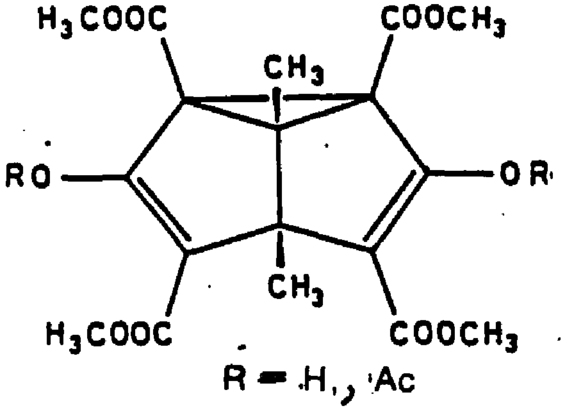
The cyclized ketone 3 was reduced with zinc under various reaction conditions. We had thought that if the zinc attacked at one carbonyl group, this could lead to a 1,4 fragmentation as shown in equation 21. Treatment of 3 with Zn and acetic acid under various reaction conditions resulted in the isolation of either tetracarbomethoxybicyclo enol 1 or 1,5-dimethylbicyclo(3.3.0)octane-3,7-dione 16.



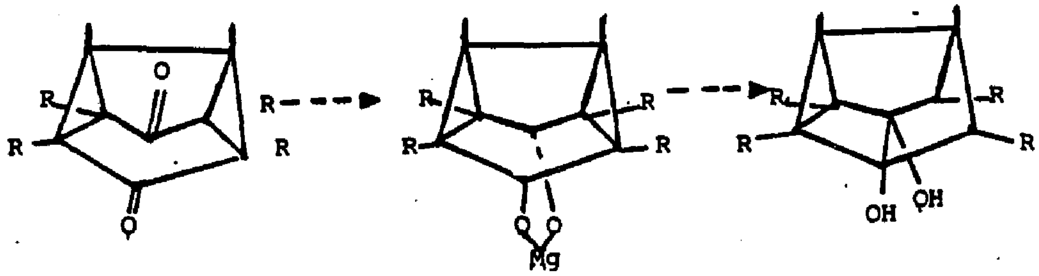
(21)

R = $COOCH_3$

These results agree with the work reported recently by Gomppers and Schwartzensteiner (56). These workers successfuly carried out the desired cleavage of 3 by using sodium dihydronaphthalide. They have reported the synthesis of the 3,7-di-hydroxy and the 3,7-di-acetoxy derivatives of Ib.



We also attempted the reduction of 3 with Mg in THF and trace of $HgCl_2$ in order to induce a pinacol type reduction which might then rearrange further (eqn 22).

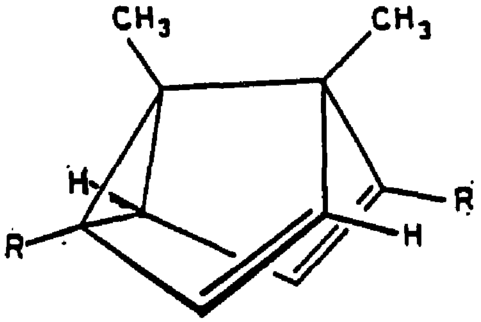


(22)

Only starting material was recovered from this reaction. These additional methods were not pursued further as the NaI treatment of 6 did yield the desired semibullvalene.

D. Synthesis of 1,5-Dimethyl-2,6 dibromosemibullvalene:

The 2,6-disubstituted semibullvalenes (Ic-Ie) were also also of interest to us. After studying the results of the X-Ray structure and the low temperature nmr spectra of the



Ic. R = Br

Id: R = $COOCH_3$

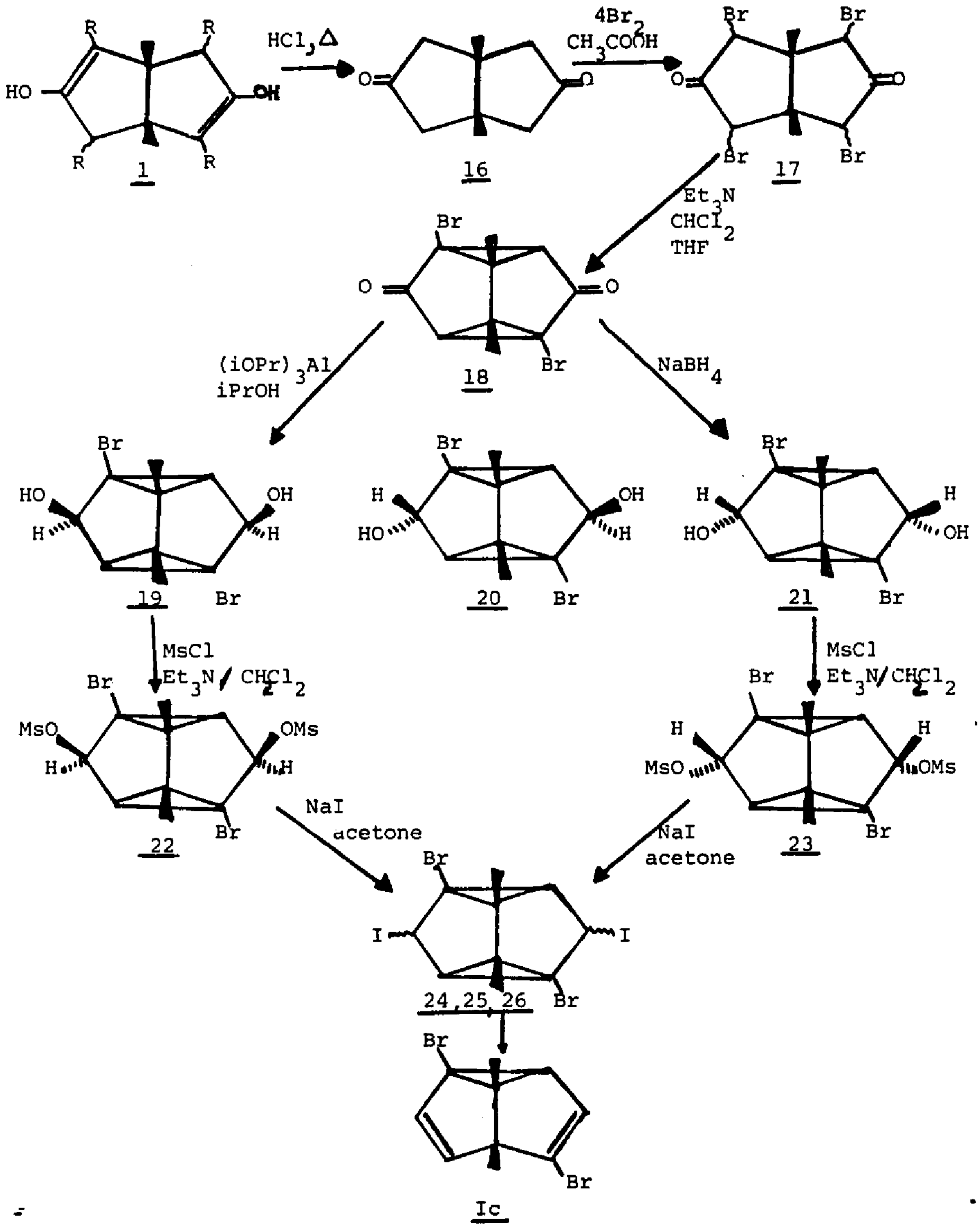
Ie: R = CN

tetracarbomethoxysemibullvalene Ib, we felt that since two of the carbomethoxy groups were not in conjugation with the cyclopropyl ring or the double bonds, it would be interesting to compare the behavior of compound Id, where two of the groups are replaced by protons, with the tetrasubstituted compound Ib. The results of our MNDO calculations (chapter 4) also suggest that the presence of electron withdrawing groups in positions 2 and 6 should stabilize the delocalized structure in the Cope rearrangement. By placing protons at positions 4 and 8 we would have sensitive probes for low temperature proton nmr studies. The dibromosemibullvalene Ic appeared to be an attractive entry into this area of semibullvalene chemistry since the bromines could probably be easily replaced by other substituents (eg) COOH, CN) (29,30). Other synthetic approaches to the disubstituted semibullvalenes Id and Ie were also investigated. The synthetic route envisaged for the preparation of Ic paralleled that used for the preparation of Ib and. therefore, if the synthesis was successful, we would have confirmed the general applicability of this new mode of entry into the semibullvalene ring system.

The preparative route followed in the synthesis of Ic is outlined in Scheme 7. The tetracarbomethoxy dienol (1) was decarboxylated to cis-1,5-dimethylbicyclo(3.3.0)ocatane-3,7-dione (16) in 78 to 90% yield following a published procedure (71). The melting point was 224-7°C which compared well with the recent finding of 220-221° (53), and was substantially higher than the original reports of 167-9°C (not well defined) (50) 158-80°C (72). The diketone 16 was brominated using four moles of bromine in acetic acid. In contrast to the tetracarbomethoxy system, this reaction always took place in the same manner although the tetrabromo adduct was difficult to characterize completely because it

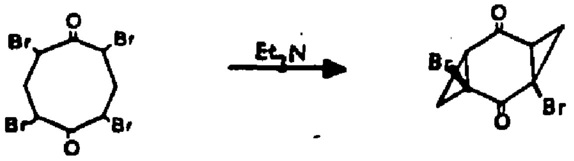
Scheme 7

SYNTHESIS OF 1,5-DIMETHYL-2,6-DIBROMOSEMIBULLVALENE - Ic



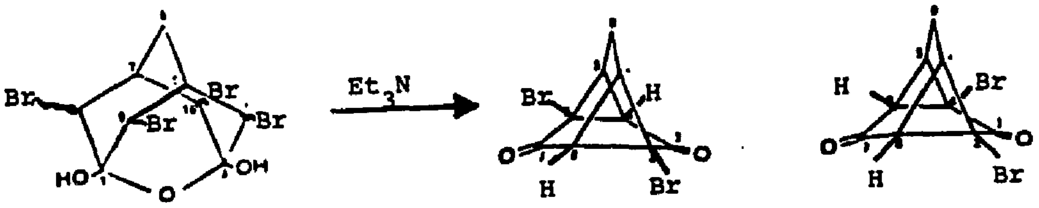
tended to decompose. However, only tetrabromo adduct (17) was isolated from the reaction mixture. Proton nmr indicated the presence of two different H-C-Br moieties (see experimental section). This compound readily lost two moles of HBr and cyclized to the tetracyclic ketone 18 upon addition of triethylamine. The proton nmr was consistent with the proposed structure displaying only two signals, a singlet at 1.72 ppm for the methyl protons and a singlet at 2.38 ppm for the two other equivalent cyclopropyl protons. At this point it was impossible to rule out the 2,4-dibromo derivative, however, this was done at a later step.

It was interesting to compare these results with some other related systems. Triethylamine induced ring closure of 2,4,6,8-tetrabromocyclooctan-1,5-dione resulted in the formation of a 1,3-dibromotetracyclic compound (eqn 23) (48).



(23)

Dehydrohalogenation of a tetrabromobicyclo(3.3.1)nonan-3,7-dione mixture with triethylamine yielded a 1:1 mixture of 2,6- and 2,4-dibromotriasteran-3,7-dione (eqn 24) (49).



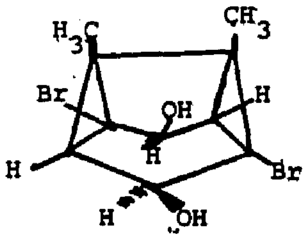
(24)

Commenting on this reaction Dreiding speculated on the possibility that the direction of dehydrobromination may depend upon the configuration of the bromine atoms in the tetrabromo precursor (49). Since we have only isolated the 2,6-dibromotetracyclic isomer from this reaction, we must assume that, in our case, the bromination only produces one stereoisomer, or, if more than one is produced, that they will all react in the same way with triethylamine.

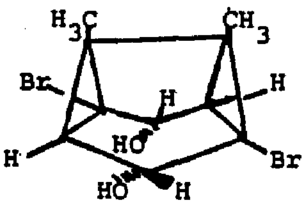
Dreiding had been able to remove the bromine atoms from the bishomoquinone system using Zinc and acetic acid (48). In the triasterane system, he could not achieve the same reaction, but was sccessful using (n-Bu)$_3$Sn (49). In the case of <u>18</u>, we were not able to remove the bromine atoms successfully by either method. When (n-Bu) $_3$Sn was used, only starting material could be isolated from the reaction. Lithium, tert-butanol in tetrahydrofaum caused extensive decomposition of the starting material while Zinc in acetic acid yielded several products.

The next step in ths scheme was the reduction of <u>18</u>.

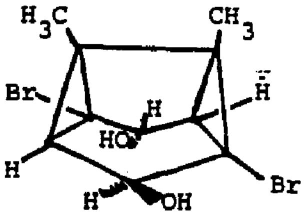
Here as in the tetracarbomethoxy series, there are three different stereoisomeric diols possible from the reduction. The same (or similar) steric factors are present in this system as in the tetracarbomethoxy compound 3 except that carbons 2 ad 6 bear bromine atoms and carbons 4 and 8 bear protons.



19



21

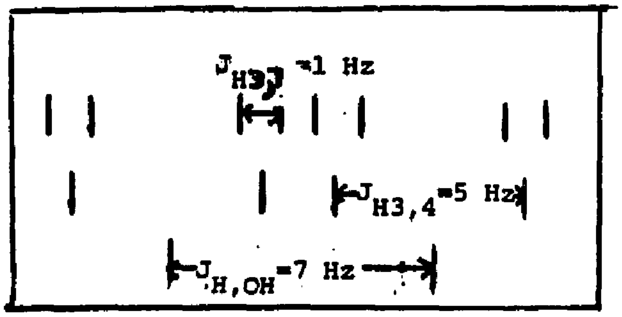


20

Sodium borohydride reduction of 18 produced a mixture of two stereoisomers, the predominant one being the di-endo diol 21 and the minor component being the endo/exo diol 20 Reduction with (i-Bu)$_3$Al produced mixtures of 19, 20 and 21. When Al(O-iPr)$_3$ in isopropanol was used as the reducing agent and a one hour reflux was followed by distillation of the solvent and the acetone formed, the major product was the di-exo diol 19 although 20 and sometimes 21 were formed in small amounts. In most instances the di-exo compound crystallized out after work-up and trituration with 10%

$CHCl_3$ in CCl_4 or ether. The isomers could also be separated by column chromatography on silica gel. The relevant spectral data for the three diols are presented in Table 6.

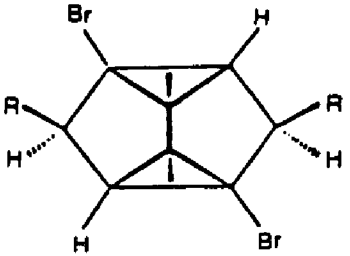
In <u>21</u>, the major isomer formed from $NaBH_4$ reduction of <u>18</u>, the 2 OH groups are pointing towards the cavity caused by the tetracyclic ring system. The salient features of the proton nmr spectrum for this compound are summarized as follows: the methyl protons appeared as a singlet at 1.4 ppm. The protons at positions 4 and 8 are split into a doublet of doublets (J= 5, 1Hz) at 1.75 ppm. The OH protons appear as a well defined doublet at 3.97 ppm (J=7Hz) which disappears upon treatment of the sample with D_2O. The carbinyl protons (H3 and H7) appear as a four spin system centered at 4.8 ppm, where the central portion has overlapped (J= 7,5, 1Hz). The splitting pattern is diagrammed schematically below:



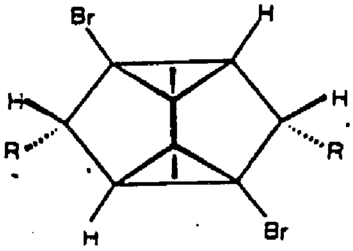
After addition of D_2O this complex pattern simplifies to a doublet of doublets (J=5,2Hz). Examination of a molecular

Table 6

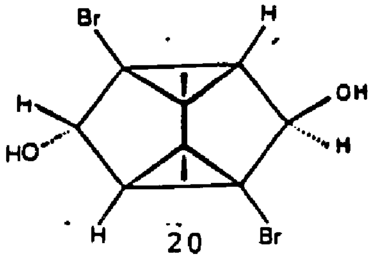
^{1}H AND ^{13}C NMR DATA FOR 1,5_DIMETHYL-2,6-DIBROMO-TETRA-CYCLO(3.3.0.0.^{2,8}0.^{4,6})OCTAN_3,7-DIOLS AND THEIR DERIVATIVES



19, 22, 25



21, 23, 26



20

^{1}H NMR

19 R=OH	21 R=OH	20
1.50 (s, 6H)	1.40 (s, 6H)	1.44 (s,3H) 1.46 (s 3H)
1.92 (s, 2H)	1.75 (dd, J=5,1Hz,2H)	1.80 (d,J=5.5Hz,1H)
		1.90 (br s 1H)
2.05 (d,J=4Hz, 2H, H4,8)	3.97 (d,J=7Hz, 2H, OH)	2.05-2.25 (br m,2H, OH)
4.08 (d,J=4Hz, 2H,H3 7)	4.80 (m,J=7,5, 1Hz,2H,H3,7)	4.52 (s,1H,H3)
		4.68 (dd,J=5.5 1Hz,1H H7)

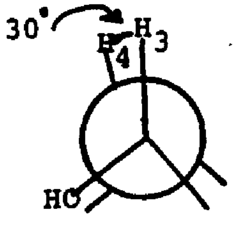
^{13}C NMR

19	21
13.8 (q)	13.6
38.4 (s)	38.6
42.2 (d)	42.1
51.1 (s)	49.5
71.6 (d)	78.2

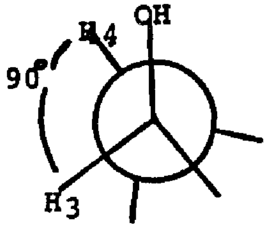
^{1}H NMR

22 R=OMs	23 R=OMs	25 R=I	26 R=I
1.55 (s,6H)	1.48 (s,6H)	1.52(1.60)	1.60(1.52) (s,6H
2.30 (s,2H)	2.10 (dd,J=5, 1Hz)	2.52 (br s, 2H)	2.32(dd,J=5,1Hz, 2H)
3.22 (s,6H)	3.20 (s,6H)		
5.28 (s,2H)	5.53 (dd,J=5 Hz, H3,7)	5.08 (br s, 2H)	4.58 (dd,J=5,1Hz, 2H, H3,7)

model of 21 confirms the fact that the dihedral angle H4-C4-C3-H3 is approximately 30-40° when H3 is in the exo position and thus the observed coupling constant of 5 Hz is



21



19

reasonable (73). The long range coupling of H_3 and H_8 (or H_4 and H_7) is an example of four bond W coupling (74).

In contrast, the di-exo diol 19 has a much simpler proton spectrum. Since the carbinyl protons are "endo", they do not experience the same spin spin coupling with either H4 or H8. The dihedral angle H4-C4-C3-H3 is now approximately 90° and thus the vicinal coupling is very small (74). Also H3 is no longer aligned in a W relationship with H8 and there is no long range coupling evident. The signal for H3 and H7 is simply a doublet at 4.08 ppm (J=4Hz) which collapses to a singlet upon the addition of D_2O. The signal for the cyclopropyl protons (H4 and H8) is a singlet at 1.92 ppm.

The endo/exo diol 20 has a proton spectrum which is a composite of the spectra of 19 and 21. The methyl groups appear as closely spaced singlets (1.44, 1.46 ppm); H8, which couples with H7, is a doublet at 1.8 ppm (J=5.5 Hz), while H4, which only experiences long range coupling with H7, appears as a broad singlet at 1.9 ppm. Both OH groups resonate at 2-2.25 ppm and do not show splitting with the geminal H3 or H7 protons in the spectrum. H3 appears as a singlet at 4.52 ppm while H7 is a doublet of doublets at 4.68 ppm (J=5.5, 1 Hz). Upon addition of D_2O the OH resonances disappear but the splitting pattern for H7 remains the same. The splitting patterns observed for the cyclopropyl and carbinyl protons in these three diols are a good example of the dependence of coupling upon molecular geometry.

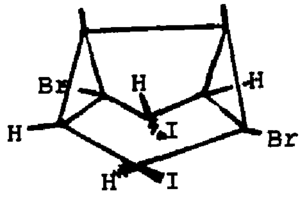
The relative chemical shifts of the protons on the three diols, 19, 20 and 21 are consistent with the assignments made for the tetracarbomethoxy series (compounds 4 & 5, Table 3) and agree well with the literature data in Table 4. The splitting patterns observed also in accord with the reported data (f in Table 4) (44,45). When the OH is exo (compound 19), the CH_3 appears further downfield than when the OH is endo (1.50 vs 1.40 ppm) (see Table 3 and 4 for comparative data). Also the cyclopropyl protons (H4 and H8 in 19 and H4 in 20) which are adjacent to an exo OH group, appear at lower field than H4 and H8 in compound 21 and H8 in compound 20, which are adjacent to an endo -OH group. Again this appears to be a deshielding effect of the exo OH groups. The carbinyl protons also show the same chemical shift pattern as in the tetracarbomethoxy series. When the proton is endo (H3 and H7 in 19 and H3 in 20) it is more shielded (4.08, 4.52 ppm) than when it is exo (H7 in 20 and H3 and H7 in 21) (4.8 and 4.68 ppm).

The ^{13}C nmr spectra are also consistent with the tetracarbomethoxy series and the literature values reported in Tables 3 and 4. The major chemical shift difference seen for the carbinyl carbon; this carbon resonates at higher field in the exo diol 19 (71.6 ppm) than in the endo diol 21 (78.2 ppm).

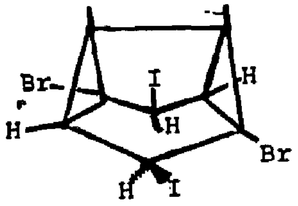
Both the proton and ^{13}C nmr spectra confirm the 2,6-dibromo structure assigned to the tetracyclic compounds (18-26). If the bromine were in positions 2 and 4 there would be 2 different chemical shifts for C3 and C7 as well as for H3 and H7 in both the di-exo ad di-endo systems. As indicated in Table 6, this is not the case; in both compounds 19 and 21 C3 and C7 and H3 and H7 are equivalent. Thus, the 2,6-dibromo substitution pattern has been verified.

Both the di-exo diol 19 and the di-endo diol 21 and mixtures of 20 and 21 reacted with methanesulfonyl chloride to form the dimesylated derivatives 22 and 23. The yield was extremely low for the di-endo dimesylate 23. However, the proton nmr (see Table 6) was consistent only with the di-endo-di-mesyl compound and exhibited the same splitting patterns and types of chemical shifts as the di-endo alcohol. This is a marked contrast to the tetracarbomethoxy series in which we could not isolate a di-endo mesylate at all; only the monosubstituted derivative of the diol was formed. All attempts at improving the yield in this reaction or of isolating other products were not successful. The di-exo diol 19 reacted with methansulfonyl chloride in much higher yield (80%) forming the di-exo dimesylate 22 in 80%. The proton nmr spectrum of this product was also consistent with the proposed structure 22 (Table 6).

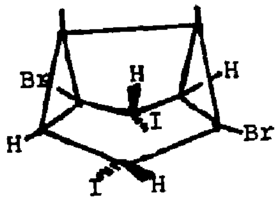
The reaction of 22 in NaI and acetone had to be carried out in the dark and at room temperature or extensive decomposition occurred. After 24 hours we were able to isolate a crystalline intermediate which could be precipitated in a mixture of CH_2Cl_2/hexanes or CH_3OH. This intermediate was also isolated from the reaction of 23 with NaI in acetone. The compound melted with decomposition at 125-9°C and appeared to have two very closely spaced tlc spots. It was not clear whether this intermediate was the exo/endo diiodiode 24 or a mixture of di-exo and di-endo diiodides, 25 and 26. The proton nmr spectrum was helpful.



24



25



26

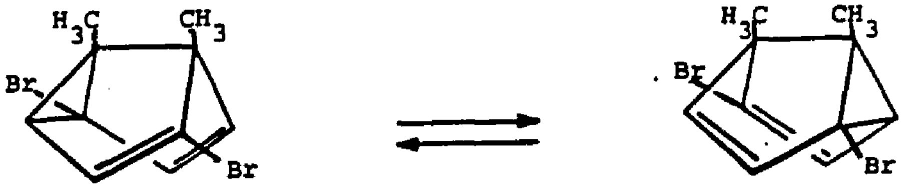
The spectrum has two methyl singlets at 1.52 and 1.60 ppm, a doublet of doublets at 2.32 ppm (J=5, 1 Hz) (H8 in 24 or H4, 8 in 26), a broad singlet at 2.52 ppm (H4 in 24 or

H4, 8 in 25), a doublet of doublets at 4.58 ppm (J=5, 1 Hz) (H3,7 in 26 or H7 in 24) and a broad singlet at 5.08 ppm (H3,7 in 25 or H3 in 24) in a ratio of 3:3:1:1:1:1. If the compound was the exo/endo dimesylate 24, H8 should not exhibit long range coupling with H3 and therefore, its nmr signal should not be a doublet of doublets. Also H4 would exhibit long range coupling with H7 and should appear as a closely spaced doublet. However, this is not the case. It appears from the spectrum that the two diiodides (25 and 26) have been formed in equal amounts. The resonances at 2.52 and 5.08 correspond to H4,8 and H3,7 in 25 and those at 2.32 and 4.58 represent the same protons in 26. Carbon 13 nmr data are also consistent with a mixture of diexo and diendo iodides. The spectrum shows signals at 13.19, 14.14, 29.18, 31.15, 42.11, 42.29, 46.14, 48.76, 51.26 and 51.36 ppm. The ratio of these isomers did not change after repeated recrystallization in CH_3OH or CH_2Cl_2/hexanes. This mixture of iodides could react further with NaI in acetone to yield the desired semibullvalene Ic.

If the dimesylate 22 was stirred in NaI and acetone for 60 hours in the absence of light, none of the intermediate was isolated. Instead 1.2 g (50%) of a new compound, m.p. 63-5°C, was isolated after crystallization in methanol. The compound was unstable to air, light and heat and had to be stored under argon, in the dark, in the freezer. It still decomposed slightly even under these conditions. Solutions of the compound appeared stable. The ^1H and ^{13}C spectral data are listed below:

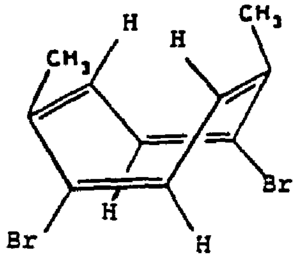
^1H: = 1.24 (s,6H, CH_3), 4.28 (d,J=4Hz, 2H, H4, 8), 5.43(d,J=4Hz, 2H, H3, 7) ppm. ^{13}C: 14.29 (q), 62.63 (s), 93.79 (s), 97.13 (d) and 124.61 (d).

These simple spectra are consistent only with a semibullvalene Ic that is rearranging rapidly on the nmr time scale at this temperature (eqn 25). The singlet at 1.24 ppm represents the two methyl groups which are equilibrating too quickly to show separate resonances; the doublet at 4.18 ppm corresponds to the two protons which are averaging between the cyclopropyl and the vinyl environments. The signal at 5.43 ppm represents the two permanently vinylic protons (H3,7). In the ^{13}C nmr spectrum, the signal at 14.39 ppm represents the equilibrating CH_3 groups and the one at 62.63 ppm corresponds to carbons 1 and 5. The singlet at 93.97 ppm represents carbons 2 and 6 and the doublet at 97.13 ppm is C4 and 8. The vinyl signal at 124.6 ppm corresonds to C3 and C7.



(25)

Although this compound is sensitive to air, light and heat, it does not appear to rearrange easily to the corresponding cyclooctatetraene derivative 27. Solutions of Ic appear to be perfectly stable as long as they are kept in the freezer away from light.



Chapter 3

X-Ray, Spectral Data and Isomerization Reactions of 1,5-Dimethyl-2,4,6,8-tetrakis(carbomethoxy)semibullvalene

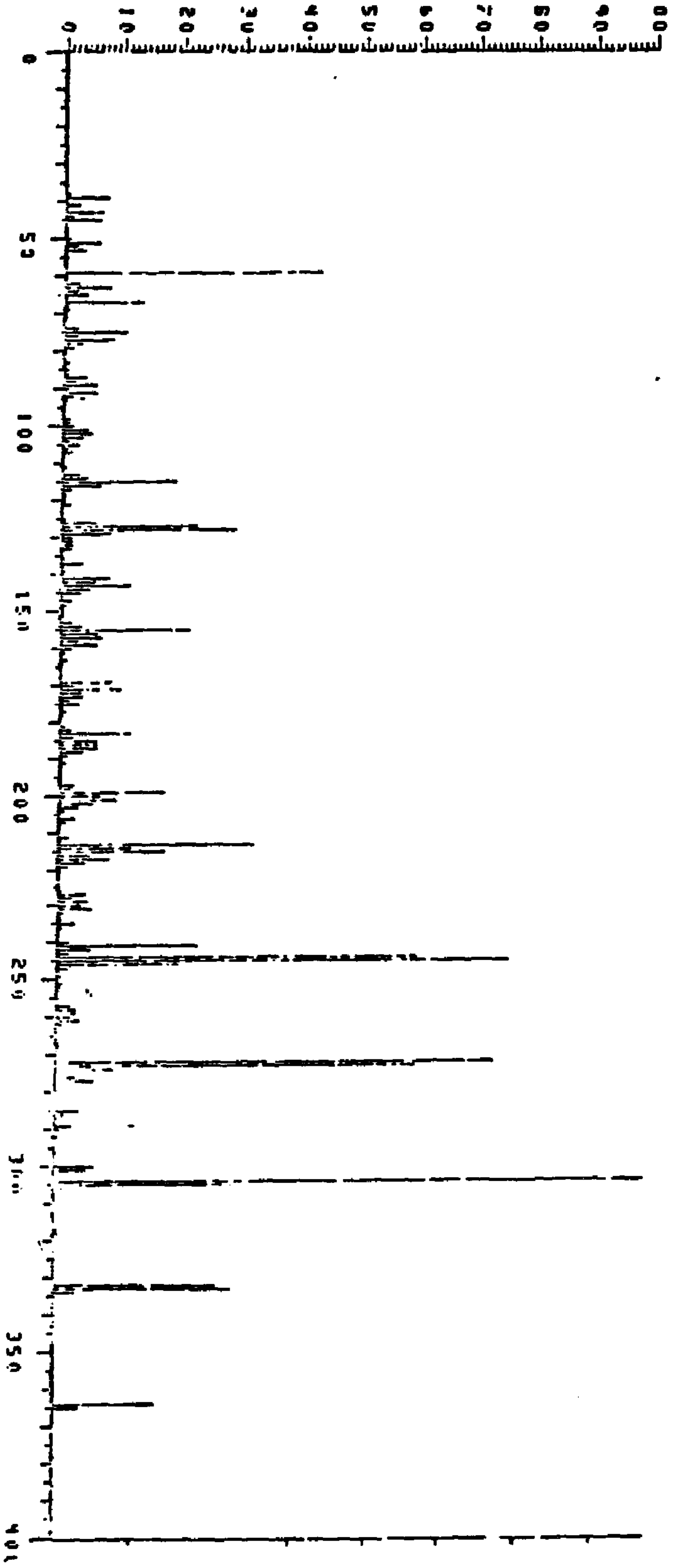
A. Overview of the Analytical and Spectral Data

Compound Ib, 1,5-dimethyl-2,4,6,8-tetrakis(carbomethoxy)semibullvalene, crystallizes from methanol as bright yellow prisms, mp = 102.5-103°C; UV $^{EtOH}\lambda$ = 230nm (ε = 12400), shoulder at 260nm; IR_{CHCl_3}: 3010, 2950, 1725, 1595, 1435, 1335, 1200-50, 1055, 1040 cm^{-1}. The nmr data are listed in Table 9. The spectra are displayed in figures 5 and 6 and are discussed in section C of this chapter. The mass spectrum is presented in Figure 1. Pertinent peaks are: m/e 364.1, parent ion 304.1, also 272.1, 245.1. Elemental analysis for $C_{18}H_{20}O_8$: Calc. C,59.34: H,5.50: 0,35.27%; Found C,59.11: H,5.40: 0,34.98%.

The yellow crystals are stable to air and light. When cooled to -78°C the crystals became colorless. Upon warming to room temperature the color is regenerated. Solutions of Ib also became colorless upon cooling. The nmr spectrum is unchanged after the solution is warmed to room temperature. Heating methanol or $CHCl_3$ solutions of Ib causes isomerization to two compounds. Prolonged storage of solutions of Ib, either at room temperature or in the refrigerator, also causes this isomerization (see section D, Chapter 3).

