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**Synthesis and investigations of 1,5 annulated semibullvalenes**

**Iyengar, Revathi, Ph.D.**

**City University of New York, 1987**

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SYNTHESIS AND INVESTIGATIONS  
OF  
1,5 ANNULATED SEMIBULLVALENES

by

REVATHI IYENGAR

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

1987

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The City University of New York

Abstract  
SYNTHESIS AND INVESTIGATIONS OF  
1,5 ANNULATED SEMIBULLVALENES

by

Revathi Iyengar

Adviser: Professor Klaus Grohmann

A new synthetic scheme was developed for annulating five-, six-, seven-, and eight membered rings at positions 1 and 5 of 2,4,6,8-tetracarbomethoxy semibullvalene. The previously synthesized 1,5-dimethyl-2,4,6,8-tetrakis (carbomethoxy) semibullvalene rearranges at 5°C (in solution) to the corresponding cyclooctatetraene. The activation energy for this process is 25 Kcal/mole, significantly lower than for the parent compound. None of the annulated semibullvalenes undergo the analogous rearrangement even on heating upto 200°C. However, the 1,5 cyclopentano and the 1,5 cyclohexano compounds absorb oxygen in both the solid state and in solution yielding well defined endoperoxides. None of the other compounds show an analogous reaction with oxygen. The X-ray structure determination of the 1,5 cyclohexano compound shows bond elongation of C2-C8 to 1.83 Å and a slight decrease in the non-bonded C4-C6 distance (2.19 Å) indicating the approach towards the symmetric transition state. The X-ray structure of the 1,5 cyclooctano compound however exhibited a degree of symmetry in the

semibullvalene part of the molecule, with C4-C6 = C2-C8 = 1.99 Å, and C2-C3 = C3-C4 = C6-C7 = C7-C8 = 1.387 Å. The free energy of activation for the Cope rearrangement in the 1,5 cyclohexano compound has been estimated to be  $3.8 \pm 0.4$  Kcal/mole at  $-160^\circ\text{C}$ . The room temperature CPDAS C-13 spectrum of the cyclooctano compound exhibited an averaged nmr spectrum for carbons 2,4,6, and 8. These results in combination with the X-ray data imply that the 1,5 cyclooctano compound is a neutral bishomoaromatic molecule. An alternative interpretation of dynamic behaviour in the solid state cannot be ruled out yet and further experiments such as low temperature solid state NMR studies need to be carried out.

A different approach was utilized towards the synthesis of 1,5-cyclopropa-2,6-dicyano semibullvalene starting from naphthalene. This route has so far led to bicyclo[3.3.0]deca-2,6-dicyano-2,6-diene, 37 (refer text). All attempts to generate the dianion of 37 have been unsuccessful. To assess the effect of an electron donor in positions 1 and 5 on the Cope rearrangement in semibullvalenes, MNDO studies have been carried out on the 1,5-dianion and 1,5-allyl bridged (cation, anion, and radical) semibullvalenes.

## ACKNOWLEDGEMENTS

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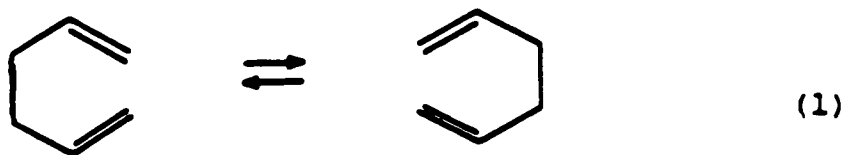
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1

CHAPTER 1  
INTRODUCTION

**BACKGROUND**

Molecules which undergo a rapid degenerate (3,3) sigmatropic shift (Cope rearrangement) have been of interest to experimental and theoretical organic chemists for a number of years. The rearrangement of 1,5-hexadiene is a prototype of this type of reaction (eqn 1) (1,2).

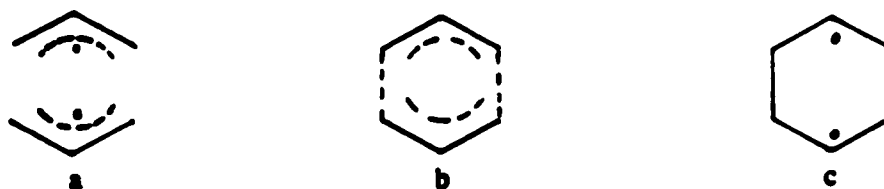


Three distinct mechanistic pathways have been considered for the rearrangement:

1. one in which the 3-4 bond is broken with the formation of two allyl radicals before the 1,6 bond is formed (a);
2. a concerted mechanism in which the bond making and

bond breaking occur simultaneously (b);

3. one in which the 1,6 bond is formed before the 3,4 bond is broken, leading to a cyclohexadiyl diradical (c);





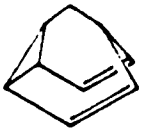

Gajewski (3) as well as others concluded that the nature of the transition state depends upon the substituents and geometric constraints present in the molecule. Dewar and Wade (4) carried out kinetic studies on 2-phenyl and 2,5-diphenyl 1,5-hexadienes and postulated a biradicaloid (type c) intermediate for this reaction. They found a 69 and 4900 times rate increase, when compared with the parent, respectively. MINDO/3 calculations also supported this hypothesis (5). Recently, Baldwin (6) has proposed this type of a transition state for the Cope rearrangement in 4-vinylcycloalkenes.

Among the various questions raised about the transition state of the Cope rearrangement, one that

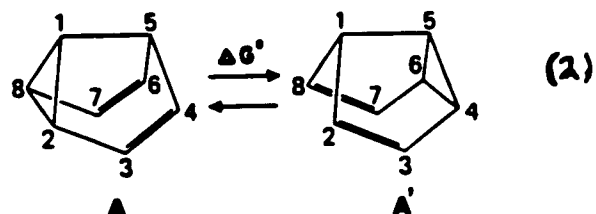
received considerable attention dealt with the chair/boat nature of the transition state. Doering (7) approached the problem from an experimental point of view while Hoffmann and Woodward (8) attacked it theoretically. Both studies led to the conclusions that the chair conformation is the preferred conformation of the transition state for the Cope rearrangement in molecules free of geometric constraints; however, in bridged cyclic compounds the rearrangement has to proceed via the boat transition state. Table 1 lists the free energies of activation for the Cope rearrangement of some bridged divinyl cyclopropanes.

Studies of the rate of the Cope rearrangement in 3,7-diphenylbarbaralane (9), 3-chloro- and 3-methoxy-6,8-dimethylbarbaralanes have discounted the 1,4-diyl transition state (10). 3,7-diphenyl substitution in the barbaralane series would have stabilized a 1,4-diyl transition state and the rate of Cope rearrangement should have increased. However a rate decrease was observed. Gajewski and others (11) have reasoned that the transition state for the Cope rearrangement in bridged polycyclic systems such as barbaralane and semibullvalene should involve more bond breaking than bond making since a bis allyl diradical would be more stable in these systems than the diyl alternative. A thermochemical argument rendered the 1,4-diyl alternative unlikely.

Table 1  $\Delta G^\ddagger$  for Scope Rearrangements

Compound	$\Delta G^\ddagger$ (kcal/mole)	ref.
 Homotropyliidene	13.6	7
 Bullvalene	12.8	8
 Barbarolane	7.8	8
 Semibullvalene	5.5	10

As shown in Table 1, semibullvalene has the lowest free energy of activation for the Cope rearrangement. Its Cope rearrangement is illustrated in Equation 2.



The potential energy diagram relating A to A' via a transition state (TS) is shown schematically in Figure 1.

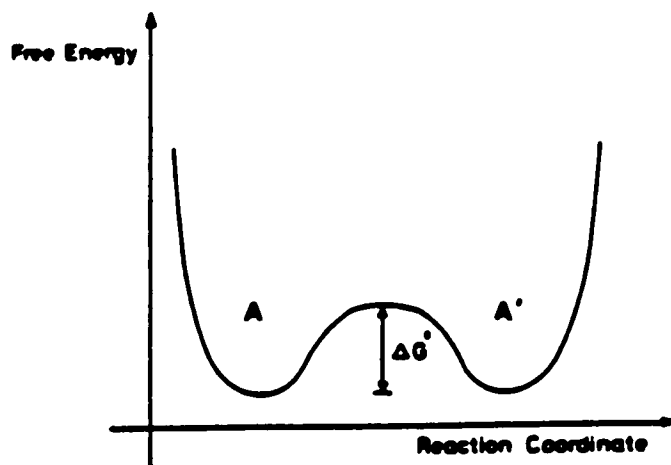
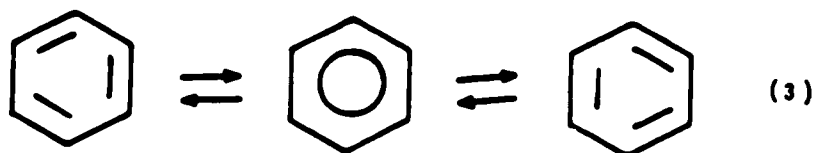


Figure 1. The potential energy curve shows a double-minimum

As stated by Hoffmann (22), "No great philosophical insight is required for the recognition that a lower activation energy can be achieved by destabilising the reactant or product, or by stabilising the TS or by some

combination of both."

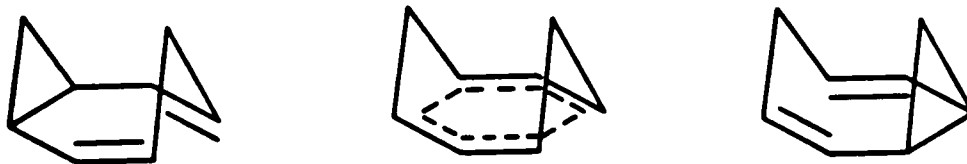
If one looks at the Kekule structures of benzene as the most extreme case of a rapidly rearranging cyclohexatriene system (Equation 3), then the proposed hypothetical "transition state", benzene itself, has a lower energy than either Kekule structure and thus, is the actual ground state of the molecule (22).



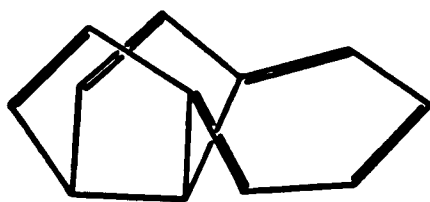
Prospects for changing the energy of the transition state relative to the ground state seemed most promising in the case of semibullvalene because it has the lowest activation energy for the Cope rearrangement. Assuming the concerted transition state, type (b) (page 2), a successful perturbation of the system could lead to the first neutral, homoaromatic molecule.

The concept of homoaromaticity was introduced into Organic Chemistry by Saul Winstein in 1967 (13). A homoaromatic molecule is defined as an aromatic system which retains its "aromatic" character even though its  $\sigma$ -backbone has been interrupted by interpolation of one or

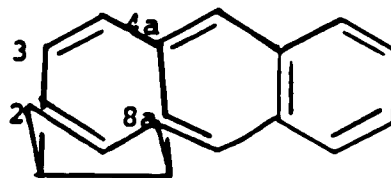
more atoms. For example, homotropyliene (a), would be considered a bishomobenzene (b) (see below).



The central problem in the characterization of a homoaromatic system is the assessment of the extent of the cyclopropane participation in lowering the energy of the system (15,14,16). One of the double bonds in the aromatic structure can be replaced by a cyclopropyl ring. A bishomoaromatic molecule has two methylene groups interspersed in an aromatic ring system. To date, no one has characterized a neutral bishomoaromatic molecule. However, there has been evidence for homoconjugative overlap (17, 18) between  $C_{4a}$  and  $C_{8a}$ , and even between  $C_2$  and  $C_3$  in compound B.



A



B

Very recently Paquette (19) reported thermo-chemical measurements on triquinacene which strongly indicate homoaromatic stabilization of this molecule relative to model compounds. However, this has been criticized by Schleyer et al. (20). The overlap integral between carbons C<sub>2</sub> and C<sub>8</sub> in molecule B was calculated from the X-ray data using a modification of the Mulliken procedure (18). The authors concluded that "mutually canted homoconjugated carbon atoms can still interact when separated by internuclear distances as large as 2.54 Å" (18). There has been some controversy concerning this conclusion (21).

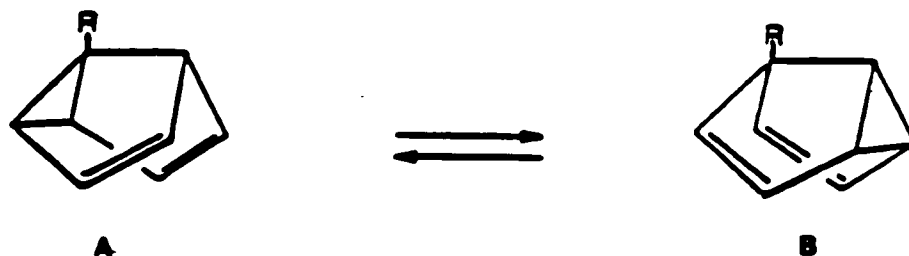
The transition state for the Cope rearrangement of semibullvalene could be described as a bishomoaromatic structure (22, 23), with the six electrons involved in the rearrangement delocalized among the six carbons. The amount of bond breaking at one end (C2-C8) is equal to the amount of bond making (C4-C6) at the other end of the molecule, i.e., C2-C8 equals C4-C6. An alternative transition state considered is the bis allyl type. The bond breaking is more advanced than the bond forming. The third possibility, the diyl transition state which involves bond formation between C4 and C6 before bond breaking is less likely because of molecular strain. Some bonding interaction between the ends of the bis allyl system (C2-C8) and (C4-C6) would still be possible. This

interaction would thus be the distinguishing feature between an allyl diradical type of a transition state and the symmetrical transition state.

The lowering of the energy of the transition state, regardless of its nature, such that the transition state geometry becomes the ground state has intrigued many chemists.

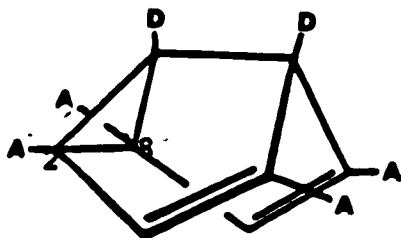
The problem was at first attacked by theoreticians in the early 1970's. Several different methods were used to calculate the geometries of ground and transition states for various substituted semibullvalenes and predictions were made concerning the energies of activation for the Cope rearrangement in these molecules. Dewar and Schoeller used MINDO/2 to study the Cope rearrangement in the bullvalene, barbaralene, semibullvalene series (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 Å apart. Since MINDO/2 overestimates the stability of cyclic compounds, the calculated energies of activation were thought to be somewhat low. In a later study by Dewar and Lo utilizing the data from MINDO/2 and applying an energy partitioning technique (23), they calculated an  $E_{act}$  of 3.6 Kcal/mole (23).

In a now classic study, Hoffmann and Stohrer used extended Huckel calculations to assess the effects of  $\pi$ -electron donating and withdrawing substituents on the ground state and transition state energies for the Cope rearrangement of semibullvalenes (22). They constructed a set of orbitals for semibullvalene by combining the Walsh orbitals of the cyclopropane and the orbitals of the penta-1,4-diene unit corresponding to the same geometry as the C3 to C7 portion of semibullvalene. This reconstruction revealed that the valence orbitals of semibullvalene compare well in symmetry with the Walsh orbitals in cyclopropane. Consider the rearrangement of A to B.



In A the substituent is on the cyclopropane ring, while in B it is on an "normal" tertiary carbon. If R is a  $\pi$  acceptor it will strengthen the 2-8 bond in A but will have little effect on B. Thus A should be more stable than B. Similarly if R is a donor it will weaken the 2-8 bond of A and shift the equilibrium to B. Using EMO Hoffmann

and Stohrer calculated 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 transition state was stabilized to a greater extent than the ground state.

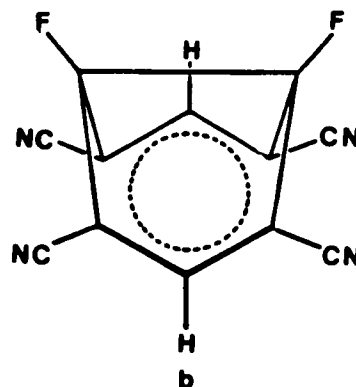
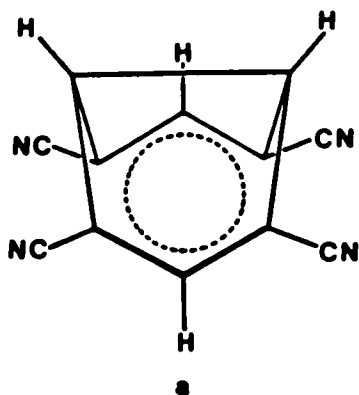


D =  $\pi$ -electron donor

A =  $\pi$ -electron acceptor

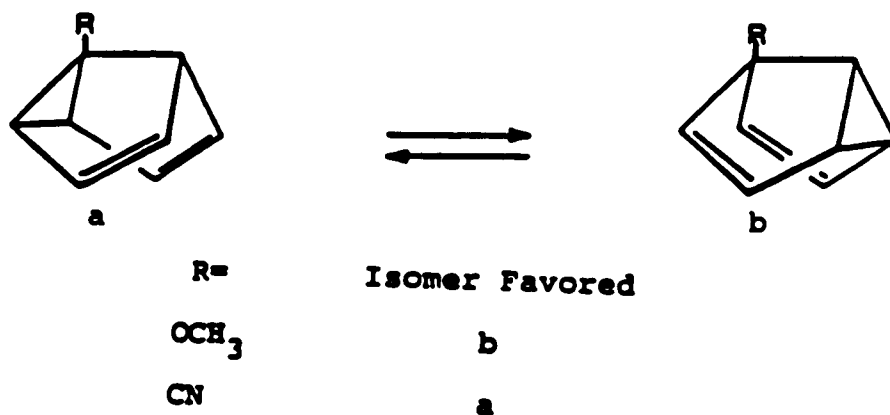
Hoffmann and Stohrer concluded that this pattern of substitution would be ideal for the stabilization of a neutral "homoaromatic" geometry. They also calculated the activation energies of several model semibullvalenes with respect to the then unknown  $E_{\ddagger}$  for semibullvalene. Semibullvalene was first prepared in 1966 by Zimmerman (25) and its nmr spectrum showed only averaged signals for H1 and H5 and H2,4,6, and 8 even at temperatures as low as  $-110^{\circ}\text{C}$ . At that time there was speculation that semibullvalene itself might exist as a "homoaromatic"

molecule, but UV spectral data (25, 11) and semiempirical calculations (23) did not support this view. Subsequently, Anet (26) determined the activation energy for the Cope rearrangement of the parent semibullvalene using low temperature proton and carbon nmr to be 5.1 Kcal/mole. Using this value of 5.1 Kcal/mole for the Cope barrier in the parent semibullvalene in combination with the theoretical predictions made by Hoffmann and Stohrer, he calculated an activation energy of -2.8 Kcals/mole for 2,4,6,8-tetracyano semibullvalene and -8.7 Kcals/mole for 1,5-difluoro-2,4,6,8-tetracyano semibullvalene. These molecules should therefore exist as neutral bishomoaromatic structures a and b respectively.



The experimental verification of these predictions would, within one class of compounds, establish a continuum between valence tautomerism, as observed in the parent semibullvalene with  $\Delta G > 0$ , and resonance as seen in benzene with " $\Delta G < 0$ " - A fascinating and challenging prospect.

Some early work did reinforce the Hoffmann-Stohrer predictions. Monosubstituted semibullvalenes which were substituted in position 1 (or 5) by a  $\pi$ -electron donating or withdrawing group were prepared by Paquette and coworkers (27, 28). Some of these compounds are listed below.



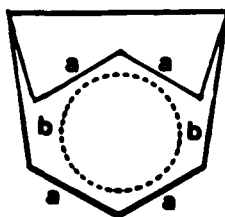
Since the two Cope rearranging structures are not equivalent, these workers could use nmr data to determine which isomer was predominant. When the substituent was methoxy, a  $\pi$ -electron donor, isomer **b** was dominant. In the cyano substituted case, isomer a was favoured. These results are in accord with the theoretical predictions (22). A  $\pi$ -electron withdrawing substituent such as CN will strengthen the cyclopropyl bond opposite it (the 2-8 bond) and thus, structure a should be favoured. The 1-cyano compound was studied in depth by Christoph and Beno (29), who determined the structure by X-ray crystallography confirming isomer a to be the preferred

structure. Conversely,  $\pi$ -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 free energies of activation for the Cope rearrangements of unsubstituted and octamethyl semibullvalenes have been determined by low temperature nmr studies. Anet (26) found that at  $-133^{\circ}\text{C}$  the average signals for protons 2,4,6, and 8 began to broaden and that the coalescence temperature was  $-143^{\circ}\text{C}$ . The actual resonances for the static semibullvalene structure were observed at  $-167^{\circ}\text{C}$ . The exchange rate constants for the Cope rearrangements in semibullvalene were determined at several temperatures which led to an activation energy of  $5.1 \pm 0.2$  Kcal/mole. The free energy of activation at  $-143^{\circ}$  was 5.5 Kcal/mole, while the enthalpy and entropy of activation were 4.8 Kcal/mole and  $-5.4 \pm 3$  eu respectively.