Figure 1

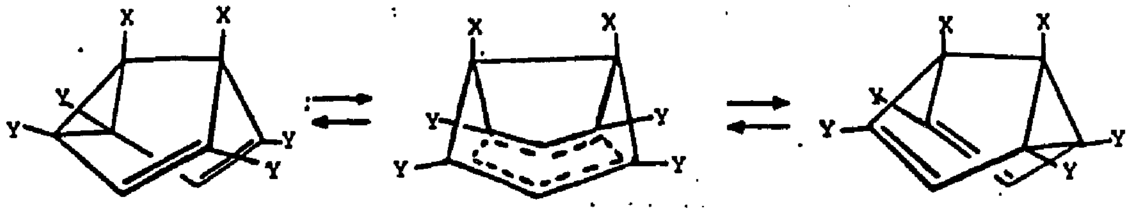
MASS SPECTRUM OF 1,5-DIMETHYL-2,4,6,8-TETRAKIS-(CARBOMETHOXY)SEMIBULLVALENE Ib



B X-ray Crystallographic Study of 1,5-Dimethyl-2,4,6,8-tetrakis(carbomethoxy)semibullvalene

i - Introduction & Background

Compound Ib, 1,5-dimethyl-2,4,6,8-tetrakis(carbomethoxy)semibullvalene was designed to test the effects of Pi-electron donor and acceptor substitution on the energy of activation for the Cope rearrangement of semibullvalene. Calculations (14,20,75) had predicted that π-electron donors at C1 and C5 and π-electron acceptors at C2,4,6,8, and 8 should lower this energy and perhaps stabilize an intermediate structure (eqn 26). The six electrons involved in the transition state might be completely delocalized among the six carbons (2,3,4,6,7,8) or the system might consist of two allyl systems (C2,3,4 and C6,7,8) whose ends could interact in a bonding manner.



(26)

X = π-electron donor
Y = π-electron acceptor

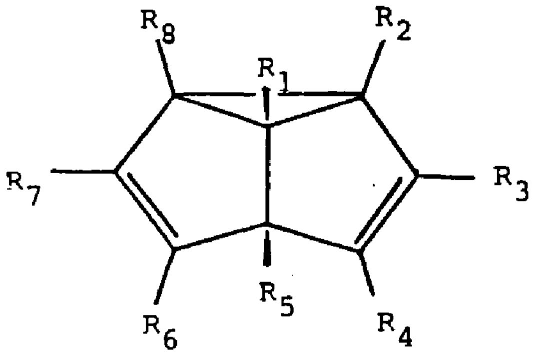
It was important to determine the structure of 1,5-dimethyl-2,4,6,8-tetrakis(carbomethoxy)semibullvalene (Ib) both as a crystal and in solution. X-ray crystallography was the method of choice for the crystal structure determination. The X-ray analysis was performed for us by Mr. Louis Todaro at Hoffmann La Roche, Inc., Nutley, New Jersey (76).

Previous structural data for semibullvalenes had been determined by gas phase electron diffraction for the parent molecule (77) and by X-ray crystallography for the 1-cyano compound (27). After completion of our investigation a communication appeared wih preliminary data for the 3,7-diacetoxy derivative of <u>Ib</u> (56). The relevant data for these compounds are listed in Table 7. These semibullvalenes appear to have localized ground state geometries. The C2-C8 bonds are all longer than an ordinary cyclopropyl bond (78). However, the cyclopropyl ring in the semibullvalene nucleus should be more strained than a free cyclopropane and this effect would be manifested in the C2-C8 bond length. The other bond lengths appear to be close to standard values (78).

The structure of the 1-cyanosemibullvalene was studied at length by Christoph and Beno (27). The C2-C8 bond distance is 1.577 A and the C1-C2 and C1-C8 distances are 1.508 A. The C4-C5-C6 bond angle at the open end of the molecule is 101^{o} and the nonbonded distance between C4 and C6 is 2.36 A. Since these authors were unsure of the accuracy of the electron diffraction results on the parent compound (77),

Table 7

ELECTRON DIFFRACTION AND X-RAY CRYSTALLOGRAPHIC DATA FOR SOME KNOWN SEMIBULLVALENES



I

Ia: R_{1-8}= H

Im: R_1= CN, R_{2-8}= H

In: $R_{1,5}$= CH_3, $R_{2,4,6,8}$= $COOCH_3$, $R_{3,7}$=$OCOCH_3$

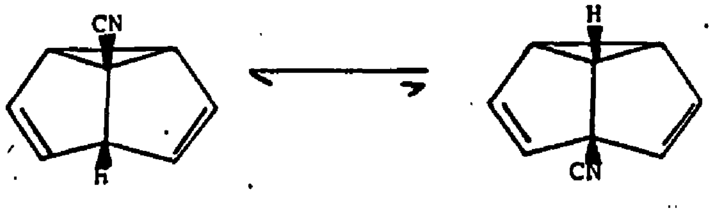
	Ia (a)	Im (b)	In (c)
C2-C8	1.600	1.577	1.643
C1-C5	1.485	1.549	
C4-C6	2.261	2.359	2.352
C2-C3	1.531	1.475	
C3-C4	1.350	1.326	
C1-C2	1.530	1.508	
C4-C5-C6	95.2	101	

(a) ref.77 - electron diffraction

(b) ref.27 - x-ray

(c) ref.56 - x-ray

they did not use this data for comparison. Molecular orbital theory had predicted that the C2-C8 bond in 1-cyanosemibullvalene should be shortened and the C1-C2 and C1-C8 bonds lengthened by the interaction of the CN group with the Walsh type orbitals in the semibullvalene cyclopropane ring (14). The authors felt that, on the contrary, the C2-C8 bond distance in a cyanosemibullvalene was long. They calculated the C4-C6 nonbonded distance that one could expect if the C4-C5-C6 bond angle were 109°. This value, 2.45 A, differed from the observed distance of 2.36 A. They also compared the dihedral angles between the five membered rings with some known values for bi- and tricyclic systems. Based on this comparison and the short nonbonded C4-C6 distance, the authors concluded that there is a small attractive bonding interaction between C4 and C6 and that this is responsible for the long C2-C8 bond. They computed bond lengths which were in good agreement with the X-ray data by assuming that the crystal actually consisted of a resonance combination of 90% a and 10% b. (eqn 27). This calculation assumed that there is a linear relationship between bond length and percent sp^3 or sp^2 character in the bond. The averaged bond lengths were weighted averages using standard C-C sp^3 and sp^2 bond lengths.



(27)

ii The Experimental Method

Crystals of the bright yellow 1,5-dimethyl-2,4,6,8-tetrakis(carbomethoxy)semibullvalene Ib suitable for X-ray crystallography were obtained by recrystallization from methanol. The crystals were orthorhombic, space group $P2_12_12_1$ with a = 6.633 (1), b = 10.841 (2), c = 24.658 (2) A, d_{calcd} 1.364 g/cm^3, d_{obsd} 1.31 g/cm^3 for Z = 4. The intensity data were measured on a Hilger-Watts difractometer (Ni filtered Cu $K\alpha$ radiation, θ-2θ scans, pulse height discrimination). A total of 1415 reflections were measured for $\theta < 57^{\circ}$, of which 1369 were considered to be observed ($I > 2.5\sigma(I)$). The structure was solved by a multiple solution procedure (Germain, G.; Main, P.; Woolfson, M.M. Acta Crystallogr., Sect. A **1971**, A27, 368) and was refined by full-matrix least squares. In the final refinement anisotropic thermal parameters were used for the nonhydrogen atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations, but their parameters were not refined. The final discrepancy indexes are R = 0.037 and wR = 0.048. The final difference map has no peaks greater than ±0.2 eA^{--3}.

iii Results & Discussion

The crystal structure of Ib is shown in Figure 2. Pertinent structural parameters are summarized in Table 8. The atomic position and thermal parameters appear in Appendix A1.

The geometry of the cyclopropane ring is particlarly unusual. There is a striking lack of symmetry in the molecule. The C2-C8 bond is very long (1.782 A) while the C1-C2 bond is shortened (1.480 A). Also, the C1-C8 bond is somewhat longer (1.530 A) than the average cyclopropane bond (1.51 A) (78). The bonds adjacent to the cyclopropane ring (C2-C3 = 1.430, C7-C8 = 1.413 A) are shorter than normal $C_{sp}2-C_{sp}2$ bonds (1.48 A) (78). The nonbonded distance at the open end of the molecule (C4-C6) is 2.21 A, and the C4-C5-C6 bond angle is 93°. These parameters are both smaller than those observed for unsubstituted semibullvalene Ia (2.261 A and 95.2°) (77) and for 1-cyanosemibullvalene (2.35 A and 101°)(27).

The cyclopropane ring asymmetry is consistent with the orientation of the carbomethoxy groups about this ring. Pi-electron acceptors are known to affect the geometry of

Figure 2a

X-RAY CRYSTALLOGRAPHIC STRUCTURE OF 1,5-DIMETHYL-2,4,6,8-TETRAKIS(CARBOMETHOXY)SEMIBULLVALENE

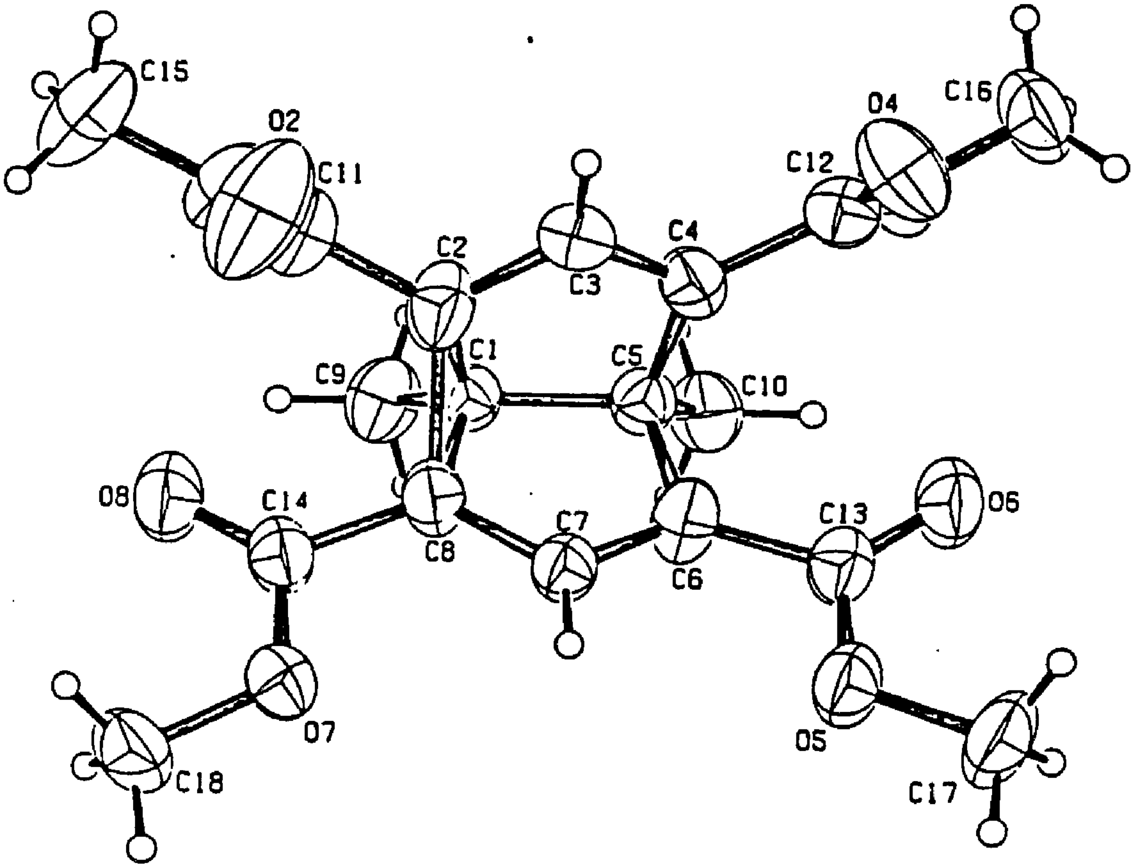


Figure 2b

X-RAY CRYSTALLOGRAPHIC STRUTURE OF 1,5-DIMETHYL-
2,4,6,8-TETRAKIS(CARBOMETHOXY)SEMIBULLVALENE

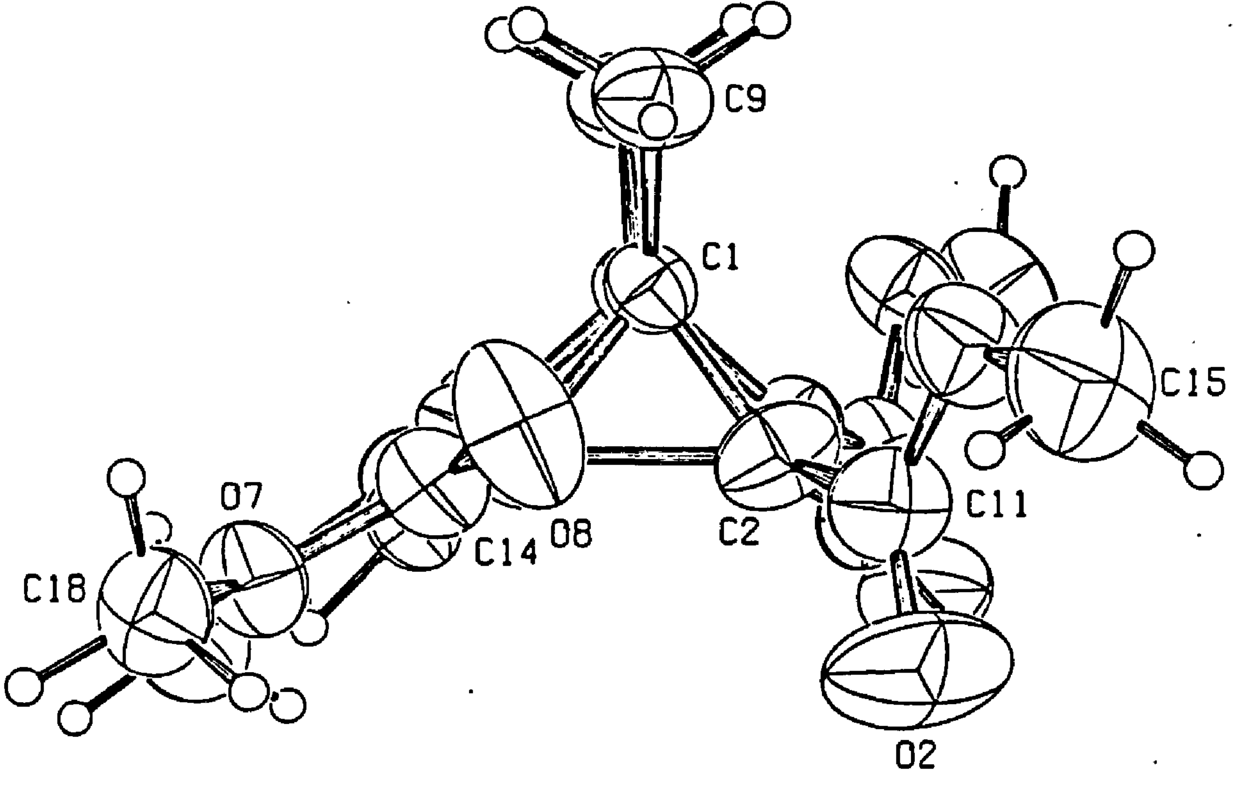
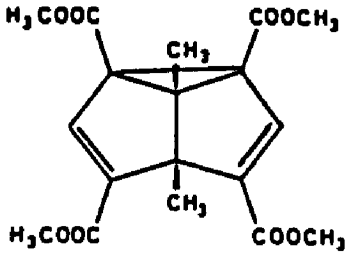


Table 8

SELECTED GEOMETRIC FEATURES OF 1,5-DIMETHYL-2,4,6,8-TETRAKIS(CARBOMETHOXY)SEMIBULLVALENE - Ib



Distance Å

C1 - C5	1.581(4)	C6 - C7	1.349(4)
C1 - C2	1.483(5)	C4 - C5	1.511(5)
C1 - C8	1.530(4)	C5 - C6	1.532(4)
C2 - C8	1.782(5)	C1 - C9	1.504(5)
C2 - C3	1.430(5)	C5 - C10	1.511(4)
C7 - C8	1.413(4)	C4 - C6	2.21
C3 - C4	1.341(4)	C3 - C7	3.05

Angle, deg

C2-C1-C8	72.5(2)	C1-C8-C7	109.7(2)
C1-C8-C2	52.5(2)	C5-C4-C3	111.1(3)
C8-C2-C1	55.0(2)	C5-C6-C7	112.0(3)
C4-C5-C6	93.1(2)	C2-C3-C4	111.3(3)
C1-C2-C3	109.5(3)	C6-C7-C8	111.4(3)

Torsional Angle, deg

O2-C11-C2-C1	147.52	O4-C12-C4-C5	-143.52
O2-C11-C2-C8	82.96	O4-C12-C4-C6	-92.90
O8-C14-C8-C1	-26.42	O6-C13-C6-C5	8.83
O8-C14-C8-C2	32.32	O6-C13-C6-C4	-35.00

cyclopropanes because of the interaction between the LUMO of the electron acceptor system and the cyclopropane HOMO of the correct symmetry (3e') (14,79). The resultant transfer of electron density from the cyclopropane to the π-electron acceptor system weakens those bonds which the 3e' orbital is bonding (the vicinal bonds) and strengthens the distal bond (for which the 3e' orbital is antibonding). The extent of this interaction is dependent on the geometric relationship of the two orbital systems. It can be assessed by measuring the dihedral angle between the carbonyl oxygen and the midpoint of the distal cyclopropane bond (e.g.,O8-C14-C8-midpoint C1-C2); 0° maximum overlap occurs, while at 90° there is no overlap.

The data from Table 8 can be used to calculate the relevant dihedral angles for compound Ib. These angles are 2.95° for the C=O bound to C8 and 115° for the C=O bound to C2. The carbonyl group bound to C2 is twisted almost completely out of conjugation with the Walsh orbitals, while that attached to C8 adopts the most favorable conformation for overlap. Therefore, the C1-C8 bond is lengthened because of the vicinal, interacting carbomethoxy substituent and is not competitively shortened by the C2 carbomethoxy group. Conversely, the C1-C2 bond is shortened as it is distal to the C8 substituent.

Applying this theory to the C2-C8 bond, one would expect a bond length similar to that of a C1-C8. A study of a series of substituted cyclopropanes has shown that the bond lengthening induced by a Pi -electron acceptor need not be equal for both vicinal bonds (79). However, the effects of these substituents is nowhere near as large as seen here for the C2-C8 distance. While molecules containing a cyclopropane ring with one long C-C bond are known (80,81), there are very few in which the bond distance is greater than 1.6 A (81) The C2-C8 bond length of semibullvalene <u>(Ia)</u> is 1.6A (77). A steric effect caused by the adjacent carbomethoxy groups might influence the C2-C8 bond length. This is unlikely as identical substitution at the open end of the Ib does not increase the C4-C6 distance with respect to the unsubstituted compounds (27,77).

It is not possible to draw exact parallels between the crystal and solution structures of <u>Ib</u> since crystal packing may affect the former. However, it appears that the pattern of substitution in Ib has led to a substantial electronic rearrangement as manifested by the unusual crystal structure. The observed geometry is consistent with a structure that is approaching the transition state for Cope rearrangement . In addition to the extremely long C2-C8 bond, the short nonbonded C4-C6 distance and the long C1-C5 bond (1.581 A), the C2-C3 and C7-C8 bonds are significantly shorter than average.

C. NMR Studies on 1,5-Dimethyl-2,4,6,8-tetrakis(carbomethoxy)semibullvalene

i. Background

Chemical systems which undergo isomerization can be studied by various methods. If the enthalpy of activation ($\Delta G^{\ddagger}$) is large (>23 kcal/mole) the various isomers are stable at room temperature and separation should be possible. As the rate of isomerization increases the $\Delta G^{\ddagger}$ will decrease and physical separation at room temperature becomes impossible. Figure 3 (82) is a schematic representation of some of the processes that can be used for the detection of intramoleclar mobility. The $\Delta G^{\ddagger}$ range indicated for nmr analysis is larger today due to the development of high field spectrometers.

Low temperature nmr spectroscopy has become an extremely effective tool for studying equilibrating systems (83). If two nuclei have different chemical environments (A different from B) or if they are interconverting so slowly that the rate constant (k_r) is very small relative to the chemical shift difference, then two separate signals for the nuclei A and B will be observed in the nmr spectrum, (we are assuming uncoupled signals whose intensities are equal). In an equilibrating system the rate constant (k_r) is a function of temperature and the nmr spectra of such systems are temperature dependent. This is shown schematically in

Figure 3

POSSIBILITIES FOR THE DETECTION OF INTRAMOLECULAR MOBILITY

Taken from H. Kessler, Angew. Chem. Intl. Ed., 1970, 9, 219-235

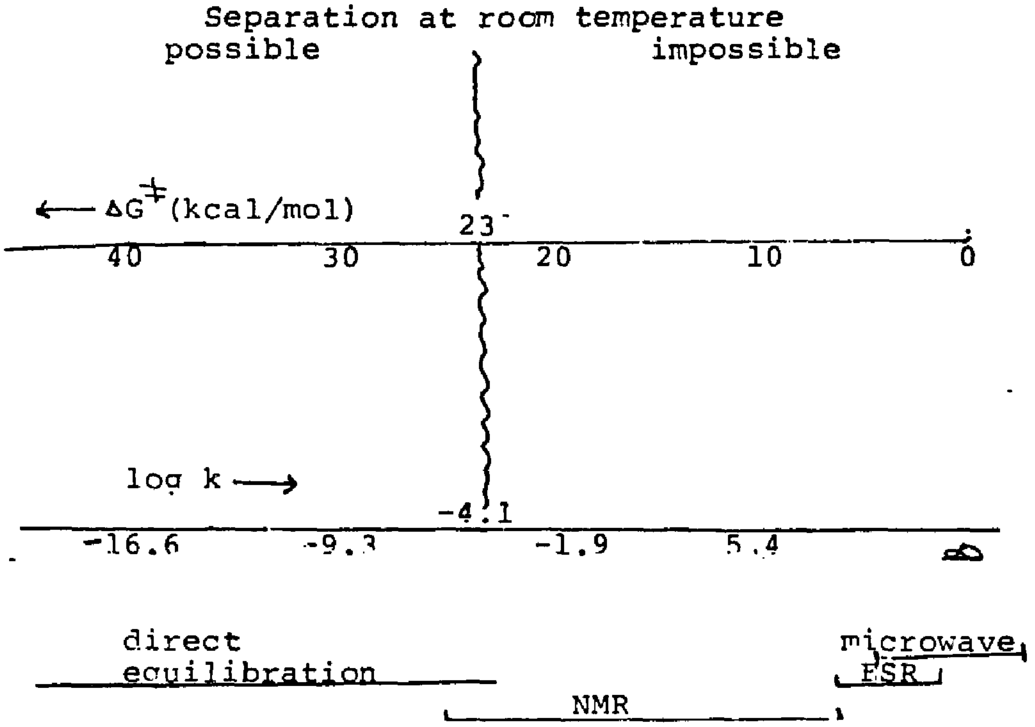


Figure 4 (84). In this illustration it is seen that at low temperatures k_r is very small (only a small percentage of the molecules are interconverting) and the rearrangement is said to be slow on the nmr time scale. Two sharp peaks are seen separated by $\Delta\nu = \nu_a - \nu_b$. As the tempeature is increased k_r increases and the signals first broaden and approach each other (c - Fig.4). At the coalescence temperature (T_c) the signals have merged into one very broad peak which is almost indistinguishable from the baseline. At the coalescence temperature the rate constant is related to the chemical sift difference for A and B by equation '28' for equally populated sites.

$$k_r = \frac{\pi}{\sqrt{2}} (\nu_a - \nu_b) \ \sec^{-1} \qquad (28)$$

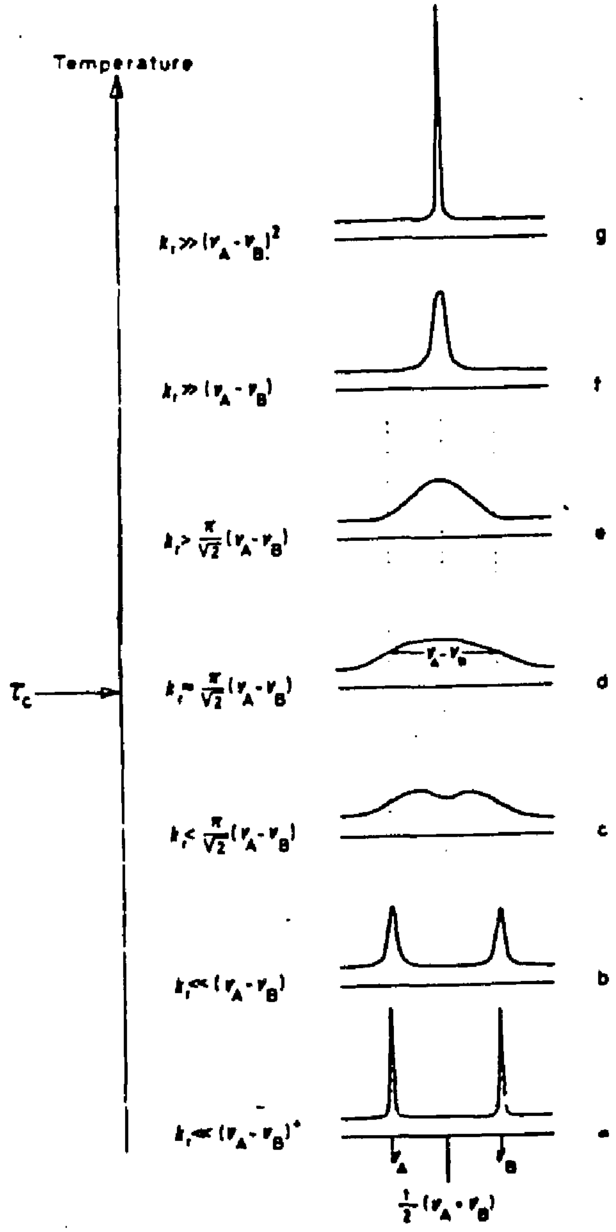
The rate increases with increasing temperature until the signals for A and B have become one sharp peak whose chemical shift is $\frac{1}{2}(\nu_a+\nu_b)$(g in Fig.4). If the coalescence temperature is known k_r can be calculating using eqn 28. If T_c is not known the rate constant can be estimated by measuring the half maximum intensity line width $\Delta\nu_{1/2(T)}$ at temperatures near T_c and using equation 29 (84).

$$k_r = 2\Delta\nu_{\frac{1}{2}(T_c)} \quad (\text{near } T_c) \qquad (29)$$

Figure 4

TEMPERATURE DEPENDENCE OF CHEMICAL SHIFTS AND LINE SHAPES DUE TO INTRAMOLECULAR MOBILITY

Taken from Breitaier and Voelter,
"^{13}C NMR Spectroscopy",
Verlag Chemie, 1974, p. 85



Once the value for k_r is determined, $\Delta G^{\ddagger}_{(T_c)}$ can be calculated for the equilibrium reaction using equation 30 (84).

$$\Delta G^{\ddagger} = 4.57\ T\ (10.32 + \log \frac{T}{k_r})\ \text{cal/mol}\ . \qquad (30)$$

The rate constant at various temperatures can be determined by measuring a series of spectra at different temperatures and comparing them to calculated spectra at these temperatures. A least squares treatment to obtain the best fitting spectra is then used to calc $k_{r(T)}$. Other thermodynaic properties (E_{act}, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$) can then be calculated (84). At low temperatures, lines may broaden for reasons other than changes in the equilibrium constant, e.g. changes in the relaxation time due to decreased tumbling of slow moving molecules (85) (see below), solvation effects, field inhomogeneity. These factors must also be taken into account when interpreting low temperature nmr data.

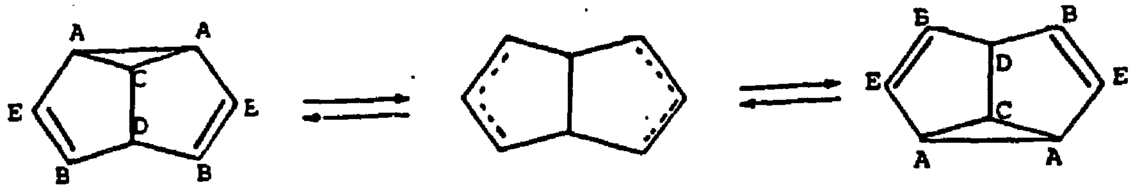
Carbon-13 nmr is useful for the study of equilibrating systems. The chemical shift differences between carbons in different environments span a large range (400 ppm) and C-C coupling is not detectable in natural abundance ^{13}C nmr spectroscopy. Since the rate constant (k_r) depends on the chemical shift measurered in Hertz, the advent of high field spectrometers has aided in the accurate determination of this parameter (eqn 31) (86).

$$\delta_{ppm}\quad \frac{\nu_{obs} - \nu_{std}}{\nu_1} \quad (\nu_1 = {}^{13}\text{C radiofrequency used}) \qquad (31)$$

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 spectrometer can be measured using a 100.6 MHz instrument.

The lower temperature limit for the determination of a spectrum is dependent upon several factors; solvent viscosity and melting points, solubility of the solute in the solvent at that temperature, ability to maintain a constant temperature at the probe. At the present time the lower limit for solution nmr using a commercial 100.6 MHz (^{13}C frequency) spectrometer is -160 to -170°C.

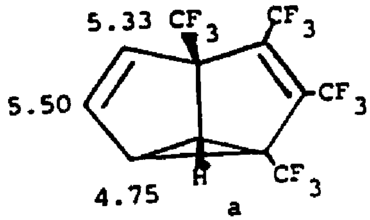
In the case of semibullvalene and its symmetrically substituted derivatives, the equilibrating species which are undergoing Cope rearrangement are degenerate (eqn 32). Thus the relative amounts of the two equilibrating species will not change with temperature, only the rate of interconversion should be affected. As indicated in eqn 32 when the equilibrium is very fast on the nmr time scale, signals for



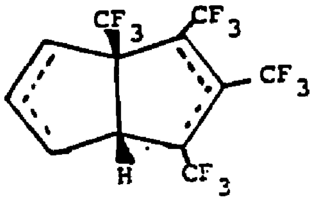
(32)

carbons (or protons) A and B will appear at averaged position as will those for C and D. The signal for E should remain unchanged with respect to any change in the rate of rearrangement. If the compound is unsymmetrically substituted one of the equilibrating species will be favored, and the relative amount of this compound as well as the rate of rearrangement, will change as the temperature is varied. Semibullvalene rearranges rapidly on the nmr time scale at room temperature (22). Its rate of rearrangement has been slowed down sufficiently at -160°C to allow the observation of the nmr resonances for the static structure. The average signal for H2,4,6 and 8 coalesced at -143°C when the spectrum was determined at 251 MHz (10). Anet has calclated an activation energy of 5.1 kcal/mole from these data and a $\Delta G^{\ddagger}_{Tc}$ of 5.5 kcal/mole at -143°C (10).

Only one semibullvalene reported in the literature might exist in a delocalized structure (36). This compound, 2,3,4,5-tetrakis(trifluoromethyl)semibullvalene exhibits a temperature independent nmr spectrum -90°C to +120°C. The proton resonances are indicated on the structural diagram. The signal for H6 is at 5.33 ppm and that for H8 is at 4.75 ppm while the signal for H7 is at 5.50ppm. The authors indicte that the signals for H8 and H6 are in a range intermediate between that expected for a cyclopropyl proton and a vinyl proton in this system. This observation coupled with the temperature invariance of the spectrum, led them to conclude that the actual structure might be the delocalized form b (diagram). The conclusion would be strengthened by recording the spectrum over a larger temperature range. The compound synthesized is not an ideal model for delocalization. We have found (MNDO calcs) (75) that substituents on one sde of the allyl system leads to a lack of interaction of the two allyl systems in the delocalized state (b). A more symmetrically substituted system might be a better model.



a



b

ii. Experimental Methods

The room temperature proton spectrum was measured in $CDCl_3$ on a Varian A60 spectrometer. The decoupled and off resonance decoupled ^{13}C spectra were measured on a JEOL-PFT-100 spectrometer in $CDCl_3$ (87). The low temperature spectra were recorded at 100 MHz on a Bruker WH-400 spectrometer in $CD_2Cl_2/CH_2{=}CHCl$ (88). The carbon spectrum was determined at -70°, -150° and $-160^{\circ}C$. The spectra can be found in figures

5 and 6 and relevant data are listed in Tables 9 and 15.

iii. Results and Discussion:

a) Room Temperature Spectra

Before attempting an analysis of the low temperature spectra, an interpretation of the room temperature data is necessary. From the data in Table 9, it is clear that averaged spectra are being recorded at room temperature; the proton spectrum shows three singlets corresponding to the methyl, methoxy and vinyl protons, while the ^{13}C spectrum consists of 6 resonances corresponding to CH_3; OCH_3; C1,5; C2,4,6,8; C3,7 and C=0.