Since it is not possible to run solution spectra at temperatures lower than  $-160 \pm 10^{\circ}\text{C}$ , it may not be possible to "freeze out" the Cope rearrangement if the  $E_{\text{act}}$  is very small. The problem can be resolved with low temperature X-ray and variable temperature solid state C-13 NMR studies. This will be discussed in detail in Chapter 3.

Unlike static semibullvalene that retains one plane of symmetry, the homoaromatic transition state structure for the Cope rearrangement is of  $C_{2v}$  symmetry. The distances 'a' and the distances 'b' are equal with 'a' not necessarily equal to 'b'.



A determination of the geometry of the molecule by X-ray crystallographic studies plays an important role in determining the dynamic behaviour or the lack thereof. Problems associated with the interpretation of X-ray data will be discussed in Chapter 3.

Another method which has been applied to the problem of distinguishing between a delocalized structure and one that is undergoing a rapid, degenerate rearrangement was developed by Saunders and coworkers (30) and recently applied to the semibullvalene system by Askani (31) and Klumpp (32). Gompper (39) used non isotopic perturbation to study valence tautomerism in fast equilibrium systems. When applied to the semibullvalene system, they found that it did not exist as a single delocalized molecule. It was undergoing the degenerate rearrangement. The technique

involves introducing a deuterium atom in the molecule and studying the  $^{13}\text{C}$  chemical shifts of a mixture of deuterated and undeuterated compounds. In addition to an intrinsic change in the  $^{13}\text{C}$  chemical shift which is due simply to the presence of deuterium in the molecule, there will also be a shift in the position of equilibrium due to the deuterium. This will not occur if the compound exists solely in a delocalized structure. This new equilibrium constant can be determined from the change in chemical shift due to equilibrium shift and from the chemical shifts of the same carbons in the static (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" (30). The ratio of the change in the chemical shifts due to the deuterium, to the difference in chemical shifts for that particular carbon in the two frozen out states, is considered to be a measure of delocalization.

#### REVIEW OF THE RECENT PERTINENT LITERATURE

L. Miller of our laboratory reported, in 1981, the synthesis of the first donor-acceptor substituted semibullvalene. (33,34). L. Todaro at Hoffmann La Roche carried out X-ray crystallographic studies on the molecule

to determine its structure. The molecule, 1,5-dimethyl-2,4,6,8-tetracarbomethoxy semibullvalene, can be described as a semibullvalene approaching the symmetrical structure. The C2-C8 bond is unusually long (1.782 Å), the nonbonded distance C4-C6 is shorter than usual, the C1-C5 bond is longer and single bonds (C2-C3, C7-C8) are shorter - changes expected for a molecule approaching the symmetrical structure (b), page 2.

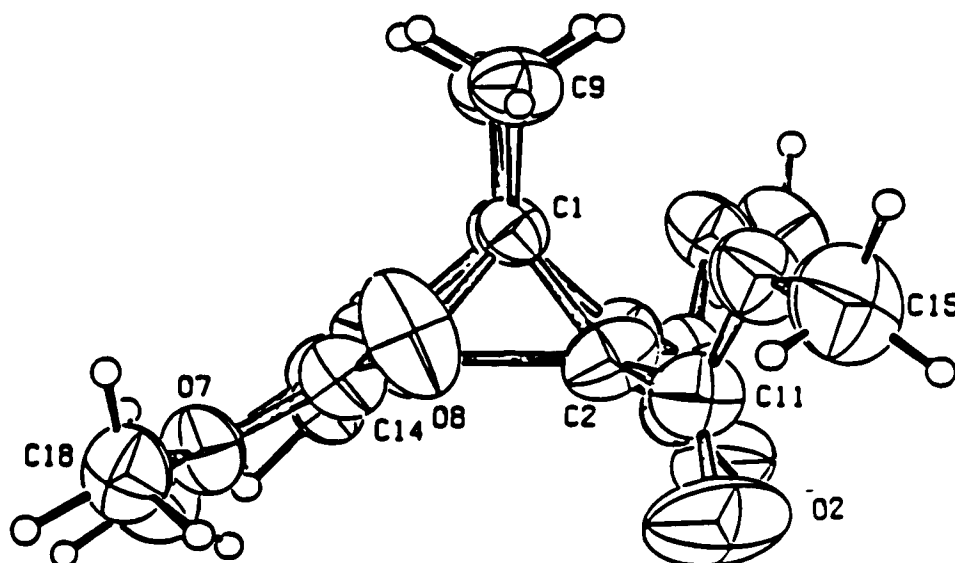
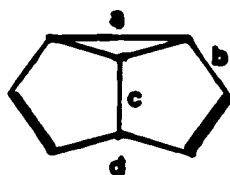


Figure 2. X-ray structure 1,5-dimethyl  
2,4,6,8-tetracarbomethoxy semibullvalene

The X-ray structure also revealed that four carbomethoxy groups to be arranged in two orthogonal planes with only two of them in conjugation with the cyclopropane ring and the double bond. The low temperature solution  $^{13}\text{C}$  nmr spectrum (Figure 3) shows broadening of the carbon signals C2, C4, C6, and C8 as well as for the methyl carbons at  $-160^\circ\text{C}$ . However, the signals for C3 and C7,

expected to remain unchanged, also broaden at  $-160^{\circ}\text{C}$ . This was interpreted (33) to be caused by the slowing down of the ester group rotation, with the molecule approaching the solid state conformation at temperatures below  $-160^{\circ}\text{C}$  (33,34,35,36); or due to presence of a low lying triplet (presence of paramagnetic species cause line broadening). The MAS (magic angle spinning) solid state  $\text{C}13$  nmr spectrum of 1,5-dimethyl 2,4,6,8-tetrakis (carbomethoxy) semibullvalene shows not only a static structure at room temperature, but also confirms the X-ray as well as the very low temperature solution nmr studies (for further details refer Chapter 3).

Table 2: Comparison of significant bond lengths (in Angstroms) with the parent semibullvalene



Molecule	a	b	c	d
1,5-dimethyl-2,4,6,8-tetrakis carbomethoxy	1.782	1.42	1.581	2.21
Parent (electron diffraction)	1.60	1.53	1.49	2.26

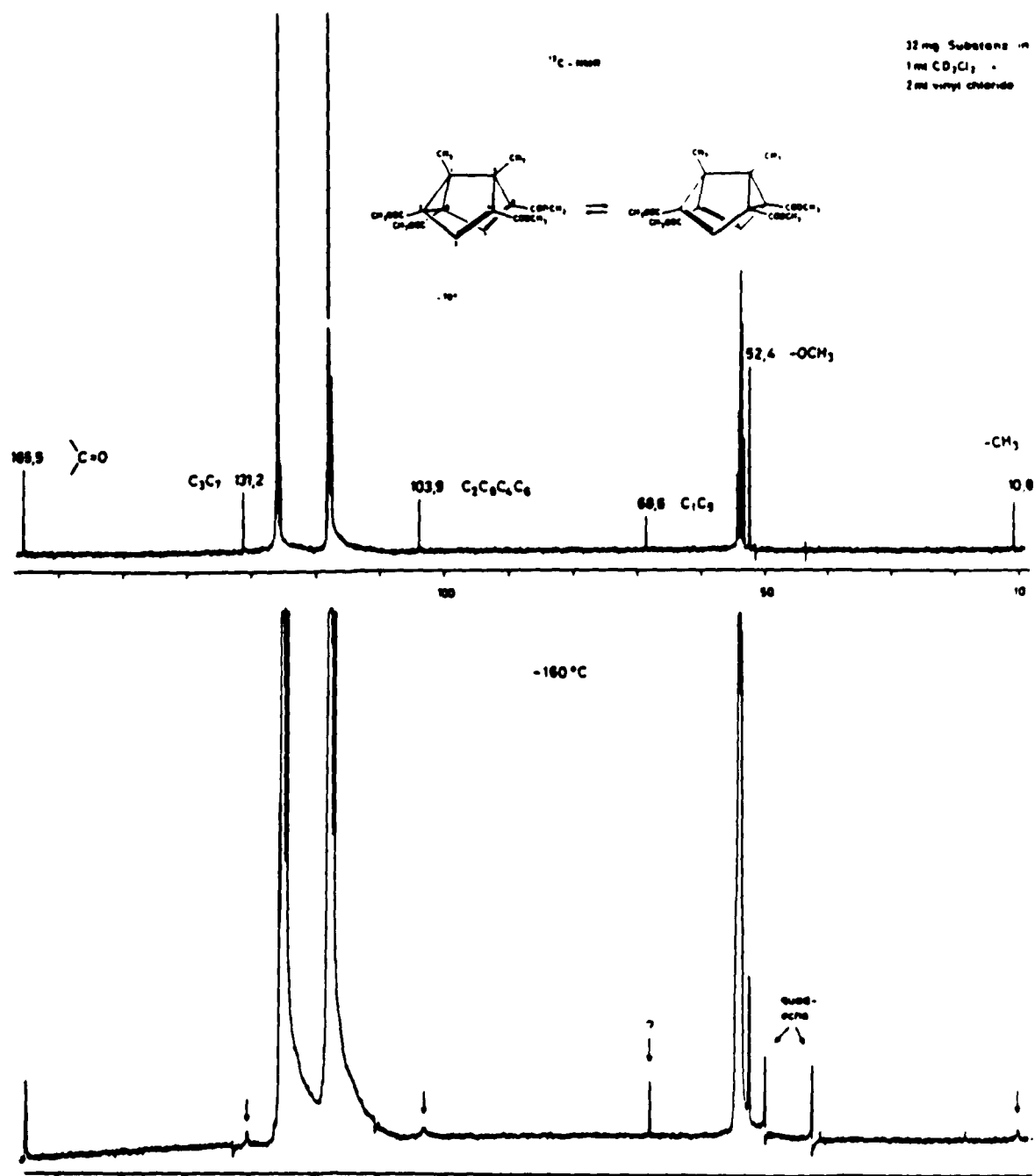


Figure 3. Low temperature solution <sup>13</sup>C NMR 1,5-dimethyl  
2,4,6,8-tetracarbomethoxy semibullvalene.

The solid state nmr measurements provided us with the chemical shifts for the non rearranging semibullvalene. Incorporating this with the dynamic solution C-13 NMR led to an upper limit for the free energy of activation for the Cope rearrangement of 1,5-dimethyl-2,4,6,8-tetrakis(carbomethoxy) semibullvalene to be  $3.8 \pm 0.4$  Kcal/mole. In spite of the orientation of the four carbomethoxy groups in two orthogonal planes, we observe a significant decrease in the activation energy ( $>1.7$  Kcal/mole) as predicted. Subsequent to the work described above, H. Quast et al. (37) and R. Askani et al. (38) reported the synthesis of 1,5-dimethyl-2,6-dicyano semibullvalene. R. Gompper et al. (39) published the synthesis of 1,5-dimethyl-2,4,6,8-tetrakis(carbomethoxy)-3,7-diacetoxy semibullvalene. J. Sauer et al. (40) and R. Quast et al (41) synthesized and investigated 1,5-dimethyl-3,7-dicyano semibullvalene. This molecule is especially interesting, as its X-ray structure showed the longest cyclopropane bond (C2-C8 = 1.835 Å) reported so far and a very short nonbonded distance C4-C6 (2.408 Å); while on the other hand, it had a higher activation energy for the Cope rearrangement than semibullvalene or the isomeric 2,6-dicyano compound (see Table 3). These results clearly add a note of caution concerning the relationship between X-ray structural data and the activation energy for the Cope rearrangement in substituted semibullvalenes (42).

Table 3: Selected Structural Data And Free Energies of Activation For Some Semibullvalenes

Semibullvalene	C2-C8 in A	C4-C6 in A	C4-C5-C6 angle	$\Delta G$ Kcal/mole
1,5-Dimethyl-2,4,6,8-tetrakis (carbomethoxy)	1.782	2.210	93.1°	4.3*
1,5-Dimethyl-2,6-dicyano	1.722	2.249	95.4°	3.1
1,5-Dimethyl-3,7-dicyano	1.835	2.048	86.2°	6.0
1,5-Dimethyl-3,7-bis (carbomethoxy)	1.596	2.277	97.6°	---
Parent	1.6	2.261	----	5.5

\* upper limit

Dashed lines in Tables (throughout the thesis) indicate that the data are not known yet.

In order to gain further insight into the effects of differently placed substituents on the relative energies of ground state and the transition state in semibullvalene, MNDO calculations with 2x2 CI and complete optimization of all internal coordinates were made (33). Some of the results are summarized in Table 4.

Table 4: Some Calculated Distances, Angles, Activation Enthalpies For Some Substituted Semibullvalenes (MNDO & 2x2 CI)

Compound	C2-C8		C4-C6		C4-C5-C6 (TS) in °	H	E <sub>a</sub>
	GS	TS	GS	TS			
Parent	1.57	2.46	2.44	2.46	109	72.2	5.7
2,4,6,8-CN-	1.60	2.50	2.45	2.50	111	202.3	-4.7*
2,6-CN-	1.58	2.52	2.45	2.52	113	134.3	-0.2
2,4-CN-	1.58	2.36	2.44	2.36	103	134.5	8.9
3,7-CN-	1.56	2.37	2.43	2.37	103	130.3	9.8
1,5-Diaza-	1.54	2.65	2.34	2.65	140	113.9	-12.4
1,5-cyclopropa-	1.60	2.47	2.48	2.47	113	137.0	-9.1
1,5-cyclobuta-	1.58	2.41	2.44	2.41	107	92.2	5.4

\* previous calculation EHMO (22) -2.8 Kcal/mole

The qualitative agreement of these predictions with subsequent experimental results of Quast (37) and Sauer (40) is quite impressive. The electron pairs in 1,5-diaza semibullvalene is the strongest possible donor substituent for positions 1 and 5 in the semibullvalene. The difference in the heat of formation between the ground state and the transition state for this semibullvalene has been calculated to be -12.4 Kcal/mole. Most of the

experimental studies have been so far concentrated on acceptor effects in positions 2,4,6, and 8. These data point towards the very strong effects of 1,5 donors.

Most remarkable is the predicted effect of annulation at positions 1 and 5. The attachment of a three-membered ring leads to a strong stabilization of the homoaromatic structure (34), while a four-membered ring is predicted to have no effect on the activation energy for the Cope rearrangement in semibullvalene. The experimental verification of these predictions involving the syntheses and investigations of annulated semibullvalenes is the subject of this thesis.

#### STATEMENT OF THE PROBLEM

The thesis problem deals with our continuing efforts directed towards the lowering of activation energy for the Cope rearrangement in semibullvalenes. The effect of annulating rings at the 1,5 positions of a 2,4,6,8-tetracarbomethoxy semibullvalene is rather dramatic. The thesis can be essentially divided into two parts - annulating cyclopropane (or cyclobutane) at the 1,5 positions and annulating larger rings (cyclopentane, cyclohexane, cycloheptane, cyclooctane) at the 1,5 positions in semibullvalene. It was intended to use

variable  $^{13}\text{C}$  NMR, solid state NMR, and X-ray structure determination to study the properties of these molecules. An important object of the syntheses of these annulated semibullvalenes was to study the mechanism of ring inversion in cyclooctatetraenes. It was also intended to study the geometries and heats of formation of selected semibullvalenes related to the series using the MNDO approximation.

CHAPTER 2  
SYNTHESES OF 1,5 ANNULATED SEMIBULLVALENES

**BACKGROUND**

As pointed out in Chapter 1, the thesis can be divided into two parts -

1. annulating cyclopropane and cyclobutane on the 1,5 positions in semibullvalene and making its 2,6-dicyano derivative;
2. annulating larger rings on the 1,5 positions of 2,4,6,8-tetrakis (carbomethoxy) semibullvalenes.

This chapter deals with the annulation of larger rings on the 1,5 positions in 2,4,6,8-tetrakis (carbomethoxy) semibullvalene.

It is appropriate at this point to discuss the significance of annulating large rings at the 1,5 positions in 2,4,6,8-tetrakis (carbomethoxy) semibullvalene.

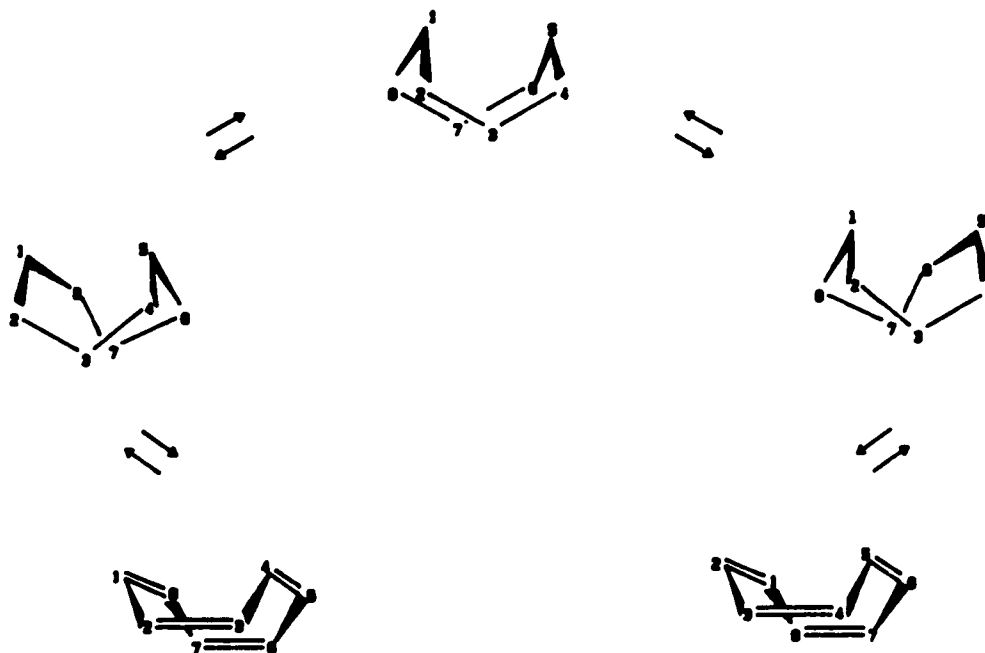
1. MNDO studies (93) indicate that the lowering of the transition state energy was in most cases accompanied by the widening of the C2-C1-C8 angle to greater than  $109.5^\circ$ . This suggests that the angle strain resulting from larger distortions of this angle could impede further reductions in the energy of the TS. In order to test the effect of annulating large rings at positions 1 and 5 on the widening of the C2-C1-C8 angle we undertook the study of annulating larger rings.
2. We were interested in the synthesis of 1,5-bridged cyclooctatetraenes in order to examine the possibility of a different mechanism for the ring inversion in cyclooctatetraenes.

Semibullvalenes and cyclooctatetraenes are known to interconvert. For example, the parent semibullvalene isomerizes to cyclooctatetraene upon pyrolysis at  $270^\circ\text{C}$ . However, 1,5-dimethyl-2,4,6,8-tetrakis (carbomethoxy) semibullvalene rearranges to the corresponding cyclooctatetraene at temperatures as low as  $5^\circ\text{C}$ . The substituents on the semibullvalene apparently lowered the barrier for the isomerization to cyclooctatetraene. We therefore expected to synthesize the 1,5 bridged cyclooctatetraenes by annulating larger rings at the 1,5 positions in

2,4,6,8 tetracarbomethoxy semibullvalene.

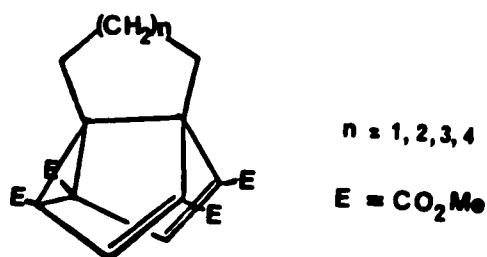
The reason for making the bridged cyclooctatetraenes was to examine an alternative mechanism for the ring inversion in cyclooctatetraenes. The generally accepted mechanism for the ring inversion in cyclooctatetraenes involves a planar transition state (47); which is an antiaromatic species involving considerable strain. Pseudo-rotation (48) is an alternative possible pathway for the process of racemization of optically active cyclooctatetraenes. The movement involved during pseudo-rotation is an exchange of C1 for C2 without disturbing the tub conformation of cyclooctatetraene; during such a motion there is always some amount of  $\pi$ -overlap and there is very little strain involved when compared to a planar transition state. The process is demonstrated on the next page. It should be noted that the two tub conformers in 1,5 bridged cyclooctatetraenes are mirror images. If racemization is detected by nmr in these annulated cyclooctatetraenes, pseudo-rotation is a conceivable mechanism via which the racemization could have occurred. It is not conceivable for a cyclooctatetraene bridged by three, four, five, or six carbons at positions 1,5 to ring invert via a planar transition state. However longer bridges could loop

around a planar transition state and hence the number of atoms in the bridge should be small to test out this hypothesis.



We intended to use the resolution techniques developed by Paquette (49) to separate the optical isomers of cyclooctatetraenes. The isolation of the two optical isomers would allow us to study the racemization process. Racemization in the bridged cyclooctatetraenes cannot proceed via the traditionally postulated planar transition state, and hence would suggest an alternative mechanism such as

pseudo-rotation. However, the 1,5 bridged cyclooctatetraenes could not be constructed using Dreiding models except in the case where a cyclooctane was bridged at the 1,5 positions. Hence the intriguing question: to what would the annulated semibullvalenes where  $n$  equals 1, 2 and 3 isomerize? To answer the above question we synthesized the following series of annulated semibullvalenes.

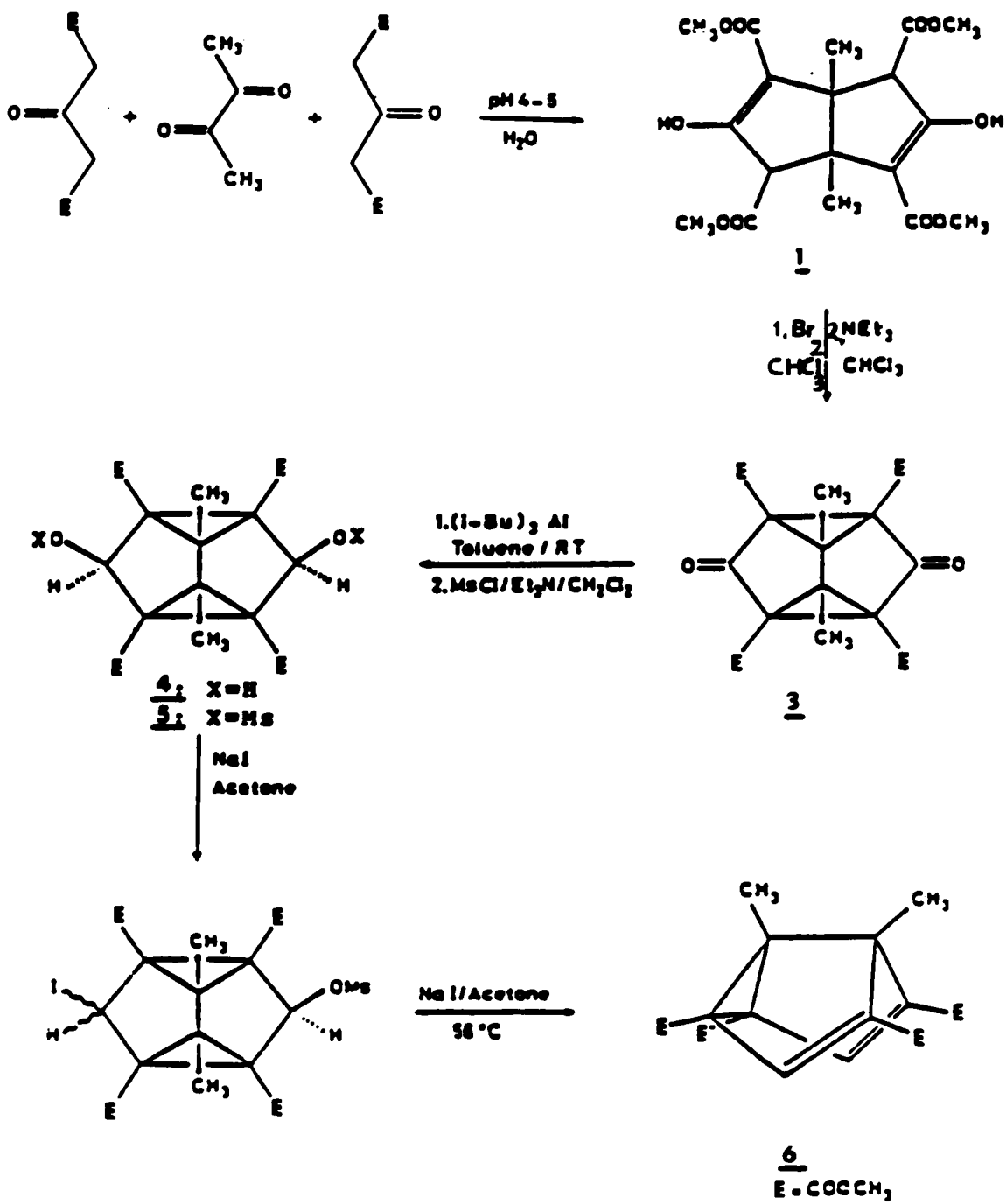


### RETROSYNTHETIC ANALYSIS

1,5-dimethyl-2,4,6,8-tetracarboxy semibullvalene was previously synthesized by L. Miller; the route shown in Scheme 1 (33). It appeared possible to use Scheme 1 to synthesize the molecules illustrated above as well. Instead of starting with an acyclic 1,2 dione, namely butane-2,3-dione, however, the cyclic 1,2 diones (cyclopentane-1,2-dione / cyclohexane-1,2-dione / cycloheptane-1,2-dione / cyclooctane-1,2-dione) would be used.

## Scheme 1

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

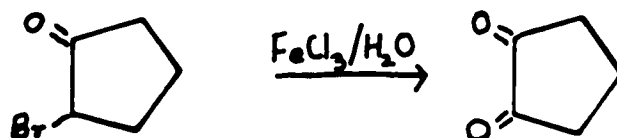


Even if we encountered difficulties with particular steps we felt confident that with the experience with these reactions in our group we could modify the sequence and attain our goal.

## SYNTHESES

The synthetic route successfully employed in the preparation of 1,5 annulated 2,4,6,8-tetrakis (carbomethoxy) semibullvalenes is outlined in Scheme 2. The first step in the syntheses involved the preparation of the cyclic 1,2 diones (this step is not shown in Scheme 2). Cyclohexane-1,2-dione, cycloheptane-1,2-dione, and cyclooctane-1,2-dione were obtained by the  $\text{SeO}_2$  oxidation of cyclohexanone (50), cycloheptanone (51), and cyclooctanone (52) respectively. Cyclohexane-1,2-dione was obtained in 60% yield (bp 75-79°C, 16 mm Hg). A difficulty with the synthesis of cycloheptane-1,2-dione was related to its distillation. A high boiling azeotrope was formed. The  $\text{SeO}_2$  oxidation of cyclooctanone to give cyclooctane-1,2-dione has been reported to be non-reproducible (53). Hence our earlier attempts in making cyclooctane-1,2-dione involved DMSO oxidation of 2-bromocyclooctanone (54), the Sharpless method (55), and acyloin condensation followed by oxidation (56,57). However  $\text{SeO}_2$  oxidation (58) using reagent grade  $\text{SeO}_2$ , and

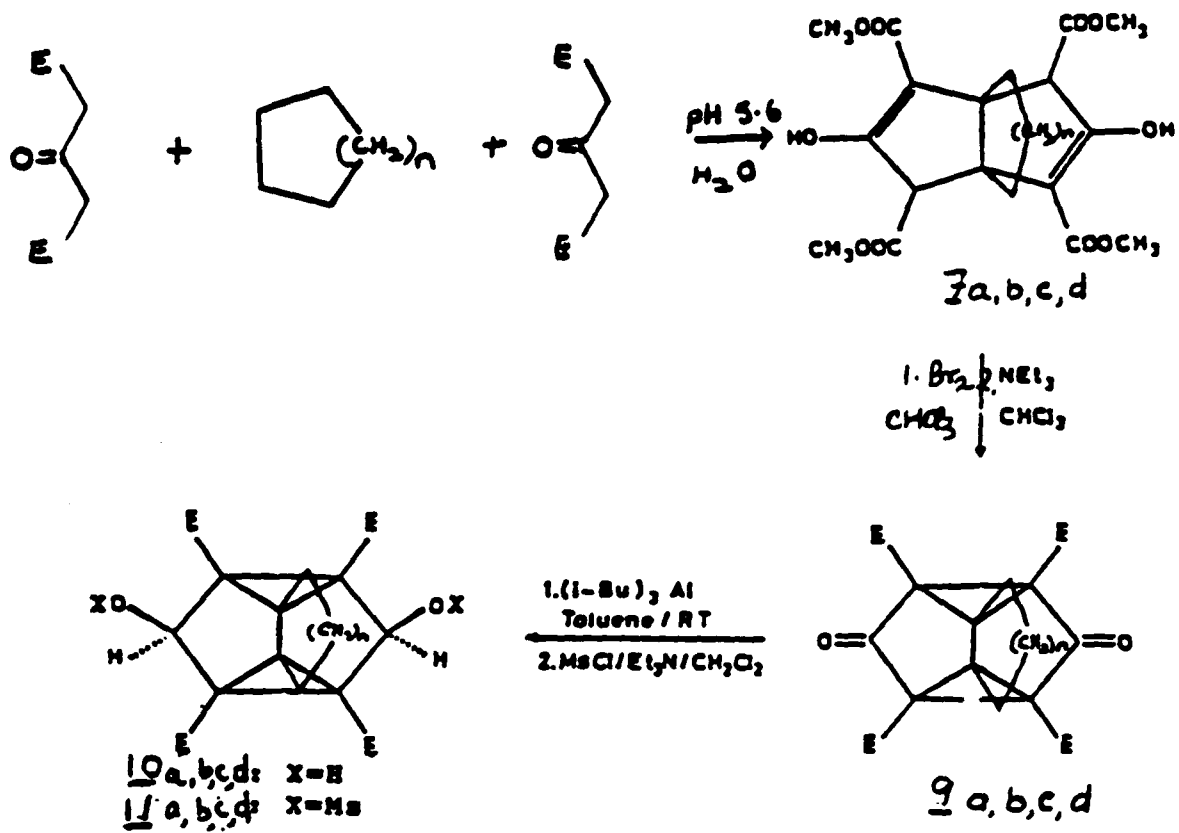
scrupulously clean dioxane (clean dioxane seems to be important) gave a 68% yield of the cyclooctane-1,2-dione (yellow oil). The synthesis of the labile cyclopentane-1,2-dione, however, posed considerable difficulties. The first attempt employed the method developed by Acheson (59), namely, treatment of 2-bromocyclopentanone with  $\text{FeCl}_3/\text{water}$ , as shown below.



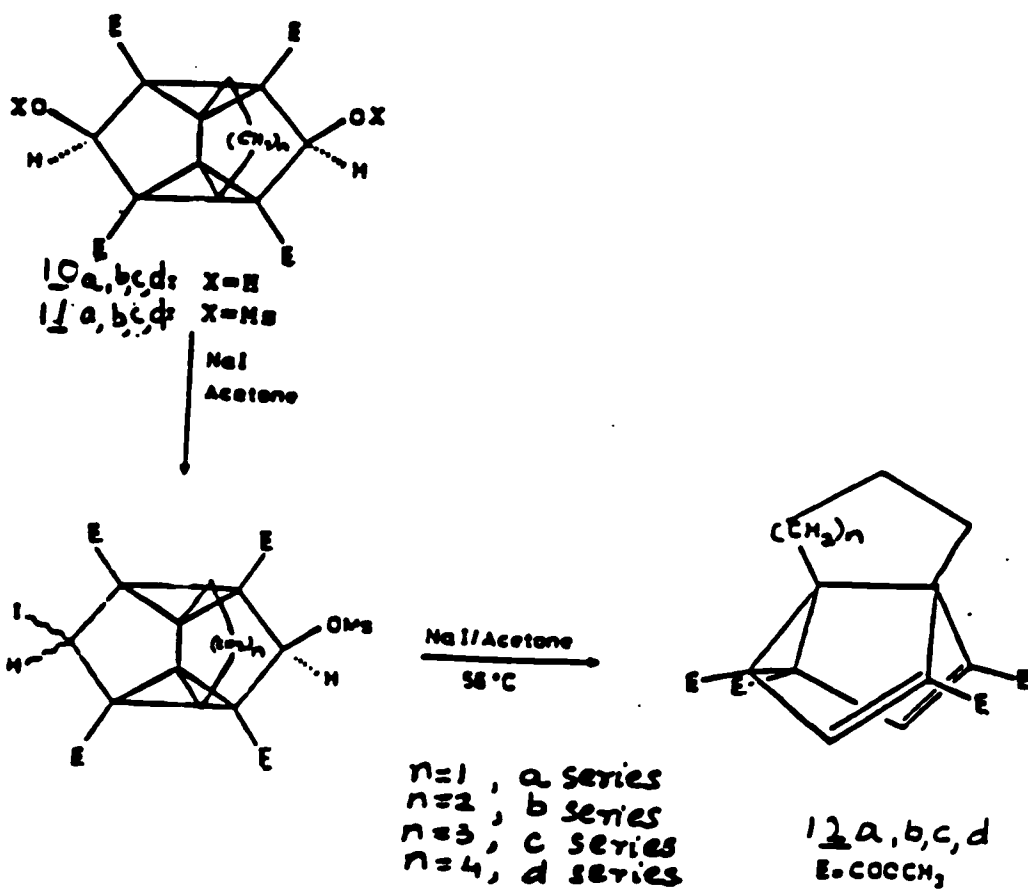
Application of Inhoffen's procedure (60) for the oxidation of 2-chlorocyclopentanone to cyclopentane-1,2-dione did not give improved yields of cyclopentane-1,2-dione. The procedure that worked well in our hands was a method reported recently by J.M.Cook (61). Reductive work-up of the ozonide of 2-cyclopentylidene cyclopentanone, obtained by the self-condensation of cyclopentanone in the presence of  $\text{NaOEt}$ , led to a near quantitative yield of cyclopentane-1,2-dione.

## Scheme 2

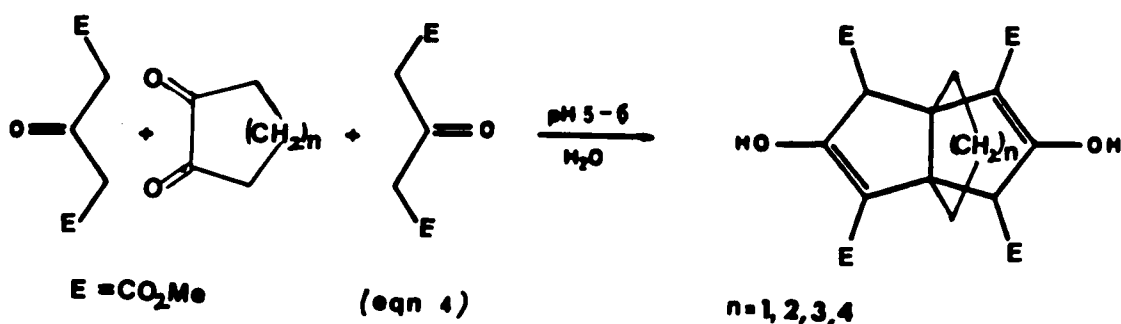
SYNTHETIC ROUTE FOR THE PREPARATION OF 1,5-ANNULATED  
2,4,6,8-TETRAKIS (CARBOMETHOXY) SEMIBULLVALENE



## Scheme 2 (continued)



The next step involved the condensation of two moles of 1,3-dimethyl acetone dicarboxylate and one mole of the cyclic 1,2-dione in an aqueous citrate-phosphate buffer using variations of the Weiss procedure, which gave the [3.3.3] (62(a)), [4.3.3] (50), [5.3.3] (63), [6.3.3] (64) propellane systems (Equation 4).



Tetramethyl [3.3.3] propellane-8,11-dione-7,9,10,12 tetracarboxylate, 7a, was obtained as a white precipitate by adding portions of cyclopentane-1,2-dione, over a period of two weeks, to an aqueous citrate-phosphate buffer solution (pH 6.6) containing dimethyl-1,3-acetone dicarboxylate. The Weiss product from the above reaction was obtained in 20% yield, melting point 156-158°C (MeOH) (lit (62(a)) 150-2°C), ir (KBr pellet) 3215 (O-H of the enol) broad peak, 2940 (C-H), 1730 (ester carbonyl), 1660  $\text{cm}^{-1}$  (C=C of the  $\beta$ -ketoester). The ir was in complete agreement with that reported by Cook.

Tetramethyl [4.3.3]-propellane-8,11-dione-7,9,10,12 tetracarboxylate, 7b, was obtained by stirring a 2:1 mixture of 1,3-dimethyl acetone dicarboxylate and cyclohexane 1,2 dione in citrate-phosphate buffer (pH 5.6) over a period of two weeks. The solid mp 154-156°C (MeOH) (lit (50) 171-5°C), ir (KBr pellet) 2940 (C-H), 1740 (ester carbonyl), 1660  $\text{cm}^{-1}$  (C=C  $\beta$ -hydroxy ester) (lit (50) ir 2940, 1730, 1650) was filtered and triturated with MeOH in 40%. The yield was 66% (lit (50) 70%) when freshly prepared cyclohexane-1,2-dione was used. The yields were higher when the pH was maintained at 8.4 and later acidified to obtain crystalline 7b. Since the condensation proved to be very sensitive to pH and a pH of 8.4 is at an extreme end of the citrate-phosphate buffer system range and, as such, difficult to maintain, we kept the pH at 5.6 and accepted the lower yields.

The [5.3.3] propellane system, 7c, has never been made using the Weiss procedure. This was attempted for the first time in our laboratories using the procedure for making the [6.3.3] system outlined below, and succeeded in obtaining the desired product, 1c, in 57% yield.

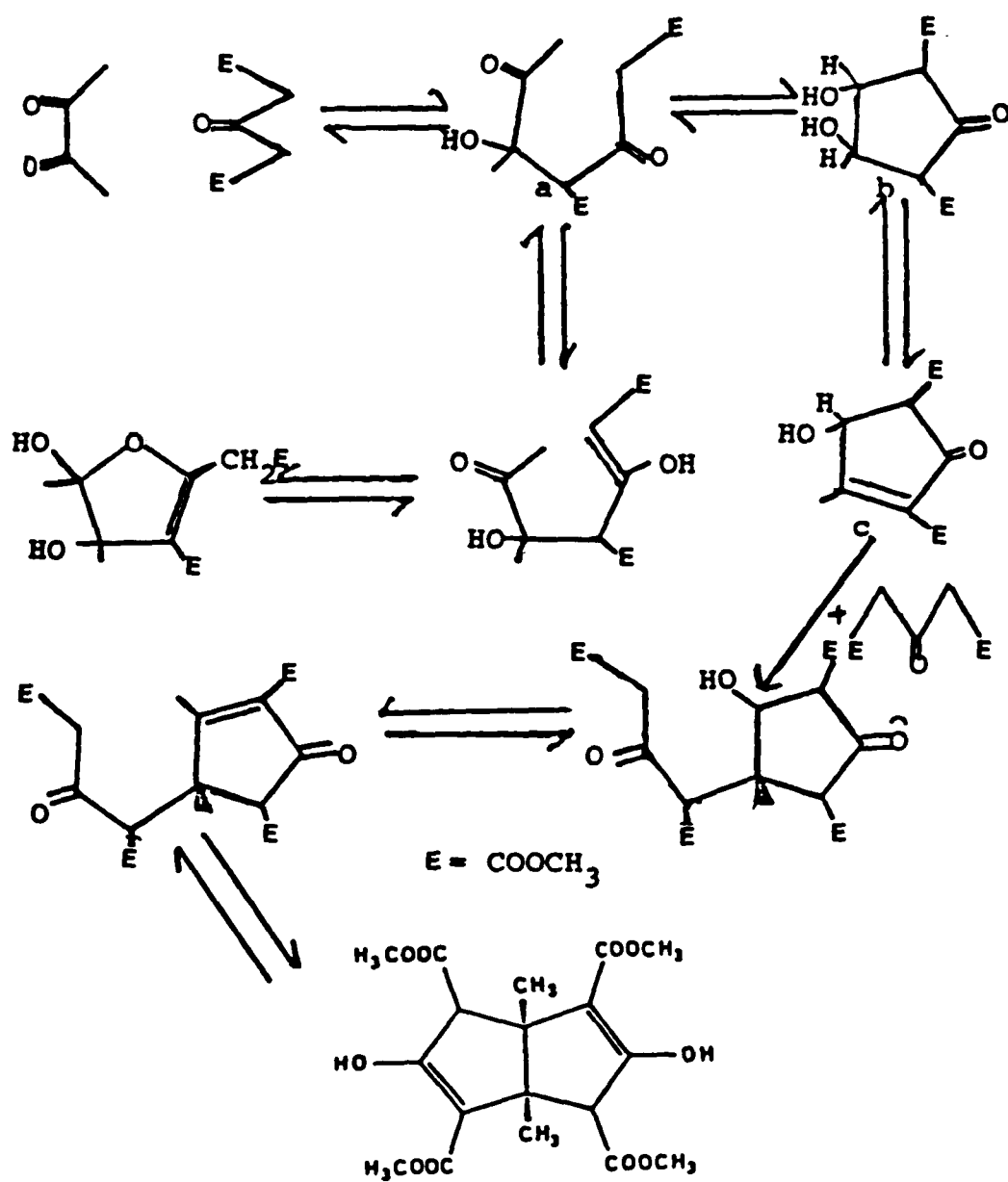
Tetramethyl [6.3.3] propellane- 7,9,10,12-tetracarboxylate, 7d, was synthesized by dissolving the cyclooctane-1,2-dione in methanol and adding the citrate-phosphate buffer (pH 6.8) till the solution became

turbid. A few drops of methanol was added to make the solution clear and the 1,3-dimethyl acetone dicarboxylate was added all in one portion. The reaction was completed within three days, and gave a 32% yield (lit (64) 80%), mp 214-216°C (lit (64) 160-3°C).