The proton chemical shifts can be compared to model compounds or to chemical shift ranges known for the types of protons present in the system. Since none of the protons are directly involved in the Cope rearrangement, their chemical shifts will not provide much information regarding this rearrangement. The carbon shifts are much more informative. As discussed above, for a rapidly rearranging system the signals for carbons 2, 4, 6 and 8 should appear at a chemical shift that is an average between the cyclopropyl and vinyl resonances expected in the static structure. Carbons 1 and 5 would also be averaged as would the two methyl carbons, the four carbonyls and the 4 methoxy groups. Only carbons 3 and 7 should appear at the chemical shift expected

Figure 5

^{1}H NMR SPECTRUM OF 1,5-DIMETHYL-2,4,6,8-TETRAKIS-CARBOMETHOXYSEMIBULLVALENE AT ROOM TEMPERATURE

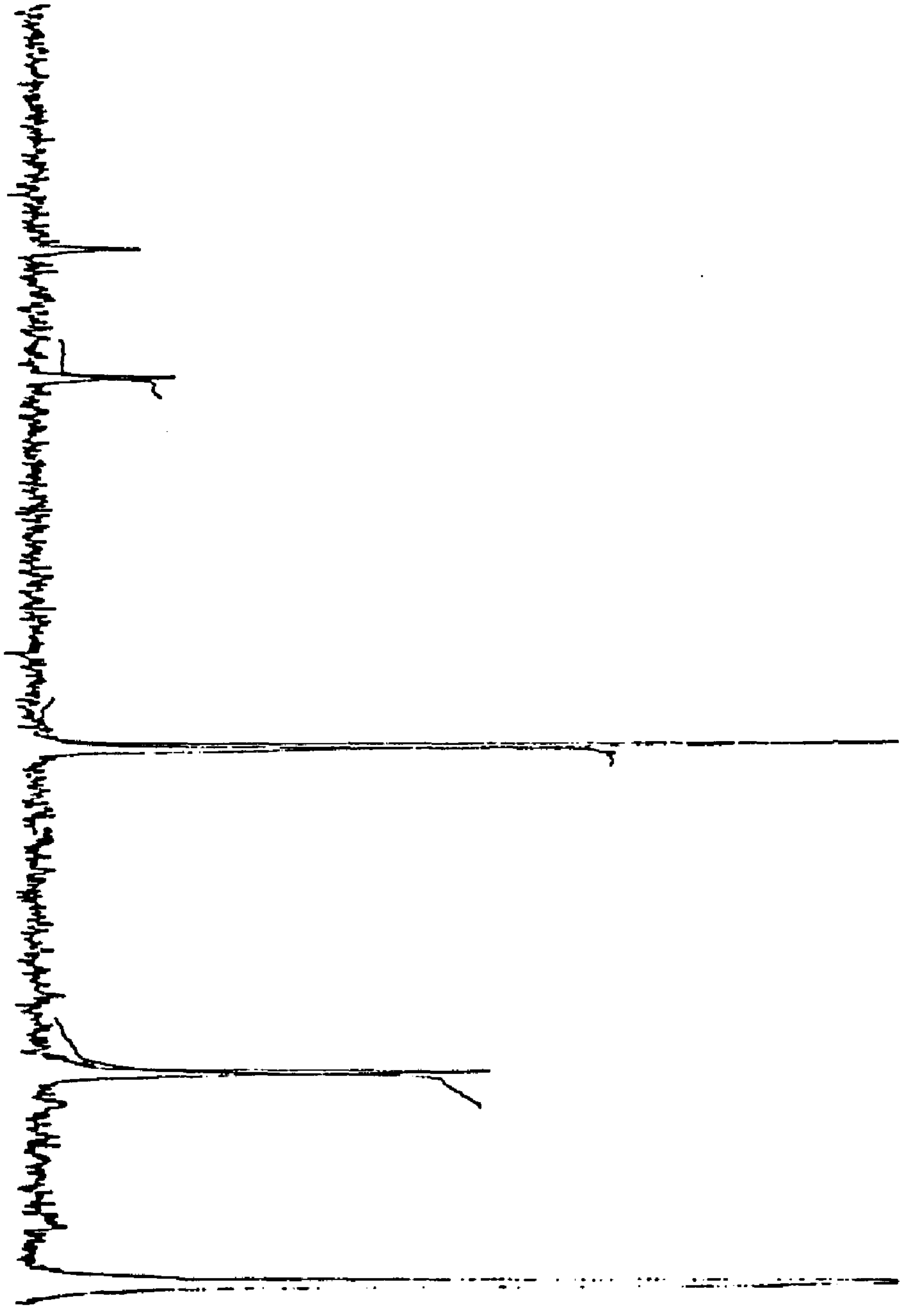


Figure 6

^{13}C NMR SPECTRA FOR 1,5-DIMETHYL-2,4,6,8-TETRAKIS-(CARBOMETHOXY) SEMIBULLVALENE - Ib

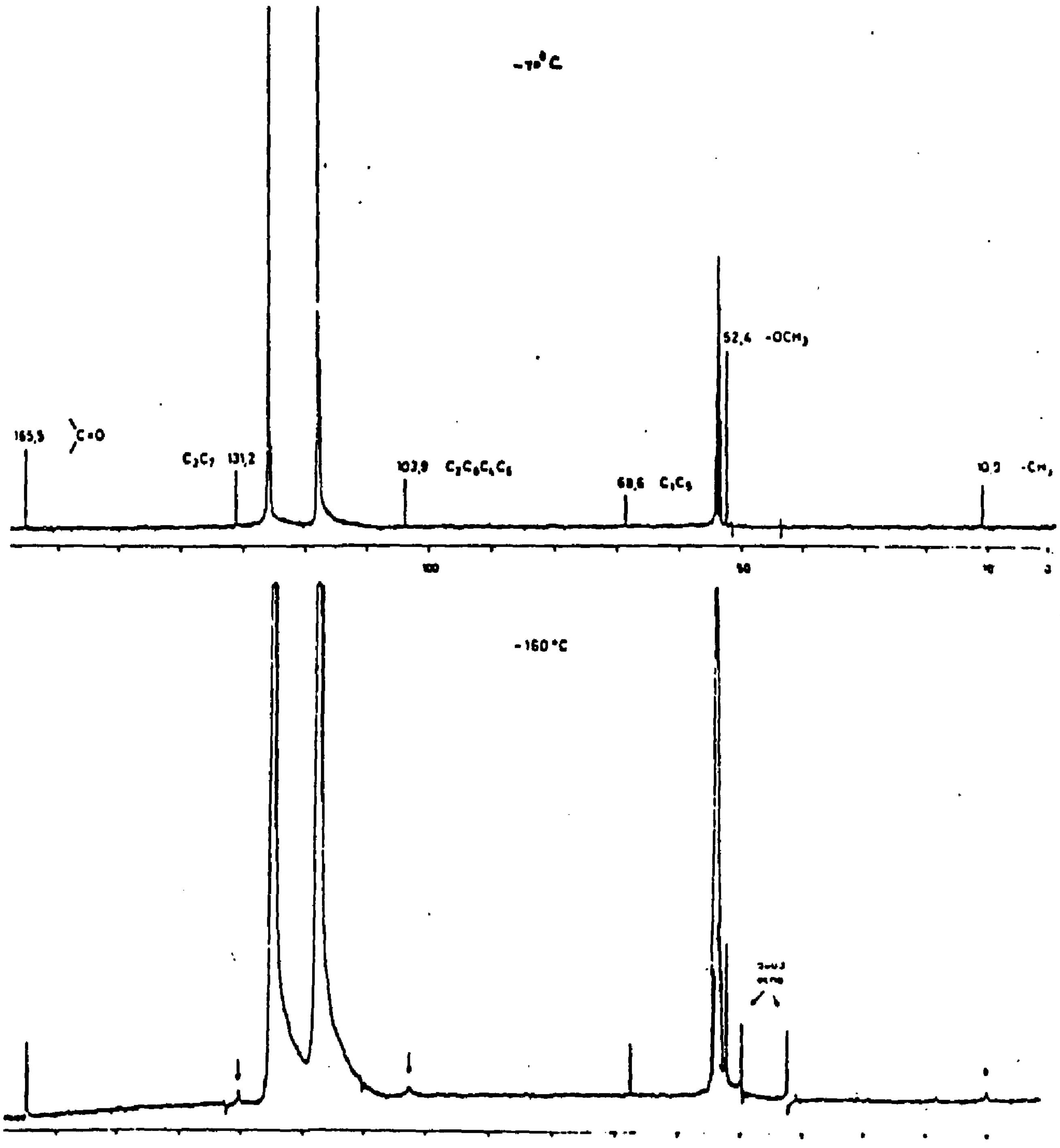
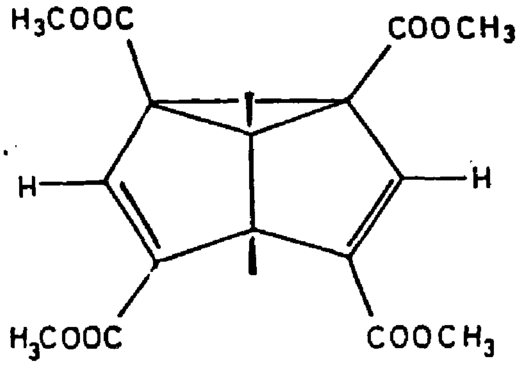


Table 9

^{1}H and ^{13}C NMR DATA FOR 1,5-DIMETHYL-2,4,6,8-TETRAKIS(CARBOMETHOXY)SEMIBULLVALENE



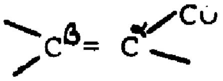
^{1}H	^{13}C		
1.45 (s, 6H, CH_3)	11.02	q	CH_3
3.67 (s, 12H, OCH_3)	52.09	q	OCH_3
6.18 (br s, 2H, H3,7)	68.67	s	C1,5
	104.07	s	C2,4,6,8
	131.23	d	C3,7
	165.47	s	C=O

All spectra obtained at room temperature in $CDCl_3$ solution for a nonequilibrating vinyl carbon in this system.

The ^{13}C data can be assessed in several different ways. One of these is to calculate the chemical shifts expected for the static (frozen out) system, obtain average values from these data and compare them with the observed values. Some ^{13}C chemical shifts can be estimated using additivity principles. Lindeman and Adams (89) deduced an additivity rule for the ^{13}C chemical shifts of alkanes based on the number and type of carbon atoms attached to the carbon in question. They calculated parameters which could be added to a base chemical shift value for an alkane. These parameters have been used to predict the chemical shifts of many branched alkanes with a high degree of accuracy (90). In brief, carbon substitution in the α and β positions shifts the carbon resonance in question downfield by approximately 9 ppm while γ substitution shifts the resonance upfield by a few ppm (90). An additivity rule has also been devised for alkenes (91). Substitution at one carbon of a vinyl group affects the chemical shifts at both vinyl carbons. For ethylene, the α-C shieldings occur over a range of approximately 70 ppm while the carbons absorb over approximately 50 ppm (92). A linear regression analysis of the olefinic shielding for alkyl substituted unsaturated carbonyl compounds yielded a series of parameters which are useful for the estimation of some of the chemical shifts in the system (93). These parameters are listed in Table 10. Polar substituent effects have been measured for cyclopro-

Table 10

SUBSTITUENT PARAMETERS FOR ALKYL SUBSTITUTION IN α,β-UNSATURATED CARBONYL DERIVATIVES



Parameter[a]	α-C (ppm)	β-C (ppm)
α	7.5±0.4	13.7±0.6
β^{Γ}	-5.4±0.4	-5.6±0.6
$\beta^{\urcorner}$	5.8±0.8	5.5±0.9
γ^{Γ}	-1.7±0.6	
$\gamma^{\urcorner}$		-1.6±1.3
cis(alkyl)	-1.3±0.6	-0.5±0.7
X=Me	-1.5±0.6	-10.3±0.9
X=OH	-10.1±0.6	-7.6±0.9
X=OMe	-10.2±0.6	-9.1±0.9
Constant term	138.3	139.2

Taken from J. B. Stothers, Carbon 13 NMR Spectroscopy 1972 Academic Press, N.Y. p 193

[a] The symbol indicates the position of substitution relative to the carbon of interest while the superscript denotes the bonding pathway to that carbon

pane (94) but there is no systematic rule for the assessment of alkyl effects. Since the additivity rules cannot be used to estimate all of the chemical shifts for 1,5-dimethyl-2,4,6,8-tetrakis(carbomethoxy)semibullvalene we will also make use of the chemical shifts of model compounds.

Another method of assessing the room temperature nmr data is by a comparison of our data with the values observed for other semibullvalenes undergoing degenerate Cope rearrangements. The third method involves an application for ^{13}C chemical shifts measured for the static structure of the parent semibullvalene (10).

Method 1

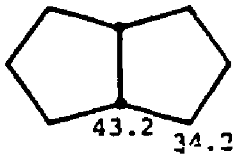
Table 11 lists the ^{13}C chemical shifts for some model compounds. Estimates for the ^{13}C chemical shifts for Ib in its static form can be made using the data in these tables as follows: The value of C1 can be estimated from the chemical shifts reported for the tetracyclic compounds f (91) in Table 11 (45-48 ppm). The substituent at C3,7 does not appear to affect this chemical shift greatly as the values found for all three compounds vary only by 3 ppm. The major difference between these model compounds and the semibullvalene Ib is that the model is tetracyclic and Ib is tricyclic and contains two vinyl groups conjugated to the cyclopropanes. The effect of a vinyl group can be estimated by looking at compound b in Table 11. Although the non allylic bridgehead carbon here is not part of a cyclopropyl ring, and therefore was not an exact model for this system,

Table 11

CARBON 13 CHEMICAL SHIFTS FOR SOME MODEL COMPOUNDS

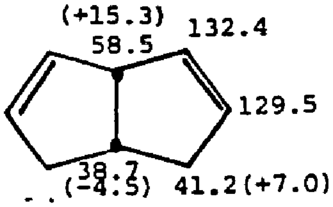
(ref)

a.



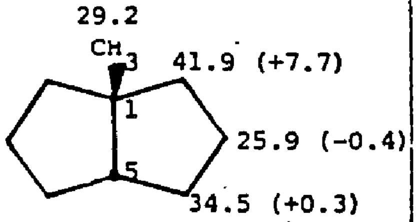
(63)

b.



(63)

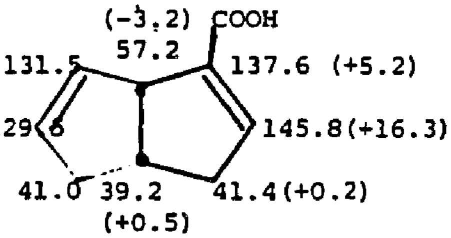
c.



C1=49.8 (+6.6)
C5=50.9 (+7.7)

b and C (changes from a)

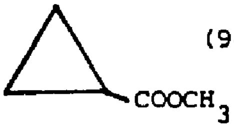
d.



(97)

d. (changes from b)

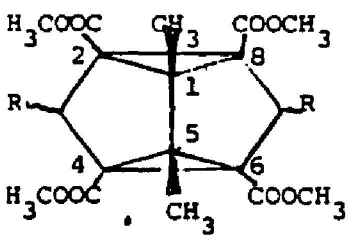
e.



(94)

αC = +16
βC = +11

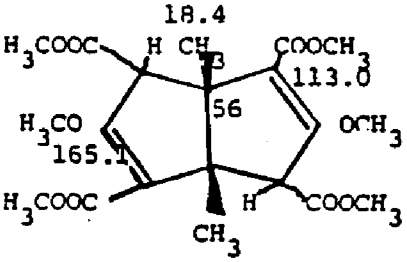
f.



(95)

R = =O; H,OH; H,OMs
C1,5 = 45-48
C2,4,6,8 = 48-50
CH_3 = 8.8-9.6

g.



(96)

one can use the data for this compound compared to the saturated analog (a in Table 11) (63) to estimate the effects of the vinyl system on the bridgehead carbon. The resonance in the unsaturated system is shifted 4.5 ppm upfield from that in the saturated analog (38.7 ppm vs. 43.2 ppm). The C1 resonance can the be estimated by a combination of the data presented above; 45-48 ppm - 4.5 ppm = 41-45 ppm.

The resonance for C5 can be estimated from the bicyclo(3.3.0)octanes c and d in Table 11 (63,97). The corresponding resonance in compound d is 57.2 ppm, to which we add the effect of a second COOR group (-1 ppm) and 6.6 and 7.7 ppm for the effects of the bridgehead CH_3 groups on this carbon; 57.2 + (-2) + 6.6 + 7.7 = 70-71 ppm.

The chemical shifts for carbons 2 and 8 in the static structure can also be estimated from the tetracyclic system (f, Table 11) (95) with contributions added in for the vinyl groups. In the tetracyclic compounds the ^{13}C resonance varies from 48-50 ppm for C2-8. In the bicyclo(3.3.0)octane systems the difference between the chemical shifts for C2 in the saturated compound (cpd a, Table 11) (63) and C4 in the unsaturated compound (d, Table 11) (97) is 7.2 ppm. Thus, the chemical shift for C2, 8 in Ib is estimated to be 48-50 + 7.2 = 55 -57 ppm.

The vinyl resonance can be estimated by using the additivity parameters for a carbomethoxy substituted vinyl group (Table 10) (93) and also from model systems. The chemical shifts for C4, 6 and C3, 7 as estimated from the data in Table 10 are listed below:

		C4,6		C3,7
Base:		138.3		139.2
OCH_3:		-10.2		-9.1
αC:	(1)	+7.5	(1)	+13.7
βC^{q}:	(3)	+17.4	(1)	+5.8
βC^{π}:	(1)	-5.8	(1)	-5.6
cis alkyl:		-1.3		
γC^{q}:			(3)	-4.8
	C4,6 =	145.4	C3,7=	139.2

Using the data from the bicyclo(3.3.0)octanes listed in Table 11, one estimates a similar chemical shift for carbons 4 and 6. Taking the value of 137.6 as a base (cpd d, carbon 2) (97) and adding in the effects of the β-CH_3 substituent (cpd c) (63) one arrives at 137.6 + 7.7 = 145 ppm.

A third estimate involves subtracting the effect of the methoxy groups at C3, 7 in the model system g (Table 1) (9). Using data from the literature (98) the effect of a methyl ether on the chemical shifts of ethylene can be estimated to be +29.9 ppm for the α-carbon and -39.2 ppm for the β carbon. In compound g, the vinyl carbons α-to the OCH_3 (C3,7) resonate at 165.1 ppm while the β-carbons resonate at 113.0 ppm. This corresponds to an estimated chemical shift of 153.2 for carbons 4 and 6 (113.0 + 39.2 = 153.2 ppm) and 135.2 ppm for carbons 3 and 7 (165.1 - 29.9 = 135.2 ppm).

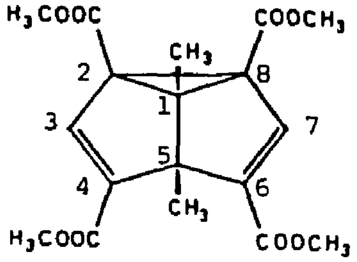
To summarize, the estimated chemical shifts for the carbons in structure <u>Ib</u> in its static state, based on additivity rules and model compounds are:

C1	41 - 45 ppm	Average = 57 ppm
C5	70 - 71 ppm	
C2,8	55 - 57 ppm	Average = 103.5 ppm
C4, 6	145 -153 ppm	
C3, 7	135 -139 ppm	

The methods used to obtain these estimates are summarized in Table 12.

Table 12

ESTIMATED CARBON 13 CHEMICAL SHIFTS FOR 1,5-DIMETHYL-2,4,6,8-TETRAKIS(CARBOMETHOXY)SEMIBULLVALENE
(Ib)



C1	45-48(f)- 4.5(d)	= 41-45 ppm
C5	57.2(d) - 1(b) +6.6(c) + 7.7(c)	= 70-71 ppm
C2,8	48 50(f) + 7.2(d)	= 55-57 ppm
C4,6	137.6(d) + 7.7(c) + 0.3(c)	= 145 ppm
	Additivity from Table 10	= 145.4 ppm
	113(g) + 39.2(OCH$_3$ on g)	= 153.2 ppm
C3,7	Additivity from Table 10	= 139.2 ppm
	165.1(g) - 29.9 (OCH$_3$ on g)	= 135.2 ppm

Compounds (a) through (g) from Table 11

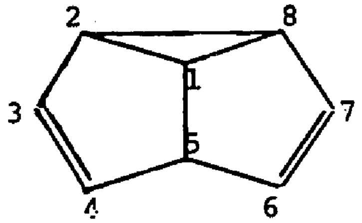
Averages	C1,5	C2,4,6,8
Calc. above	57 ppm	103.5 ppm
Exp.	68.7 ppm	104.1 ppm

The average values observed for Ib are C1,5 = 68.7 ppm, C2,4,6,8 = 104. ppm and C3,7 = 131.7 ppm. The observed data for C2,4,6,8 agree well with the values calculated above. Also, the calculated difference in chemical shift between C2,8 and C4,6 of 91 ppm (147-56 ppm) is in excellent agreement with the low temperature data for the parent semibullvalene (see Table 14) (10). The average chemical shifts estimated for C1,5 do not agree well with the observed value. The calculated chemical shift difference would be 30 ppm for C1 and C5 in their static states. This seems like a large difference for a cyclopropyl and a allylic sp^3 carbon. The chemical shift observed for C3,7 is slightly upfield from that calculated by the various methods above. Some reasons for these anomalies will be discussed below.

A second way of looking at the ^{13}C nmr data for Ib is to compare the values observed with data from known semibullvalenes. Relevant literature data are recorded in Table 13 along with the differences from the parent compound. Here again the average resonance for C1 and C5 seems too far downfield. In all other 1,5-dimethylsemibullvalenes listed in Table 13 the average chemical shift difference from the unsubstituted compound for C1,C5 is approximately 9 ppm. In Ib this difference is 18 ppm. The average signal for the methyl group in Ib and its diacetate derivative appear upfield from all the other 1,5-dimethyl semibullvalenes. This method of comparison is difficult for the other carbons since the known compounds have very different substituents

Table 13

CARBON 13 CHEMICAL SHIFTS FOR SOME SUBSTITUTED SEMIBULLVALENES

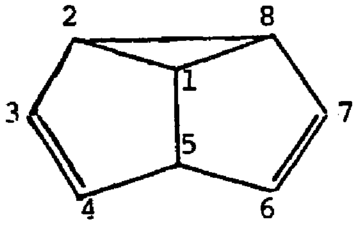


Compound	C1,5	C2,4,6,8	C3,7	CH_3	Reference
all H	50.7	87.2	121.7	--	10
1,5-di-Me	59.8 (+9.1)	93.0 (+5.8)	119.0 (-2.7)	15.6	29
1,5-di-Me-3,7-di-COOMe	60.6 (+9.9)	93.7 (+6.5)	127.2 (+5.5)	14.9	41
1,5-di-Me-3,7-di-Ph	58.5 (+7.8)	88.7 (+1.5)	128.4 (+6.7)	15.8	41
1,3,5,7-tetra-Me	59.0 (+8.3)	92.9 (+5.7)	127.4 (5.7)	15.8 16.3	41
1,5-di-Me-2,4,6,8-tetra COOMe-3 7-di-OAc	60.3 (+9.6)	94.2 (+7.0)	145.1 (+23.4)	11.4	56
1,5-di-Me-2,4,6,8-tetra COOMe	68.7 (+18.0)	104.1 (+16.9)	131.2 (+9.5)	11.0	This work

(Values in parantheses denote differences from the unsubstituted compound)

Table 14

VARIABLE TEMPERATURE NMR DATA FOR UNSUBSTITUTED SEMIBULLVALENE (10)



Proton NMR (δ, ppm from TMS)

Room Temperature	-160	Difference (Δδ)
2.98 (H1,5)	2.83 (H1)	0.33
	3.16 (H5)	
4.17 (H2,4,6,8)	2.79 (H2,8)	2.80
	5.59 (H4,6)	
5.07 (H3,7)	5.08 (H3,7)	

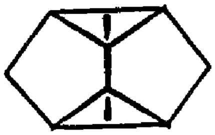
Carbon NMR (δ ppm from TMS)

Room Temperature	-160	Difference (Δδ)
50.7 (C1,5)	48.7 (C1)	5.1
	53.1 (C5)	
87.2 (C2,4,6,8)	42.2 (C2,8)	89.6
	131.8 (C4,6)	
121.7 (C3,7)	121.7 (C3,7)	

and the effects on averaged chemical shifts is hard to assess. In summary, the method employed here indicates that the average chemical shifts observed for C1,5 and the methyl carbons for compound Ib are anomalous when compared to known substituted semibullvalenes.

The third method of comparison makes use of the known chemical shifts of unsubstituted semibullvalene (Ia), in its frozen nonequilibrating state (10). The ^{13}C spectral data obtained by Anet et al are listed in Table 14. The chemical shift difference between C1 and C5 is 5.1 ppm while that between C2,8 and C4,6 is 89 ppm. If we assume that the differences in chemical shift for the carbons in the static structure is comparable for the unsubstituted semibullvalene and Ib, we can estimate the expected resonances for Ib in its static state. The chemical shift difference between C1 and C5 would be expected to be 5.1 ppm. Using the observed average value of 68.6 ppm for C1,5 in Ib, we obtain chemical shifts for carbons 1 and 5 of 66 and 71 ppm respectively (68.6 ± 2.6 ppm). Applying the same method to carbons 2,4,6 and 8 the shifts are 59.3 ppm for C2 and 8 and 148.9 for carbons 4 and 6 (104 ± 44.8 ppm). Except for C1 all the calculated chemical shifts agree with the values estimated by using model compounds and additivity effects.

Perhaps the problem with the chemical shift of C1 lies in the choice of model. The model cmpound chosen is the tetracyclic ring system shown below.



In the unsubstituted semibullvalene, C1 is further downfield than C2,8 (48.0 vs. 42.2 ppm - see Table 16). However, the answer to the question of the correct assignment for the C1 chemical shift awaits the aquisition of more data or better model compounds.

In summary, the results of the comparative studies of the ^{13}C chemical shifts of 1,5-dimethyl-2,4,6,8-tetrakis-(carbomethoxy)semibullvalene (Ib) indicate that the averaged shifts observed for C2,4,6,8 are in the correct range for a rapidly Cope rearranging system. The chemical shift of C1,5 does not agree well with that calculated from model compounds, probably due to an anomalous shift for C1. The shift observed for C3,7 appears somewhat upfield from the calculated values (131.7 vs 135.9). The proton resonance for H3,7 also appears upfield from the analogous resonance in the cyclooctatetetraene <u>7</u> (6.19 vs 7.3 ppm).

These discrepancies have not been totally resolved.

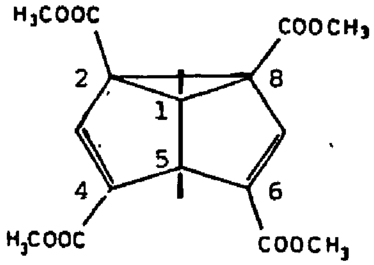
b. Low Temperature Spectra:

The low temperature nmr spectrum can be found in Figure 6 and a schematic representation of the results in Table 15. Assuming that Ib is a rapidly Cope rearranging system, the low temperature nmr spectra should follow a pattern similar to that observed for the parent compound (10). As the temperature is decreased the signal for C2,4,6,8 should broaden first, followed by the resonances for C1,5, the methyl, methoxy and carbonyl carbons. We would expect the largest chemical shift difference in the frozen out state between C2, 8 and C4, 6 as one set of carbons will become part of a cyclopropyl ring and the other set will be vinylic. Carbons 3 and 7 should be equivalent in both equilibrating structures and should not show broadening due to changes in the rate of Cope rearrangement. If the compound exists in a single delocalized structure in solution, the resonances should not change due to an equilibrium rate change upon cooling.

The ^{13}C spectrum at -70° shows no change from the room temperature measurement. The spectra at $-150^{\circ}C$ and $-160^{\circ}C$ appeared to be identical. The signal for C2,4,6,8 is broadened at these temperatures but has not yet coalesced. The signal has not broadened to a width anywhere near the expected 90 ppm chemical shift difference for C2,8 and C4,6 in the static structure. The resonances for the methoxy and carbonyl carbons are still sharp, as is the resonance for

Table 15

VARIABLE TEMPERATURE CARBON 13 NMR DATA FOR 1,5-DIMETHYL-2,4,6,8-TETRAKIS(CARBOMETHOXY)SEMIBULLVALENE

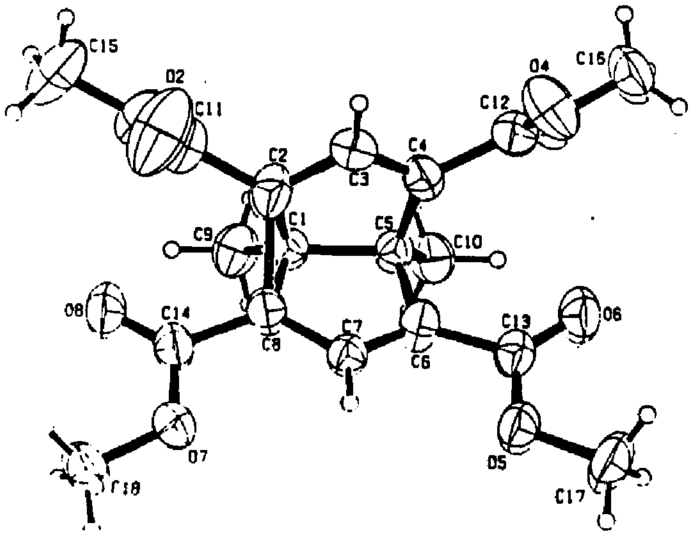


ppm from TMS in $CD_2Cl_2/CH_2{=}CHCl$

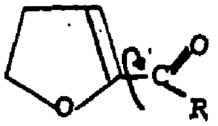
Carbon	-70°	-150 (-160)°
CH_3	10.9	broad (reduced height)
OCH_3	52.4	sharp
C1,5	68.6	sharp
C2,4,6,8	103.9	broad (reduced height)
C3,7	131.2	broad (reduced height)
C=O	165.5	sharp

C1,5. The signals for the vinylic carbons, C3, 7 and the methyl carbons are broadened. This pattern of broadening does not fit in with the results expected based on a decrease in the rate of the Cope rearrangement only. There are three possible explanations for these unusual results.

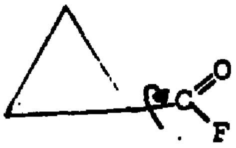
The X-ray analysis indicated that the carbomethoxy groups are not symmetrically disposed in the crystal. If one looks at the crystal structure (below) it is clear that C3 and C7 are in different environments with respect to the carbomethoxy groups, i.e. the carbomethoxy groups are no longer conjugated with the C3-C4 double bond nor with the cyclopropyl ring at C2. It is possible that at low temperatures the rate of rotation of the carbomethoxy groups about the single bond may be slowing down.



Hindered rotations around C-C single bonds have been reported in some systems (99,100).



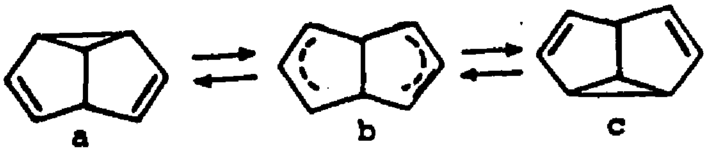
$\Delta G^{\ddagger}_{T_c}$ = 10-11 kcal/mol T_c = -57°C

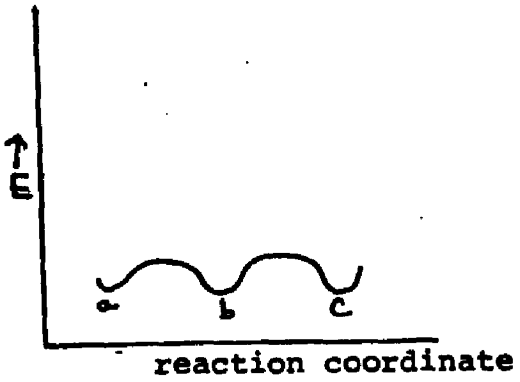


$\Delta G^{\ddagger}_{T_c}$ = 5.5 kcal/mol

We can estimate the effects of hindered rotation on our system in the following way. If the carbonyl group is frozen completely out of conjugation with the vinyl carbons, then it should not contribute any shielding to the vinyl carbon resonances. If the carbonyl group is frozen into conjugation with the double bond, the shielding expected at the β- carbon could be estimated to be twice that observed when the group is freely rotating (2 x 7 ppm) (98). Configurations that are frozen out in intermediate positions would experience effects between these two extremes. The maximum difference in ^{13}C chemical shift for the β-vinylic carbon (C3,7 in our compound) would then be 14 ppm (2 x 7 - 0). This corresponds to a frequency difference of 1400 Hz on the spectrometer used for the low temperature studies and an estimated k_r = 2800 sec^{-1} (eqn 29). If we estimate a $\Delta G^{\ddagger}$ of 5.5 - 9 kcal/mole then the coalescence temperature expected can be estimated using equation (30) and varies from -70°C to -135°C depending upon the $\Delta G^{\ddagger}$ picked (e.g. if $\Delta G^{\ddagger} = 8.5$ kcal/mole, then $T_c = -70$°C using equation 30). If $\Delta G^{\ddagger}$ is near this value we should have seen line broadening for the C3,7 peaks at -70°C. This is not the case. It could be that the $\Delta G^{\ddagger}$ for this rotation is on the same order as that for the Cope rearrangement. Even then, line broadening would not be expected at the same temperature for the two processes as the difference in chemical shifts for the frozen out species are very different (90 ppm vs 14 ppm). A more complete series of low temperature spectra will help elucidate this situation.