The Weiss reactions leading to 7a and 7b were very sensitive to pH (the product did not precipitate out of the reaction mixture when the pH maintained was incorrect); however the Weiss reaction leading to 7d proved rather insensitive to pH. We did not separate and identify the isomeric products from the Weiss reaction, suffice it to say there were other compounds formed besides the desired product (based on mp's). These could have been different stereoisomers or keto/enol tautomers of the Weiss product. The accepted mechanism involves a sequence of aldolizations and Michael additions (62). A plausible sequence, shown in Scheme 3, can be formulated and is consistent with all information known to date. Initial 1:1 aldol condensation leads to species a which can undergo a second intramolecular aldol condensation to form b (Scheme 3). This molecule will easily lose water forming the key intermediate c (Scheme 3), which can then add another molecule of 1,3-dimethyl acetone dicarboxylate via an intermolecular Michael reaction followed by an intramolecular Michael addition.

## Scheme 3

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



7a, tetramethyl [3.3.0] propellane-8,11-dione-7,9,10,12-tetracarboxylate, exists in the symmetric bisenolic form as is evident from the proton NMR - a broad singlet appears at 10.43 ppm for the enol hydroxy hydrogens (Table 5). Additional confirmation of the structure was obtained by quantitative conversion of enol 7a to its dimethyl ether using diazomethane in ether without a catalyst. Table 5 summarizes the nmr data for the Weiss products, 7a,b,c,d.

The next step involved conversion of 7a,b,c,d to the diketones 9a,b,c,d, respectively, (refer to Scheme 2). Bromination of the Weiss products with two moles of bromine led to dibromides of unknown stereochemistry. During the reaction of the 1,5-dimethyl-2,4,6,8-tetrakis (carbomethoxy) bicyclo [3.3.0] octa-2,6-diene-3,7-diol, 1, with two moles of bromine a small amount of the non-halogenated cyclised product was isolated from the reaction mixture. This led to a one pot approach for the transformation of the Weiss products to the cyclised diketones.

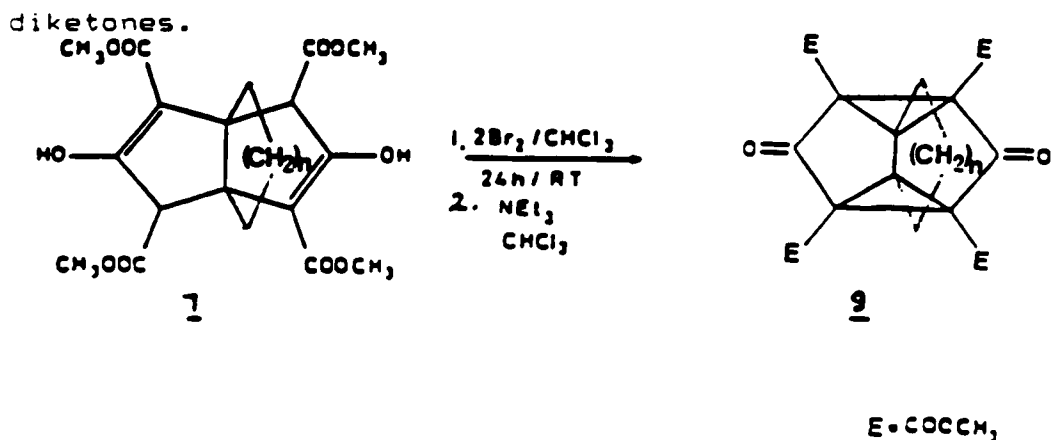
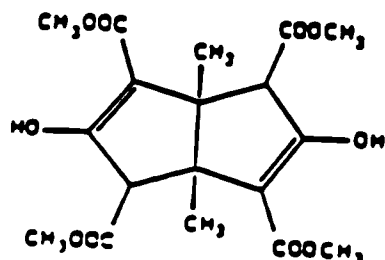


Table 5: H-1 NMR ( $\delta$  in ppm) data for the Weiss product  
(CDCl<sub>3</sub>)

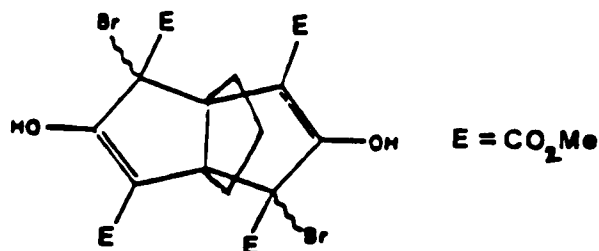


Compound	OH (2H br s)	H 4,8 (2H s)	COOMe (two 6H s)	cycloalkane H's (multiplet)
1	10.80	3.92	3.88, 3.75	1.30
7a	10.43	3.84	3.78, 3.72	1.71
7b	10.95	3.7	3.7, 3.7	1.95, 1.5

(overlapping singlets)

The tetraesters 7a,b,c,d were treated with two equivalents of bromine in CHCl<sub>3</sub> overnight at room temperature. 7d posed solubility problems - it did not dissolve in CHCl<sub>3</sub> or AcOH, however, it dissolved easily in a 1:1 mixture of AcOH and CHCl<sub>3</sub>. The excess bromine was removed by washing the chloroform solution with aqueous NaHSO<sub>3</sub>. The solution of dibromo tetraesters 8a,b,c,d were then dehydrobrominated by the addition of a solution of triethylamine in CHCl<sub>3</sub>.

The oil obtained during the synthesis of 9a, 1,7,8,10 tetrakis (carbomethoxy) pentacyclo[5.3.1.0<sup>2,4</sup>.0<sup>3,5</sup>.0<sup>6,8</sup>.1<sup>0</sup>] undeca-9,11-dione on trituration with ether yielded a colorless compound (mp 196-197°C with decomposition MeOH). Microanalysis of the colorless compound indicated the presence of two bromine atoms - elemental analysis for C<sub>17</sub>H<sub>16</sub>Br<sub>2</sub>O<sub>10</sub>: Calc. C, 40.3; H, 3.20; Br, 28.23%; Found C, 40.22; H, 3.46; Br, 28.18%. The compound responded positively to the Beilstein test. IR (KBr pellet) indicated the presence of hydroxy (3190 cm<sup>-1</sup>, broad peak), ester (1750 cm<sup>-1</sup>), and C=C (1670 cm<sup>-1</sup>) groupings in the molecule. The proton NMR consists of a multiplet between 1.7-1.8 and 2.0 ppm for the six cyclopentane protons, two singlets at 3.85 and 3.87 ppm for the twelve carbomethoxy methyls and the two enolic protons appear at 10.83 ppm suggesting the following structure for the compound, 8a. The stereochemistry, however, is not known.



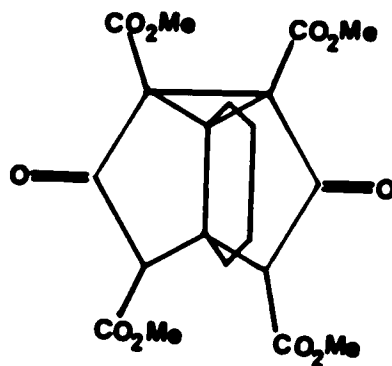
The structure was further confirmed by its C-13 spectrum which showed a triplet at 26.4 ppm corresponding to the

middle carbon of the cyclopentane ring, another triplet at 35.4 ppm to the other two carbons of the cyclopentane ring, an overlapping quartet for the carbomethoxy methyls at 51.9 and 53.4 ppm. The two carbons at the junction of the three rings appear at 67.4 ppm, and the quaternary carbons bearing the bromine and the carbomethoxy groups appear as a singlet at 71.4 ppm, the two enolic carbons appear at 108.6 ppm, the  $sp^2$  carbons bearing the carbomethoxy groups show up at 166.8 ppm, and finally the carbonyl carbons of the ester groups appear at 168.9 and 169 ppm. Compound 8a decomposes at room temperature in two days in solution.

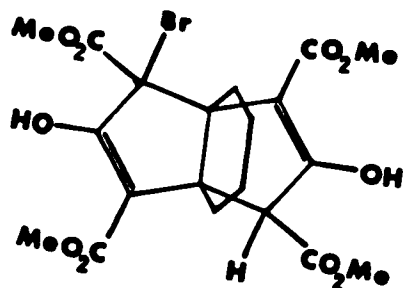
After several fractional recrystallizations the dione 9a, 1,7,8,10-tetrakis (carbomethoxy) pentacyclo[5.3.1.0<sup>2,4</sup>.0<sup>3,5</sup>.0<sup>6,8</sup>.0<sup>9,11</sup>] undeca-9,11-dione crystallized finally with great difficulty. The mother liquor after removal of the dione apparently contains another compound which appears to be the starting material 7a, tetramethyl [3.3.3.0<sup>1,3</sup>] undecane-3,7-dione-2,4,6,8-tetracarboxylate.

Trituration (ether) of the oil obtained from the bromination - dehydrobromination sequence leading to 9b (refer Scheme 2), yielded three crops of the dione mp 162-3°C; pure dione mp 170-2°C. The fourth crop differed from the diketone, 9b, and exhibited a mp 147-150°C (decomp.). This compound gave a positive Beilstein test.

After long storage and recrystallization from methanol, the mp raised to 242-244°C. Elemental analysis corresponded to  $C_{20}H_{22}O_{10}$ : Calc, C, 56.87; H, 5.25%; Found C, 56.60; H, 5.28%. This compound contains two more H's than the dione 9b. IR (KBr pellet) suggested the presence of ester ( $1780\text{ cm}^{-1}$ ), and two other C=O groups ( $1750$  &  $1720\text{ cm}^{-1}$ ). The proton NMR exhibits the cyclohexane protons as multiplets at 1.7, 2.27 and 2.35 ppm, the carbomethoxy methyl protons at 3.79 and 3.82 ppm, and the remaining two protons at 4.17 ppm. The compound apparently exists in the diketonic form as no enolic protons were visible. We suggest the following structure.



However the C-13 spectrum, suggests three different carbonyls (one ester and two ketonic carbonyls). Hence the structure of the compound could not be resolved. There were other products as well, in the reaction. The precursor to the above compound could very well be envisioned as follows.



The bromination-dehydrobromination sequence led to a variety of products from which the diketones 9a,b,c,d had to be separated by careful fractional recrystallizations. The relevant NMR's, IR's and mps of the diones 9a,b,c,d are listed in Table 6. The tetracyclic ketones 9b,c,d were isolated in percentage yields of 39%, 33%, 52% respectively. 9a could not be crystallized - a variety of solvents and solvent mixtures were employed in attempts to crystallize 9a, with limited success. A part of it crystallized (mp 169-171°C), but most of it remained in the mother liquor - hence, the yield of pure recrystallised 9a could not be determined. 9a was carried over in the crude form to the next step.

Table 6a: MP's (in °C) and IR's (KBr pellet) in  $\text{cm}^{-1}$  of the cyclised diketones

Compound	MP's	C-H	COOMe	C=O
3	185-8	---	---	---
9a	169-171	2950	1770 and 1745	1720
9b	170-2	2950	1770 and 1740	1715
9c	161-2	---	---	---
9d	200-3	---	---	---

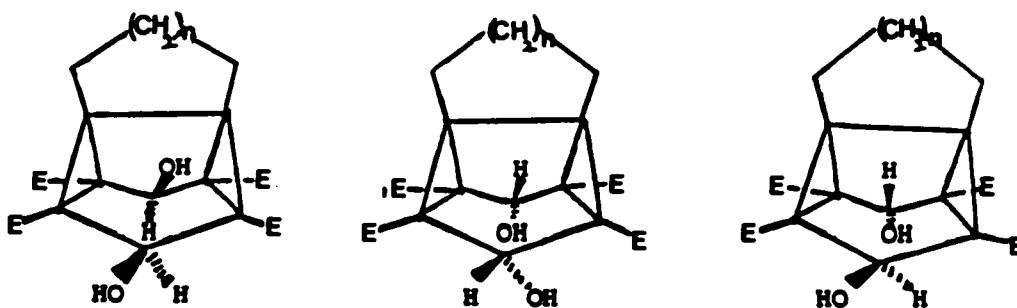
Table 6b: H-1 NMR's ( $\delta$  in ppm) of the cyclised diketones ( $\text{CDCl}_3$ )

Compound	COOMe (12H s)	cycloalkane H's (multiplet)
3	3.8	1.8
9a	3.77	2.47, 2.2
9b	3.8	2.2, 1.85
9c	3.8	2.3, 1.8
9d	3.8	2.4, 1.45

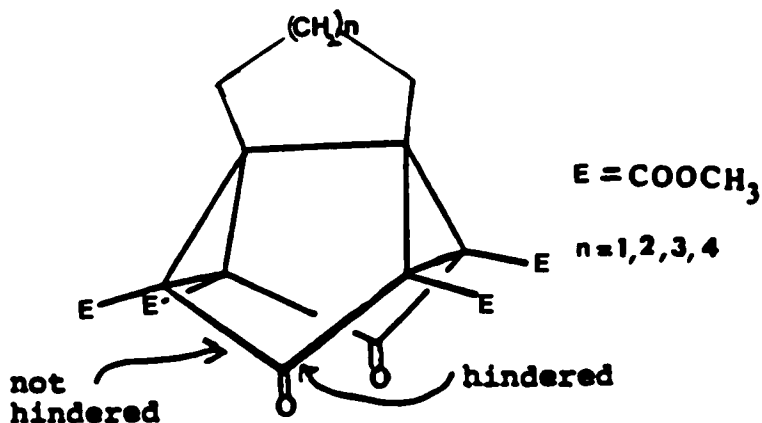
Table 6c: C-13 NMR's ( $\delta$  in ppm) of the cyclised diketones (CDCl<sub>3</sub>)

Compound	C=O	COOMe	OMe	C 2,4 6,8	C 1,5	cyclo- alkane C's
	s	q	q	s	s	t
3	189.6	162.0	53.2	49.8	48.1	8.5
9a	189.9	162.06	54.68	53.21	48.59	26.52, 24.85
9b	189.9	162.0	53.3	49.6	49.1	19.7, 18.2

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 of the carbonyls while still leaving the carbomethoxy groups and the ring system intact. However, stereochemistry of the product diol was an important issue. It is apparent that three different diols could form in the reduction reaction (see below).



Lebel suggested (66) that  $\text{NaBH}_4$ , and other unhindered reducing agents would deliver a hydride anion in an exo manner to form the diendo 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. Triisobutyl aluminium is known to be a mild reducing agent which was known to reduce hindered ketones to the more thermodynamically favored isomer (67, 68). Reduction of the diones 9a,b,c,d with  $(i\text{Bu})_3\text{Al}$  in toluene as the reducing agent led to the diexo-diols. The diol, 4 (Scheme 1), was found to be more soluble in EtOAc than in  $\text{CH}_2\text{Cl}_2$ , and the yield was raised to 70% selecting EtOAc as the solvent for extraction.

It is interesting to note that while other workers often obtained endo/exo mixtures when they reduced diketones (69), no trace of the endo/exo diol was seen in the reduction of 3 (Scheme 1). Furthermore, the diexo

product was never isolated from the NaBH<sub>4</sub> reduction, nor was diendo product recovered from the (iBu)<sub>3</sub>Al reaction. Hence the reagent of choice for the conversion of 9a,b,c,d to 10a,b,c,d, respectively, was triisobutyl aluminum. The diexo diols 10a,b,c,d were obtained as the only products in 65%,63%,68%,88% yields, respectively. The diendo alcohol obtained during the NaBH<sub>4</sub> reduction of 3 (Scheme 1) on mesylation led to the monohydroxy monomesylate compound. However, the diexo diol 4 (Scheme 1) formed the dimesylate readily. The diexo stereochemistry of the diols 10a,b,c,d was therefore based on the reaction with methane sulfonyl chloride to yield the dimesylates readily. Table 7 summarizes the MP's and spectral data for the diexo diols 10a,b,c,d.

Table 7a: MP's (in °C) and relevant IR-bands (KBr pellet) in cm<sup>-1</sup> of the diols 10a-c.

Compound	MP's	OH	C-H	C=O of COOMe
4	200-4	---	---	---
10a	199-202	3490	2980, 2960	1730, 1700
10b	213-215.5	3420	2920	1720
10c	195-203	---	---	---

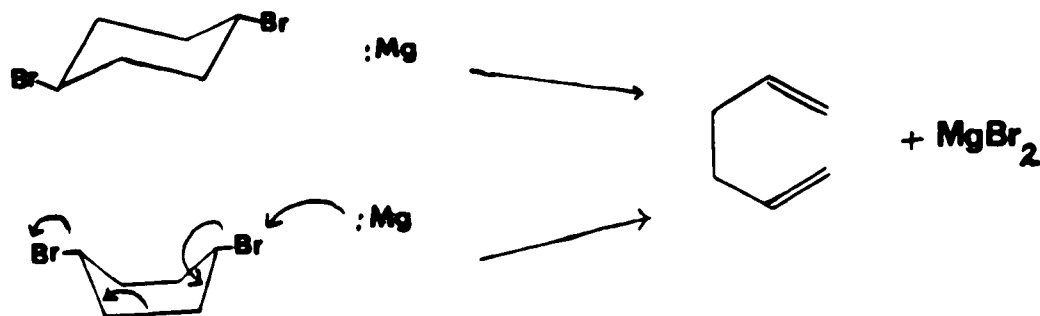
Table 7b: H-1 ( $\delta$  in ppm) NMR data of the diols (CDCl<sub>3</sub>)

Compound	H 3,7 (2H s)	OH (2H d)	COOMe (12H s)	cycloalkane H's (multiplet)
4	4.60	3.80	3.72	1.70
10a	4.84	3.57	3.7	2.35, 2.25
10b	4.6	3.75	3.7	2.2, 1.8
10c	4.9	4.1	3.9	2.2, 1.9

Diols 10a,b,c,d reacted readily with two equivalents of distilled methane sulfonyl chloride in distilled methylene chloride yielding the dimesylates 11a,b,c,d, respectively in yields of 66%, 63%, 73%, and 60%. Non-reproducible results were obtained if either the solvent or the methane sulfonyl chloride was not distilled prior to use. The reaction was complete after two hours. Table 8 summarizes the mp's, IR, and NMR data of 11a,b,c,d.

The key step in our synthesis of semibullvalenes involves a Grob fragmentation which converts the pentacyclic system into a semibullvalene containing the 1,5-hexadiene unit. The stereoelectronic requirement for the Grob fragmentation (shown below) is a parallel

alignment of the orbitals involved in bond breaking.



While a variety of reagents have been reported to achieve this transformation, namely, KI in polyhydrogen fluoride (70), NaI in HMPA (71), *t*BuLi (72), Na/K alloy in THF (72), Na/NH<sub>3</sub>, (72) and P<sub>2</sub>I<sub>4</sub> (73), we employed the reagent used for the conversion of 5 to 6 (Scheme 1).