Another interpretation of the low temperature spectra is suggested by results of our MNDO study on the Cope rearrangement of some substituted semibullvalenes (see Chapter 4). The results suggest that there could be a triple minimum on the energy surface for the 2,4,6,8-tetracyanosemibullvalene and the 2,6-dicyano compound. That is, there is another species comparable to a bis allyl intermediate which is very close in energy to the Cope-rearranging ground state (eqn 33).





At room temperature the three structures are equilibrating rapidly and averaged nmr signals are observed. This could account for some of the unusual chemical shifts discussed above. Since the bis allyl type structure could be expected to have different chemical shifts from the classical Cope rearranging species, the average values observed at room temperature would be different from those calculated in the previous section . As the temperature is lowered the rate of rearrangement would decrease and the ratio of classical compound to intermediate would also change if their energies are different. This should cause some of the ^{13}C resonances to broaden and shift. The chemical shifts in this study were not measured with the accuracy necessary to determine any slight changes. This will be studied when the additional nmr spectra are obtained.

A third effect which leads to broadening of nmr lines is a change in the relaxation time due to a decrease in the tumbling rate of the carbons at low temperatures. Spin-spin relaxation, as characterized by T_2 becomes important in solids and liquids with slow tumbling molecules. If one is in the region when T_1 T_2 then slower motion of molecules leads to line broadening. This is accelerated when the nuclei participate in a dipolar bond (e.g O-H, C-H)$_6$ (85). Carbons bearing protons should experience this effect more readily as the temperature is decreased. This would explain the broadening observed for C3,7 and the methyl carbons, however, the OCH_3 carbons do not broaden. The broadening of C2,4,6,8 could still be caused by the decrease in the rate of Cope rearrangement with decreasing temperature. The signal for C1,5 may not broaden until a lower temperature is reached as the difference in chemical shifts between C1 and 5 is probably not large.

In our studies coalescence of the signals for C2,4,6,8 has not been reached at -160°C. Since we do not have a series of spectra at different temperatures, a line shape analysis is not possible (83). We can, however, estimate an upper limit for $\Delta G^{\ddagger}$ of the Cope rearrangement. The difference in chemical shift between C2,8 and C4,6 is probably on the order of 90 ppm based on our estimations and the data obtained by Anet for the parent molecule (10) at 62.5 MHz. Since our study was carried out at a ^{13}C frequency of 100 MHz, instrument. The difference in signals between C2,8 and C4,6 would be approximately 9000 Hz (90 ppm x 100

MHz). The rate constant can be applying by equation 29.

$$k_r \cong 2\Delta\nu_{\frac{1}{2}}(T_c) \quad \text{near } T_c$$
$$k_r \cong 2\ (9000) \approx 18000\ \text{sec}^{-1}$$

These data can be used to calculate an upper limit to G at an approximate T_c (-160°C) using eqn 30.

$$\Delta G^{\ddagger} \leq 4.57\ T\ (10.32 + \log \frac{T}{k_r}) \qquad T = 113°K \quad k_r = 18000$$
$$\Delta G^{\ddagger} \leq 4.19\ \text{kcal/mol}$$

This value, 4.19 kcal/mole, is lower than that obtained for the parent compound and is in accord with the theories presented in this thesis. The results of a more complete nmr study should give us reliable numbers for $\Delta G^{\ddagger}$ and E_{act} for the Cope rearrangement of 1,5-dimethyl-2,4,6,8-tetrakis-(carbomethoxy)semibullvalene.

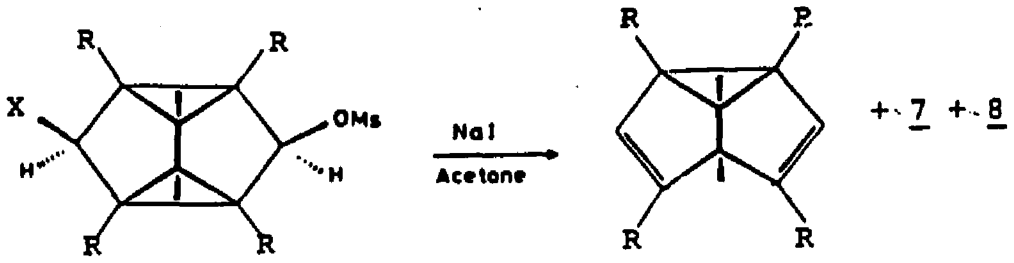
D. Isomerizations of 1,5-Dimethyl-2,4,6,8-tetrakis-(carbomethoxy) semibullvalene Ib

D - 1 To the Cyclooctatetraene Derivative:

i. Preparation and Properties:

During the synthesis of Ib we have noted the formation of another major reaction product (7) (see page). This compound was after the prolonged treatment of the dimesylate or the iodomesylate with NaI in acetone (eqn 34). The pecentage of this compound was increased at the expense of

Ib if a higher boiling solvent was used or if the reagents were refluxed in acetone for more than one to two hours. The unknown could be separated from Ib on a silica column using CH_2Cl_2 as eluent. The unknown eluted before Ib. Compound Ib rearranged to this unknown compound under extremely mild conditions. Solutions of Ib in methanol or



X = OMs   R = $COOCH_3$

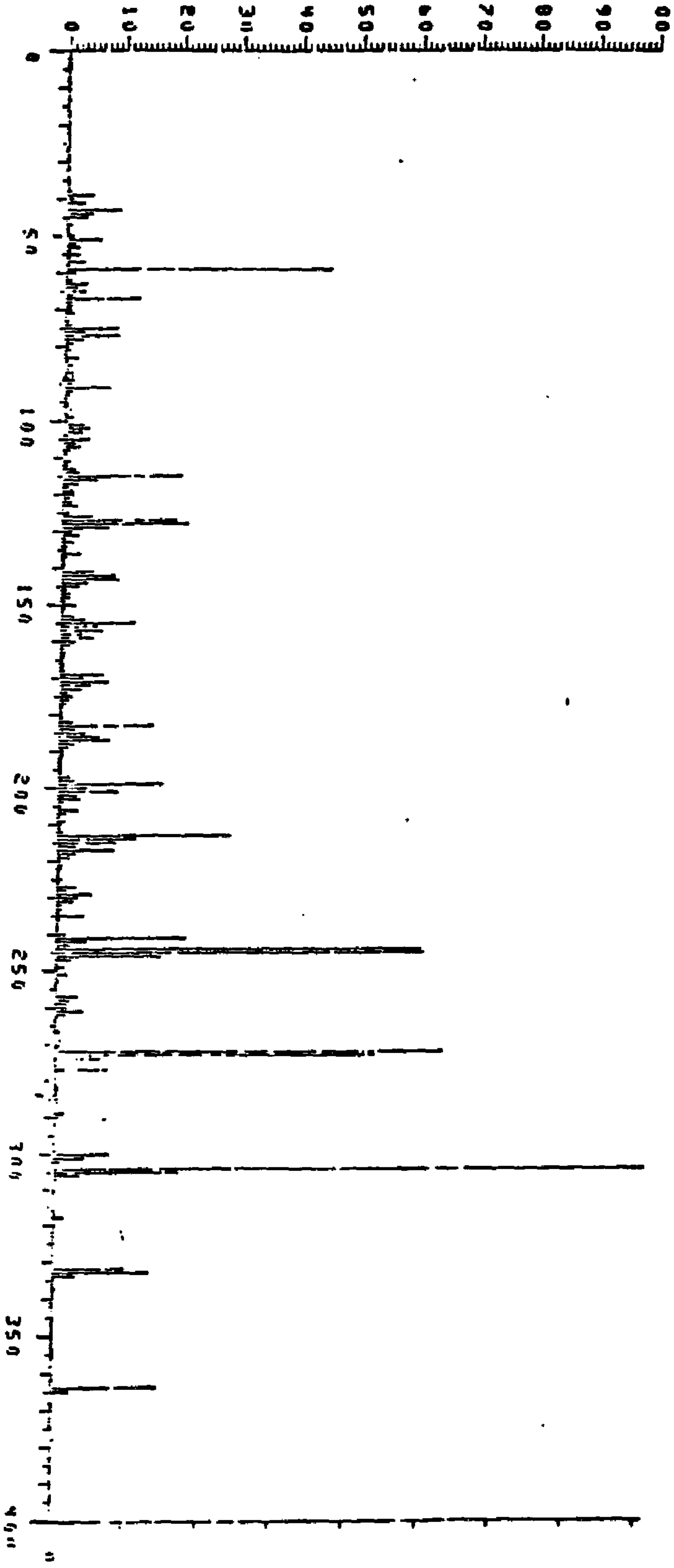
X = I

chloroform isomerized to this product in the refrigerator after several weeks. A solution of Ib in $CDCl_3$ was heated at 50^oC. After 48 hours the solution consisted of 40% cpd Ib, 40% cpd 7 and approximately 20% of another rearranged product (see D-2).

Compound 7 is a colorless crystalline solid, m p = 104-106°C; elemental analysis for $C_{18}H_{20}O_8$: Calc, C,59.34; H,5.50; O,35.27%; Found C,59.33; H,5.52; O,35.26%; UV^{EtOH} = 273 nm (   ), IR_{CHCl_3} = 3125, 2960, 1725, 1563, 1440, 1265, 1200-50, 1060 cm^{-1}; mass spectrum (Figure 7) m/e =

Figure 7

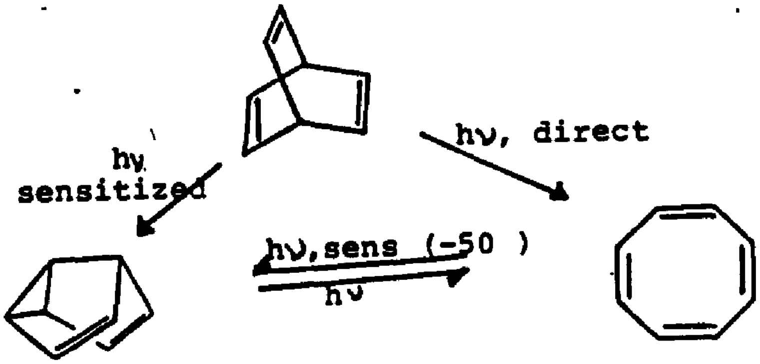
MASS SPECTRUM OD 2,6-DIMETHYL-1,3,5,7-TETRAKIS-(CARBOMETHOXY)CYCLOOCTATETRAENE 7



364.1 (parent ion) 304.1, other peaks 272.1, 245.1. The fragmentation pattern is similar to that seen for the semibullvalene Ib. The nmr data are listed in Table 16 and figure 8. The compound is stable to air, light, and heat remaining unchanged in $CHCl_3$ solution at 50°C.

ii. Background

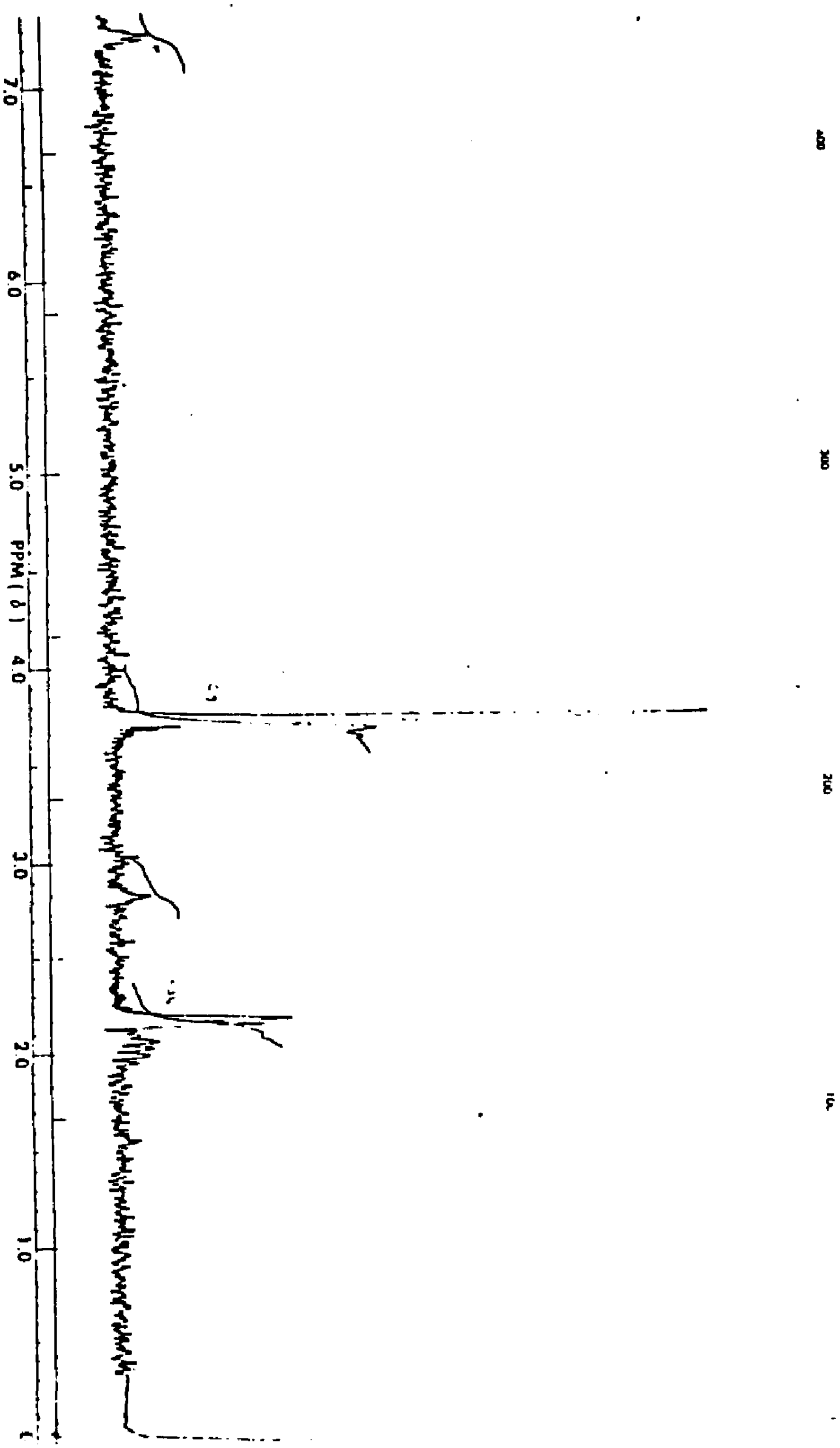
Semibullvalenes and cyclooctatetraenes are known to interconvert. Unsubstituted semibullvalene has been prepared by the acetone sensitized irradiation of cyclooctatetraene (33). In 1969 Zimmerman and coworkers studied the photochemical interconversions of barrelene, semibullvalene and cyclooctatetraene (34) (eqn 35). Another study (23) showed that 1,3,5,7-tetramethylcyclooctatetraene underwent conversion to 1,3,5,7-tetramethylsemibullvalene, mesitylene and 2,4,6,8-tetramethylsemibullvalene when heated at 250°C for 20 hours in a total of 10% yield (eqn 36). Acetone sensitized irradiation of 1,3,5,7-tetramethylcyclooctatetraene yielded no semibullvalene product, only mesitylene was observed. When 1,3,5,7-tetramethylsemibullvalene was irradiated with an acetone sensitizer a 58% yield of 1,3,5,7-tetramethylcyclooctatetraene was recovered (eqn 36).

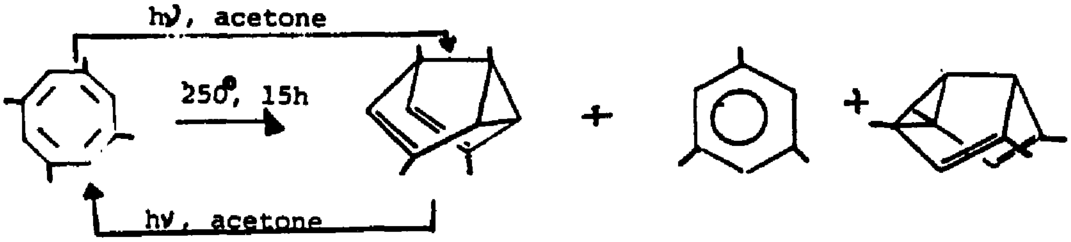


(35)

Figure 8

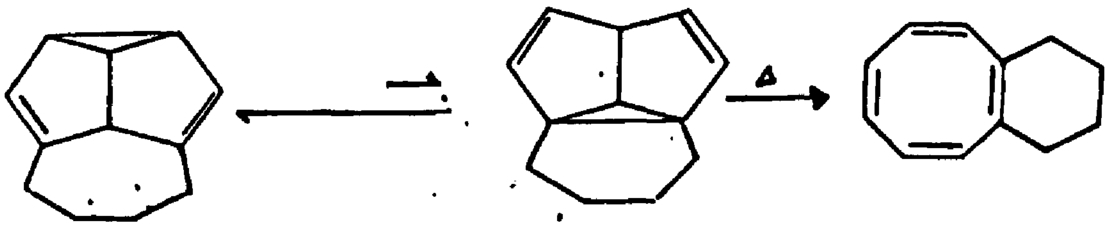
^{1}H NMR SPECTRUM OF 2,6-DIMETHYL-1,3,5,7-TETRAKIS-(CARBOMETHOXY)CYCLOOCTATETRAENE AT ROOM TEMPERATURE



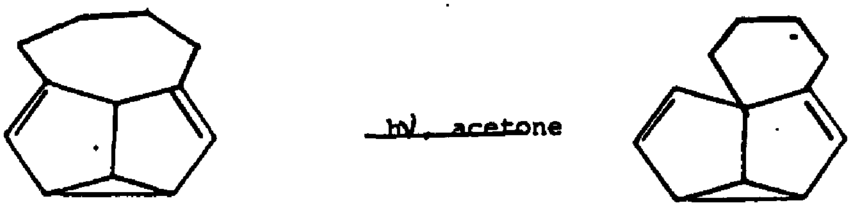


(36)

Thermal isomerizations of semibullvalenes to cyclooctatetraenes have been observed for sme other semibullvalenes. Several dimethylsemibullvalenes have been pyrolyzed at 390°C to produce 70-80% yields of the corresponding cyclooctatetraenes (101). In a related thermal isomerization, 2,8-tetramethylenesemibullvalene yielded a rearranged cyclooctatetraene (eqn 37) while acetone sensitized irradiation of this compound led to a rearranged semibullvalene (eqn 38) (102). This is only one example of a semibullvalene-semibullvalene interconversion.



(37)

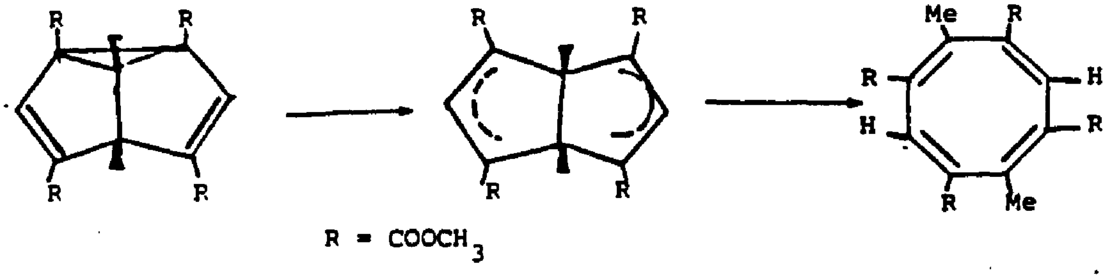


(38)

All literature examples of semibullvalene isomerizations occur under extreme reaction conditions. We believe the observed isomerization reaction of 1.5-dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene is the first example of such a facile rearrangement, one that even occurs at 5°C.

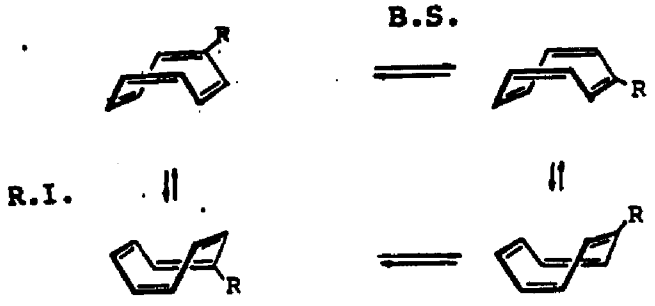
iii. Assignment of Structure (Compound 7)

After studying the spectral data we assigned the following structure to the unknown compound; 2,6-dimethyl-1,3,5,7-tetrakis(carbomethoxy)cyclooctatetraene 7 . We envision its formation as shown in equation 39. This facile isomerization is not surprising if one considers the X-ray data. The C2-C8 bond distance is already extremely long in Ib and it apparently takes very little energy to complete its rupture. The mass spectrum rules out a dimeric form.



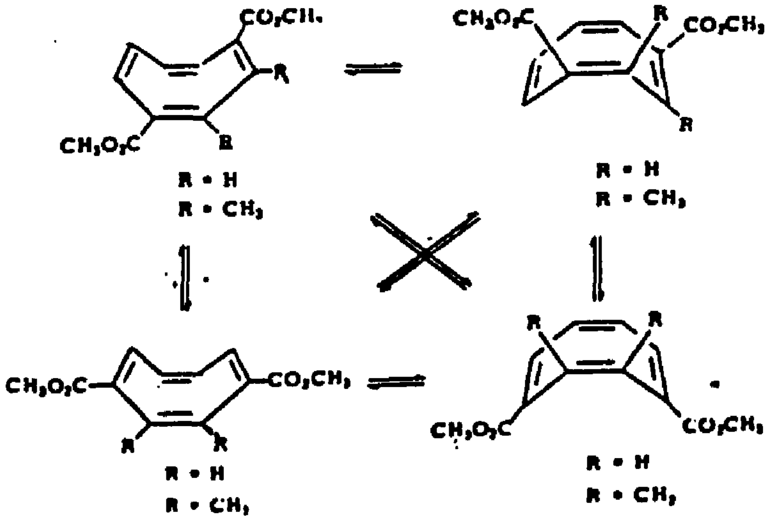
(39)

Cyclooctatetraenes are known to exist in a tub shaped conformation (103) which can undergo both ring inversion and bond shifting (BS) as shown below:

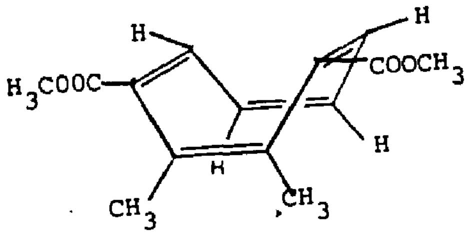


In the parent molecule and monosubstituted derivatives, both R.I. and B.S. can occur at room temperature. The nmr spectra show resonances for the different isomers (103,104). As the samples are heated the rates of interconversion increase and averaged spectra are obtained. However, as more substituents are placed on the ring, the E_{act} for both RI and BS increases due to an increase in strain for the formation of a planar transition state. An nmr study of bond shifts in 1,3,5,7-tetramethylcyclooctatetraene showed no change in the spectrum from -80° to 90°C. (105). Above 120° the compound was rapidly interconverting between the two bond shift isomers. The results of this study led to a calculation of $\Delta G^{\ddagger}$ = 22.5 kcal/mole for bond shifting in this molecule.

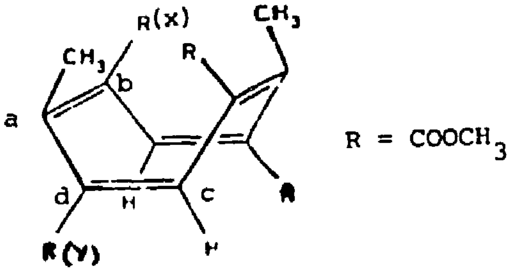
Subsequently, Paquette and others (103-105) have calculated the energy barriers to ring inversion and bond shifting for a number of di-, tri, tetra- and pentamethylcyclooctatetraenes from their temperature dependent nmr spectra. As the number of contiguous substituents increases, the energy for rearrangement increases. A recent study shows interesting differences between dimethylcyclooctatetraene-1,4-dicarbooxylate and its 2,3-dimethyl derivative (106).



The proton spectrum of the 1,4-disubstituted compound shows three broad olefinic resonances which coalesce at 71°C and collapse to a singlet at 120°C. This corresponds to interconverting isomers at room temperature and a $\Delta G^{\ddagger} = 16.8$ kcal/mole. In contrast to this, the 2,3-dimethyl derivative exhibits an AA'BB' spin system for the olefinic protons which does not change upon heating. The ^{13}C spectrum for this compound consists of seven signals. Both of these results support a rigid structure as shown below.



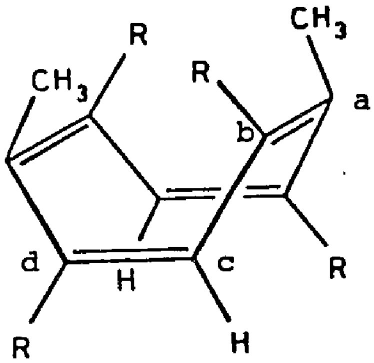
The data presented for the unknown compound (7) are compatible with a rigid, non-interconverting cyclooctatetraene as pictured below:



Several features of the 'H and ^{13}C nmr spectra (Table 16) are noteworthy. In the proton spectrum, the methyl and

Table 16

^{1}H and ^{13}C NMR DATA FOR 2,4-DIMETHYL-1,3,5,7-TETRAKIS(CARBOMETHOXY)CYCLOOCTATETRAENE <u>(7)</u>



R = COOCH$_3$

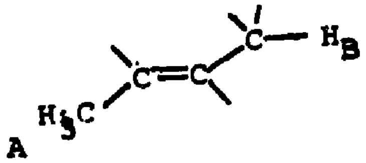
^{1}H NMR ppm (CDCl$_3$)

2.24	d (J = 1.8 Hz)	6H	CH$_3$
3.75	s	6H	OCH$_3$
3.77	s	6H	OCH$_3$
7.30	q (J = 1.8 Hz)	2H	$\underline{H}$-C=C-COOCH$_3$

^{13}C NMR ppm (CDCl$_3$)

20.30	q	CH$_3$
51.75	q	OCH$_3$
51.94	q	OCH$_3$
127.22	s	b
136.25	s	d
138.87	d	c
149.90	s	a
164.53	s	C=O

vinyl proton exhibit long range spin-spin coupling (J = 1.8 Hz). This was confirmed by double irradiation experiments. This type of homoallylic coupling (107) has been observed in a number of systems consisting of four single and one double bond arranged as pictured below (108):



$J_{AB} = 0\text{-}4$ Hz

The chemical shifts of the methyl and vinyl protons are consistent with the assigned structure. The methyl group resonates at 2.24 ppm which is reasonable for a methyl group attached to a vinyl carbon (109). The vinyl proton (δ = 7.3 ppm) is a beta to a carbomethoxy group and is expected to resonante at low field (109). There are two sets of carbomethoxy groups as evidenced from the two methoxy signals in the proton and carbon spectra. Assuming a rigid cyclooctatetraene structure as indicated in the diagram on page the COOOCH$_3$ marked X is different from the one marked Y .

and should have a different chemical shift.

In the ^{13}C nmr spectrum the vinyl carbons appear as four signals. They have been assigned as follows (see Table 16). The doublet at 138.87 is assigned to carbon c, which is the only carbon bearing a proton and also a carbomethoxy group. The resonance at 149.9 ppm is assigned to carbon a. This carbon bears both an α-CH_3 and a β-$COOOCH_3$ group. Both of these substituents shift the vinyl carbon resonance downfield (91,93). Carbons b ad d bear an α-$COOOCH_3$ substituent. Carbon b, also bears a β-CH_3 substituent while carbon d only has a proton at this position. Since β -CH_3 substituents connected through the pi-system cause an upfield shift (93), the resonance at 127.22 ppm is assigned to carbon b.

The vinyl carbon resonances can be estimated using the data from Table 10. The values compare favorably with the observed signals.

Vinyl C	a	b	c	d
Base:	139.2	138.3	139.4	138.3
OCH_3	-9.1	-10.2	-9.1	-10.2
C	(2) +27.4	(1) +7.5	(1)+13.7	(1) +7.5
C				(1) +5.8
C	(1) -5.6	(2)-10.8	(1) -5.6	(1) -5.4
Calc:	151.9	125.8	138.2	136.0
Obs:	149.9	127.2	138.9	136.3

The proton nmr spectrum remained unchanged as the temperature was increased to 150°C at which time the methyl and vinyl peaks appeared as broad singlets and the coupling was no longer visible. The long range coupling could be affected by an increased rate of bond shifting. Since the bond shift isomerss are identical only the coupling would be affected by changes in the rate of isomerization.

CHAPTER 4

A MNDO STUDY OF THE COPE REARRANGEMENT OF SOME SEMIBULLVALENES

A. Introduction

Concurrently with the experimental work we carried out a theoretical study of the Cope rearrangement of some substituted semibullvalenes. Our goal was to look at a series of semibullvalenes, both in their ground states and during Cope rearrangement, in order to determine what types of alterations (substituent patterns, geometry changes) in the semibullvalene nucleus would have the best chance of lowering the activation energy for this reaction so that the homoconjugated structure (110) would become the preferred species at room temperature. Several groups had studied the Cope rearrangement of semibullvalene using the MINDO/2 and extended Huckel (EH) methods of calculations. Only the EH study (14) attempted a systematic assessment of the effects of electron donor and acceptor substituents on the energies of the ground and transition state structures. However, the EH method is not sufficiently accurate to be used for calculations of energies or geometries; only relative energies could be predicted.

For our initial study we chose a series of cyano substituted semibullvalenes and the parent semibullvalene for comparison. The cyano group was chosen for several reasons:

a. We wanted to assess the effects of the same π-

electron acceptor at various positions on the semibullvalene ring. The cyano group is a good model for a π-electron acceptor.

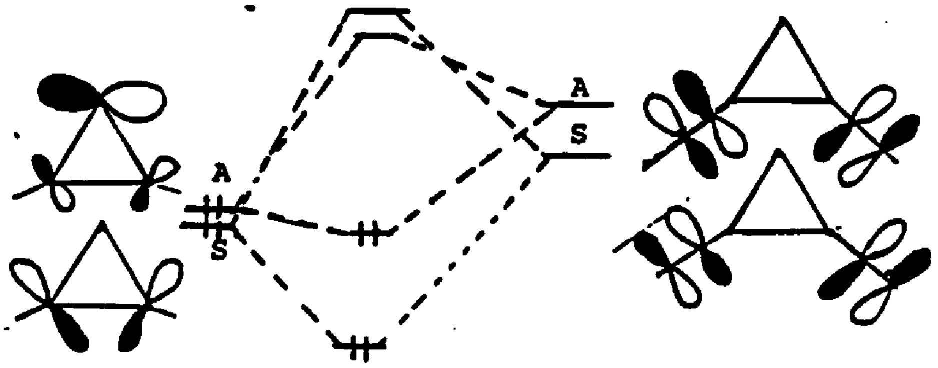
b. The cyano group is linear and would not present steric problems in the geometry. The orbitals of the CN would always be able to interact conjugatively with the semibullvalene orbitals.

c. The cost of the calclations would be significantly lower if CN was used as a typical π-electron acceptor rather than with a group wth more atoms (e.g. $COOCH_3$).

d. If the calculations suggested that a particular CN substituted semibullvalene would be more stable in the delocalized state, a synthesis would be attempted. Incorporation of the cyano group into the semibullvalene molecule would be synthetically feasible (see Chapter 5).

While cyano groups can interact with both the ground and transition state orbitals of semibullvalene, the extent of this interaction is determined by the placement of the groups on the ring. A decrease in the activation energy for the Cope rearrangement can be brought about by destabilizing the classical ground state, stabilizing the homoconjugated structure or a combination of these effects. Therefore, the interaction of the cyano groups with both the ground and transition state orbitals must be studied.

In the ground state the low lying unoccupied orbitals of the cyano groups at positions 2 and 8 can interact with the Walsh type orbitals of the cyclopropane portion of semibullvalene.