Table 8a: MP's (in °C) and IR (KBr pellet) in cm<sup>-1</sup> of the dimesylates

Compound	MP's	C-H	C=O of COOMe
5	140-2	---	---
11a	136-7	2960	1740-1725
11b	111-2	2960	1720 (br peak)

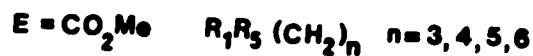
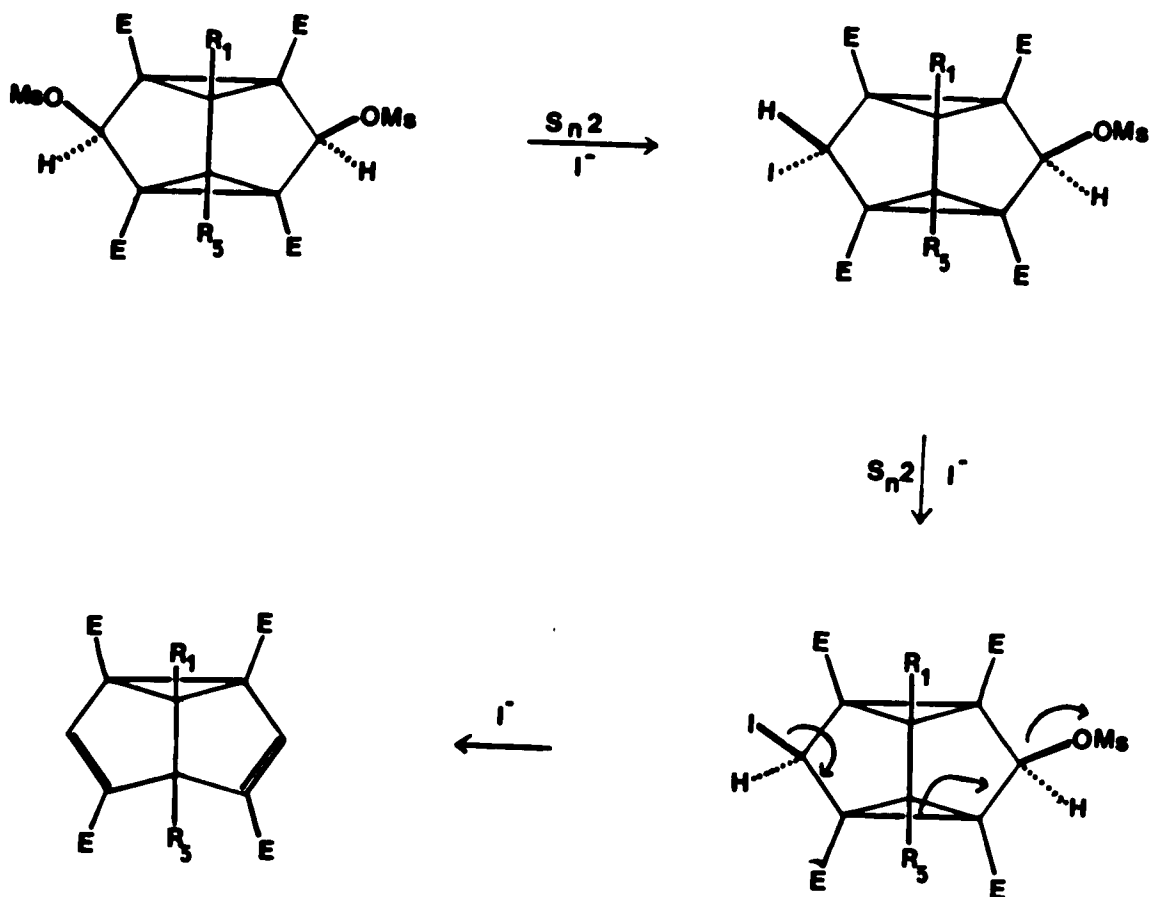
Table 8b: H-1 NMR's ( $\delta$  in ppm) of the dimesylates (CDCl<sub>3</sub>)

Compound	H 3,7 (2H s)	COOMe (12H s)	SOOMe (6H s)	cycloalkane H's (multiplet)
5	5.73	3.75	3.08	1.80
11a	5.73	3.67	3.04	2.42, 2.26
11b	5.7	3.65	3	2.3, 1.8
11c	5.75	3.7	3.1	2.35, 1.73
11d	5.65	3.7	3.0	2.4, 1.6

Refluxing the dimesylates 11a,b,c,d in dry acetone with an excess of anhydrous NaI produced a mixture of products. To study the mechanism, the reaction producing 12b was worked up at an earlier stage. A colorless compound was obtained. On the basis of its proton NMR 1.8 (8H, multiplet, 3.8 (12H, singlet), 5.2 (1H, singlet), 6.45 (1H, singlet) it was identified as the mono-iodo mono-mesylate of unknown stereochemistry. This was analogous to that observed in the case of 6 (Scheme 1).

The mechanism for the conversion of the dimesylates to the semibullvalenes is outlined below. A double displacement by iodide converts the dimesylate first to an endo-iodo-exo mesylate, then to an exo-iodo exo mesylate

(not isolated). Iodide induced reductive 1,4 fragmentation of the exo-iodo exo-mesylate then takes place leading to the semibullvalenes.



Semibullvalene 12b crystallised from methanol as shiny yellow flakes, in a 64% yield; 12a (yellow crystals) was isolated in a crude yield of 60%. The melting points, IR, NMR are summarised in Table 9. A detailed analysis of the proton and C-13 nmr will be given in Chapter 3.

Table 9a: MP's (in °C) and IR's (KBr pellet) in  $\text{cm}^{-1}$  of the semibullvalenes

Compound	MP's	C-H	C=O of COOMe	C=C
6	102.5-103	2960	1710	1590
12a	105-7	2950	1720	1580
12b	128-9	2940	1720	1590
12c	95-7	---	---	---
12d	169.5-170.5	--	---	---

Table 9b: H-1 NMR's ( $\delta$  in ppm) of the semibullvalenes ( $\text{CDCl}_3$ ) at room temperature.

Compound	H 3,7 (vinylic) (2H s)	COOMe (12H s)	cycloalkane H's multiplet
6	6.18	3.67	1.45
12a	6.43	3.77	2.22, 1.66
12b	6.42	3.75	2.05, 1.45
12c	6.45	3.8	2.2, 1.5
12d	6.3	3.7	2.3, 1.3

Table 9c: C-13 NMR's ( $\delta$  in ppm) of the semibullvalenes  
(CDCl<sub>3</sub>) at room temperature.

Compound	C=O s	C 3,7 d	C 2,4,6,8 s	C 1,5 s	OMe q	cyclo- alkane C's t
6	165.47	131.23	104.07	68.67	52.09	11.02
12a	165.36	132.41	103.91	76.8	52.12	28.57, 27.99.
12b	165	132.5	106.5	70	52	18

CHAPTER 3  
REACTIVITY AND PHYSICAL MEASUREMENTS

REACTIVITY

This shall be discussed under the following subheadings:

1. Thermal isomerization
2. Endoperoxide formation by reaction with triplet oxygen

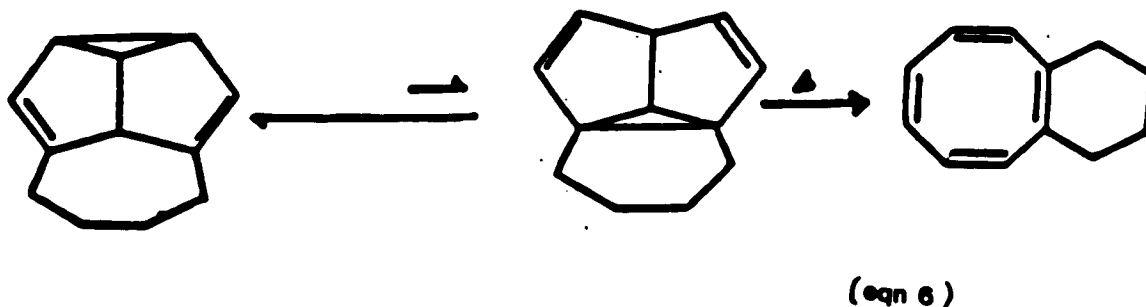
Thermal isomerisation:

Pyrolysis of several dimethyl semibullvalenes at 390° produced the corresponding cyclooctatetraenes in 70-80% yields (75, 74, 76) (equation 5).



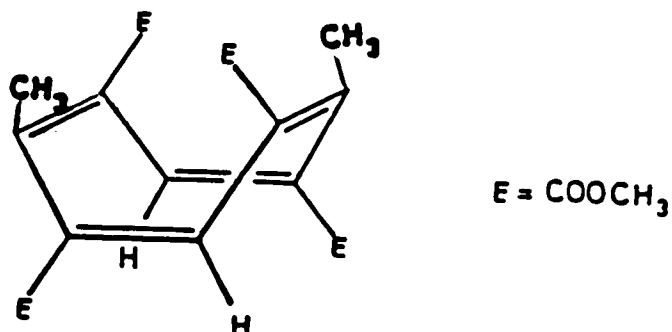
In a related thermal isomerization, 2,8-tetramethylene

semibullvalene yielded a rearranged cyclooctatetraene (equation 6).



The parent semibullvalene gets converted to cyclooctatetraene by pyrolysis at 270°C. 1,5-Dimethyl-2,6-dicyano semibullvalene synthesized by Quast et al., isomerizes to the corresponding cyclooctatetraene in a yield of 98% (capillary GC) in solution at 130°C (77). However the conversion of 1,5-dimethyl-2,4,6,8-tetracarbomethoxy semibullvalene, 6, to the corresponding cyclooctatetraene, 13, is the most facile of all occurring even at refrigerator temperatures of 5° C. The synthesis of 1,5-dimethyl-2,4,6,8-tetrakis (carbomethoxy) semibullvalene, 6, was always accompanied by the formation of a white material identified as 13. 13 was formed even at room temperature in solution, but not in the solid state; it was formed on prolonged standing in

solution at refrigerator temperatures.



### 13

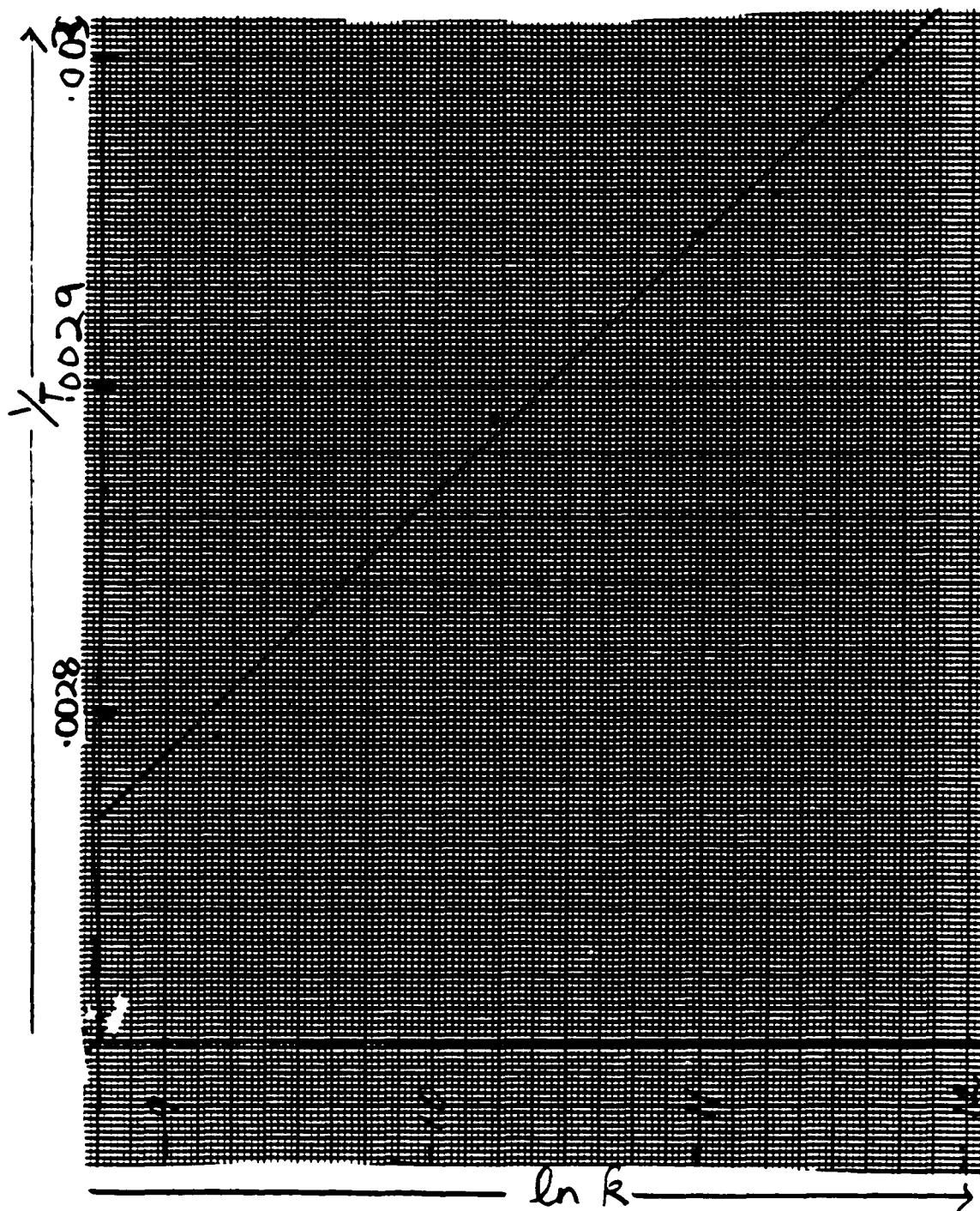
In order to quantitate the facile conversion of 6 to 13, the activation energy was obtained from the rate constants at three different temperatures using the Arrhenius equation. The reaction was found to be irreversible. Refluxing the cyclooctetraene at 74°C in carbon tetrachloride led to only 4% of the semibullvalene. The rate constants were therefore determined assuming an irreversible reaction. It was done by integrating peaks at 6.2 ppm (semibullvalene vinylic H) and 7.2 ppm (cyclooctatetraene vinylic H) leading to the following values (for further experimental details refer Chapter 7):

$k=1.28 \times 10^{-6} \text{ sec}^{-1}$ ,  $t_{1/2}=15 \text{ hrs.}$ , at 65°.

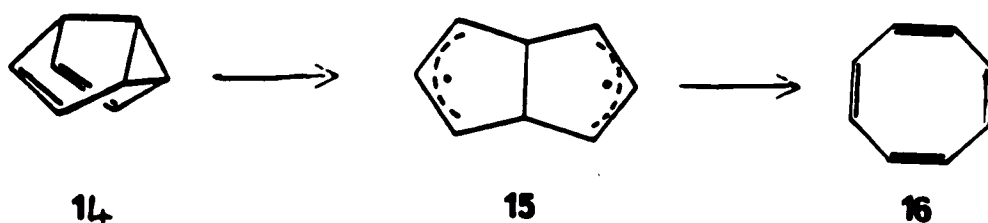
$k=3.59 \times 10^{-6} \text{ sec}^{-1}$ ,  $t_{1/2}=5.4 \text{ hrs.}$ , at 73°.

$k=1.014 \times 10^{-5} \text{ sec}^{-1}$ ,  $t_{1/2}=1.9 \text{ hrs.}$ , at 85°.

Incorporating the above values into the Arrhenius' equation led to an activation energy of  $25.6 \pm 0.1$  Kcal/mole and an A value of  $1.97 \times 10^{11}$  for the conversion of 6 to 13.

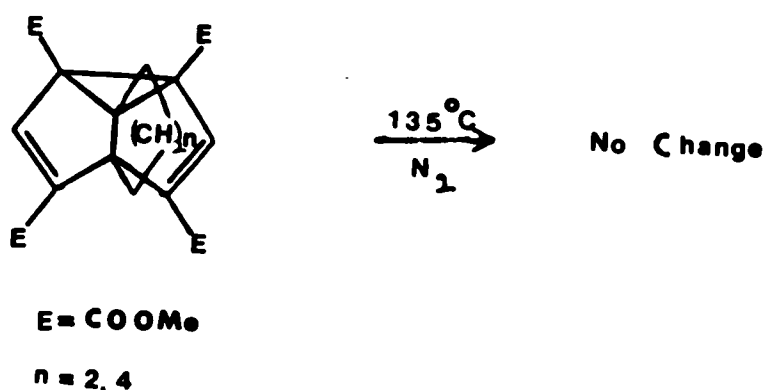


The activation energy for the conversion of the parent semibullvalene to cyclooctatetraene was reported to be 39 Kcal/mole (78). The mechanism for the conversion of semibullvalene to cyclooctatetraene is thought to occur via the diradical 15 (79).



The ease of conversion of 1,5-dimethyl-2,4,6,8-tetrakis (carbomethoxy) semibullvalene, 6, to the corresponding cyclooctatetraene, 13, when compared to the parent semibullvalene clearly indicates that the substituents have lowered the activation energy for the conversion of semibullvalene to cyclooctatetraene. The 1,5 annulated semibullvalenes were therefore expected to rearrange to bridged cyclooctatetraenes. However, refluxing 1,5-cyclohexano-2,4,6,8-tetrakis (carbomethoxy) semibullvalene, 12b, and 1,5-cyclooctano-2,4,6,8-tetrakis (carbomethoxy) semibullvalene, 12d, in xylene for 24 hrs under  $N_2$  produced no change in the semibullvalenes. The semibullvalenes were recovered quantitatively. 12d was

pyrolysed (without solvent) in an NMR tube to 200°C leading to a product unidentifiable by NMR.

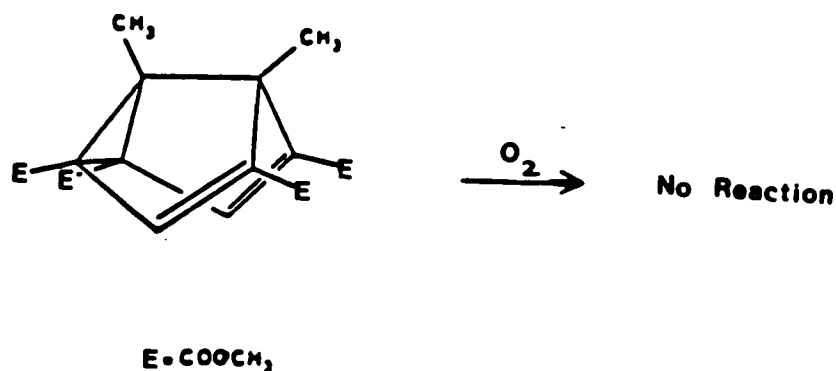


Drieding molecular models allow the construction of 1,5-hexamethylene cyclooctatetraene while the 1,5-pentamethylene, 1,5-tetramethylene, 1,5-trimethylene bridges introduce considerable strain in the molecule. This is a qualitative explanation for the inability of the annulated semibullvalenes to rearrange to the corresponding cyclooctatetraenes.

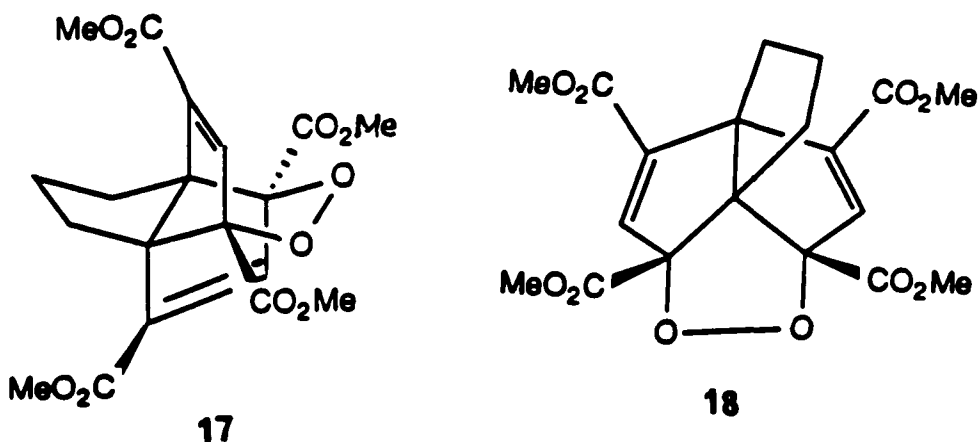
Endoperoxide formation by reaction with triplet oxygen:

Endoperoxide formation of semibullvalene has been reported earlier in the case of octa methyl semibullvalene. Legoff reported the isolation of a compound containing two extra oxygen atoms during the synthesis of octacarbomethoxy semibullvalene (43). However, we have not able to isolate any endoperoxide in

the case of 1,5-dimethyl-2,4,6,8-tetrakis (carbomethoxy) semibullvalene by bubbling  $O_2$  through a solution of the semibullvalene in acetone.