Since there is more electron density in the symmetrical Walsh orbital the interaction of this orbital with the symmetric combination of the acceptor orbitals will be stronger than the interaction of the antisymmetric orbitals. (14) This will lead to a weakening of the 2-8 bond in semibullvalene. Similarly, the cyano LUMOs of correct symmetry can interact with the HOMOs of the diene portion of the semibullvalene molecule if they are attached to C3, 4, 6, or 7. In summary, the effect of cyano substiuents on semibullvalene will be stabilizing, with conjugation of the cyano groups and the double bonds having a greater effect than the conjugation with the Walsh orbitals. In this case of dicyano substitution at positions 2, 8, (or 4, 6), Hoffmann and Stohrer have calculated that the 4,6-dicyano isomer would be favored (eqn 41) (14).

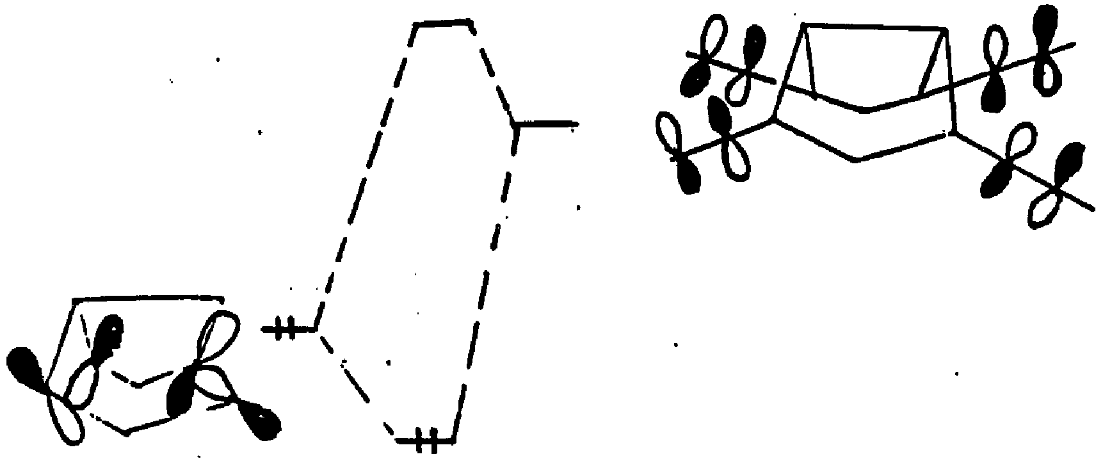
41

Substitution of the cyano groups at the 3,4 (or 2,3) positions should also favor the structure with these groups on the double bond. This compound has been synthesized (33) and the ^{1}H nmr data confirm this prediction. (Eqn. 42)

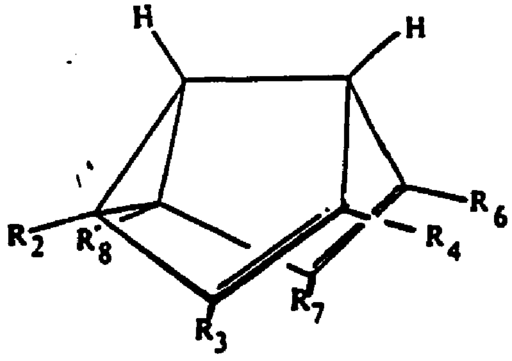
(42)

Since the equilibrium for the Cope rearrangement favors one of the isomers in these two systems, they were not considered for this study. We wanted to assess the effects of cyano groups on semibullvalenes whose Cope rearrangement would be degenerate.

In the homoconjugted structure cyano groups at positions 2,4,6 and 8 can interact with the HOMO of the bis allyl system, while substituents at positions 3 and 7 can only interact with the next lowest orbital. Substiuents at positions 1 and 5 would not be expected to interact with these orbitals. If the substituents were only on one of the allyl moieties there would be a difference in the resultant energies of the two allyl systems, thus removing their degeneracy. An example of the interaction of the bis allyl HOMO of semibullvalene and the LUMO of four cyano groups symmetrically substituted in positions 2,4,6 and 8 is shown schematically.



In order to test these predictions and to calculate meaningful geometries and energies for the species involved in the Cope rearrangements of cyano substituted semibullvalenes, we chose the series of compounds listed below for our MNDO study. The 3,4 and 4,6-dicyano compounds were not included as discussed above. Also the 1,5-dicyano compound was not studied as we would not expect significant interaction with the homoconjugated state and the ground state and the ground state would be expected to stabilized (14).



Ia: $R_{2,3,4,6,7,8} = H$

If: $R_{3,7} = H$; $R_{2,4,6,8} = CN$

Ig: $R_{3,4,7,8} = H$; $R_{2,6} = CN$

Ih: $R_{3,6,7,8} = H$; $R_{2,4} = CN$

Ii: $R_{2,4,6,8} = H$; $R_{3,7} = CN$

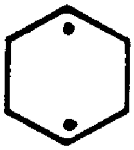
The second series of compound studied by theoretical methods was chosen on the basis of the results of the first study. These will be discussed in section iii.

B. Related Theoretical and Experimental Studies

Theoreticians as well as experimentalists have studied Cope rearrangements in order to further understand their mechanism and to elucidate the structure of the transition states. Historically the Cope rearrangement was postulated to occur through a pericyclic mechanism (b) (1). Experimental and theoretical studies have raised questions as to the actual transition state structures in various Cope rearrangements. The six atoms involved in the transition state can be thought of as a combination of two allyl radicals which interact to different degrees. The nonconcerted extremes can be visualized as two separated allyl radicals (a) or a diyl system (c) (3). It has been suggested that the transition state for the Cope rearrangements of a series of related compounds is dependent upon the type and position of substituents and could approach either of the extremes (a or c) dependng upon the pattern of substitution in the compound (2,3,111).

a

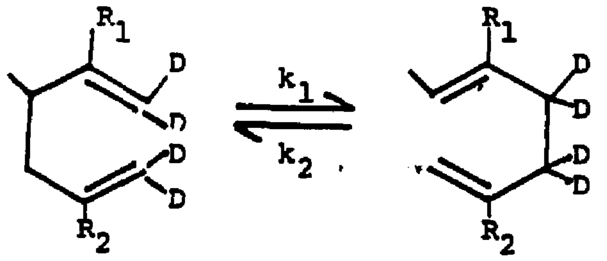
b



c

The Cope rearrangement of 1,5-hexadiene has been studied by several methods to ascertain the structure of the transition state. Kinetic studies showed that 2-phenyl- and 2,5 diphenyl-1,5-hexadiene rearrange 69 and 4900 times faster than the parent compound at 189.1° C indicating some radical character at C2 and C5 in the transition state (4). In conjunction with the kinetic studies Dewar and coworkers performed MINDO/2 calculations for the degenerate Cope rearrangement of 1,5-hexdiene and related compounds (5). They concluded that this arrangement takes place via an intermediate consisting of equilibrating biradicals related to the 1,5-cyclohexadiyl radical. In a related study, Wehrli and Schmidt reached similar conclusions based on the rates of rearrangement of 2,5-dicyano-1,5-hexadiene (111).

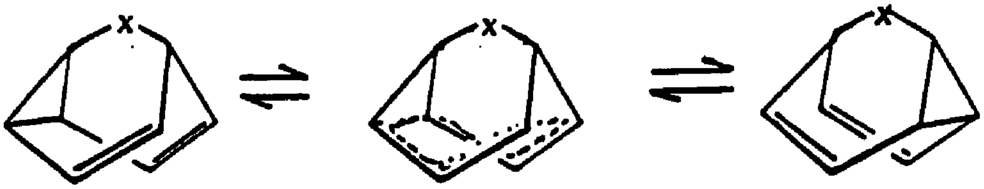
Gajewski studied the Cope rearrangements of various methyl substituted 1,5-hexadienes by measuring their α-secondary kinetic isotope effects of deuterio substituted compounds (3). If one looks at the two extreme structures for the Cope rearrangement transition states (a and c), it is clear that for the cyclic diyl, bond making (BM) is more important than bond breaking (BB). The reverse is true for the bis allyl alternative. Gajewski synthesized a series of deuterio substituted methyl-1,5-hexadienes, with and without phenyl substituents at the 2 and 5 positions. The deuteriums were either at the 1,6 (cpds x) or the 3,4 (cpds y) positions as shown in equation 43. If bond making is more important than bond breaking in the transition state, the kinetic isotope effect (KIE) will be greater for the forward (k_1) reaction. If bond breaking is more important a greater effect will be seen for the reverse (k_2) reaction.



$R_1 = R_2 = H$
$R_1 = H$, $R_2 = Ph$
$R_1 = R_2 = Ph$

The bond making isotope effects (BMKIE) and the bond breaking effects (BBKIE) were measured for the series of compounds listed in equation 43. Each effect was then expressed as a percent increase or decrease relative to the nondeuterated compound (BMKIE - 1 or BBKIE -1). The ratio of these values (BMKIE/BBKIE) was compared for the series of compounds with increasing phenyl substitution. This ratio increased in favor of bond breaking from 1.8 for the unsubstituted case to 8.1 for the 2,5-diphenyl substituted compound. The authors devised a scheme by which the transition state structure could be predicted depending upon the secondary deuterium KIEs. They stated that "...stabilizing either of the two nonconcerted alternatives- that from either pure bond breaking or pure bond making - (a diallyl or diyl transition state) will draw the transition state in the direction of stabilization." (3).

The first theoretical study of the Cope rearrangemets in the bullvalene, barbaralane, semibullvalene series (eqn 44) was reported by Dewar and Schoeller in 1971 (24). They used MINDO/2 to calculate the geometries and energies for the ground states and the transition states of these compounds. The relevant data are collected in Table 17 along with their results for 1,5-hexadiene, the experimentally determined values and the results of a similar study carried out by Iwamura and coworkers using both MINDO/1 and MINDO/2 (112).



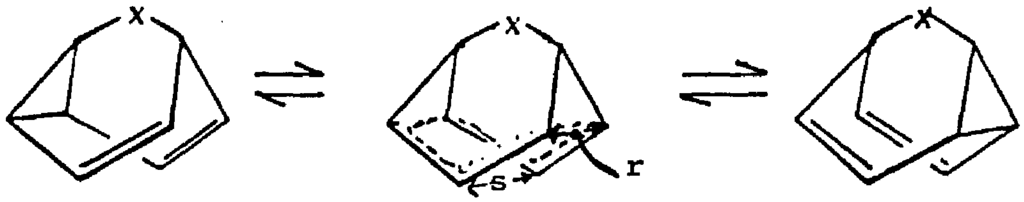
(44)

The data reproduces the observed decrease in activation energy as the size of the bridge is decreased.

Shortly thereafter, Dewar and Lo published a detailed analysis of the Cope rearrangement for the same series of compounds utilizing the data obtained from the MINDO/2 calculations and applying an energy partitioning technique (20). They concluded that as the size of the bridge in this series of compounds decreased, the transition state for the Cope rearrangement becomes more like a pair of allyl radicals and is stabilized by a drift in a charge from the rest

Table 17

CALCULATED AND EXPERIMENTAL DATA FOR SOME COPE REARRANGEMENTS



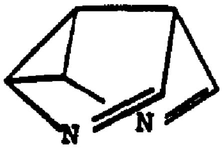
Compound	E_{act}			
	calc	exp	transition state interatomic distance r (calc)	s
1,5-hexadiene	30.6^{x}	41.2^{a}	1.628^{x}	2.577^{x}
bullvalene	11.3^{x}	11.8^{b}	1.626^{x}	2.808^{x}
X= -CH=CH-	9.1	12.8^{c}	1.770	2.557
barbaralane	5.9^{x}	8.6^{d}	1.720^{x}	2.680^{x}
X= $-CH_2-$	6.7		1.798	2.768
semibullvalene	2.3^{x}	4.8^{e}	1.753^{x}	2.805^{x}
X= --	0.6		1.771	2.844

a. W. Von F. Doering and W R. Roth, Tet, 1962, 18, 67
b. M. Saunders, Tet Lett, 1963 1699
c. A. Allerhand, H. S. Gutowsky, JACS, 1965, 87 4092
d. W. Von F. Doering, B. M. Ferrier, E. T Fossel, H. J. Harentstein, M. Jones Jr, R. M. Rubin, J. Klumpp M. Saunder, Tet 1967, 23, 3943
e. Ref (10)

x: All data labeled "x" from Ref. (24)
All unlabeled calc data from Ref (112)

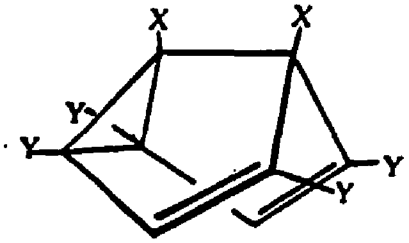
of the molecule to the six atoms involved. They predicted that substitution of electron withdrawing groups at the ends of the allyl moieties will lower the activation energy for the Cope rearrangement by stabilizing the transition state.

In another related study, Dewar and coworkers used MINDO/2 to study 3,7-diazasemibillvalene and the corresponding bishomopyrazine (113). They chose this system based on the conclusions of their energy partitioning study (20). The calculations for the delocalized bishomopyrazine proceeded



normally. However, when the authors tried to calculate the geometry of the classical ground state, the bond lengths and bond angles changed progressively with each iteration until the final structure was identical with the delocalized one. From these results the authors predicted that 3,7-diazasemibullvalene should exist in the delocalized form. They also predicted that substitution of nitrogen for carbon at positions 2 and 6 in the semibullvalene nucleus, or substitution of CN for H at these carbons should lead to delocalized nonclassical ground states. Until the present report, no studies have been published testing these predictions, either theoretically or experimentally.

At about the same time, Hoffmann and Stohrer published their study of the Cope rearrangement of semibullvalene and the effects of substituents on this reaction (14). The calculations were performed using the EH method. The methodology used and the conclusions drawn were discussed at length in Chapter 1. To summarize, Hoffmann and Stohrer concluded that the pattern of substitution indicated below would stabilize the transition state to a greater extent than the ground state and thus reduce the activation energy for the Cope rearrangement.



X = π-electron donor

Y = π-electron acceptor

C. Methodolgy

i. Review of the MNDO and MINDO Methods:

Semiempirical methods have been used with varying degrees of success to study molecular geometry and reaction paths. Several previous semiempirical methods (MINDO/1,2,3) had utilized a modification of the INDO (Intermediate Neglect of Differential Overlap) method for simplification of the Roothaan-Hall-SCF-LCAO-MO method. The MNDO method uses NNDO (Neglect of Diatomic Differential Overlap). (115) In the MINDO treatments many of the energy terms were set equal to parametric functions which contained adjustable parameters (114a).

The INDO and NDDO methods treat two-center electron repulsion integrals and the two-center core electron attractions differently. In the INDO method all integrals involving differential overlap except for the one-electron core repulsion integral and the one-center exchange integrals are neglected. The NDDO approximation retains all two-center terms involving monoatomic differential overlap and provides a closer approximation to the full Fock matrix. In INDO, two-center electron-electron repulsions and core electron attractions are spherically averaged whereas in NDDO they show an angular dependence. The directionality in chemical bonding is also included in the two-center electron-electron repulsions and the core-electron attractions in NDDO while in INDO the directionality is only represented in the resonance integrals.

Although NDDO seems a more logical basis for semiempirical treatments, until the development of MNDO it was too difficult and costly to parametrize a semiempirical method using this approximation. Dewar and Thiel used a new proceedure for estimating the NDDO repulsion integrals and were able to reparametrize the NDDO approximation for H, C, N and O. From these parameters, which were calculated to fit experimental heats of formation, a new semiempirical method MNDO (Modified Neglect of Diatomic Overlap) evolved (115).

A comparison of results for a number of compounds using MINDO/3 and MNDO are presented in Table 18. The absolute error for most ground state properties is reduced by one-half in going from MINDO/3 to MNDO. Although MNDO contains many fewer adjustable parameters than MINDO/3, the cost of performing and equivalent calculation is only about 20% greater using this method (116).

ii. Other Studies Using MNDO

The MNDO method with 2x2 CI (configuration interaction) appears to give reliable geometries and heats of formation (H_f) for species along a reaction path that involves neutral diradicals. Dannenberg and Rocklin (117) studied the mechanism of the thermal decomposition of azoalkanes and 1,1-diazenes using MNDO. The calculated energies of activation for the decomposition reations and the geometries of the reactants agreed well with the experimental measurements. In calculating these reactions paths 2x2 CI was included when the species were diradical-like. Few other detailed studies of reaction paths using MNDO calculations have been reported, but other results from our laboratories support the contention that the MNDO method is particularly useful for the study of reactions involving neutral free radicals and radical pairs (118). The calculated heat of formation agree well with the experimental results.

iii. Methods of Calculation Used in the Study

Table 18

A COMPARISON OF MNDO AND MINDO/3

Mean Absolute Errors $\Delta(\Delta H_f)$ for Heats of Formation

Class of Compound	No.	$\Delta(\Delta H_f)$, kcal/mol MNDO	MINDO/3
All compounds	138	6.3	11.0
Hydrocarbons	58	6.0	9.7
with aromatic rings	5	1.7	12.1
with 3 membered rings	8	5.2	11.7
acyclic hydrocarbons	26	3.5	6.9
cyclic hydrocarbons	32	8.0	11.9
bicyclic hydrocarbons with 5 and 6 membered rings	5	2.9	22.3
Nitrogen Compounds (C H N)	34	6.5	17.3
amines	11	4.1	6.9
cyanides	8	4.6	19.6
All Compounds[a]	122	5.0	10.9

[a] Excluding those with 4-membered rings, tert-butyl groups, or NO bonds

The MNDO approximation to molecular orbital theory was used for this study (115). Geometrical optimization was performed using the Fletcher, Powell, Davidson algorithm incorporated in the MNDO program (119,120). For all diradical like species 2x2 CI was included in the calculation. There was no elements of symmetry imposed on the molecules. Two possible reaction coordinates were tried for each Cope rearrangement studied, opening the 2-8 bond and closing the 4-6 bond. In all cases the lowest energy path was the one where the 2-8 bond was opened.

The energy and geometry of the ground states were calculated using complete geometric optimization. The number of independent variables optimized ranged from 36 in the unsubstituted semibullvalene to 46 in the tetracyano compound. This does not include several pairs of C-H bonds which were coupled by symmetry (see Appendix). Each reaction path was studied by stepping through the appropriate reaction coordinate without CI while optimizing internal coordinates individually. This procedure allowed us to locate the approximate geometry for the homoconjugated structure of the unsubstituted semibullvalene; however, for the cyano compounds the energy surface was quite flat around the col in the direction of the reaction coordinate and the approximate homoconjugated structure could only be located after the inclusion of 2x2 CI. Since the cost of the MNDO calculations with 2x2 CI varies approximately with the square of the number of parameters to be optimized, we could not optimize all the parameters at once. Initially only the parameters for the atoms involved directly in the Cope rearrangement were optimized. The parameters for these atoms were then held constant and the other atomic parameters were optimized. This procedure was repeated until the energy for the homoconjugated species did not change. Once the geometry was optimized for this species, the calculations were repeated holding the C2-8 and C4-6 ends of the molecule equal. This procedure led to a lower energy for the homoconjugated structure (~1 kcal/mole). A few points around the col were also recalculated using CI to make sure that the energy of points on either side was decreasing. In some instances, after the inclusion of CI, the homoconjugated structure corresponded to a minimum on the energy surface. In these cases, the energy and geometry were optimized in the usual way. In all cases, the energy for the homoconjugated state was lowered by 7-15 kcal/mole by the inclusion of 2x2 CI.

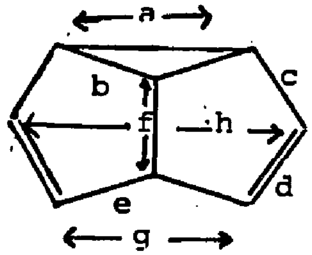
D. Results and Discussion

i. Unsubstituted Semibullvalene:

Table 19 compares the ground state for semibullvalene as determined by several different methods. The only experimental study has been the gas phase electron diffraction determination by Wang and Bauer (77). The other calculated values were obtained by the MINDO/2 and MINDO/3 methods (20,24,112,114b). The geometry calculated in the current study agrees quite well with the experimental data except

Table 19

A COMPARISON OF EXPERIMENTAL AND CALCULATED GEOMETRIES FOR SEMIBULLVALENE



method	ref	a	b	c	d	e	f	g	h
electron diffraction	77	1.60	1.53	1.53	1.35	1.53	1.49	2.26	
MNDO	a	1.57	1.54	1.50	1.36	1.54	1.57	2.44	3.17
MINDO/2	20 24	1.54	1.49	1.48	1.35	1.51	1.53	1.93	
MINDO/2	112	1.51	1.51	1.48	1.34	1.53		2.15	
MINDO/3	114b	1.57	1.53	1.53	1.36	1.53	1.57		

a. This Work

for two distances. The C1-C5 distance is smaller in the experimental work than in any of the calculations. Also, the distance at the open end of the molecule (C4-C6) differs in all the reported studies. Wang and Bauer commented on the short C1-C5 distance which they obtained from the electron diffraction data and, in fact tried to use the models where this distance was longer, but could not get a satisfactory fit with the experimental values (77). The structures of some substituted semibullvalenes have been determined by x-ray crystallography. For 1-cyanosemibullvalene the C1-C5 distance is 1.55 Å (27) and in 1,5-dimethyl-2,4,6 8-tetrakis(carbomethoxy)semibullvalene Ib, the distance is 1.58 Å (121). Thus, the calculated value of 1.57 Å is not unreasonable.

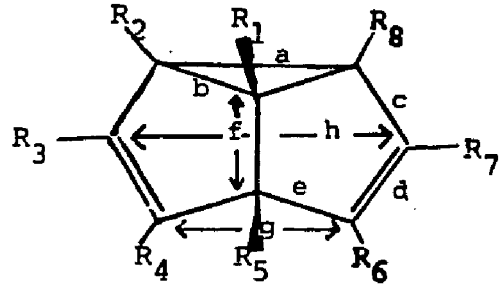
The differences in the observed and calculated nonbonded distance (C4-C6) might be due to the energy surface beng fairly flat with respect to that distance. We have calculated the energy and geometry for semibullvalene keeping the 4-6 distance at 2.30 and 2.35 Å while optimizing all the other parameters and have found that the geometry changes very little overall and the energy increases by approximately 1.5 kcal/mole. The C2-C8 distance found experimentally (1.60 Å) is reproduced well by the MNDO calculation (1.57 Å). The calculated geometry (MNDO) also agrees well with the MINDO/3 results (114b).

ii. Cyano Substituted Semibullvalenes

Table 20 lists the geometries calculated for the cyano

Table 20

GROUND STATE GEOMETRIES FOR SOME CYANO SUBSTITUTED SEMIBULLVALENES USING MNDO (no CI)



Ia. R_1-R_8 = H
If: $R_{1,3,5,7}$=H, $R_{2,4\ 6,8}$=CN
Ig: $R_{1,3,4,5,7,8}$=H, $R_{2,6}$=CN
Ih: $R_{1,3,5,6,7,8}$=H, $R_{2,4}$=CN
Ii: $R_{1,2,4,5,6,8}$=H, $R_{3,7}$=CN

Distance (C—C) A

Compound	a	b	c	d	e	f	g	h
Ia	1.57	1.54	1.50	1.36	1.54	1.57	2.44	3.17
If	1.60	1.55	1.50	1.36	1.54	1.56	2.45	3.14
Ig	1.58	1.55 1.54	1.51 1.50	1.36 1.37	1.53 1.54	1.57	2.45	3.15
Ih	1.58	1.56 1.54	1.51	1.36	1.54 1.53	1.57	2.44	3.15
Ii	1.56	1.54	1.51	1.37	1.53	1.56	2.43	3.15

substituted semibullvalenes and the parent molecule in their classical ground states. There is very little difference in most of the geometric parameters. Although no elements of symmetry were imposed upon the system, the calculated geometries show similar bond lengths for all pairs of bonds related by a C_{2v} plane of symmetry except for variations of 0.01A in the 2,6- and 2,4-diCN derivatives.

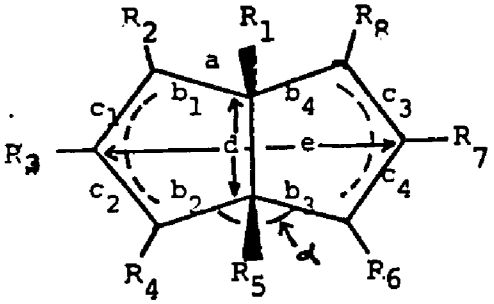
This is in marked contrast to the crystal structure of 1,5-dimethyl 2,4,6,8-tetrakis(carbomethoxy)semibullvalene, Ib, which was remarkably unsymmetrical. Although crystal packing may have caused some of this effect, the orientation of the carbomethoxy group is the overwhelming factor responsible for this asymmetry (121). With cyano substituents this problem appears to be circumvented.

The C2-C8 bond varies from 1.56 A in the 3,7-diCN compound Ii to 1.60 A in the tetracyano derivative If. The results are in accord with the predicted interaction of a cyano group with the Walsh type orbitals in semibullvalene (14). The cyclopropyl bonds which have cyano groups directly attached to one or both carbons are longer than those which are unsubstituted. The effect is greatest in the tetracyano compound.

The geometries for the homoconjugated structures are listed in Table 21. Here again symmetry constraints were not imposed on the carbocyclic system. In most cases the four bonds which could be equivalent if there are two planes

Table 21

GEOMETRIES OF HOMOCONJUGATED STRUCTURES FOR CYANO SUBSTITUTED SEMIBULLVALENES USING MNDO AND CI



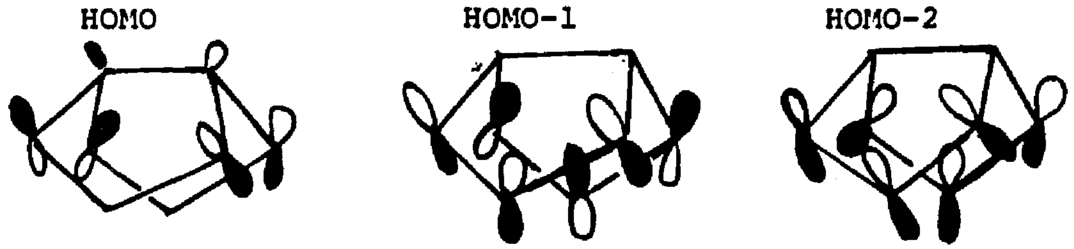
Ia: R_{1-8} = H
If: $R_{1,3,5,7}$=H, $R_{2,4,6,8}$=CN
Ig: $R_{1,3,4,5,7,8}$=H $R_{2,6}$=CN
Ih: $R_{1,3,5,6,7,8}$=H, $R_{2,4}$=CN
Ii: $R_{1,2,4,5,6,8}$=H, $R_{3,7}$=CN

	Distance (C--C) A					Angle
Compound	a	b	c	d	e	α
Ia	2.46	1.51	1.40	1.59	3.72	109
If	2.50	1.52	1.40	1.60	3.71	111
Ig	2.52	$1.51_{b2,4}$ $1.52_{b1,3}$	$1.39_{c2,3}$ $1.41_{c1,4}$	1.60	3.80	113
Ih	2.36	1.51	1.41	1.59	3.63	103
Ii	2.37	1.51	1.40	1.59	3.63	103

of symmetry in the molecule (see Table 21) (c1-c4 ad b1-b4) are equal after optimization. In the 2,6-dicyano compound the bonds adjacent to the CN groups (c1,4 ad b1,3) are slightly longer than those which are substituted by protons. The C-C bond lengths of the Cope rearranging portion of the molecule are approximately equal to the C-C bond length in benzene. Figure 9 depicts some representative orbitals estimated from the results of the molecular orbital calculations for the homoconjugated structures. The orbitals resemble two interacting allyl systems and the ordering is the same as that calculated by Hoffmann ad Stohrer (14). The two orbitals below the HOMO are almost degenerate in all but one case and correspond to the AS and SS combination of the two allyl systems. It can be seen that when the cyano substituents are on the same allyl group (the 2,4-dicyano compound) these two orbitals are very different from those seen for the other semibullvalenes studied and are no longer degenerate. (Fig. 9) Thus there is little interaction of the two allyl systems in this molecule.

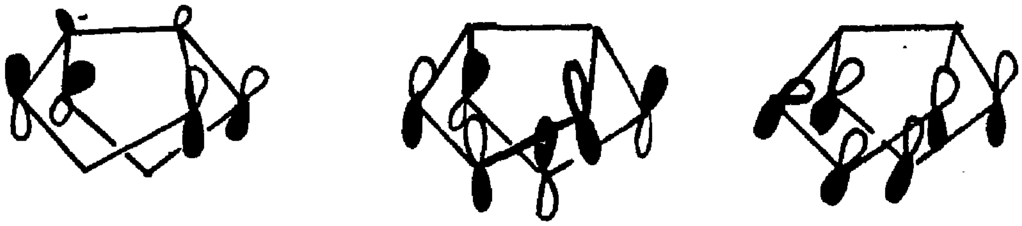
The distance between the ends of the allyl systems (C2-C8) and (C4-C6) varies for the homoconjugated structures studied, while in the ground states the nonbonded distance (C4-C6) is fairly constant (2.43 - 2.45 A). The differences are noteworthy:

Figure 9
SCHEMATIC REPESENTATION OF SOME MOLECULAR ORBITALS FOR THE HOMOCONJUGATED STATES OF SEVERAL SEMIBULLVALENES

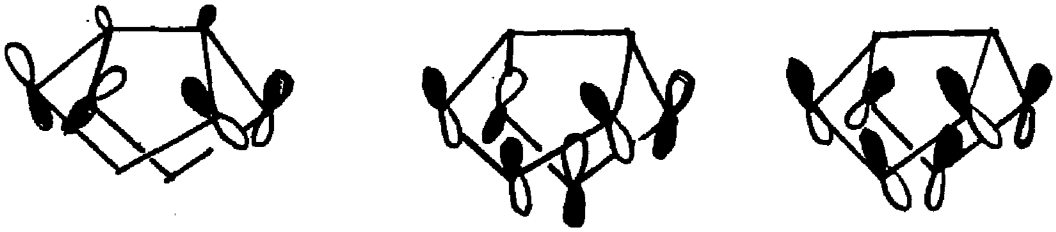


Unsubstituted Semibullvalene

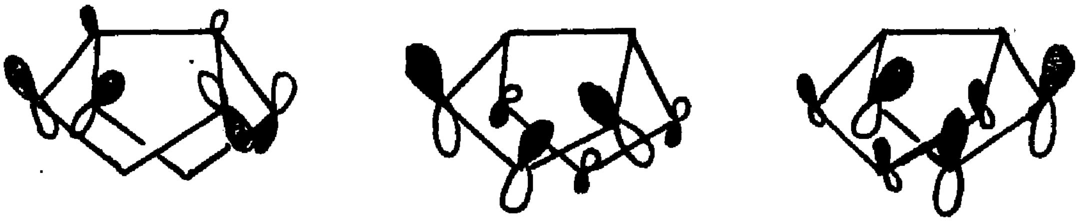
2,4,6,8-Tetracyanosemibullvalene



2,6-Dicyanosemibullvalene



3,7-Dicyanosemibullvalene



2,4-Dicyanosemibullvalene

Cpd	G. S.	Homoconj.	Subst.
Ia	2.44	2.46	H
If	2.45	2.50	(2,4,6,8-CN)
Ig	2.44	2.52	(2,6-CN)
Ih	2.44	2.36	(2,4-CN)
Ii	2.43	2.37	(3,7-CN)

The 2,4 ad 3,7-dicyanosemibullvalenes have nonbonded distances of 2.36 and 2.37 A in the homoconjugated states while the 2,6-dicyano and the 2,4,6,8-tetracyano compounds have distances of 2.50 and 2.52 A respectively. In the unsubstituted compound the distance is almost the same for both states. The bond angle (C4-C5-C6) varies in te same way; it is the largest for the 2,6- and tetracyano compounds (111 and 113°). This is also evident in the nonbonded C3-C7 distance (Table 21). As the ends of the allyl system move further apart the middle carbons do also. In the MO diagram (Fig 9) it can also be seen that there is a large antibonding interaction between C3 and C7 in the orbital below the HOMO. This would be lessened as carbons three and seven move further apart. In none of the systems studied did the homoconjugated ground state resemble a 1,4-diyl structure. When the nonbonded distance between the ends of the allyl systems was decreased, the energies increased greatly. It appears that not only is the C2-C8 bond almost completely broken before the transition state, but that the C4-C6 distance is increased slightly before bond formation begins at that end of the molecule.

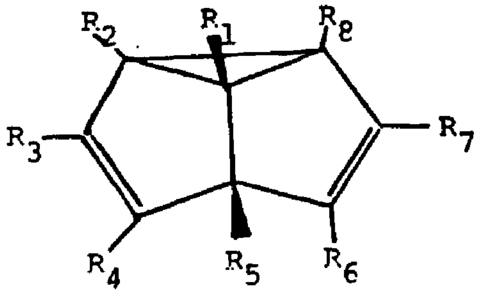
There is some electron density in the antibonding orbital for the protons bound to C1 and C5 in the HOMO for all the systems studied. It is possible that as the ends of the allyl systems move further apart there is a through-bond interaction involving these orbitals which stabilizes the homoconjugated states.

The significance of the results presented above is clear when the $\Delta H^{\ddagger}$ for the systems are compared. These results, along with the heats of formation (ΔH_f) for the compounds studied are listed in Table 22. Our calculated value of $\Delta H^{\ddagger} = 5.7$ kcal/mole compares favorably with Anet's experimentally determined value of 4.8 kcal/mole for the parent molecule (10). The $\Delta H^{\ddagger}$ for the tetracyano substituted compound is also surprisingly close to that calculated by Anet considering that his calculations were based on EH energy differences (10).

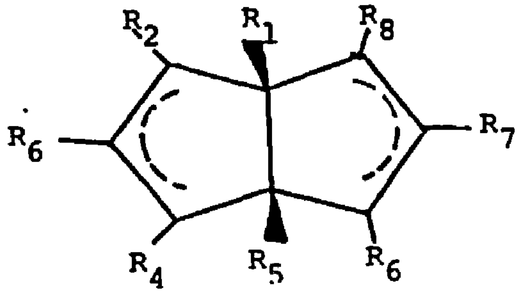
The heats of formation for the ground states of the three isomeric dicyano semibullvalenes are interesting. The 3,7-dicyano substituted compound has two cyano groups which can interact with the diene portion of semibullvalene while in the 2,4 and 2,6 disubstituted compounds only one cyano group is in conjugation with the diene. The heats of formation for the 2,6 and 2,4 dicyano compounds are the same (134.3 and 134.5 kcal/mole), while that for the 3,7-disubstituted compound is 130.3 kcal/mole. The effect of one cyano group can be estimated as 4.2 kcal/mole on the ground state the ΔH_f. In the homoconjugated state the ΔH_fs for the dicyano compounds are all different. The highest value is seen for the 2,4-dicyano compound, 143.4 kcal/mole. We

Table 22

HEATS OF FORMATION (ΔH_f) AND ENTHALPIES OF ACTIVATION ($\Delta H^{\ddagger}$) OF SOME SEMIBULLVALENES (MNDO)



Ground State



Homoconjugated State

kcal/mol

Compound	Description	ΔH_f(g.s.)	ΔH_f(homo-conj)	$\Delta H^{\ddagger}_{calc}$	$\Delta H^{\ddagger}_{obs}$
Ia	all H	72.2	77.9	5.7	4.8[a]
If	2,4,6,8-tetra-CN	202.3	197.6	-4.7[b]	
Ig	2,6-di-CN	134.3	134.1	-0.2	
Ih	2,4-di-CN	134.5	143.4	8.9	
Ii	3,7-di-CN	130.3	140.1	9.8	

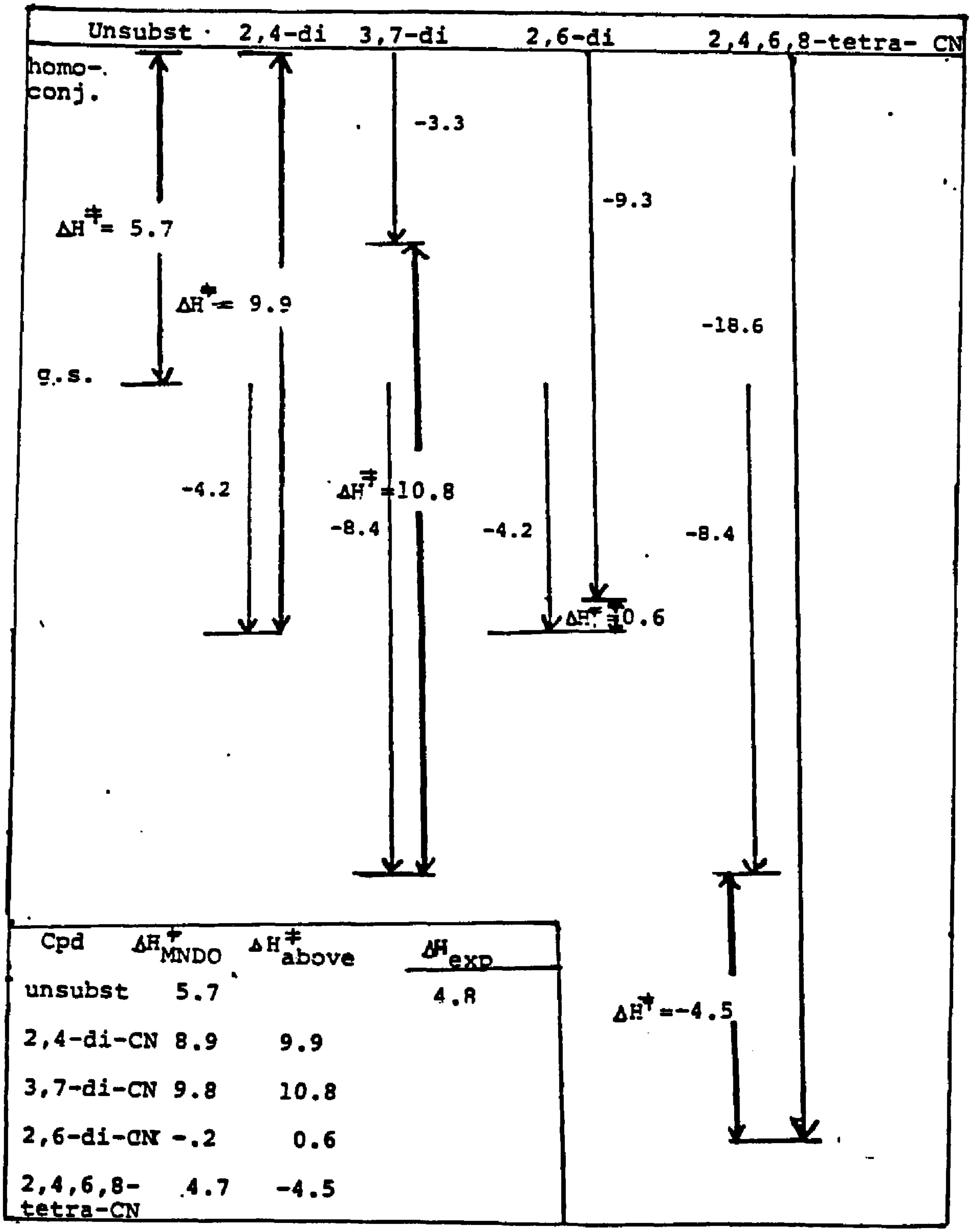
a. Ref 10
b. Calc (ref 10) = -2.8 kcal/mol

can assume that there is no stabilization of the homoconjugated state for this compound as the cyano groups are only interacting with one of the allyl systems. The ΔH_f for the 3,7-dicyano compound is 140.1 kcal/mole. This could be due to a stabilization occuring through an interaction of the AS orbital (second highest HOMO) of the allyl system and the 3,7 cyano substitutents. In the 2,6-disubstituted compound for the ΔH_f is 134.1 kcal/mole, which is 9.3 kcal lower than that calculated for the 2,4-dicyano compound. Figure 10 depicts these effects quantitatively and the ΔH^{*} for the Cope rearrangement of the series of compounds studied is estimated based on the effect per cyano group on the ground and homoconjugated states. The additivity of these effects is evident in the calculated ΔH^{*} for the tetracyano case. The method used here reproduces the ΔH^{*}s calculated by MNDO quite well. In summary the 2,4-and the 3,7-dicyanosemibullvalenes appear to have a higher ΔH^{*} for Cope rearrangement than the parent molecule, mainly due to stabilization of the ground state. The 2,6-dicyanosemibullvalene has a ΔH^{*} of almost zero; that is, the ground state and the homoconjugated state have almost the same energy, while the tetracyanosemibullvalene has a stabilized homoconjugated state ($\Delta H^{*} = -4.7$kcal/mole) and would be expected to exist in this form at room temperature.

We have attempted to calculate the energy barrier between the homoconjugated and classical ground states for the tetracyano compound. Using 2x2 CI and a reaction coordinate

Figure 10

RELATIVE STABILIZATION OF GROUND AND HOMOCONJUGATED STATES OF SOME CYANO SUBSTITUTED SEMIBULLVALENES



Cpd	$\Delta H^{\ddagger}_{MNDO}$	$\Delta H^{\ddagger}_{above}$	ΔH_{exp}
unsubst	5.7		4.8
2,4-di-CN	8.9	9.9	
3,7-di-CN	9.8	10.8	
2,6-di-CN	-.2	0.6	
2,4,6,8-tetra-CN	4.7	-4.5	

method we have obtained a preliminary ΔH_f of 212 kcal/mole for a transition state where the two ends of the molecule are 2.2 and 2.4 A apart. This transition state has been very hard to locate as the energy surface is quite flat with respect to the reaction coordinate for distances of several tenths of an angstrom on either side of the col. We had hoped to refine this point further but have been unsuccessful.

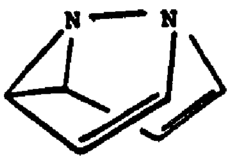
The homoconjugated structures for the parent and tetracyanosemibullvalene were also calculated for the triplet state. The energy and geometries were very similar to those calculated for the singlets and these states might be accessible.

If one returns to the geometric parameters listed in Tables 20 and 21, it is clear that the homoconjugated structures whose energies are equal to or lower than the classical ground states (If and Ig) are those in which the two ends of the molecule (C2-C8 and C4-C6) are separated by the largest distances. This is manifested by a flattening of the ring system ($\measuredangle$C4-C5-C6 = $\measuredangle$C2-C1-C8 $>$109) and a concomitant increase in the C3-C7 nonbonded distance.

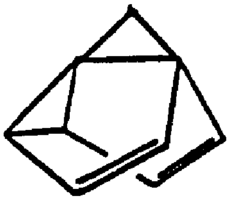
ii. Other Semibullvalene Systems

We wished to apply the results of the cyano substituent study to predict what other types of modifications of the semibullvalene molecule would lower the activation energy of the Cope rearrangement. We noted above that flattening of the bicyclic allyl system (opening the C4-C5-C6 bond to values greater than 109^{o}) occurred in compounds where the homoconjugated structure was stabilized with respect to the ground state. Since this involves opening the bridgehead angles greater than 109^{o}, we wanted to devise compounds in which the strain involved in tis procedure would be minimized. This could be accomplished by introducing nitrogen instead of carbon at positions 1 and 5 in the semibullvalene nucleus. Annelating a small ring to positions 1 and 5 would also cause the C4-C5-C6 angle to open.

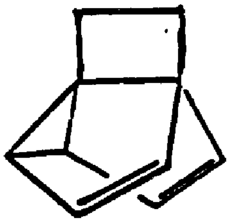
We used the MNDO method to study 1,5-diazasemibullvalene and the semibullvalene having a three and four membered ring annelated to positions 1 and 5 (Ij, Ik, Il).



Ij



Ik



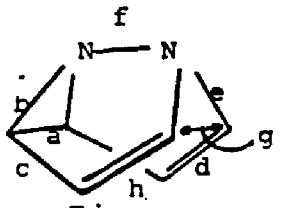
Il

We calculated the classical ground state structures and homoconjugated states for these compounds but have not studied the reaction paths.

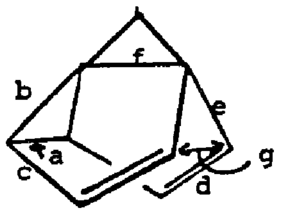
Tables 23 and 24 list the relevant geometries and heats of formation for these compounds in the classical ground state and the homoconjugated state. The diaza compound exists preferentially as the known diazapentalene (122). In this case it is possible that the Cope rearrangement pro-

Table 23

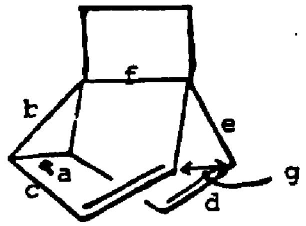
GROUND STATE GEOMETRIES AND HEATS OF FORMATION FOR SOME SEMIBULLVALENES CALCULATED BY MNDO



Ij



Ik

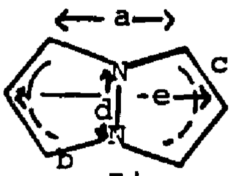


Il

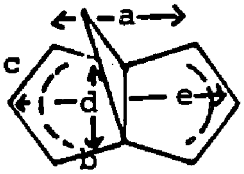
	Distances (C—C) A								kcal/mol
Compound	a	b	c	d	e	f	g	h	ΔH_f
unsubst.	1.57	1.54	1.53	1.36	1.54	1.57	2.44	3.17	72.2
Ij	1.54	1.52	1.50	1.36	1.48	1.42	2.35		113.9
Ik	1.60	1.51	1.51	1.36	1.51	1.60	2.48		137.0
Il	1.58	1.53	1.51	1.36	1.52	1.59	2.44	3.17	92.2

Table 24

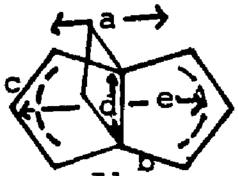
HOMOCONJUGATED STATE GEOMETRIES AND HEATS OF FORMATION FOR SOME SEMIBULLVALENES AND ENTHALPIES OF ACTIVATION FOR THEIR COPE REARRANGEMENTS (MNDO)



Ij



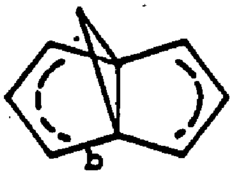
Ik



Il

	Distances (C--C) A					deg	kcal/mol	
Compound	a	b	c	d	e	α	ΔH_f	$\Delta H^{\ddagger}$
Ia unsubst	2.46	1.51	1.40	1.59	3.72	109	77.9	5.7
Ij	2.65	1.41	1.41	1.37		140	101.4	-12.4
Ik	2.47	1.47	1.41	1.64	3.78	113	127.9	-9.1
Il	2.41	1.5-	1.39	1.61	3.69	107	97.5	5.4

ceeds through a different transition state since the disrotatory opening of this semibullvalene to diazapentalene is an eight electron process and is forbidden. The cyclopropyl fused analog (<u>Ik</u>) is most interesting. The calculations predict the homoconjugated structure to be more stable than the classical ground state by 9.1 kcal/mole. In the homoconjugated state the bridgehead angle is opened to 113°, while the nonbonded distance between the ends of the two allyl systems is 2.47 A, not very different from the unsubstituted semibullvalene Ia (2.46 A). The major difference is in the geometry of the five membered rings .



The distance b in the cyclopropyl annelated compound is shorter than in any of the other carbocyclic semibullvalenes studied. This allows the rings to flatten with less strain while not forcing the nonbonded ends of the allyl systems as far apart as they are in the cyano substituted cases. In the cyclobutyl annelated system, <u>Il</u>, the homoconjugated structure is calculated to have an energy 5 kcal/mole higher than the ground state.

E. Conclusions

We have systematically studied the geometries and energies for the Cope rearrangement of semibullvalene and some of its substituted derivatives using the MNDO method of calculation and including 2x2 CI for all diradical like species. All the compounds rearrange via a bis allyl type transition state. When cyano groups are substituted at the ends of the allyl systems (2,4,6,8-tetracyano-) the energy of the homoconjugated structure is lower than that of the classical ground state which should cause the delocalized structure to be favored at room temperature. In the 2,6-dicyano substituted compound, the ground state and homoconjugated states are almost equal in energy. Placing cyano groups at positions 3 and 7 or 2 and 4 increases the $\Delta H^{\ddagger}$ for the Cope rearrangement with respect to the parent compound. The additional MNDO studies indicate that the cyclopropyl annelated semibullvalene <u>Ik</u> should exist preferentially in the homoconjugated structure. The method of calculation appears to reproduce the energies and geometries of the rearranging species well and shows good agreement with the experimental value for the $\Delta H^{\ddagger}$ of the Cope rearrangement of the unsubstituted semibullvalene as determined by Anet (10).

Chapter 5

CONCLUSIONS

A. Summary

With the synthesis of 1,5-dimethyl-2,4,6,8-tetrakis-(carbomethoxy)semibullvalene Ib, we have prepared the first semibullvalene substituted with pi-electron acceptors at the specific positions predicted by the theoretical calculations to lower the E_{act} for the Cope rearrangement (14). The synthetic sequence presents a new route for the preparation of semibullvalenes. We have utilized this route for the successful synthesis of 1,5-dimethyl-2,6-dibromosemibullvalene Ic.

Compound Ib has been studied by X-ray crystallography and nm . The X-ray structure shows the molecule to be unsymmetrical, with two sets of carbomethoxy groups, one able to interact conjugatively with the semibullvalene orbitals and one twisted out of conjugation. The C2-C8 bond is very long (1.782 A) and the non-bonded C4-C6 distance is shorter than in the unsubstituted compound. The interaction of the carbomethoxy groups with the cyclopropyl orbitals is not sufficient to explain the extremely long C2-C8 bond (22). We concluded that the pattern of substitution in Ib has led to a substantial electronic rearrangement as manifested by the unusual crystal structure. The observed geometry is consistent with a structure that is approaching the transition state for the Cope rearrangement.

The results of the nmr studies are interesting, although not definitive. The room spectra temperature show averaged signals for the Cope rearranging carbons and protons. The positions of the signals for C1,5, C3,7 and H3,7 raise questions as to whether there is another species of similar energy equilibrating with the Cope rearranging molecules. The low temperature ^{13}C spectra shows broadening of the signals for C2,4,6,8, C3,7 and the methyl carbons at --150°C which remains unchanged at -160°C. These data have been interpreted using several hypotheses all of which assume that the broadening of the C2,4,6,8 resonance is caused by the decreased rate of Cope rearrangement with decrease in temperature.

a) The carbomethoxy rotation is also slowing down thus causing an inequivalence between carbons 3 and 7;

b) There is also a delocalized species of similar energy which is equilibrating with the Cope rearranging molecules and this equilibrium is changing with decreasing temperature;

c) The broadening of some of the signals is due to a decrease in the tumbling rate of these carbons as manifested by a short T_2.

MNDO calculations on the cyano substituted semibullvalenes indicated that 2,4,6,8-tetracyano and 2,6-dicyano derivatives should have delocalized structures which are equal or lower in energy than the classical ground states. The semibullvalene with a methylene group annelated to C1 and C5 is also predicted to have a homoconjugated structure of lower energy than the classical ground state.

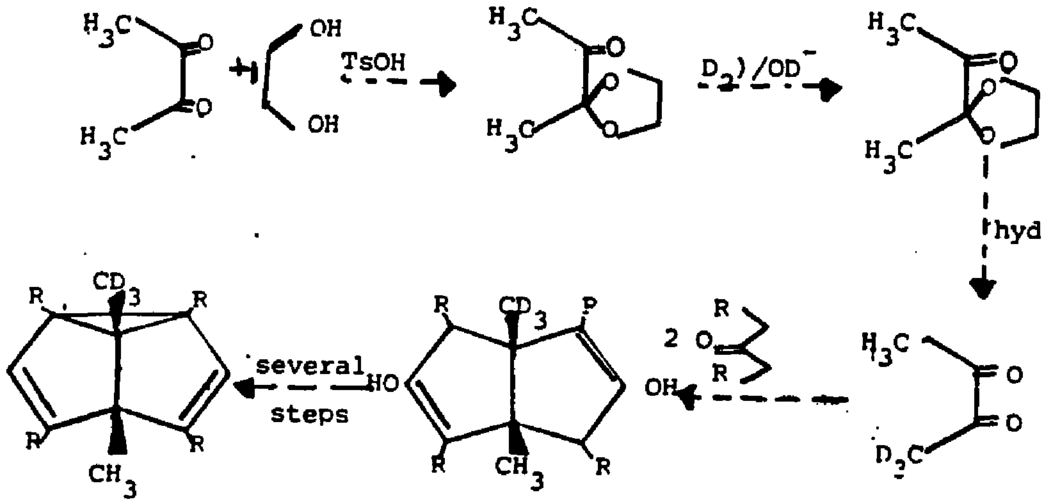
B. Suggestions for Spectral Work

i In order to obtain more information about the solution behavior of Ib a series of low temperature ^{13}C spectra where the temperature will be varied from -70° to -160° will be obtained and the pattern of signal broadening studied as well as any subtle changes in chemical shift.

ii Another method which can be used for the study of rapidly equilibrating species having low activation energies is low-temperature, high resolution solid state ^{13}C nmr (123). The solid state ^{13}C nmr of semibullvalene measured by Miller and Yannoni showed resonances corresponding to the static structure at room temperatures as high as -110°C. The authors estimated that the rate constant at -110°C to be 400 sec^{-1} as compared to a rate constant in solution of 2.2 x 10^5 at this temperature as measured by Anet and coworkers (10). Using this method, it should be possible to distinguish between equilibrating or symmetrical species even for rearrangements where the E_{act} is too small to be measured by low temperature solution nmr spectroscopy. Once the di-or tetracyano substituted semibullvalene is synthesized it should be studied by this method as well as by solution nmr.

iii Isotopic Perturbation Study

The isotopic peturbation 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 (28, 29, 30, 124). It may be possible to substitute deuterium at some position in Ib, or in the tetra or dicyanosemibullvalene and study the effects using ^{13}C nmr. The most obvious position to substitute is one of the methyl groups in Ib (eqn 45).



(45)

The CD_3 group should remove the degeneracy from the Cope rearranging species. The ^{13}C NMR spectra of mixtures of the deuterated and nondeuterated compounds would be determined at different temperatures. If the compound actually exists as a delocalized species, there would be no effect on the ^{13}C resonances except for an intrinsic isotope effect which decreases rapidly with distance from the deuterium. If the equilibrium is sufficiently altered by the CD_3 group, different chemical shifts would be measured for the formerly equivalent carbons (e.g. C2,8 ad C4,6). These data would serve to differentiate between the two alternatives (a rapid Cope-rearranging species and a delocalized structure). Since we know that the tetracarbomethoxysemibullvalene <u>Ib</u> experiences broadening of the C2,4,6,8 signal at -150°C in solution, the tetracyano compound would serve as a better model for a study of a delocalized system.

<u>iv</u> Low temperature UV/visible spectroscopy might provide some useful information regarding the thermochromicity of compound <u>Ib</u>. Since it was observed that the intense yellow color disappears upon cooling of the crystals or a solution of the compound, a study of the temperature dependence of this phenomenom would be of value. A preliminary study of the solid state UV/visible spectra of <u>Ib</u> was inconclusive. (125)

C Suggestions for Experimental Work

The results of the MNDO calculations and the interesting X-ray and nmr data obtained for Ib suggested several semibullvalenes which should be synthesized and their properties studied. The following represents some of the synthetic plans.

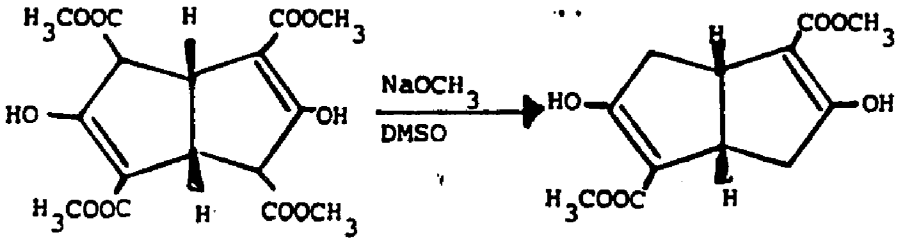
Di-COOMe ad Di-CN Compounds:

The X-ray analysis of Ib indicated tht 2 of the carbomethoxy groups are not in conjugation with the semibullvalene orbitals. The MNDO study indicated that 2,6-dicyanosemibullvalene should have a delocalized structure that is of approximately the same energy as the classical ground state. The synthesis of both 2,6-dicarbomethoxy- and the 2,6-dicyanosemibullvalenes would be of great value.

One method of synthesizing these compounds utilizes existing precursor molecles. The following procedures were tried, with little success:

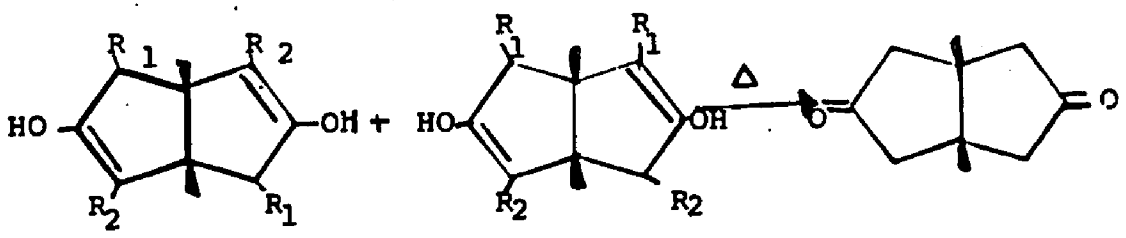
1. Decarboxylation of the enol-ester (1)

The enol ester with protons at the brigehead positions has been reported to react with sodium methoxide in DMSO to yield the diester (no CH_3 groups) in 90% yield (eq 46) (6). We repeated this reaction several times and could not isolate the diester. Each time, the same product was isolated. It was soluble in base and precipitated in acid (bubbled). When heated neat at 150°C it bubbled vigorously



(46)

and turned red after 10 minutes. After 16 hours at 150°C the proton nmr showed signals only for the completely decarboxylated 1,5-dimethylbicyclo (3.3.0) octane <u>(16)</u>. The temperature and time for the reaction was varied with no change in the results. The products obtained from this reaction may be a mixture of partially deesterfied compounds which decarboxylated completely with heat (eqn 47).



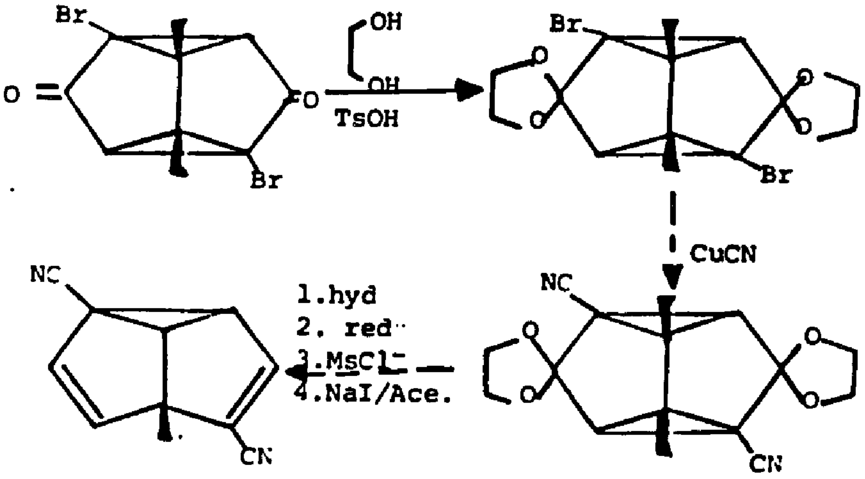
R_1=COOH

R_2=CCOCH$_3$

(47)

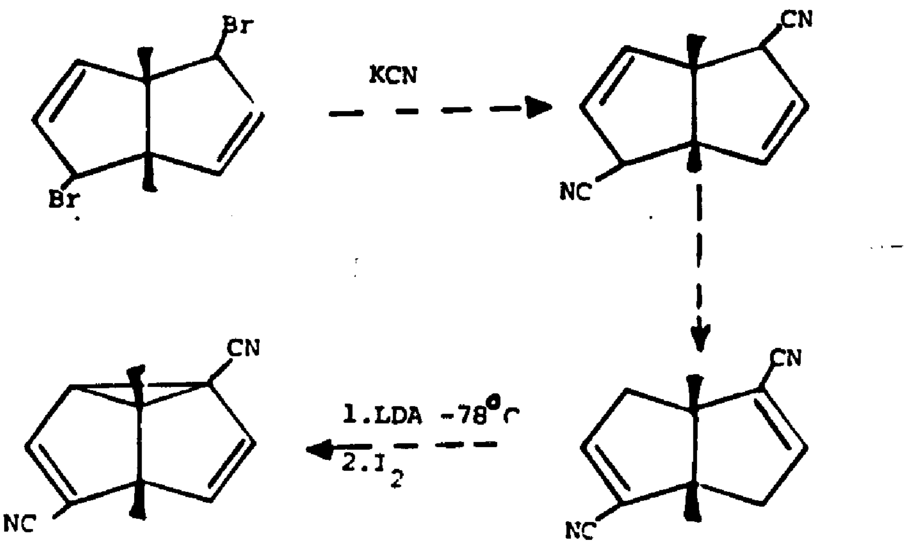
2. Substitution of CN for Br:

The substitution reaction was attempted on various brominated precursor molecules using CuCN in DMF, quinoline and N-Me-pyrrolidone. These reactions were all unsuccessful resulting in intensive decomposition if the carbonyl groups are protected before the CN attacks the following sequence should prove effective. (eqn 48)



(48)

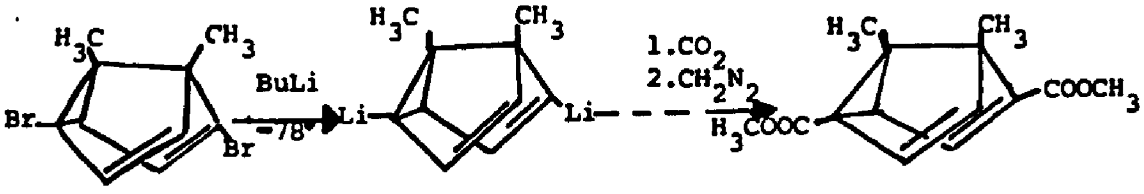
Another molecule which has been synthesized by Askani and coworkers (126) is 1,5-dimethyl-4,8-dibromobicyclo(3.3.0)oct-2,6-diene. Treatment of this compound with KCN should produce the dicyano bicyclooctadienes (eqn 49). Formation of the dianion with LDA and subsequent oxidation with I_2 would yield the 1,5-dimethyl-2,6-dicyanosemibullvalene.



(49)

3. Manipulation of Existing Semibullvalenes

Because of its lability, the 1,5-dimethyl-2,4,6,8-tetrakis(carbomethoxy)semibullvalene is not a good starting material for any conversion reactions. However, the 2,6-dibromosemibullvalene (Ic) offers a promisng route for the preparation of other 2,6-disubstituted semibullvalenes. It should be possible to form the dilithium compound by treating Ic with BuLi at -78°C. Addition of CO_2 followed by CH_2N_2 should produce the dicarbomethoxy derivative (eqn 50).



(50)

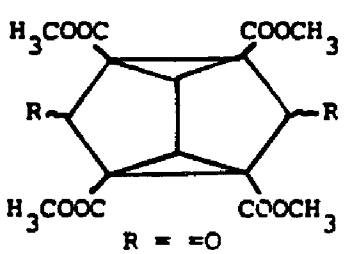
A preliminary experiment produced a very small amount of a solid whose ^1H nmr spectrum showed signals for CH_3, OCH_3 and vinyl protons: however, the ratios of these signals were not correct for the dicarbomethoxy derivative. It is possible that a mixture of mono- and di-carbomethoxy compounds were formed.

In a related study Klumpp and coworkers were unable to isolate any 2 (or 4)-COOMe semibullvalene from 2 (or 4)-lithiosemibullvalenes which was prepared from the corresponding monobromo compound using lithium p,p'-ditertbutylphenyl as the lithiating agent (30). The metallation reaction was successful for substituting H, D, CH_3, and Cl for the lithium. Askani and coworkers also prepared the 2 (or 4) deuteriosemibullvalene by treatment of 1,5-dimethyl-2 (or 4)bromosemibullvalene with tert-butyllithium followed by D_2O (19). The application of these methods to 1,5-dimethyl-2,6-dibromosemibullvalene should be pursued further.