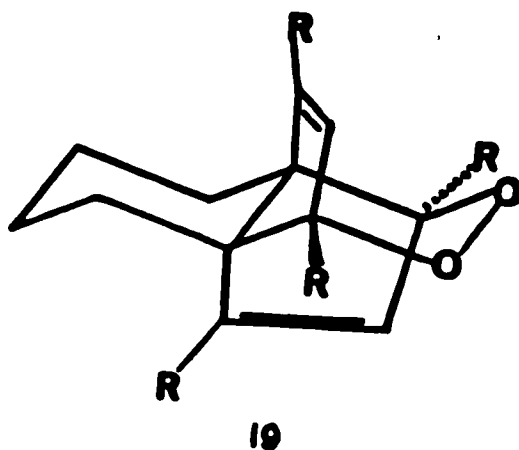


On the other hand, during the isolation of 1,5-cyclopentano-2,4,6,8-tetrakis (carbomethoxy) semibullvalene, 12a, it was apparent that the yellow semibullvalene was transformed very quickly to a colorless mixture of three components, as is evident by TLC (9 Et<sub>2</sub>O : 1 CH<sub>2</sub>Cl<sub>2</sub>) under UV. The nmr of the mixture showed two olefinic and three carbomethoxy signals indicating the presence of at least two compounds. Structures 17 and 18 have been assigned to the two compounds based on NMR. Oxygen absorption occurs thirty times faster for 12a than for compound 12b. NMR of the endoperoxide 17  $\delta$  ppm : 1.85 (4H multiplet, the four outer H's in cyclopentane) and 2.24 (2H triplet, the middle H's in cyclopentane), 3.88 (two 6H singlets, OMe), 6.36 (2H singlet, vinylic H's).



The mother liquor from the synthesis of 1,5-cyclohexano-2,4,6,8-tetrakis (carbomethoxy) semibullvalene, 12b, initially showed a single spot on TLC (9:1, Et<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub>) the R<sub>f</sub> of which corresponded very well with the R<sub>f</sub> of 1,5-dimethyl-2,4,6,8-tetrakis (carbomethoxy) semibullvalene, 6 (Scheme 1). When the TLC when repeated after a couple of days it indicated the presence of two components. The R<sub>f</sub> of the second component compared well with 2,6-dimethyl-1,3,5,7-tetrakis (carbomethoxy) cyclooctatetraene, 13. Microanalysis of the new compound indicated the formula C<sub>28</sub>H<sub>28</sub>O<sub>10</sub>: calc , C,56.87; H,5.25; found C,56.89; H,5.33. This suggested the presence of two extra oxygens. A high resolution mass spectrum of the compound confirmed the presence of the two extra oxygens. The proton NMR fits well with the structure δ 1.1 (2H, t), 1.25 (2H, t), 1.4 (2H distorted triplet), 2.3 (2H, br doublet), 3.75 (two 6H s, OMe), 7.0 (2H s, vinylic H's). The C-13 NMR data: δ 22 (t, cyclohexane carbons), 52 (two q, OMe), 66 (s, the

carbons at the junction of the two five membered rings and the cyclohexane ring), 92.2 (s, the tertiary carbons bearing the ester groups and the oxygen), 140 (d, for the vinylic CH and a singlet for the double bond carbons bearing the ester groups), 164 (s, carbonyl of one set of esters), 165 (s, carbonyl of the other set of esters). X-ray crystallography finally proved the structure of endoperoxide 19, which indicated the addition of one mole of oxygen to the semibullvalene giving the endoperoxide, shown below.



The X-ray crystallography was done by L. Todaro at Hoffman La-Roche. Note that the cyclohexane ring exists in the chair conformation in the endoperoxide. In the 1,5-cyclohexano semibullvalene it exists in the boat conformation (refer the section on X-ray studies in this Chapter). One of the driving forces for the reaction towards oxygen may be related to the conformation of the cyclohexane.

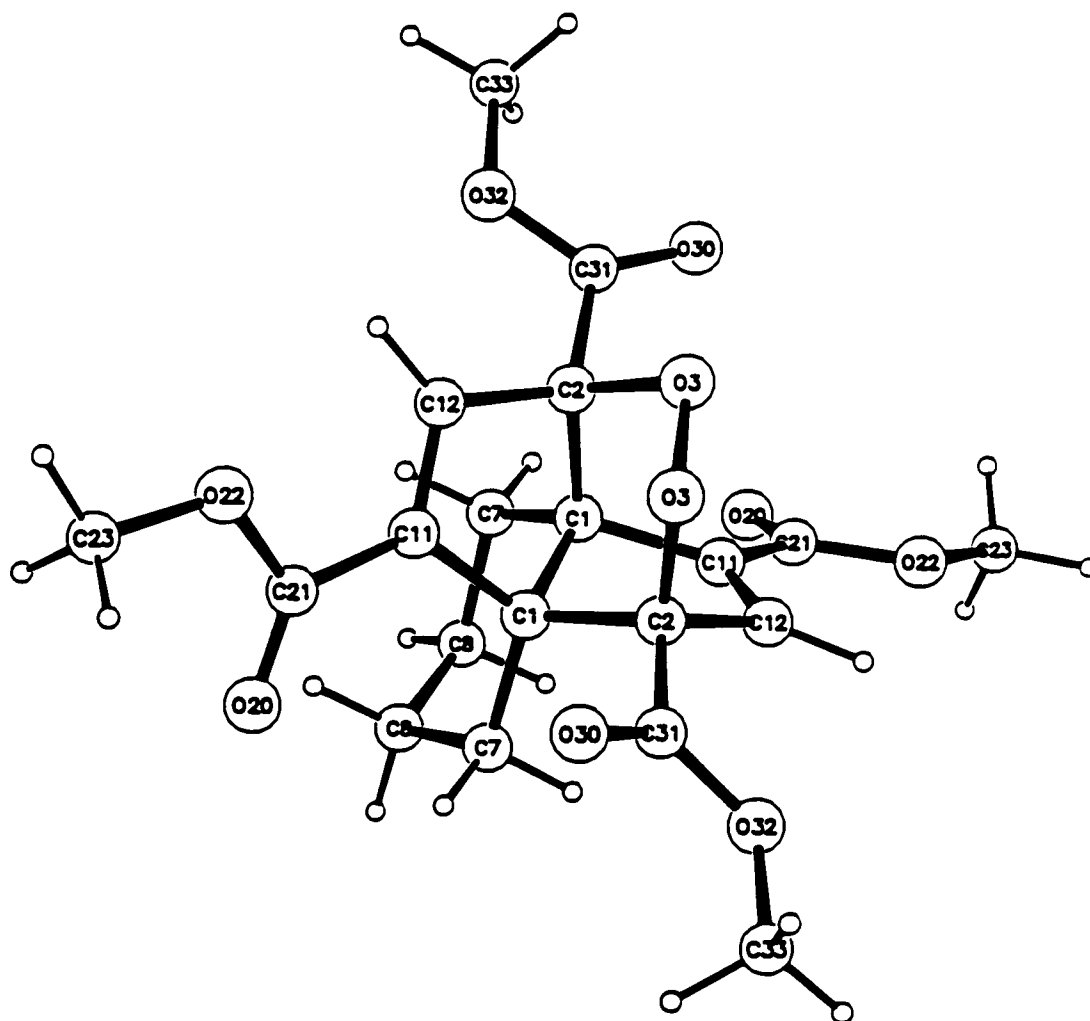


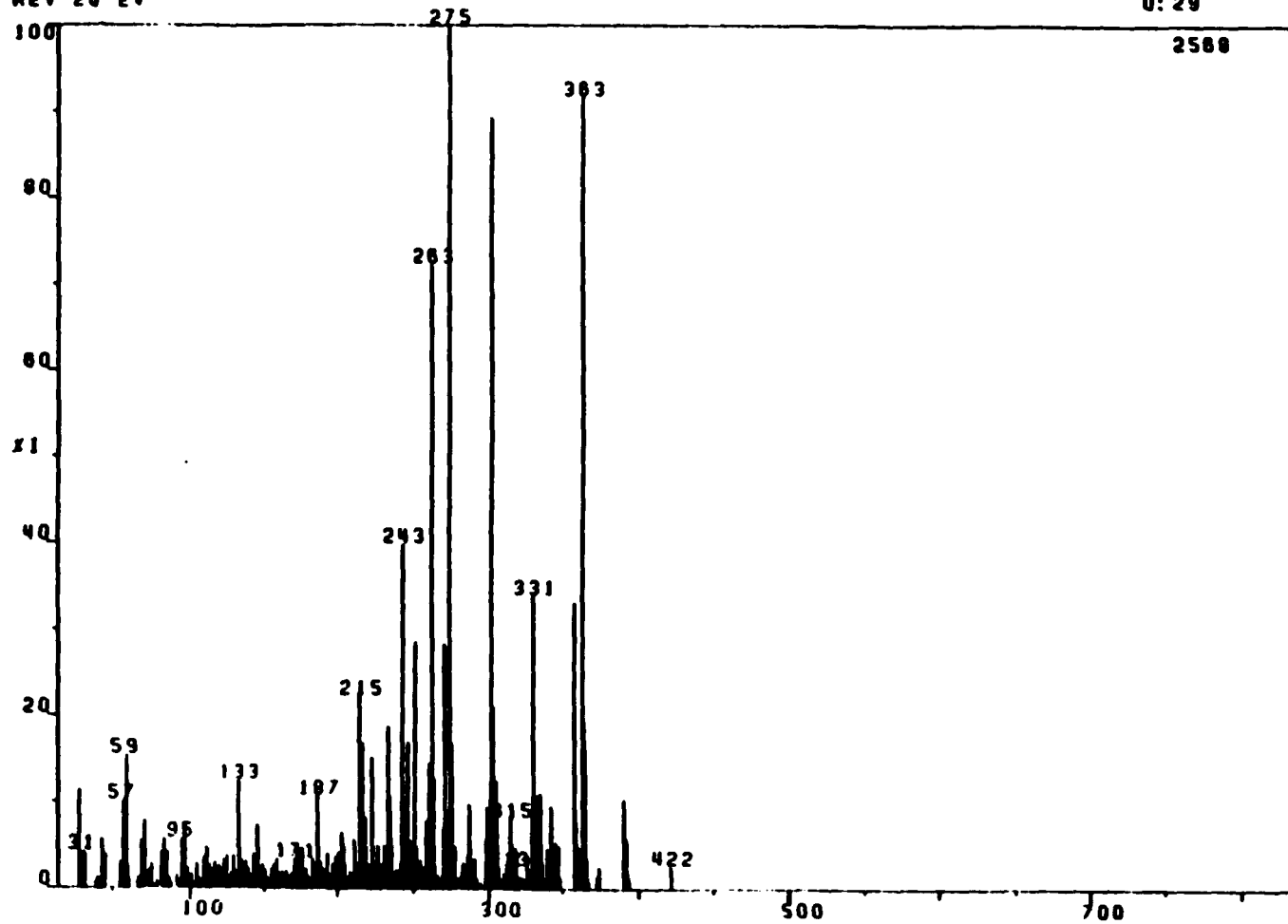
Figure 4. Xray structure 10,11-dioxatetracyclo [7.6.0.0  
 1.0.0.1.0] 7,13-diene- 7,9,12,14-tetracarboxylic  
 acid tetramethyl ester.

KLAUSI. 5  
REV 20 EV

CAL:CCD

STA: BG SCAN = 4

0:29



The melting point of the endoperoxide, 19, was found to be 151.5-153°C (MeOH); during the determination of the melting point the colorless crystalline endoperoxide turned yellow suggesting its conversion to the yellow semibullvalene 12b. To study the details of the loss of oxygen from the endoperoxide, 19, it was sublimed at 150°C and 5 mm of Hg, and the sublimate as well as the residue were examined by 400 MHz NMR. The NMR indicated a mixture of two products, different from the semibullvalene and endoperoxide, which were not further identified.

1,5-cyclohexano-2,4,6,8- tetrakis (carbomethoxy) semibullvalene, 12b, converted to the endoperoxide, 19, in the solid state at room temperature in the dark. 12b absorbed oxygen slower than 12a, as measured by the color change of yellow semibullvalenes to colorless endoperoxides. To quantitate the rates of oxygen absorption by 12a and 12b, the rate constant values were obtained as follows: the semibullvalene was dissolved in carbon tetrachloride and oxygen was bubbled through the solution. NMR's were obtained every hour. The vinylic H's for semibullvalene and endoperoxide appear at 6.2 and 7 respectively in the case of the 1,5-cyclohexano compound. The area under these peaks were integrated and the concentration of semibullvalene was obtained by dividing the area under the peak at 6.2 by the sum total of areas under the peaks at 6.2 and 7 (look for further

experimental details in Chapter 7).

$k = 4.8 \times 10^{-4} \text{ sec}^{-1}$ , at 24°C and 759 mm of Hg (oxygen flow rate 16 ml/min.) for 12a.

$k = 1.6 \times 10^{-4}$ , at 26°C and 758.2 mm of Hg (oxygen flow rate 16 ml/min) for 12b.

The reactions followed first order kinetics with respect to the semibullvalene in each case.

Wilson and Geiser (84) interpret the ease of formation of endoperoxides of trimethylmethane biradicals with oxygen, to the existence of an accessible and long-lived triplet ground state. The reaction of semibullvalenes 12a and 12b with oxygen is therefore suggestive of low lying triplets.

1,5-Cycloheptano-2,4,6,8- tetrakis (carbomethoxy) semibullvalene, 12c, does not absorb oxygen in solution. Oxygen was bubbled through a solution of 5 mg of the semibullvalene in 15 mL of carbon tetrachloride; the nmr of the solution remained unchanged. The 1,5- cyclooctano-2,4,6,8- tetrakis (carbomethoxy) semibullvalene, 12d, also does not absorb oxygen. The reason for the stability of 12d became obvious after carrying out X-ray crystallographic studies to determine its structure. X-ray structure determination and variable low temperature C-13 NMR studies were carried out only on 12b and 12d. This will be discussed in subsequent sections.

## NMR STUDIES

NMR studies on 1,5-cyclohexano-2,4,6,8-tetrakis (carbomethoxy) semibullvalene and 1,5-cyclooctano-2,4,6,8-tetrakis (carbomethoxy) semibullvalene:

### Background:

Chemical systems which undergo isomerization can be studied by various methods. If the free energy of activation ( $\Delta G^\circ$ ) is large ( $>23$  Kcal/mole), the various isomers are stable at room temperature and separation should be possible. As the rate of isomerization increases  $\Delta G^\circ$  decreases and physical separation at room temperature becomes impossible. Figure 5 is a schematic representation of some of the processes that can be used for the detection of intramolecular mobility. Low temperature solution nmr spectroscopy is an extremely valuable tool for studying equilibrium systems (85). If two nuclei have different chemical environments and if they are interconverting slowly; then two separate signals will be observed in the nmr spectrum in the case where the signals are not coupled and are of equal intensities. In an equilibrating system the rate constant is a function of temperature and the nmr spectra of such systems are temperature dependent. This is shown schematically in Figure 6 (86).



In this illustration it is seen that at low temperatures 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  $\delta U = U_a - U_b$ . As the temperature is increased the rate of interconversion,  $k_r$ , increases and the signals first broaden and approach each other (c - Figure 6). At the coalescence temperature ( $T_c$ ) the signals have merged into one very broad peak (d - Figure 6) which is almost indistinguishable from the baseline. At the coalescence temperature the rate constant is related to the chemical shift difference by equation 7 for equally populated sites.

$$k_r = \pi/\sqrt{2} (U_a - U_b) \text{ sec}^{-1} \quad (\text{eqn 7})$$

The rate increases with increasing temperature until the signals have become one sharp peak whose chemical shift is  $1/2(U_a + U_b)$  (g in Figure 6). Once the value for  $k_r$  is determined,  $\Delta G^\circ_{(T_c)}$  can be calculated for the equilibrium reaction using equation 8 (86).

$$\Delta G^\circ = 4.57 T (10.32 + \log T/k_r) \text{ cal/mole} \quad (\text{eqn 8})$$

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.

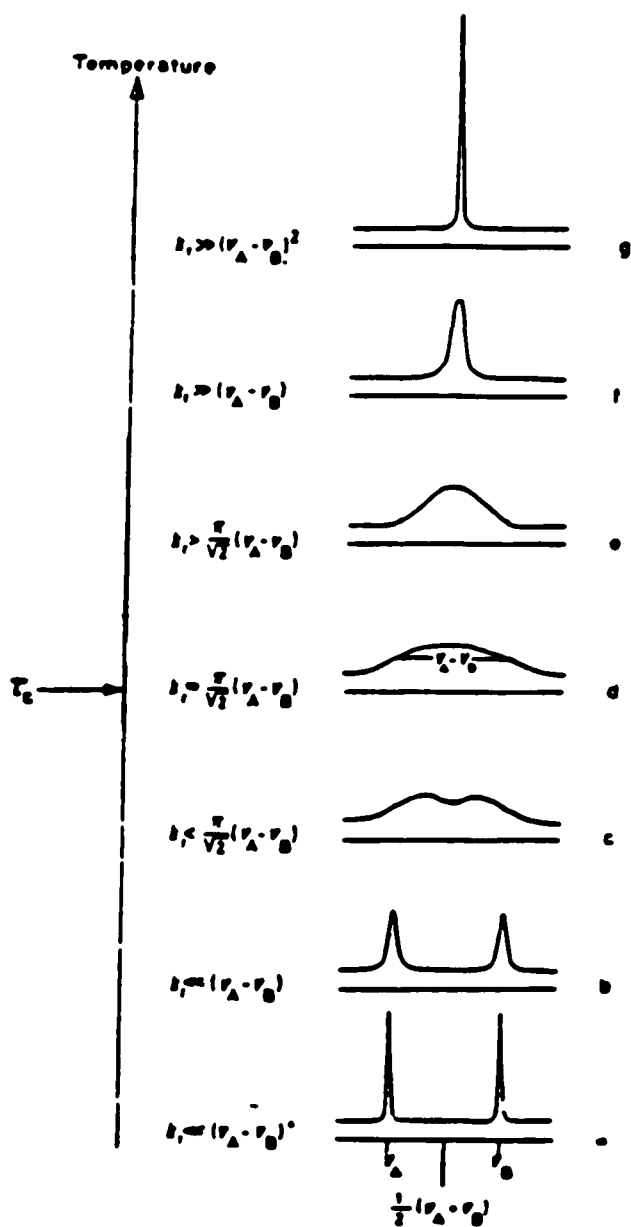


Figure 6. Temperature dependence of chemical shifts and line line shapes due to intramolecular mobility

Taken from Breitauer and Voelter,  
 "<sup>13</sup>C NMR Spectroscopy",  
 Verlag Chemie, 1974, p. 85

A least squares treatment to obtain the best fitting spectra is then used to calc  $k_{12}$ . Other thermodynamic properties ( $E_{act}$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$ ) can then be calculated (86). 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 (87) (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 studying 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  $^{13}\text{C}$  nmr spectroscopy. Since the rate constant ( $k_r$ ) depends on the chemical shift differences between the exchanging nuclei (measured in Hertz), the advent of high field spectrometers has aided in the accurate determination of this parameter (88).

The lower temperature limit for the determination of a spectrum is dependent on several factors; solvent viscosity and melting points, solubility of the solute and the 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 ( $^{13}\text{C}$  frequency) spectrometer is  $-160$  to  $-170^\circ\text{C}$ .

In the case of semibullvalene and its symmetrically substituted derivatives, the equilibrating species which are undergoing Cope rearrangement are degenerate (eqn 2). 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 9 when the equilibrium is very fast on the nmr time scale, signals for carbons (or protons) 2,8 and 4,6 will appear at averaged positions as will those for 1,5.



The signal for 3,7 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 will change as the temperature is varied. Semibullvalene rearranges rapidly on the nmr time scale at room temperature (25). Its rate of rearrangement has been slowed at  $-160^{\circ}\text{C}$  to allow

observation of the nmr resonances for the static structure. The signals for H 2,8 and H 4,6 coalesced at  $-143^{\circ}\text{C}$  when the spectrum was determined at 251 MHz (26). Anet has calculated a free energy of activation from these data and reached at a value of 5.5 Kcal/mole.