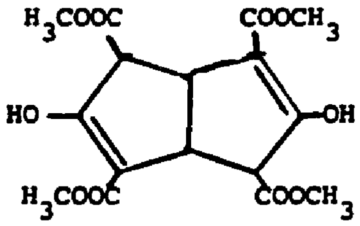
1. Approaches to the Tetracyanosemibullvalene

Manipulation of Existing Compounds

We attempted to convert various tetracarbomethoxy substituted precursor compounds to the tetracyano derivatives via the dehydration of the tetraamides. All attempts to convert the esters (below) to amides using liquid NH_3 and Na or $NaOCH_3$ under pressure or at low temperatures failed. When the diol (4a) was treated with aqueous NH_3 and CH_3OH at reflux a new compound was formed which appeared to be a



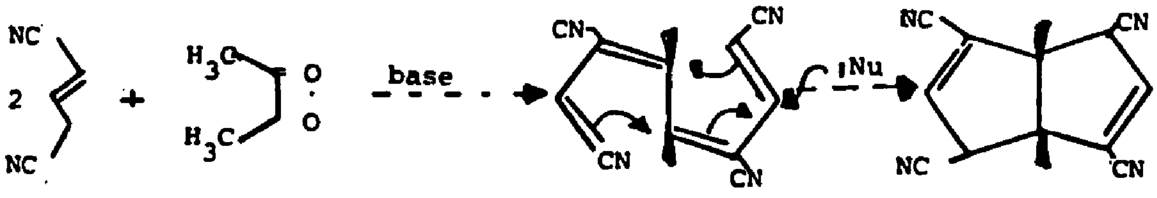
R = =O
R = H,OH
R = H,OMs



diester-diamide. Longer reaction times did not change the composition of this product. There are several approaches to the synthesis of 1,5-dimethyl-2,4,6,8-tetrakis(cyano)-semibullvalene which should be more successful. These are outlined below.

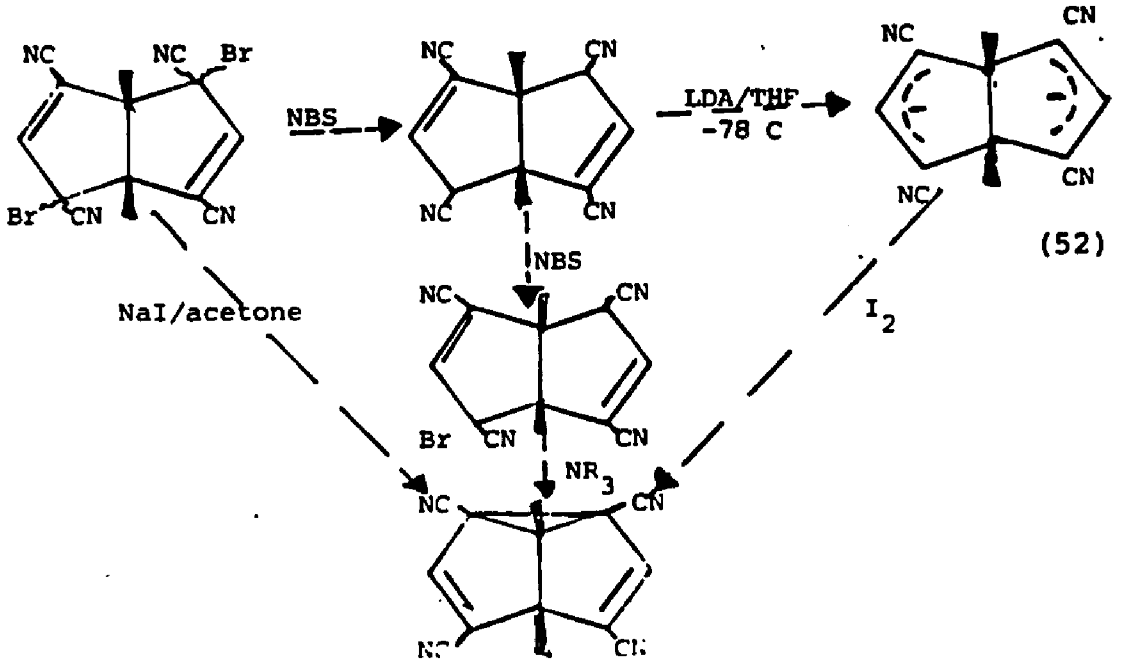
2. Other Routes:

The first route involves the synthesis of the tetracyanobicyclo(3.3.0)octadiene from 1,3-dicyanopropene



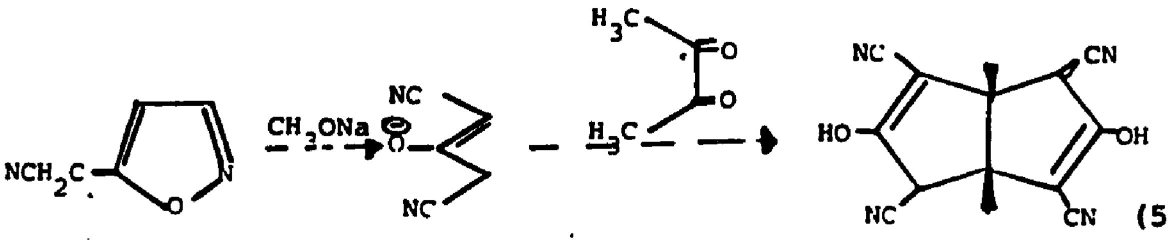
(51)

and 2,3-butanedione by a combination of aldol condensations and intramolecular Michael additions (Michael Induced Ring Closure, MIRC). It may be possible to find a base/nucleophile which effects the aldol condensation and the MIRC. The bicyclooctadiene could then be converted into the semibullvalene by one of several routes (eqn 52).



(52)

Another route involves the in situ trapping of 1,3-dicyanoacetone by 2,3-butandione. The 1,3-dicyanoacetone could be generated from 5-cyanomethylisoxazole and CH_3ONa in the presence of the dione (127). If conditions are optimum, the enol would be formed (equ 53) and could be transformed onto the desired semibullvalene following the route used for

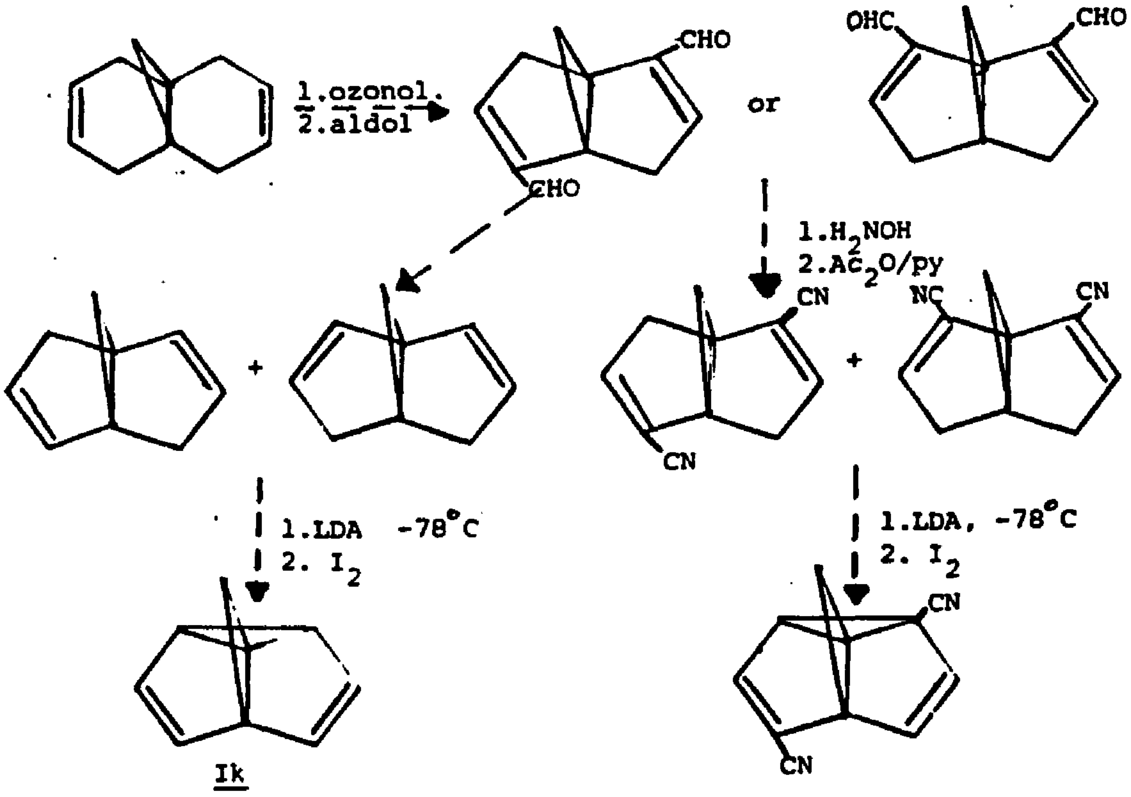


(53)

the 1,5-dimethyl-2,4,6,8-tetrakis(carbomethoxy)semibullvalene Ib.

Approaches to the Cyclopropyl annalated semibullvalene (Ib)

The equation below (equ 54) indicates one route that could be followed for the preparation of the cyclopropyl fused semibullvalene system. Ozonolysis followed by aldol condensation would lead to the tricyclo(3.3.0^{1,5}) nonane system. Removal of the aldehyde groups would yield cyclopropyl annelated semibullvalene IR, while the conversion of the aldehydes to cyano groups leads to the inclusion of both the fused cyclopropyl ring and the 2,6-dicyano substituents in one molecule, a fasicnating prospect.



(54)

E. Theoretical Studies:

Additional MNDO studies should be carried out to further refine the pathways between the low energy species calculated in this work. A study of the Cope rearrangement of cis-divinylcyclopropane and cis-divinylcyclobutane should be undertaken. It is known that the cyclopropane compound rearranges much faster than the cyclobutane (2). The MNDO study should clarify the geometry of the transition states and aid in our understanding of this process.

CHAPTER 6

EXPERIMENTAL

All solvents were purified by literature procedures.

IR spectra were obtained on a Beckman 4240 spectrometer in $CHCl_3$ solution. UV-Visible spectra were run on a Beckman DU-8 spectrometer in 95% EtOH solution. Routine ^1H NMR were recorded at 60 MHz on a Varian A60 or a Varian EM-360L spectrometer in $CDCl_3$ or CD_3COCD_3 solution using an internal TMS reference. The routine ^{13}C NMR were determined at 25.03 MHz on a JEOL PS/PFT 100 spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, New York.

"Usual" or "standard" workup refers to the following procedure: the reaction mixture was poured onto ice-water containing dilute HCl or $NaHSO_3$ (for I_2 and Br_2 producing reactions) and extracted three times with CH_2Cl_2. The combined organic layers were washed with dilute HCL and saturated $NaHCO_3$ (if necessary) solutions followed by saturated NaCl and dried over $MgSO_4$ or Na_2SO_4. After filtration the organic solvent was evaporated <u>in vacuo</u> using a Buchi Rotavapor-R.

Preparation of 1,5-Dimethyl-2,4,6,8-tetrakis(carbomethoxy)bicyclo(3.3.0)octa-2,6-diene-3,7-diol. (1)

Compound 1 was prepared by a modification of the procedure of Weiss and Edwards (50). To 1700 ml of a pH = 5 aqueous acetate buffer solution, 100 ml (106.7 g (90%), 0.61 m) dimethyl acetone-1,3-dicarboxylate and 30 ml (29.4g, 0.34 m) butane-2,3-dione was added. The solution was stirred for 24 hours at room temperature. The solid was collected, washed with water and air dried. It was triturated with methanol. The yield of colorless crystals was 110 g (0.28 m, 90%). mp 158-62°C (lit. (50) mp 144-6, (53) mp 153-5); nmr data see Table 2.

Preparation of 1,5-Dimethyl-2,4,6,8-tetrakis(carbomethoxy)tetracyclo(3.3.0.0.^{2,8}0.^{4,6})octa-3,7-dione (3)

The tetracyclic ketone 3 was prepared from 1 by a two-step reaction. A solution of 7 ml (21 g, 0.13 m) Br_2 in 50 ml $CHCl_3$ was added to a solution of 25.0 g (0.063 m) 1 in 250 ml $CHCl_3$ over a period of one hour. The bromine did not completely react. The solution was stirred at room temperature overnight. It was washed with saturated $NaHSO_3$ to remove the excess bromine. The organic layer was then washed with saturated NaCl and dried over $MgSO_4$. The $CHCl_3$ solution contaning the dibromo adduct 2, was chilled and a solution of 24 ml (17.4 g, 0.17 m) triethyl amine in 50 ml $CHCl_3$ was added to it over a period of 30 minutes. After stirring for 2 hours the solution was worked up in the usual way. The crude product was triturated with CCL_4. The yield of shiny. colorless crystals of 3 was 10.1 g (0.026 m 41%). m.p. 185-8, (lit. (56) mp 185); nmr see p ; 2,4-DNP mp 236-8; Anal. Calc for $C_{18}H_{18}O_{10}$: C, 54.82; H 4.57. Found: C, 54.99; H, 4.57.

Preparation of 3 via the Tetrabromo Adduct 2a.

A solution of 7 ml Br_2 (21 g, 0.13m) in 20 ml acetic acid was added dropwise to a solution of 12 g (0.03m) 1 in 150 ml acetic acid over a period of 30 minutes. The solution did not decolorize and was stirred overnight. It was poured into 500 ml ice-water to which some $NaHSO_3$ had been added. A precipitate was formed and the excess bromine was destroyed. The crude solid (25-30 g) was collected, washed with water and air dried. It was suspended in 130 ml CH_3OH, heated to boiling and the insoluble material was filtered off. This proved to be the tetrabromo product 2a and was used without further purification. The yield was 11 g (0.015 m, 51%)

To a solution of 25 g (0.17 m) NaI in 160 ml dry acetone, 7.57 g (0.011 m) 2a was added in small portions. The solution turned color progressively from yellow to dark brown and a yellow precipitate was evident. After 18 hours the product 3 was isolated by dilution of the reaction mixture with a solution saturated with NaCl and $NaHSO_3$, and extraction with CH_2Cl_2. After the usual workup 3.6 g (0.09 m, 82%) 3 was isolated, mp 183-5; spectral properties identical to those of 3 prepared via the dibromo adduct of 1.

Preparation of 2 Using the Acetic Acid Method.

The dibromo adduct of 1 could be isolated in variable yield from the bromination of 1 in acetic acid. Compound 2 was more soluble in acetone than the tetrabromo adduct 2a, and separation could be achieved by relative solubilities. After several recrystallizations (CH_3OH and CCl_4) the product had a mp of 176-8.5°C (dec) and was completely enolized; nmr see Table 5.

Preparation of 1,5-Dimethyl-2,4,6,8-tetrakis(carbomethoxy)tetracyclo(3.3.0.$0^{2,8}0^{4,6}$)octane-3,7-diol. (4a)

A chilled suspension of 4.6 g (11.7 mmole) 3 in 60 ml toluene was stirred under argon. Sixty five ml of a solution of $(i\text{-Bu})_3Al$ in toluene (25% soln 1.06M, 69.5 mmole) was added (59). The clear yellow solution was stirred at room temperature for one hour. A 3M HCl solution (25 ml) was added cautiously to the cooled reaction. The mixture was poured into ice water which was diluted with HCl and CH_2Cl_2, stirred for several hours and the layers separated. After three additional CH_2Cl_2 extractions, the combined organic layers were washed in the usual way. The crude diol was recrystallized from an ethyl acetate-hexane solvent pair. Colorless crystals. 2.0 g (5.03 mmole, 43%) were obtained. mp 200-4; nmr see Table 3; Anal: Calc for $C_{18}H_{22}0_{10}$: C, 54.27; H 5.53; Found: C, 54.14. H, 5.53.

Preparation of the Di(methanesulfonyl) Derivative of 4a (5a)

A solution of 2.0 g (5.0 mmole) 4a, 3.75 ml triethylamine (2.72 g, 27 mmole) in 50 ml CH_2Cl_2 was cooled and 2.2 ml (3.26 g 28 mmole) methanesulfonyl chloride in 8 ml CH_2Cl_2 was added over a period of 30 minutes. The solution was stirred at room temperature overnight. The product was isolated by dilution with ice water and HCL, followed by extraction with CH_2Cl_2. After the standard workup the oily solid obtained was recrytallized from an ethyl acetate-hexane solvent pair. The yield of white solid was 1.8g (3.25 mmole, 65%). mp 133-4°C(dec). An analytical sample was obtained by recrystallization from an ethyl acetate-hexane mixture. mp 140-2°C(dec); nmr see Table 3; Anal. Calc. for $C_{20}H_{26}S_20_{14}$: C, 43.32; H, 4.69; S, 11.55; Found; C, 43.58; H 4.78; S, 11.45.

Preparation of Diendo-1,5-Dimethyl-2,4,6,8-tetrakis-

(carbomethoxy)tetracyclo(3.3.0.0^{2,8}0^{4,6})octan-3,7-diol (4b)

A solution of 2.5 g (6.25 mmole) 3 in 50 ml CH_2Cl_2 was added to a solution of 0.53 g (15 mmole) $NaBH_4$ in 100 ml methanol and stirred for one hour. The reaction was hydrolyzed by the addition of 13 ml 30% acetic acid and the solvents evaporated *in vacuo* to 3-5 ml. Water was added and the crude product extracted with CH_2Cl_2. After the standard workup, the solvent was evaporated leaving 2.0 g (5.03 mmole, 80%) diol. Recrystallization from ethyl acetate-hexane yielded 1.2 g 4b mp 174-80; nmr see Table 3.

Reaction of 4b and methanesulfonyl chloride

One gram (2.5 mmole) of the diendo diol 4b was dissolved in 20 ml CH_2Cl_2 to which 1.04 ml (0.76 g, 7.5 mmole) triethylamine had been added and the solution chilled in an ice bath. A solution of 0.43 ml (5.5 mmole, 0.63 g) methanesulfonyl chloride in 5 ml CH_2Cl_2 was added slowly to the diol solution. After a few minutes a precipitate was evident. The reaction was stirred for 30 minutes, poured into ice-water-HCl and extracted wth several portions of CH_2Cl_2. The crude oily product obtained after standard workup was stirred in 3 ml CH_3OH for 2 days. A yield of 0.43 g (0.90 mmole, 36%) beige solid was obtained. Spectral data indicated a mono-mesyl mono-hydroxy structure, 5b, see Table 3.

mp 110-12^{o}C (bubbles).

Preparation of 1,5-Dimethyl-2,4,6,8-tetrakis(carbomethoxy)-semibullvalene, (<u>Ib</u>)

To a solution of 14 g (.095 m) NaI in 50 ml dry acetone 1.8 g (3.25 mmole) <u>5a</u> was added in portions. The solution turned yellow and then cloudy and brown. It was stirred at room temperature for 48 hours. The mixture was then poured into a solution of $NaHSO_3$ in ice water and extracted with several portions of CH_2Cl_2. After the usual workup, the crude products were suspended in 5 ml CCl_4 and the insoluble white solid separated. This solid, 1.0 g, (1.7 mmole) proved to be the intermediate <u>6</u>, mp 140-2; nmr see Table 3. The yellow CCl_4 filtrate was evaporated, the residue suspended in 2 ml CH_3OH and left in the freezer for 24 hours. A mixture of 0.22 g yellow and white crystals was collected which contained both <u>6</u> and <u>Ib</u>. These crystals were treated with CCl_4 twice, the insoluble white portion separated and the residue again suspended in methanol. After several days 51 mg (.14 mmole) <u>Ib</u>, mp 102-5, were collected.

One gram of the solid (<u>6</u>) originally isolated was resuspended in a solution of 10 g (.068 m) NaI in 50 ml acetone and stirred at room temperature for 2 days. After the same workup as above 66.7 mg <u>Ib</u> (.18 mmole) was isolated; mp 102-5^{o}; nmr see Table 9: x-ray structure, see chapter 3; other spectral data see chapter 3; Anal. Calc.

for $C_{18}H_{20}O_8$; C, 59.34; H 5.50; O, 35.17; Found C, 59.11; H 5.40; O, 34.98.

Preparation of 2,6-Dimethyl-1,3,5,7-tetrakis(carbomethoxy)-cyclooctatetraene (7) from Ib, 5a or 6.

The cyclooctatetraene 7 could be obtained from semibullvalene Ib by heating a solution of Ib or by prolonged storage of solutions of Ib in the refrigerator or at room temperature. The product was also obtained during the preparation of Ib if the NaI and acetone solutions were refluxed for more than one hour or if higher boiling solvents were used. The two compounds, Ib and 7 could be separated on a silica column using CH_2Cl_2 as eluent. The semibullvalene eluted first followed closely by compound 7. The compound is colorless, mp 104-6, spectral data see chapter 3; Anal: Calculated for $C_{18}H_{20}O_8$; C, 59.34; H, 5.50; O 35.17; Found; C, 59.33; H 5.51; O, 35.26.

Preparation of Cis-1,5-Dimethylbicyclo(3.3.0)octan-3,7-dione (16)

The compound was prepared following the method of Weiss et al (71). Thirty g (0.077m) 1 was refluxed wih 700 ml 6N

HCl overnight. Afer several hours of refluxing compound 1 dissolved. The pink, clear solution was diluted with an equal volume of ice-water and extracted with CH_2Cl_2. After the usual workup 11.5 g (0.069 m, 90%) of crude product, mp 218-223 was isolated. It was triturated with CCl_4 to yield 10.0 g (78%) 16. mp 224-7 (lit ( ) mp 167-9, (53) mp 220-1); ^1H NMR: 1.22 (s, 6H, CH_3), 2.28 (s, 2H, ring H).

Preparation of Cis-1,5-Dimethyl-2,4,6,8-tetrabromobicyclo(3.3.0)octane-3,7-dione (17)

Eighteen g (0.11 m) of diketone 16 was dissolved in 200 ml glacial acetic acid. A solution of 24 ml (0.44 m) Br_2 in 80 ml of acetate acid was added over a 2 hour period to the cooled diketone solution. The Br_2 decolorized as soon as it reacted. After 30 minutes a precipitate was observed. The reaction mixture was stirred for an additional 1.5 hours after which it was poured onto 1.5 L ice-H_2O-$NaHSO_3$. The product precipitated and was collected. The crude product melted with decomposition at 181-90°C. It was extremely difficult to purify as it decomposed easily. ^1H nmr showed the presence of two different H-C-Br moieties. ^{1}Hnmr: 1.60 (s, 6H, CH_3), 5.10 (s, 2H, H-C-Br), 5.27 (s, 2H, H-C-Br). The crude product was used directly for the next step.

Preparation of 1,5-Dimethyl-2,6-dibromotetracyclo(3.3.0.0^{2,8}0^{4,6})octan-3,7-dione (18)

To a chilled solution of 31 g (0.066 m) 17 in freshly distilled THF a solution of 16.0 ml (0.115 m) triethylamine in 40 ml THF was added slowly. The reaction was stirred at room temperature for 1.5 hours. The THF was stripped off *in vacuo* and the resultant crude solid was extracted with CH_2Cl_2. A large volume of organic solvent had to be used as the solubility of the product was not very great. After the standard workup ca. 10 ml of CH_2Cl_2 was left and four times this volume of CCl_4 was added. The colorless product, 11.5 g (.035 m, 53%) melted at 218-22°C. ^1H NMR: CD_3COCD_3); 1.72 (s, 6H, CH_3), 2.38 (s, 2H, ring H).

The reaction could also be run using CH_2Cl_2 as solvent.

Preparation of Diendo-1,5-Dimethyl-2,6-dibromotetracyclo-(3.3.0.0^{2,8}0^{4,6})octan-3,7-diol (21) and the endo/exo diol (20)

A solution of 2.0 g (6.25 mmole) 18 in 50 ml CH_2Cl_2 was added to a solution of 0.6 g (17.0 mmole $NaBH_4$ in 100 ml CH_3OH and the mixture stirred for 1.5 hours. The excess $NaBH_4$ was destroyed by the addition of 13 ml 30% acetic acid. The solvents were evaporated to a volume of 3-5 ml and the reaction mixture was extracted with CH_2Cl_2 after the addition of ice-water. After the usual workup 1.7 g (5.2 mmole) of diols were isolated. TLC (10% ethyl acetate/CH_2Cl_2) indicated two products. The diols were separated on a silica column using 15% ethyl acetate/CH_2Cl_2. The diendo diol 21 eluted first; mp 128-9°C (dec) followed by the endo/exo diol 20, mp 105-10°C. A complete analysis of the nmr data appears in chapter 2 and the data are listed in Table 6.

Preparation of Diexo-1,5-Dimethyl-2,6-dibromotetracyclo(3.3.0.0^{2,8}0^{4,6})octan-3,7-diol (19)

A mixture of 1 g (37 mmole) Al (washed twice with CCl_4), a catalytic amount of $HgCl_2$ and 125 ml i-PrOH was stirred in an oil bath at 70-80°C overnight. Hydrogen was evolved and grey-black solid was suspended in the solvent. To this hot suspension, 4.8 g (15 mmole) 18 was added and the reaction was refluxed for one hour. A distillation head was attached and the solvent and the acetone formed in the reaction were distilled over a period of several hours. The distillation was continued until only a few ml of solvent remained. After cooling, the aluminum complexes were hydrolyzed with dilute HCl and the mixture extracted with CH_2Cl_2. After the usual workup a crude white solid was isolated by trituration with CCl_4. An additional trituration with 10% $CHCl_3$-CCl_4 provided 1.8 g (5.55 mmole) colorless solid. mp 148-50°C (dec). IR 3350 cm^{-1}; nmr, see Table 6. Mixtures containing some endo/exo and endo/endo diols were also obtained.

Preparation of the Dimesylate 22 from the diexo diol 19

A solution of 1.6 g (4.93 mmole) 19, 2 ml triethylamine (14 mmole) and 100 ml CH_2Cl_2 was chilled in an ice bath. A solution of 1.0 ml (12.8 mmole) methanesulfonyl chloride in 7 ml CH_2Cl_2 was added slowly to the chilled solution of diol. The reaction was stirred overnight during which time a white solid precipitated in the yellow solution. The reaction mixture was poured into ice-H_2O-HCl and worked up in the usual way. A large volume of CH_2Cl_2 was used for extraction due to the poor solubility of the product. After trituration with CCl_4 1.95 g (4.06 mmole) 22 was isolated. mp 142.3°C (dec). In some runs the mp was 125-130°C but the spectral data was the same; nmr see Table 6.

Preparation of the Dimesylate 23 from the diendo diol 21.

The procedure used to prepare the diexo dimesylate 22 was repeated using 1.4 g (4.32 mmole) 21. The volume of CH_2Cl_2 used for the reaction was reduced to 50 ml since the diendo diol was much more soluble than the diexo isomer. The product did not precipitate during the reaction. After the usual workup 0.5 g (1.04 mmole) 23 was isolated. The yield could not be improved. mp 118-21°C (dec), nmr see Table 6.

Preparation of 1,5-Dimethyl-2,6-dibromosemibullvalene

(Ic)

To a solution of 27 g (.18 mmole) NaI in 120 ml dry acetone, 4.0g (8.3 mmole) diexo dimesylate 22 was added in portions. The solution turned cloudy and yellow. It was stirred at room temperature in the dark for 60 hours at which time it was very dark brown. The reaction mixture was poured onto ice-H_2O-$NaHSO_3$ at which time all the color disappeared. After the standard workup approximately 5 ml methaol was added to the crude oil. After 1.5 hours in the freezer, 1.2 g (4.1 mmole) Ic was isolated as a colorless solid. mp 63 = 5°C (cloudy until 90°C). A second crop of 373 mg (1.27 mmole) Ic was isolated from the filtrate after several weeks in the freezer. The compound had to be stored in the dark, in the freezer, under argon or nitrogen. The nmr data are listed and discussed in chapter 2.

Isolation of Diiodides from Above Reaction

If the reaction described above was stopped after 24 hours a white crystalline solid could be isolated by precipitation in CH_2Cl_2-hexanes or methanol. It appeared to be a mixture of the endo-endo and endo-exo diiodides 25 and 26. Two very close spots were seen on TLC. mp 125-9°C (dec); nmr data listed in Table 6.

Preparation of Dimethyl Ether of 1 (13)

A diazomethane solution was prepared as follows: To a cold mixture of 100 ml of 40% KOH and 100 ml diethyl ether, 2.5 g (25 mmole) N-nitroso-N-methylurea was added. The mixture was stirred in an ice-salt bath for 1.5 hour. The ether was decanted into a clean dry flask containing KOH pellets. The etheral solution of CH_2N_2 was added to a solution of 2 g (5.0 mmole) enol ester 1 in 45 ml THF and the mixture stirred at 0°C. After allowing the solution to warm to room temperature, the excess CH_2N_2 was destroyed by the careful addition of 10% acetic acid in ether. Solid $NaHCO_3$ and $MgSO_4$ were added to the ether solution, it was filtered and the ether evaporated *in vacuo*. After trituration with methanol, 1.2 g (2.8 mmole) 13 was isolated. m.p. 158-62; nmr see Table 5.

Preparation of Diacetate Derivative of 1 (12)

A solution of 2.0 g (5 mmole) 1 and 20 ml acetic anhydride were stirred in an 85-90°C oil bath. A small amount of TsOH was added and the reaction kept at 80°C overnight. It was cooled and poured into ice-H_2O-NaOH and extracted with CH_2Cl_2. After the usual workup 1.0 g (2.08 mmole) 12 was isolated, mp 135-9. nmr see Table 5.

Preparation of Dimesylate of 1 (11)

A solution of 1.0 g (2.5 mmole) 1, 1.4 ml (10 mmole) triethylamine and 20 ml CH_2Cl_2 was chilled in an ice bath. A solution 0.7 ml (10 mmole) methanesulfonyl chloride in 3 ml CH_2Cl_2 was added over a period of 15 minutes. A precipitate formed. The reaction was stirred at room temperature for one hour after which it was worked up in the usual way. After several triturations with methanol 0.6 g (1.01 mmole) 11 was isolated, mp 132-4; nmr, see Table 5.

Preparation of the Dimethyl Ether of 2 (15)

Compound 15 was prepared from 2 following the same procedure as that used for the preparation of 13; see Table 5.

Preparation of Diacetate Derivative of 2 (14)

The diacetate 14 was prepared from 2 following the same procedure as that used for the preparation of 12; nmr see Table 5.