Experimental Methods:

Results and discussion:

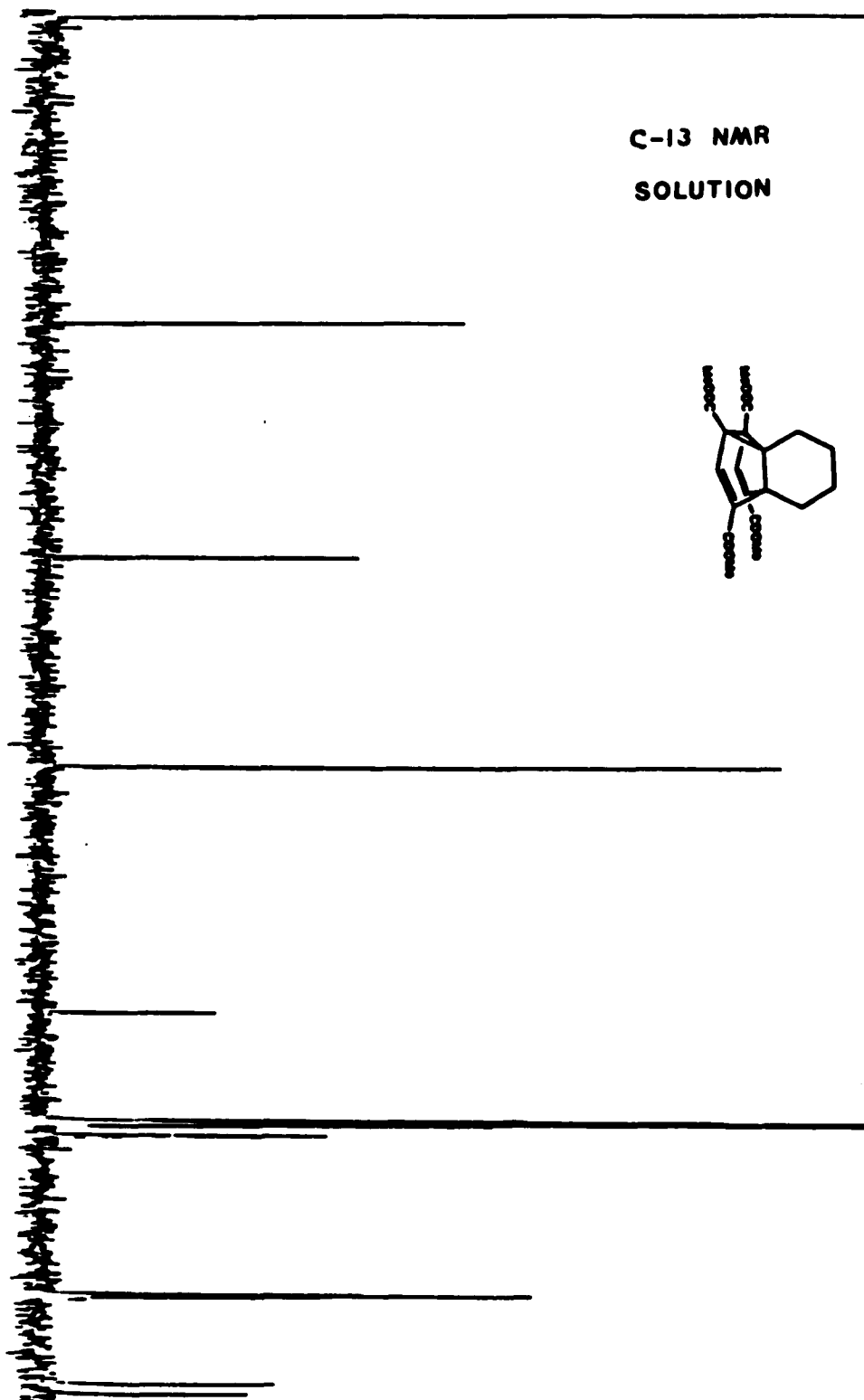
Before attempting an analysis of low temperature spectra, an interpretation of the room temperature data is necessary. The resonances for H 3,7; C 2,4,6,8; and C 3,7 are summarized below.

Room temp. nmr's for the annulated semibullvalenes

Compound	H 3,7	C 2,4,6,8	C 3,7
6 (Scheme 1)	6.18	104.07	131.23
12a (Scheme 2)	6.43	103.91	132.41
12b (Scheme 2)	6.42	106.5	132.5
12c (Scheme 2)	6.45	---	---
12d (Scheme 2)	6.3	104.32	130.90

From the data above, it is clear that averaged spectra are being recorded at room temperature. The  $^{13}\text{C}$  spectrum exhibits C 2,8 and C 4,6 as a single peak. Since the positions 2,4,6,8 are substituted with ester groups, none of the protons are directly involved in the Cope

rearrangement, proton chemical shifts will not provide much information regarding this rearrangement.

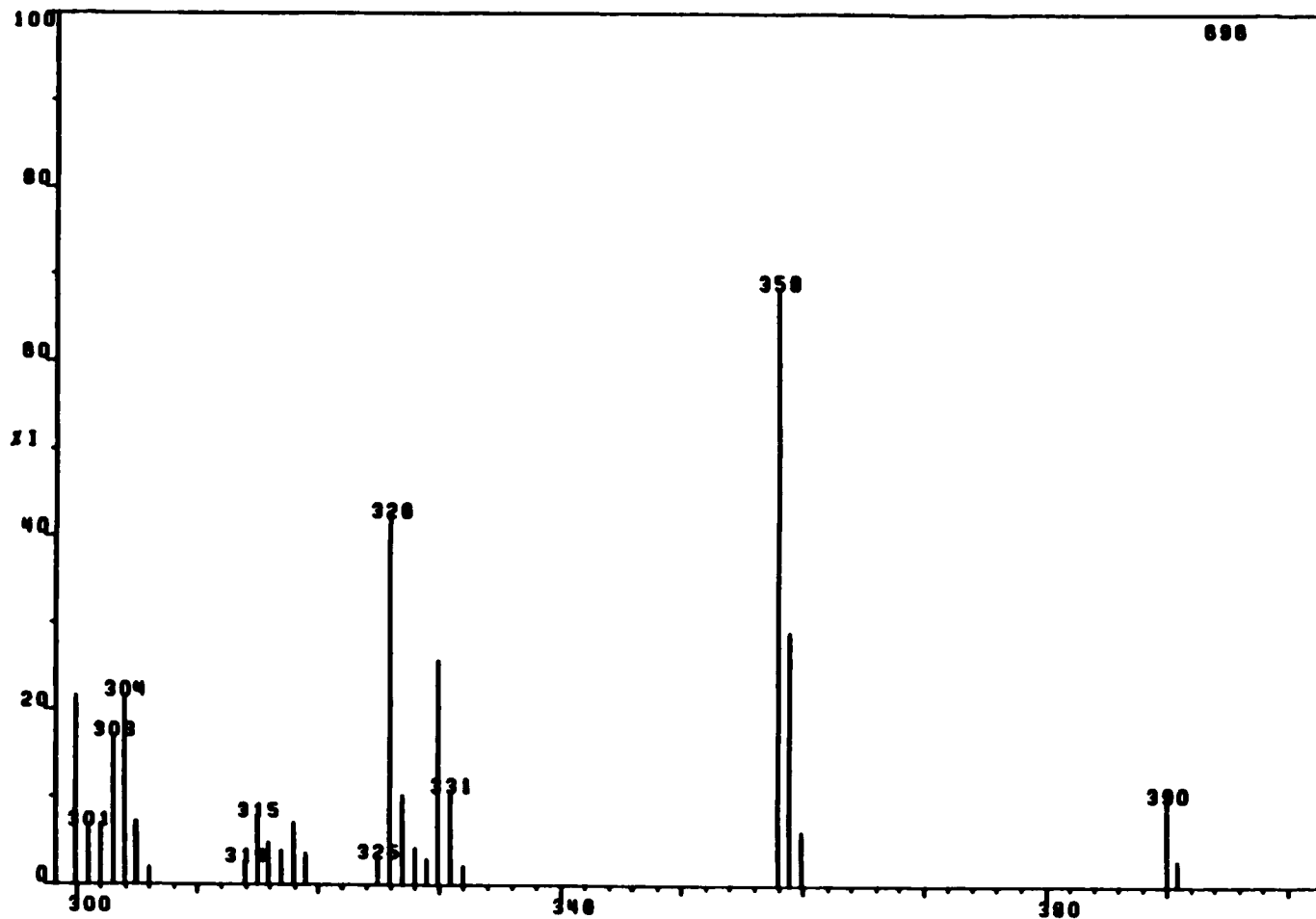


SB-CO 14

CAL:CCO

STA: 00 SCAN = 0

1: 1



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 carbons attached at the 1,5 positions, the four carbonyls and the four methoxy groups. Only carbons 3 and 7 should appear at the chemical shift expected for a nonequilibrating vinyl carbon in the system.

Analysis of low temperature dynamic C-13 NMR in solution:

Assuming that 1,5-cyclohexano and 1,5-cyclooctano semibullvalenes 12b and 12d are rapidly undergoing Cope rearrangement, the low temperature nmr spectrum should follow a pattern similar to that observed for the parent compound (26). 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 to be between C2,8 and C4,6 as one set of carbons will become a 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 show no 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.

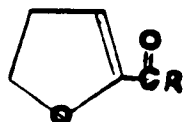
At  $-95^{\circ}\text{C}$  the C-13 spectrum of 1,5-cyclohexano-2,4,6,8-tetrakis (carbomethoxy) semibullvalene, 12b, shows no change from the room temperature measurement. The signal for C3,7 and C2,4,6,8 decrease in height as the temperature is lowered. This is evident from the spectra at  $-103$ ,  $-123$ ,  $-143$  and  $-153^{\circ}\text{C}$ . At  $-153^{\circ}\text{C}$  the signal for C3,7 broadens, while the peak at 106.5 ppm (C2,4,6,8) is still sharp. The resonances for the methoxy, and carbonyl carbons and C1,5 are still sharp. No definitive statement can be made about the broadening of the peak for the cyclohexane carbons due to the solvent (ethyl chloride) peak. Solvents used for low temperature nmr measurements should have have a good anti-freeze ability; this limits our choice of solvents. We had to avoid vinyl chloride which is a good solvent for detemining low temperature nmr's. In order to avoid solvent interference in the vinylic region which is very crucial for the present study. It appears however that the peak for cyclohexane has not broadened even at  $-153^{\circ}\text{C}$ . Table 10 summarizes the dynamic NMR studies of semibullvalene 12b.

The broadening of the signals for the vinylic carbons, C3,7 was not expected on the basis of decrease in the rate of Cope rearrangement only. There are three possible

explanations for this unexpected broadening:

1. The X-ray analysis indicated that the carbomethoxy groups are not symmetrically disposed in a crystal. If one looks at the crystal structure (below) it is clear that C3 and C7 are different environments with respect to the carbomethoxy groups, i.e., the carbomethoxy groups are no longer conjugated with the C3-C4 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 (89,90).



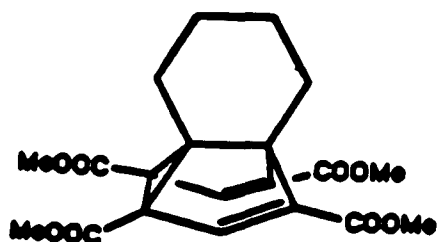
$$\Delta G_{T_c}^{\ddagger} = 10-11 \text{ kcal/mol}$$

$$T_c = -57^{\circ}\text{C}$$



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

Table 10. Variable Temperature C-13 NMR for 1,5-cyclohexano-2,4,6,8-tetrakis (carbomethoxy) semibullvalene



ppm from TMS in deuterated methylene  
chloride/vinyl chloride

Carbon	-95	-103	-123	-143	-153 in °C
cyclo- alkane*	18	not obvious	not obvious	not obvious	not obvious
OMe	52	sharp	sharp	sharp	sharp
C1,5	70	sharp	sharp	sharp	sharp
C2,4,6,8	106.5	height reduced	height reduced	height reduced	height reduced (sharp)
C3,7	132.5	height reduced	height reduced	height reduced	height reduced (broad)
C=O	165	sharp	sharp	sharp	sharp

\* it is not obvious due to the solvent peak

We can estimate the effects of hindered rotation on our system in the following way. If the carbonyl group is 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 in conjugation with the double bond, the shielding expected at the  $\beta$ -carbon could be estimated to be twice that observed when the group is freely rotating ( $2 \times 7$  ppm) (91). Configurations in intermediate positions would experience effects between these two extremes. The maximum difference in C-13 chemical shift for the  $\beta$ -vinylic carbon (C3,7 in our compound) would then be 14 ppm ( $2 \times 7 - 0$  ppm). This corresponds to a frequency difference of 1408.4 Hz on the spectrometer used for low temperature studies and an estimated  $k_r = 3129 \text{ sec}^{-1}$ . The C3,7 peak begins to broaden at  $-153^\circ\text{C}$ . The upper limit for the free energy of activation for the rotation of the carbomethoxy groups is 5 Kcal/mole. This type of broadening of the C3,7 peak was observed at  $-150^\circ\text{C}$  in the case of 1,5-dimethyl-2,4,6,8-tetrakis (carbomethoxy) semibullvalene (33) which would once again suggest a value of 5 Kcal/mole for the free energy of activation for the rotation of the carbomethoxy groups. The signal for cyclohexane appears to be sharp even at temperatures as low as  $-153^\circ\text{C}$ . A study of the dynamics of the cyclohexane

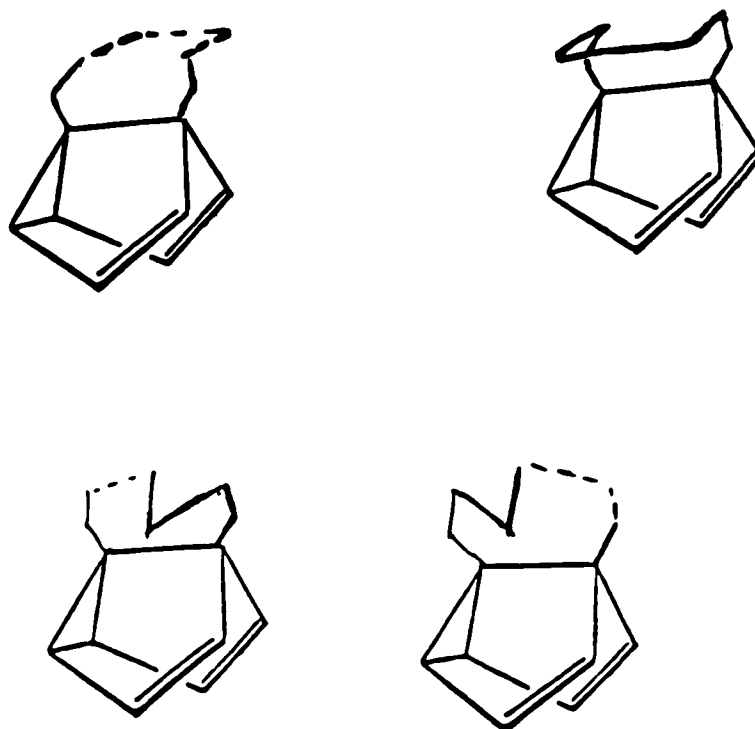
ring movement should provide useful information. Though one expects the cyclohexane ring movements to cause differences in the resonances of C3,7, it appears from a comparison of the low temperature C-13 solution NMR's of the dimethyl compound and the cyclohexane compound that these resonances remain unaffected (the broadening of C3,7 resonances start to occur at about  $-150^{\circ}\text{C}$  for both the compounds). The reason for the broadening thus appears to be more fundamental and related to the semibullvalene skeleton itself.

2. Another interpretation of low temperature spectra is suggested by results of the MNDO study (33) on the Cope rearrangement of some substituted semibullvalenes. The results suggest that there could be a triple minimum on the energy surface for the 2,4,6,8-tetra cyano semibullvalene and the 2,6-dicyano compound. There appears to be another species comparable to a bisallyl intermediate which is very close in energy to the Cope rearranging ground state. At room temperature the three structures are probably equilibrating rapidly and average NMR signals are observed. This could account for some of the unusual chemical shifts discussed above. 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 C-13 resonances to broaden and shift. The chemical shift in this study were not measured with the accuracy necessary to determine any slight changes. This will be studied when additional NMR spectra are obtained.

3. A third effect which could have caused the broadening of the C3,7 signal, is a change in the relaxation time due to a decrease in the tumbling rate of the carbons at low temperatures. Spin-spin relaxation becomes important in solids and liquids with slow tumbling molecules. 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) (87). Carbons bearing protons should experience this effect more readily as temperature is decreased. This would explain the broadening observed for C3,7. However, the cyclohexane carbons and the OMe carbons do not broaden.

In case of the 1,5-cyclooctano compound the ring movements of the cyclooctane complicates the situation. Some of these motions are shown below.



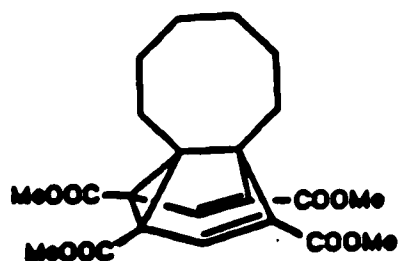
This process occurs very rapidly on an nmr time scale (the kinetics of the ring movements are currently under study at our laboratories) at room temperature in solution, thus not causing any differences in the resonances for C 2,4 and C 6,8. However, while obtaining nmr's at lower temperatures this process of ring folding slows down, causing a difference in the carbons 2,4 versus carbons 6,8 as is evident from the nmr at  $-33^{\circ}\text{C}$ . The peak for C2,4,6,8 begins to broaden at  $-33^{\circ}\text{C}$  and splits into two broad peaks at  $-95^{\circ}\text{C}$  due to the folding of the cyclooctane ring. This assumption is based on the chemical shift difference between the split peaks (3 Hz.). The other problem with dynamic solution nmr of this compound is that

it crystallizes out of the deuterated vinyl chloride / dichloromethane mixture used as a solvent at  $-130^{\circ}\text{C}$ . Alternatives to circumvent these problems are currently under study in our laboratories.

Since the ring movements cause differences in carbons 3 and 7, the signal for C3,7 begins to broaden at  $-33^{\circ}\text{C}$  and splits into two separate signals at  $-95^{\circ}\text{C}$ . The signals are 3 ppm apart, which is identical to the difference in the splitting for C2,4,6,8. The remaining signals are sharp at  $-95^{\circ}\text{C}$ . Table 11 summarizes the dynamic C-13 NMR of 1,5-cyclooctano 2,4,6,8-tetrakis (carbomethoxy) semibullvalene.