Appendix A

Final Atomic Parameters for 1,5-dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene (<u>Ib</u>)*

Atom	X	Y	Z	B
O(1)	0.2931(4)	0.0307(2)	0.10421(9)	**
O(2)	0.1481(6)	0.1051(3)	0.17882(14)	**
O(3)	0.2959(4)	0.5598(2)	0.01639(8)	**
O(4)	0.0980(5)	0.5909(3)	0.08791(10)	**
O(5)	0.7063(4)	0.6366(2)	0.18634(9)	**
O(6)	0.5852(5)	0.6692(2)	0.10258(9)	**
O(7)	0.7451(4)	0.1931(2)	0.24313(8)	**
O(8)	0.6240(6)	0.0517(2)	0.18670(11)	**
C(1)	0.5648(5)	0.2555(3)	0.10356(11)	**
C(2)	0.3636(6)	0.2363(3)	0.12840(15)	**
C(3)	0.2375(5)	0.3400(3)	0.1168(12)	**
C(4)	0.3384(5)	0.4272(3)	0.08934(12)	**
C(5)	0.5602(5)	0.3947(3)	0.08448(11)	**
C(6)	0.6162(6)	0.4645(3)	0.13633(12)	**
C(7)	0.6245(5)	0.3892(3)	0.17983(11)	**
C(8)	0.5902(6)	0.2651(3)	0.16509(12)	**
C(9)	0.6779(6)	0.1626(3)	0.07053(14)	**
C(10)	0.6786(6)	0.4259(3)	0.03395(12)	**
C(11)	0.2593(6)	0.1169(3)	0.14084(15)	**
C(12)	0.2319(6)	0.5366(3)	0.06607(13)	**
C(13)	0.6339(5)	0.6001(3)	0.13845(13)	**
C(14)	0.6526(6)	0.1578(3)	0.19845(13)	**
C(15)	0.1974(9)	-0.0876(4)	0.11422(19)	**
C(16)	0.1934(8)	0.6576(3)	-0.01244(15)	**
C(17)	0.7238(8)	0.7684(3)	0.19454(16)	**
C(18)	0.8173(6)	0.0947(3)	0.27782(13)	**
H(3)	0.093	0.347	0.1278	4.0
H(7)	0.652	0.418	0.2177	4.0
H(9)A	0.668	0.079	0.0884	5.0
B	0.823	0.186	0.0677	5.0
C	0.618	0.157	0.03333	5.0

H(10)A	0.667	0.516	0.0263	5.0
B	0.624	0.378	0.0025	5.0
C	0.824	0.404	0.0395	5.0
H(15)A	0.232	-0.146	0.0843	9.0
B	0.048	-0.076	0.1157	9.0
C	0.246	0.122	0.1496	9.0
H(16)A	0.254	0.667	-0.0493	8.0
B	0.208	0.737	0.0081	8.0
C	0.047	0.637	-0.0160	8.0
H(17)A	0.779	0.785	0.2316	8.0
B	0.588	0.807	0.1911	8.0
C	0.816	0.804	0.1666	8.0
H(18)A	0.885	0.131	0.3104	6.0
B	0.915	0.043	0.2574	6.0
C	0.701	0.043	0.2896	6.0

* Standard Deviations are in paranthesis

** Anisotropic thermal parameters are given in the next table.

Appendix A'

Final Anisotropic Thermal Parameters for 1,5-dimethyl-2,4,6,-8-tetracarbomethoxysemibullvalene (Ib)^{a,*}

Atom	B11X10^4	B22X10^4	B33X10^5	B12X10^4	B13X10^4	B23X10^5
O(1)	370(9)	95(2)	208(5)	-74(4)	0.(2)	-31(9)
O(2)	600(13)	142(4)	370(8)	-100(7)	82(3)	-22(15)
O(3)	387(8)	98(2)	147(4)	48(4)	-16(2)	49(8)
O(4)	334(8)	139(3)	247(5)	94(5)	7(2)	70(12)
O(5)	359(8)	60(2)	181(4)	-7(3)	-10(2)	-19(7)
O(6)	404(9)	70(2)	206(5)	-7(4)	-12(2)	93(9)
O(7)	279(6)	80(2)	157(4)	-2(3)	-13(1)	78(7)
O(8)	553(12)	64(3)	272(5)	-18(4)	-50(2)	51(9)
C(1)	207(8)	59(3)	127(5)	3(4)	-3(2)	-15(10)
C(2)	256(10)	71(3)	243(7)	-11(5)	18(2)	60(13)
C(3)	185(8)	86(3)	745(6)	3(5)	-5(2)	3(11)
C(4)	224(8)	71(3)	141(5)	14(5)	-4(2)	33(11)
C(5)	204(8)	63(3)	117(5)	-5(4)	0(2)	14(10)
C(6)	325(11)	62(3)	140(5)	-11(5)	6(2)	2(11)
C(7)	225(8)	59(3)	126(5)	-3(4)	-5(2)	-3(10)
C(8)	305(10)	60(3)	138(5)	14(5)	-11(2)	4(10)
C(9)	304(11)	77(3)	197(7)	8(5)	8(2)	-79(12)
C(10)	275(10)	91(3)	149(5)	3(5)	6(2)	43(11)
C(11)	310(11)	79(3)	216(7)	-23(6)	8(3)	23(14)
C(12)	250(9)	83(3)	159(6)	0(6)	-12(2)	3(12)
C(13)	225(9)	63(3)	174(6)	-10(5)	6(2)	34(12)
C(14)	274(10)	66(3)	158(6)	5(5)	-6(2)	51(12)
C(15)	521(19)	122(5)	367(12)	-130(9)	4(4)	-75(19)
C(16)	481(16)	97(4)	228(8)	50(7)	-36(3)	93(15)
C(17)	464(15)	60(3)	273(8)	-47(6)	-7(3)	-60(13)
C(18)	297(11)	111(4)	189(6)	8(6)	-13(2)	177(14)

The anisotropic temperature factor has the form exp. (-(h^2 B11 + K^{2}B22 - 1^{2}B33 + 2hK B12 + 2hl B13 + 2kl B23))

(a) atoms labeled as in Figure 2; * std. dev. in parenthesis

Appendix B

Optimized Geometry for Unsubstituted Semibullvalene - G. S.

```
        SEMIB-GS

 HEAT OF FORMATION                      7[illegible].[illegible]565[illegible] KCAL/MOLE
 IONIZATION POTENTIAL                    9.28783 EV
 DIPOLE MOMENT                          0.05[illegible]3[illegible] DEBYE

  ATOM     ATOMIC    BOND LENGTH    BOND ANGLE    TWIST ANGLE
 NUMBER    NUMBER    (ANGSTROMS)    (DEGREES)      (DEGREES)
   I                     J I          K J I         L K J I      J     K     L

   1         6
   2         6      [illegible] *                                 1
   3         6      1.3[illegible] *  1[illegible]4.5[illegible] *                     2     1
   4         6      3.1697  *      74.856  *    -0.6[illegible]4 *      3     2     1
   5         6      1.5[illegible]2[illegible] *  110.555 *    -39.741  *      1     4     [illegible]
   6         6      [illegible] *  [illegible] *      5.375  *      4     1     5
   7         6      1.5[illegible] *  [illegible] *  [illegible] *      [illegible]     [illegible]     [illegible]
   8         6      1.5427  *     105.578  *     -8.481  *      7     [illegible]     [illegible]
   9         1      [illegible] *  [illegible] *  1[illegible].523 *      3     2     5
  10         1      [illegible]        [illegible]        [illegible] *      4     1     5
  11         1      1.0[illegible]26  *     127.6[illegible]6 *     -1.0[illegible] *      [illegible]     [illegible]     5
  12         1      [illegible]        127.626         0.902  *      1     4    10
  13         1      [illegible] *  [illegible] *  [illegible] *      [illegible]     3     [illegible]
  14         1      1.0[illegible]33       116.7[illegible]4 *   -[illegible] *      [illegible]     [illegible]    10
  15         1      [illegible] *     114.602  *     38.597  *      [illegible]     [illegible]    1[illegible]
  16         1      [illegible] *  1[illegible].1[illegible] *     12.5[illegible] *      [illegible]     7    13
```

Appendix B-2

Optimized Geometry for Unsubstituted Semibullvalene - Homoconjugated State

```
          SEMIB-TS-CI

LOWEST EIGENVALUES - HEATS OF FORMATION IN KCAL/MOLE

          1           2
     77.934     154.896

IONIZATION POTENTIAL                      6.88211  EV
DIPOLE MOMENT                             0.33622  DEBYE

 ATOM     ATOMIC    BOND LENGTH     BOND ANGLE   TWIST ANGLE
NUMBER    NUMBER    (ANGSTROMS)     (DEGREES)     (DEGREES)
   I                    J I           K J I        L K J I        J     K     L

   1        6
   2        6          2.4580 *                                   1
   3        6          1.3929 *      114.658 *                    2     1
   4        6          3.7169 *       64.535 *    -1.764 *        3     2     1
   5        6          1.5121 *      111.262 *   -40.627 *        1     4     3
   6        6          1.4049 *      111.002 *     1.565 *        4     1     5
   7        6          2.4580        115.483 *    -0.710 *        6     4     3
   8        6          1.5092 *      111.244 *     4.901 *        7     3     2
   9        1          1.0855 *      124.651 *   176.458 *        3     2     5
  10        1          1.0855        124.693     180.823 *        4     1     5
  11        1          1.0816 *      126.495 *    -0.737 *        2     3     9
  12        1          1.0816        126.455       3.207 *        1     4    10
  13        1          1.0810 *      126.205 *     3.748 *        7     3     5
  14        1          1.0810        126.209      -1.780 *        6     4    10
  15        1          1.1045 *      113.466 *    55.260 *        5     1    12
  16        1          1.1062 *      113.023 *    53.923 *        8     7    13
```

Appendix B-3

Optimized Geometry for 2,4,6,8-Tetracyanosemibullvalene - GS

```
HEAT OF FORMATION                    [illegible] KCAL/MOLE
IONIZATION POTENTIAL                 10.[illegible] EV
DIPOLE MOMENT                         0.80057 DEBYE

 ATOM    ATOMIC    BOND LENGTH   BOND ANGLE   TWIST ANGLE
NUMBER   NUMBER    (ANGSTROMS)   (DEGREES)    (DEGREES)
   I                    J I        K J I       L K J I

   1       6
   2       6        1.4459 *                                1
   3       6        1.3629 *    105.285 *                   1    2
   4       6        [illegible] *  74.846 *      -0.037 *   3    2    1
   5       6        [illegible] *  [illegible] * [illegible] *  1    4    3
   6       6        1.5078 *    111.889 *        5.[illegible] *  [illegible]  1  [illegible]
   7       6        1.[illegible] *  120.316 *  -0.168 *    6    4  [illegible]
   8       6        [illegible] *  [illegible] *  -6.556 *  7    3    2
   9       6        1.4[illegible] *  [illegible] *  -1[illegible] *  [illegible]  [illegible]  [illegible]
  10       6        1.4166 *    126.908 *      173.410 *  [illegible]  [illegible]  [illegible]
  11       6        [illegible] *  [illegible] *  1[illegible] *  1    4    6
  12       6        1.4[illegible] *  [illegible] *  1[illegible] *  [illegible]  4    1
  13       7        1.1610 *    180.000        180.000    [illegible]  [illegible]  [illegible]
  14       7        1.1620 *    180.000        180.000     10    2    6
  15       7        [illegible] *  [illegible]  [illegible]   11    1    7
  16       7        1.1610 *    180.000        180.000    1[illegible]  [illegible]  [illegible]
  17       1        1.1[illegible] *  115.100 *  -215.708 *  [illegible]  [illegible]  [illegible]
  18       1        [illegible] *  [illegible] *  -0.075 *  8    5   17
  19       1        1.0[illegible] *  [illegible] *  -[illegible] *  [illegible]  [illegible]  1[illegible]
  20       1        1.0851 *    126.888 *        3.238 *    4    1   11
```

Appendix B-4

Optimized Geometry for 2,4,6,8-Tetracyanosemibullvalene-Homoconjugated State

```
  ATOM    ATOMIC        BOND LENGTH         BOND ANGLE           TWIST ANGLE
 NUMBER   NUMBER       (ANGSTROMS)         (DEGREES)            (DEGREES)
   (I)                   (I-NA)             (I-NA-NB)          (I-NA-NB-NC)      NA          NB          NC
    1       6
    2       6         2.50423  *                                                  1
    3       6         1.40406  *        114.79457  *                              2           1
    4       6         2.[illegible]186  *        [illegible]  *       -1.39191  *       3           2           1
    5       6         1.51875  *        110.76190  *       [illegible]  *       1           4           3
    6       6         1.40[illegible]71  *        111.64702  *       [illegible]  *       2           1           [illegible]
    7       6         [illegible]            116.12195  *        -0.67302  *       6           4           [illegible]
    8       6         1.519[illegible]8  *        110.08[illegible]  *       [illegible]  *       7           3           2
    9       6         1.41283  *        126.06584  *       [illegible]  *       [illegible]           3           2
   10       6         1.41[illegible]  *        125.17918  *        172.44063  *       2           [illegible]           7
   11       6         1.41[illegible]           [illegible]          [illegible]  *       1           4           6
   12       6         1.41283           126.06[illegible]          [illegible]  *       [illegible]           4           1
   13       7         1.16194           180.00000           180.00000          [illegible]           [illegible]           1
   14       7         1.16186           180.00000           180.00000         10           [illegible]           [illegible]
   15       7         1.16189           180.00000           180.00000         11           1           7
   16       7         1.16191           180.00000           180.00000         12           [illegible]           [illegible]
   17       1         1.10[illegible]  *        114.17856  *      -231.50910  *       5           [illegible]           [illegible]
   18       1         1.10[illegible]  *        11[illegible]  *       [illegible]  *       8           5          17
   19       1         1.08059           124.26967           [illegible]          [illegible]           2          10
   20       1         1.0[illegible]           124.25369            4.14268          4           1          11
```

Appendix B-5

Optimized Geometry for 2,4-Dicyanosemibullvalene - G. S.

[illegible]

```
HEAT OF FORMATION                    134.54412 KCAL/MOLE
IONIZATION POTENTIAL                  10.1[illegible] EV
DIPOLE MOMENT                          2.[illegible] DEBYE
```

ATOM NUMBER I	ATOMIC NUMBER	BOND LENGTH (ANGSTROMS) J I	BOND ANGLE (DEGREES) K J I	TWIST ANGLE (DEGREES) L K J I	J	K	L
1	6						
2	6	2.4436 *			1		
3	6	1.3[illegible] *	1[illegible]5.[illegible]3 *		2	1	
4	6	[illegible].14[illegible] *	7[illegible].[illegible] *	[illegible].1[illegible] *	[illegible]	[illegible]	1
5	6	1.5314 *	110.968 *	-38.754 *	1	[illegible]	[illegible]
6	6	1.4[illegible] *	11[illegible].7[illegible] *	8.689 *	4	1	5
7	6	1.5[illegible] *	[illegible] *	-[illegible] *	6	4	3
8	6	1.5557 *	10[illegible].[illegible]57 *	-[illegible] *	[illegible]	[illegible]	[illegible]
9	6	1.4342 *	115.735 *	-149.820 *	7	3	2
10	6	1.41[illegible] *	[illegible] *	1[illegible]4.[illegible] *	2	3	7
11	7	1.1610 *	180.000	180.000	[illegible]	[illegible]	1
12	7	1.162[illegible] *	180.000	180.000	10	[illegible]	[illegible]
13	1	1.1[illegible] *	114.[illegible]3 *	-215.723 *	5	2	3
14	1	1.0[illegible] *	[illegible] *	-[illegible]4 *	[illegible]	[illegible]	1[illegible]
15	1	1.0850 *	127.230 *	-2.646 *	[illegible]	[illegible]	1[illegible]
16	1	1.[illegible] *	1[illegible]17 *	1[illegible]4.853 *	4	1	5
17	1	1.0[illegible] *	1[illegible] *	1.[illegible] *	1	4	16
18	1	1.0940 *	11[illegible].47[illegible] *	-[illegible]7.[illegible] *	[illegible]	[illegible]	1[illegible]

Appendix B-6

Optimized Geometry for 2,4-Dicyanosemibullvalene - Homoconjugated State

```
            SEMIBCNIMTAD.CT

LOWEST EIGENVALUES - HEATS OF FORMATION IN KCAL/MOLE
       1            2
   143.352      221.954

IONIZATION POTENTIAL                8.66533 EV

DIPOLE MOMENT                       4.03533 DEBYE

 ATOM    ATOMIC    BOND LENGTH    BOND ANGLE   TWIST ANGLE
NUMBER   NUMBER    (ANGSTROMS)    (DEGREES)     (DEGREES)
   I                  J I          K J I        L K J I       J     K     L

   1       6
   2       6        2.3886                                    1
   3       6        1.4084       116.437                      2     1
   4       6        1.6051        62.347        -0.352        3     2     1
   5       6        1.5061      110.988 *     -42.628 *       1     4     3
   6       6        1.4049      110.653 *       1.834         4     1     5
   7       6        2.3556       116.432        0.719 *       6     4     2
   8       6        1.4444      111.718 *       4.113         7     3     2
   9       6        1.4115       124.425     -175.558         2     3     4
  10       6        1.4149       125.045      175.074         2     3     4
  11       7        1.1601 *     180.000      180.000         9     7     1
  12       7        1.1602 *     180.000      180.000        10     4     5
  13       1        1.1019 *     115.950     -232.482         8     4     4
  14       1        1.1045 *     114.045        0.484         8     5    13
  15       1        1.0845 *     125.431       -4.050 *       3     2    10
  16       1        1.0845 *     125.124      180.144 *       4     1    16
  17       1        1.0859 *     126.156        3.903         1     4    16
  18       1        1.0909 *     125.305       -3.788         6     4    16
```

Appendix B-7

Optimized Geometry for 3,7-Dicyanosemibullvalene - G. S.

```
            [illegible]-MIND

  HEAT OF FORMATION                      130.28423 KCAL/MOLE
  IONIZATION POTENTIAL                   1[illegible] EV
  DIPOLE MOMENT                          [illegible] DEBYE

  ATOM    ATOMIC    BOND LENGTH    BOND ANGLE    TWIST ANGLE
 NUMBER   NUMBER   (ANGSTROMS)    (DEGREES)     (DEGREES)
   (I)               (I-J)         (I-J-K)      (I-J-K-L)        J      K      L

   1        6
   2        6        2.4289 *                                    1
   3        6     [illegible] *   [illegible] *                  2      1
   4        6     [illegible]     [illegible]   [illegible] *    [illegible]  2  1
   5        6        1.5326       111.062       -[illegible]     [illegible]  [illegible]  [illegible]
   6        6     1.[illegible] * 110.476 *      7.468 *         [illegible]  1  5
   7        6     [illegible]     [illegible]   [illegible] *    [illegible]  4  3
   8        6        1.5431       105.834       -[illegible]     [illegible]  [illegible]  [illegible]
   9        6     1.4[illegible] * 127.141 *    175.453          [illegible]  [illegible]  [illegible]
  10        6     [illegible] *   [illegible] * [illegible] *    4      1      5
  11        7     [illegible]     [illegible]   [illegible]      [illegible]  [illegible]  [illegible]
  12        7        1.1615 *     180.000       180.000         10      4      [illegible]
  13        1     [illegible] *   [illegible] * [illegible] *    7      3      9
  14        1     1.0[illegible]  [illegible]   -[illegible] *   [illegible]  4  1[illegible]
  15        1        1.0833       127.594       -1.[illegible]   [illegible]  [illegible]  [illegible]
  16        1     1.[illegible]   127.594         1.549 *        1      4     10
  17        1     [illegible]     [illegible] * [illegible] *    [illegible]  1  16
  18        1        1.0855       120.776       -[illegible]     [illegible]  [illegible]  [illegible]
```

Appendix B-8

Optimized Geometry for 3,7-Dicyanosemibullvalene - Homoconjugated State

```
          [illegible]

LOWEST EIGENVALUES - HEATS OF FORMATION IN KCAL/MOLE
    140.068   [illegible]

IONIZATION POTENTIAL                  [illegible] EV
DIPOLE MOMENT                         3.4[illegible] DEBYE

 ATOM     ATOMIC     BOND LENGTH     BOND ANGLE    TWIST ANGLE
NUMBER    NUMBER    (ANGSTROMS)      (DEGREES)     (DEGREES)
  (I)                   NA I           NB NA I     NC NB NA I     NA    NB    NC

   1         6
   2         6        2.3742                                        1
   3         6        [illegible]     115.478                       2     1
   4         6        [illegible]     [illegible]   [illegible]     [illegible]  [illegible]  1
   5         6        1.5056          111.259       [illegible]     [illegible]  [illegible]  [illegible]
   6         6        [illegible]     [illegible]   2.131           4     1     [illegible]
   7         6        [illegible]     [illegible]   [illegible]     [illegible]  4     3
   8         6        1.5159          [illegible]   [illegible]     [illegible]  [illegible]  [illegible]
   9         6        [illegible] *   125.473 *     176.265         3     2     5
  10         6        [illegible] *   [illegible] * [illegible]     4     1     5
  11         7        1.1615 *        180.000       [illegible]     [illegible]  [illegible]  [illegible]
  12         7        1.1616 *        180.000       180.000         10    4     [illegible]
  13         1        [illegible] *   [illegible] * 2.269           7     3     9
  14         1        [illegible] *   [illegible] * [illegible]     [illegible]  4     [illegible]
  15         1        1.0828 *        126.471 *     -2.913          [illegible]  [illegible]  [illegible]
  16         1        [illegible] *   [illegible] * 7.317           1     4     10
  17         1        [illegible] *   [illegible] * [illegible] *   5     1     16
  18         1        1.1004 *        [illegible] * [illegible] *   [illegible]  [illegible]  17
```

Appendix B-9

Optimized Geometry for 2,6-Dicyanosemibullvalene - G. S.

```
                  [illegible]

   HEAT OF FORMATION                  [illegible]4.32774 KCAL/MOLE
   IONIZATION POTENTIAL                1C.18595 EV
   DIPOLE MOMENT                       [illegible] DEBYE

   ATOM     ATOMIC      BOND LENGTH      BOND ANGLE     TWIST ANGLE
  NUMBER    NUMBER      (ANGSTROMS)      (DEGREES)      (DEGREES)
    I                        J I             K J I          L K J I        J      K      L

    1         6
    2    [illegible]   [illegible]     *                                    1
    3         6        1.[illegible]   *  [illegible]   *                   2      1
    4         6        3.1484          *  74.[illegible] *  -C.1[illegible] *  [illegible] [illegible] 1
    5    [illegible]   1.543C          *  11C.261       *  -38.601       *  1      4   [illegible]
    6    [illegible]   1.[illegible]   *  [illegible]   *  [illegible]   *  4      1      5
    7         6        1.5830          *  [illegible]   *  -C.[illegible] * [illegible] [illegible] [illegible]
    8    [illegible]   1.[illegible]42 *  1C5.453       *  -7.049        *  7  [illegible] [illegible]
    9    [illegible]   1.[illegible]   *  [illegible]   *  -149.641      *  7      3      2
   10         6        1.4[illegible]  *  [illegible]   *  [illegible]   *  1  [illegible] [illegible]
   11         7        1.1612          *  1EC.CCC          180.000         [illegible] [illegible] 1
   12    [illegible]   1.[illegible]   *  [illegible]      1EC.C00         10     1      7
   13         1        1.[illegible]   *  [illegible]   *  -[illegible]  *  [illegible] 2  3
   14         1        1.0862          *  [illegible]      -C.[illegible] * [illegible] [illegible] [illegible]
   15         1        1.C[illegible]  *  121.795       *  27.483        *  3      7      9
   16         1        1.[illegible]   *  [illegible]   *  1.[illegible] *  4      1     1C
   17         1        1.0829          *  1[illegible]  *  -1.[illegible] * [illegible] [illegible] [illegible]
   18         1        1.C[illegible]36 * 116.252       *  -27.268       *  [illegible] [illegible] [illegible]
```

Appendis B-10

Optimized Geometry for 2,6-Dicyanosemibullvalene-Homoconjugated State

```
          SEMIBCNOPP

LOWEST EIGENVALUES - HEATS OF FORMATION IN KCAL/MOLE
       1          2
    134.126    204.938

IONIZATION POTENTIAL                  7.73241 EV
DIPOLE MOMENT                         0.33556 DEBYE

 ATOM    ATOMIC    BOND LENGTH    BOND ANGLE    TWIST ANGLE
NUMBER   NUMBER   (ANGSTROMS)     (DEGREES)      (DEGREES)
  I                   J I          K J I          L K J I       J     K     L

  1        6
  2        6        2.5156 *                                    1
  3        6        1.3929 *     116.753 *                      2     1
  4        6        3.7934 *      63.359 *       -0.422 *       3     2     1
  5        6        1.5189       110.970        -37.009         1     4     3
  6        6        1.3901 *     110.627 *        4.134 *       4     1     5
  7        6        2.5155       117.834 *        0.055 *       6     4     3
  8        6        1.5202       110.412          6.029 *       7     3     2
  9        6        1.4120 *     125.762       -173.348 *       7     3     2
 10        6        1.4133 *     125.773        185.518 *       1     4     6
 11        7        1.1610 *     180.000        180.000         9     7     1
 12        7        1.1620 *     180.000        180.000        10     1     7
 13        1        1.1088 *     112.403 *     -234.812 *       5     2     3
 14        1        1.1083 *     112.447 *       -0.601 *       8     5    13
 15        1        1.0855 *     124.572 *        3.961 *       3     7     9
 16        1        1.0855 *     124.526 *        3.806 *       4     1    10
 17        1        1.0817 *     126.508 *       -2.563         2     3    15
 18        1        1.0807 *     126.438 *       -2.028         6     4    16
```

Appendix B-11

Optimized Geometry for Diazasemibullvalene - G. S.

```
                  DIAZASEMIBULLVALENE  GS

HEAT OF FORMATION                     113.91641 KCAL/MOLE
IONIZATION POTENTIAL                    9.20457 EV
DIPOLE MOMENT                           3.18138 DEBYE

  ATOM    ATOMIC    BOND LENGTH     BOND ANGLE    TWIST ANGLE
 NUMBER   NUMBER    (ANGSTROMS)     (DEGREES)      (DEGREES)
   I                    J I           K J I         L K J I      J     K     L

   1        6
   2        6        2.3486 *                                    1
   3        6        1.3607 *     106.349 *                      2     1
   4        6        3.1534 *      73.373 *      -0.338 *        3     2     1
   5        7        1.4849 *     111.100 *     -40.339 *        1     4     3
   6        6        1.4974 *     107.595 *       5.401 *        4     1     5
   7        6        1.5369 *     122.664 *      -0.241 *        6     4     3
   8        7        1.5172 *     104.107 *      -7.541 *        7     3     2
   9        1        1.0803 *     128.675 *     177.243 *        3     2     5
  10        1        1.0803       128.675       181.265 *        4     1     5
  11        1        1.0835 *     131.425 *      -1.877 *        2     3     9
  12        1        1.0835       131.425         0.866 *        1     4    10
  13        1        1.0971 *     117.190 *      35.007 *        7     3     9
  14        1        1.0971       116.734       -34.281 *        6     4    10
```

Appendix B-12

Optimized Geometry for Diazasemibullvalene (Diazapentalene) Homoconjugated State

```
                DIAZSEMIB-TS-

HEAT OF FORMATION                  101.40161 KCAL/MOLE
IONIZATION POTENTIAL                 7.15126 EV
DIPOLE MOMENT                        0.03115 DEBYE

 ATOM    ATOMIC    BOND LENGTH    BOND ANGLE    TWIST ANGLE
NUMBER   NUMBER    (ANGSTROMS)    (DEGREES)     (DEGREES)
  I                    J I          K J I         L K J I       J     K     L

  1        6
  2        6        2.6525 *                                   1
  3        6        1.4094 *      125.941 *                    2     1
  4        6        2.2572 *       94.121 *      -0.454 *      3     2     1
  5        7        1.4080 *      106.115 *       0.145 *      1     4     3
  6        6        1.4142 *      108.674 *      -0.855 *      4     1     5
  7        6        2.6525        125.767 *       0.114 *      6     4     3
  8        7        1.4044 *      106.521 *       0.591 *      7     3     2
  9        1        1.0813 *      125.812 *     178.921 *      3     2     5
 10        1        1.0813        125.812       180.203 *      4     1     5
 11        1        1.0785 *      132.500 *      -0.632 *      2     3     9
 12        1        1.0785        132.500         1.031 *      1     4    10
 13        1        1.0784 *      132.223 *       0.582 *      7     3     9
 14        1        1.0784        132.205        -0.655 *      6     4    10
```

Appendix B-13

Optimized Geometry for 1,5-Methylenesemibullvalene - G. S.

```
                 [illegible]

HEAT OF FORMATION                     133.01208 KCAL/MOLE
IONIZATION POTENTIAL                    9.26479 EV
DIPOLE MOMENT                           0.14[illegible]71 DEBYE

  ATOM     ATOMIC     BOND LENGTH      BOND ANGLE       TWIST ANGLE
 NUMBER    NUMBER     (ANGSTROMS)      (DEGREES)        (DEGREES)
   I                     NA I           NB NA I         NC NB NA I      NA    NB    NC

   1         6
   2         6          2.4882 *                                         1
   3         6        [illegible] *    [illegible] *                     2     1
   4         6          3.2069 *       74.806 *         -0.149 *         3     2     1
   5         6          1.5098 *      109.538 *        -36.460 *         1     4   [illegible]
   6         6        [illegible] *    [illegible] *      8.328 *         4     1     5
   7         6        [illegible] *    [illegible] *    -0.1[illegible] * 6     4   [illegible]
   8         6          1.5080 *      104.977 *         -8.028 *         7   [illegible] [illegible]
   9         6        [illegible] *     96.843 *        146.896 *         5     8     6
  10         1        [illegible] *    [illegible] *   [illegible] *     3     2     5
  11         1          1.0831        [illegible]      [illegible] *     4     1   [illegible]
  12         1          1.0822 *      127.973 *         -0.491 *         2     3    10
  13         1        [illegible]      [illegible]      [illegible] *    1     4    11
  14         1          1.0926 *      117.066 *        [illegible] *  [illegible] [illegible] 10
  15         1          1.0926        117.086          -25.974 *         6   [illegible] 11
  16         1        [illegible] *    [illegible] *    110.067 *         9     5     8
  17         1        [illegible] *    [illegible] *   [illegible] *  [illegible] [illegible] [illegible]
```

Appendix B-14

Optimized Geometry for 1,5-Methylenesemibullvalene - Homoconjugared State

```
          SEMIB-TS-CYCPROP

LOWEST EIGENVALUES - HEATS OF FORMATION IN KCAL/MOLE
        1          2
     127.654    200.875

IONIZATION POTENTIAL                    6.93939 EV
DIPOLE MOMENT                           0.45243 DEBYE

  ATOM    ATOMIC     BOND LENGTH     BOND ANGLE    TWIST ANGLE
 NUMBER   NUMBER    (ANGSTROMS)     (DEGREES)      (DEGREES)
   I                    J I           K J I         L K J I       J      K      L

   1        6
   2        6          2.4692 *                                   1
   3        6          1.3967 *     116.301 *                     2      1
   4        6          3.7775 *      63.322 *     -1.074 *        3      2      1
   5        6          1.4734 *     109.605 *    -36.324 *        1      4      3
   6        6          1.4041 *     113.400 *      0.628 *        4      1      5
   7        6          2.4692       116.373 *     -1.324 *        6      4      3
   8        6          1.4727 *     109.074 *      0.489 *        7      3      2
   9        6          1.5356 *      57.331 *    118.844 *        5      8      6
  10        1          1.0867       123.222      177.951 *        3      2      5
  11        1          1.0867       123.222      180.786 *        4      1      5
  12        1          1.0811       126.539 *      0.705 *        2      3     10
  13        1          1.0811       126.539       -2.262 *        1      4     11
  14        1          1.0909       126.499 *     -3.126 *        7      3     10
  15        1          1.0908       126.499        0.321 *        6      4     11
  16        1          1.0569 *     119.338 *    111.154 *        9      5      8
  17        1          1.0966 *     119.495 *    109.399 *        9      8      5
```

Appendix B-15

Optimized Geometry for 1,5-Dimethylenesemibullvalene - G.S.

```
          SEMIB-CYCB[illegible]

   HEAT OF FORMATION                       [illegible] KCAL/MOLE
   IONIZATION POTENTIAL                    9.34877 EV
   DIPOLE MOMENT                           [illegible] DEBYE

  ATOM     ATOMIC      BOND LENGTH      BOND ANGLE    TWIST ANGLE
 NUMBER    NUMBER      (ANGSTROMS)      (DEGREES)      (DEGREES)
   (I)                    NA:I           NB:NA:I      NC:NB:NA:I       NA      NB      NC

    1        6
    2        6        [illegible] *                                     1
    3        6        [illegible] *   [illegible] *               [illegible]  1
    4        6           3.1680 *       74.776 *     -0.281 *     [illegible] [illegible] 1
    5        6        [illegible] *    110.32[illegible] *  -38.785 *      1       4       3
    6        6        [illegible] *   [illegible] *  [illegible] *     4       1       5
    7        6           1.5774 *      121.597 *  [illegible] *  [illegible] [illegible] [illegible]
    8        6           1.5268 *      105.011 *     -8.261 *      7       3       2
    9        6        [illegible] *   [illegible] *  [illegible] *     5       8       6
   10        6           1.5113 *       91.497 *  [illegible] *  [illegible] [illegible] 1
   11        1           1.0832 *      126.755 *    175.424 *  [illegible] [illegible] [illegible]
   12        1        [illegible]     [illegible]     184.063 *      4       1       5
   13        1        [illegible] *   [illegible] *  [illegible] *  [illegible] [illegible] 11
   14        1           1.0822        127.596         0.964 *      1       4      [illegible]
   15        1        [illegible] *   [illegible] *     26.658 *      7       3      11
   16        1        [illegible]     [illegible]    [illegible] *     6       4      12
   17        1           1.1047 *   [illegible] *  [illegible] *  [illegible] [illegible] [illegible]
   18        1           1.1046 *      114.770 *   -117.148 *      9       5       8
   19        1           1.1047     [illegible]    [illegible] *    10       8       5
   20        1           1.1046        114.770    [illegible] *    10   [illegible] [illegible]
```

Appendix B-16

Optimized Geometry for 1,5-Dimethylenesemibullvalene-Homocinjugated State

```
                SEMIB-TS-CYCAUT

          LOWEST EIGENVALJES - HEATS OF FORMATION IN KCAL/MOLE
                1            2
             97.500     175.352

          IONIZATION POTENTIAL                6.93587 EV
          DIPOLE MOMENT                       0.23098 DEBYE

   ATOM    ATOMIC    BOND LENGTH    BOND ANGLE    TWIST ANGLE
  NUMBER   NUMBER    (ANGSTROMS)    (DEGREES)      (DEGREES)
    I                    J I          K J I         L K J I       J     K     L

    1        6
    2        6          2.4056 *                                  1
    3        6          1.3961 *     114.299 *                    2     1
    4        6          3.5860 *      64.550 *     -3.556 *       3     2     1
    5        6          1.5032 *     109.831      -43.960         1     4     3
    6        6          1.4026 *     112.813 *     -3.196         4     1     5
    7        6          2.4055       113.714 *     -1.814 *       6     4     3
    8        6          1.5149 *     111.797 *      0.310 *       7     3     2
    9        6          1.5440 *      89.011 *    123.995         5     8     6
   10        6          1.5432 *      89.198 *   -128.664         8     5     1
   11        1          1.0842       124.374      175.430         3     2     5
   12        1          1.0842       124.374      179.386         4     1     5
   13        1          1.0812       126.259       -3.001         2     3    11
   14        1          1.0812       126.258        0.203         1     4    12
   15        1          1.0816       125.885       -0.099 *       7     3    11
   16        1          1.0851       125.885       -2.450 *       6     4    12
   17        1          1.1046       114.397      118.375         9     5     8
   18        1          1.1046       114.682     -116.716         9     5     8
   19        1          1.1047       114.397      118.358        10     8     5
   20        1          1.1046       114.682     -115.803        10     8     5
```

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