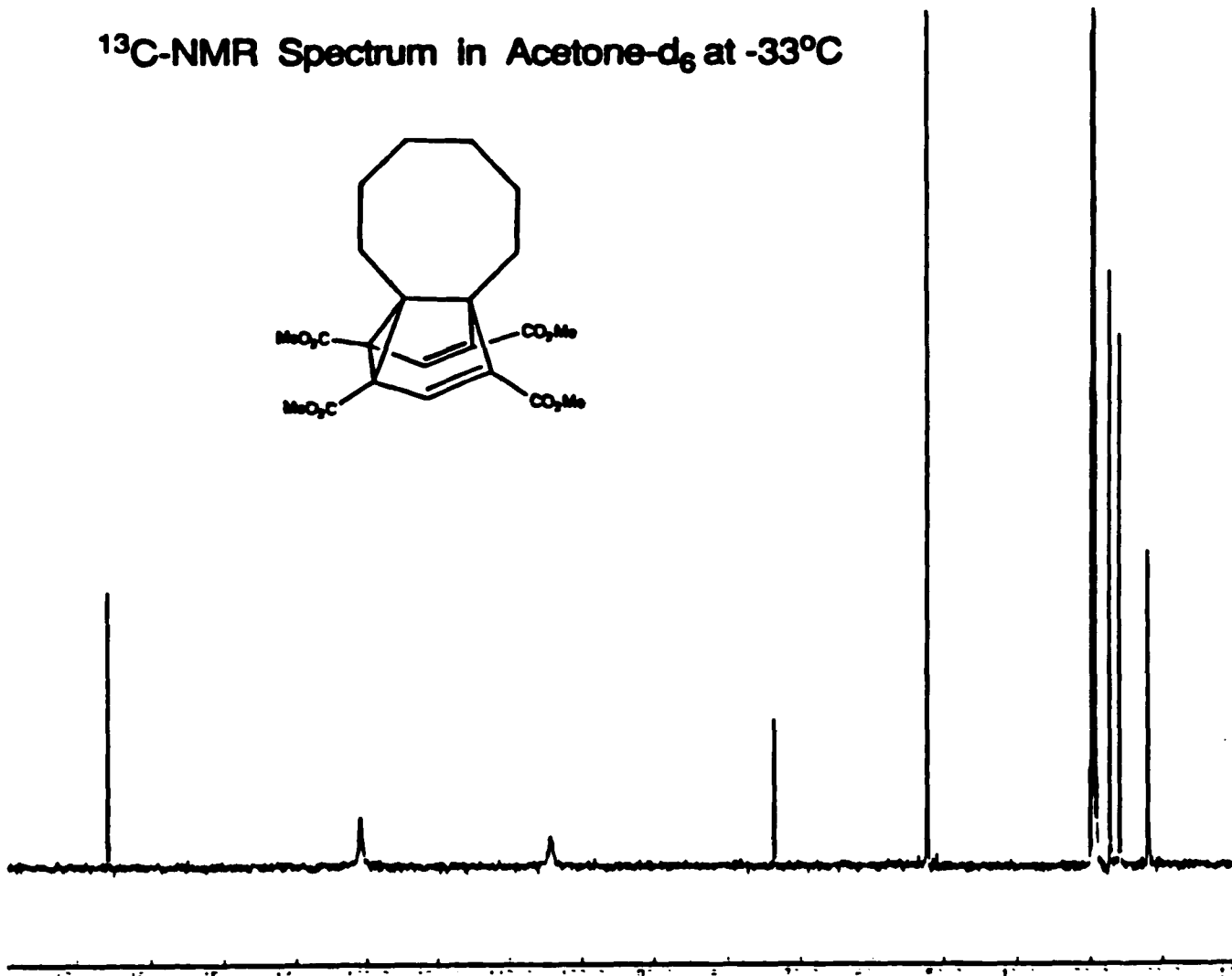
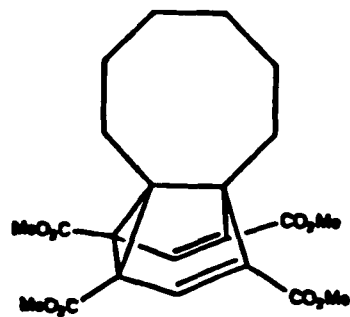
The reason for the broadening of the peak at 104.32 (C2,4,6,8) at  $-95^{\circ}\text{C}$  is probably related to the motions of the cyclooctane ring. It cannot be due slowing down of the Cope rearrangement because that would be contradictory to the structure of the molecule determined by X-ray crystallographic studies (this is taken up in the third section of this Chapter).

Table 11. Variable Temperature Carbon 13 NMR Data For  
1,5-cyclooctano-2,4,6,8- tetrakis (carbomethoxy)  
semibullvalene

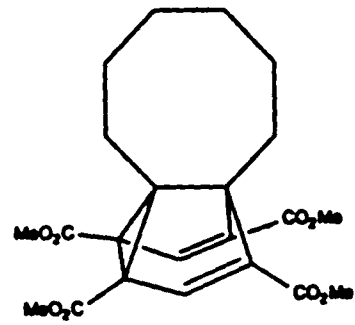


ppm from TMS in deuterated methylene  
chloride / vinyl chloride

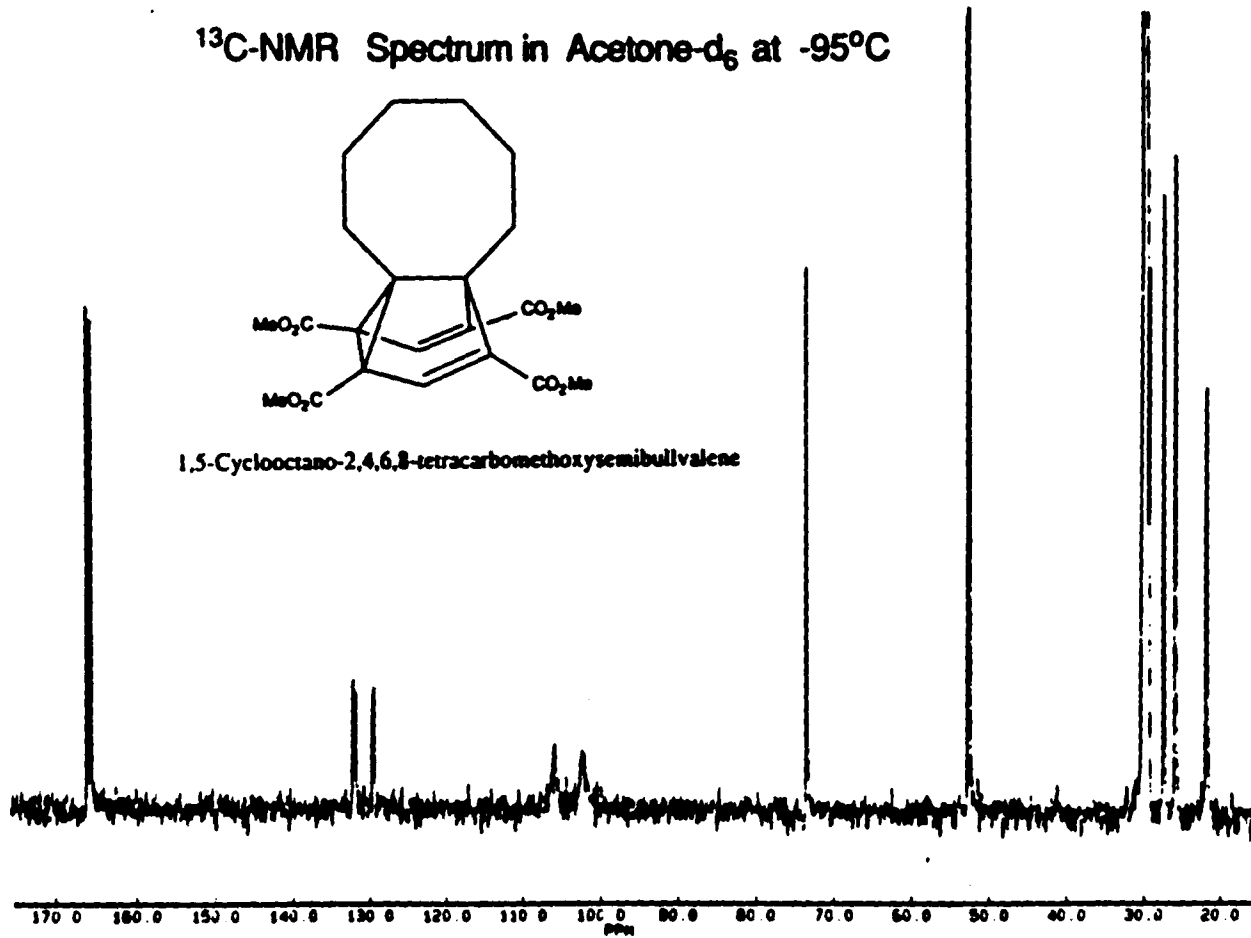
Carbon	-33	-95 in °C
cyclooctane carbons	25.75	sharp
OMe	52.29	sharp
C1,5	73.64	sharp
C2,4,6,8	104.32	two br peaks (short br)
C3,7	130.90	two sharp peaks (short br)
C=O	165.75	sharp

$^{13}\text{C}$ -NMR Spectrum in Acetone- $d_6$  at  $-33^\circ\text{C}$ 

$^{13}\text{C}$ -NMR Spectrum in Acetone- $\text{d}_6$  at  $-95^\circ\text{C}$



1,5-Cyclooctano-2,4,6,8-tetracarboxysemibullvalene



Calculation of activation energies:

The chemical shift difference between the carbons 2,8 and carbons 4,6 in 1,5-dimethyl-2,4,6,8-tetrakis (carbomethoxy) semibullvalene was determined from the CPMAS C-13 spectrum. This was found to be 44.75 ppm. This value was estimated by L. Miller to 90 ppm (33). Table 12 compares the C-13 resonances of 1,5-dimethyl-2,4,6,8-tetrakis (carbomethoxy) semibullvalene in the solid and solution phases. The carbon resonances differ by no more than 1.33 ppm (C3,7 resonances). This clearly indicates that there is no major crystal packing effects in this compound and the difference of the C2,8 and C4,6 can be safely used from the solid state measurements. Incorporating the value of 44.75 ppm in equation 7, the rate constant was found to be  $10003.4 \text{ sec}^{-1}$ . Low temperature dynamic C-13 NMR studies of 1,5-dimethyl-2,4,6,8-tetrakis (carbomethoxy) semibullvalene, 6 (Scheme 1), show that the peak for C2,4,6,8, just begins to broaden at  $-160^\circ\text{C}$ .

Table 12. Comparison of the C-13 NMR of 1,5-dimethyl-2,4,6,8-tetrakis (carbomethoxy) semibullvalene in the solid and solution phases

Carbon	solid	solution
Methyls	11.5	11.02
OMe	----	52.09
C1,5	67.75	68.67
C2,4,6,8	105.4	104.07
C3,7	131.23	129.9
C=O	165.9	165.47

Assuming the coalescence temperature to be  $-160^{\circ}\text{C}$  and employing a value of  $10003.4 \text{ sec}^{-1}$  for the rate constant in equation 9, the upper limit for the free energy of activation for the Cope rearrangement in this molecule was found to be 4.3 Kcals/mole. Since we do not have a series of spectra at different temperatures, a line shape analysis (85) is not possible. Such an analysis could lead to an exact coalescence temperature thus allowing us to accurately predict the activation energy for the Cope rearrangement.

With the 1,5 cyclohexano-2,4,6,8-tetrakis (carbomethoxy) semibullvalene, 12b, the resonances for

C2,4,6,8 remained a sharp singlet even at  $-153^{\circ}\text{C}$  (solution nmr). We have not yet obtained the CPMAS C-13 nmr spectrum of this compound. It is reasonable, however, to assume that the chemical shift difference between carbons 2 and 8 and carbons 4 and 6 is in the order of 45 ppm (there is a striking similarity in the structural features of the 1,5-dimethyl and 1,5-cyclohexano compounds; this will be taken up in detail in the section dealing with X-ray structure determination). Hence it appears that the free energy of activation for the Cope rearrangement in 12b is even lower than  $3.8 \pm 0.5$  Kcal/mole.

In case of the 1,5-cyclooctano compound, we need a more complete series of spectra to be able to calculate the activation energy for the Cope rearrangement. In order to study the molecule in the solid state, a CPMAS C-13 nmr of the 1,5-cyclooctano compound, Figure 7, was obtained. The most striking feature of the spectrum is that the signal for C 2,4,6,8 appears as two broad peaks at 100-110 ppm differing by 5 ppm. The signal for the vinylic carbons 3 and 7 appear as two peaks differing by 5 ppm. All the remaining signals are sharp. The splitting of the peaks for C2,4,6,8 and C3,7 can be attributed to the cyclooctane ring being folded on one side of the semibullvalene causing carbon 3 to differ from carbon 7, and also cause differences between C2,4 and C6,8.

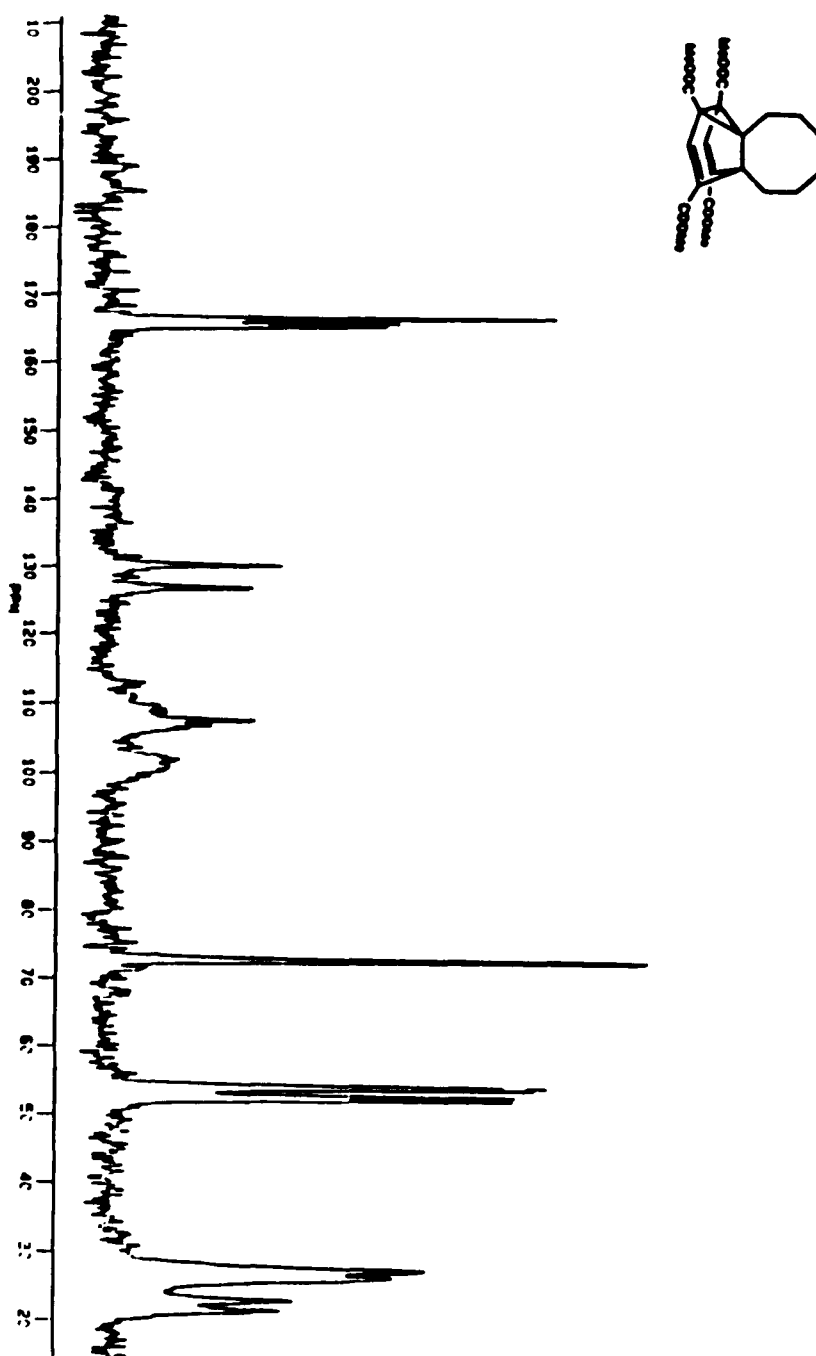


Figure 7. RT-CP-MAS solid State  $^{13}\text{C}$ -NMR of:  
1,5-cyclooctano-2,4,6,8-tetrakis (carbomethoxy)  
semibullvalene

This agrees well with the structure of the molecule determined by X-ray crystallographic methods. However, the peak at 100-110 ppm is broad. This suggests that the molecule is undergoing a rapid Cope rearrangement in the solid state at room temperature (98); or, that the molecule has a low lying triplet. This can be resolved by carrying out low temperature solid state NMR measurements. If the molecule is Cope rearranging at room temperature, the spectrum would change at lower temperatures. The broadening of the C2,4,6,8 peak is not related to large solid-state perturbations on the molecular electron distributions. This is evident by comparing the solution C-13 NMR with the solid state NMR (92). Table 15 summarizes (at the end of this Chapter) the comparison of the carbon resonances of 12d in the two phases.

This broadening is expected on the basis of its X-ray structure which reveals that the C2-C3, C3-C4, C6-C7, C7-C8 distances are all equal (refer to the section on X-ray studies). Hence the broadening is not due to an effect originating from the method used to determine the solid state nmr. In fact it is definitely not an artifact of the instrument, as the measurement was done on three different instruments (Jeol, Bruker, Varian).

The solid state C-13 nmr of the parent semibullvalene measured by Miller and Yannoni (134) showed resonances

corresponding to the static structures at temperatures as high as  $-100^{\circ}\text{C}$ . The authors estimated that the rate constant at  $-110^{\circ}\text{C}$  to be  $400\text{ sec}^{-1}$ , compared to a rate constant in solution of  $0.22\text{ sec}^{-1}$  at this temperature, as measured by Annet and coworkers (88). Using this method it should be possible to distinguish between equilibrating and symmetrical species even for rearrangements where the  $E_{\text{act}}$  is too small to be measured by solution dynamic NMR spectroscopy.

### X-RAY STUDIES

The X-ray structure determination of 1,5-dimethyl-2,4,6,8-tetrakis (carbomethoxy) semibullvalene showed an elongation of the C2-C8 bond and a shortening of the C4-C6 distance (34). This was attributed (Chapter 1) to a molecule approaching a symmetrical structure; however, the revelation (from X-ray) that two of the carbomethoxy groups are twisted out of plane diminishes the electron withdrawing ability of the esters at positions 6 and 8. This creates a difference in the two halves of the molecule about the C1-C5 bond, in the solid state. In solution, the carbomethoxy groups can freely rotate making the semibullvalene symmetrical; such systems have been predicted by MNDO (93) studies to have a low activation energy for the rearrangement. Since the observations are

in accord with the calculations, it is reasonable to assume that the transition state is diallylic in character, as predicted by MNDO. The lowering of the activation energy might also be related to the electron donating effect of the methyls at positions 1,5. This was suggested by some recent findings by Quast and Gunther (unpublished results). Low temperature solution dynamic NMR studies indicate that the free energy of activation for the 1,5-dimethyl semibullvalene to be lower than  $3.8 \pm 0.5$  Kcal/mole.

Following the synthesis of 1,5-dimethyl-2,4,6,8-tetrakis (carbomethoxy) semibullvalene, Sauer et al., synthesized 1,5-dimethyl-3,7-dicyano semibullvalene. The activation energy for the Cope rearrangement of this compound was found to be 6 Kcal/mole. This value qualitatively agrees with the theoretical predictions made by Dannenberg et al., once again suggesting that the transition state for the Cope rearrangement in semibullvalenes is diallylic in character. X-ray data showed a very long C2-C8 cyclopropane bond (1.835 Å) and a short non bonded distance C4-C6 = 2.048 Å. In an attempt to correlate the structural features with the high activation energy, the authors suggest this to be specific to the crystal lattice. To test if the crystal lattice effects are indeed the explanation to the situation, the authors should compare the CPMAS  $^{13}\text{C}$  NMR spectrum with a

solution carbon spectrum.

Finally, also note that the activation energy for the 2,6-dicyano semibullvalene studied by using MNDO (93), agrees qualitatively with the value obtained subsequently for the 1,5-dimethyl 2,6-dicyano semibullvalene.

The experimental method:

Crystals of the bright yellow 1,5-cyclohexano-2,4,6,8-tetrakis (carbomethoxy) semibullvalene 12b suitable for X-ray crystallography were obtained by recrystallization from methanol. The crystals were monoclinic, space group  $P2_1/C$  with  $a = 10.798$ ,  $b = 7.681$ ,  $c = 22.872$  Å,  $\beta_{angle} = 95.86^\circ$ ,  $d_{calc} = 1.374$  g/cm<sup>3</sup>, for  $z=4$ .  $Volume_{cell} = 1837.03$ . The intensity data were measured on a CAD 4 diffractometer (Cu K $\alpha$  radiation, graphite monochromated). A total of 3898 reflections were measured for  $\theta < 75^\circ$ , of which 3343 were considered to be observed ( $I > 3\sigma(I)$ ). The structure was solved by a multiple solution procedure (Germain, G., Woolfson, M.M.; Acta crystallogr., Sect. A 1971, A27, 368; Peter Main et. al. 1982, Multan, 11/82) and was refined 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  $R = 0.054$  and  $wR = 0.082$ . The final difference map has

no peaks greater than  $\pm 0.3$ .

Results and discussion:

The crystal structure of 12b is shown in Figure 8. Pertinent structural parameters are summarised in Table 13.

The atomic positions and thermal parameters appear in Appendix A. The cyclohexane ring assumes a boat shape. The geometry of the cyclopropane ring is particularly unusual. There is a striking lack of symmetry in the molecule. The C2-C8 bond is very long (1.83 Å) while the C1-C2 bond shortened (1.48 Å). The C1-C8 bond measures 1.51 Å. The nonbonded distance at the open end of the molecule (C4-C6) is 2.195 Å, and the C4-C5-C6 bond angle is 75.23°. These parameters are both smaller than those observed for the unsubstituted semibullvalene (2.261 Å and 95.2°) (94) and for 1-cyano semibullvalene (2.35 Å and 101°) (29).

The folding of the cyclohexane about the cyclopropane and the orientation of the carbomethoxy groups create asymmetry in the cyclopropane ring. The cyclopropane ring asymmetry is also  $\pi$ -Electron acceptors are known to affect the geometry of cyclopropanes because of the interaction between the LUMO of the electron acceptor system and the cyclopropane HOMO of the correct symmetry ( $3e'$ ) (22,95).

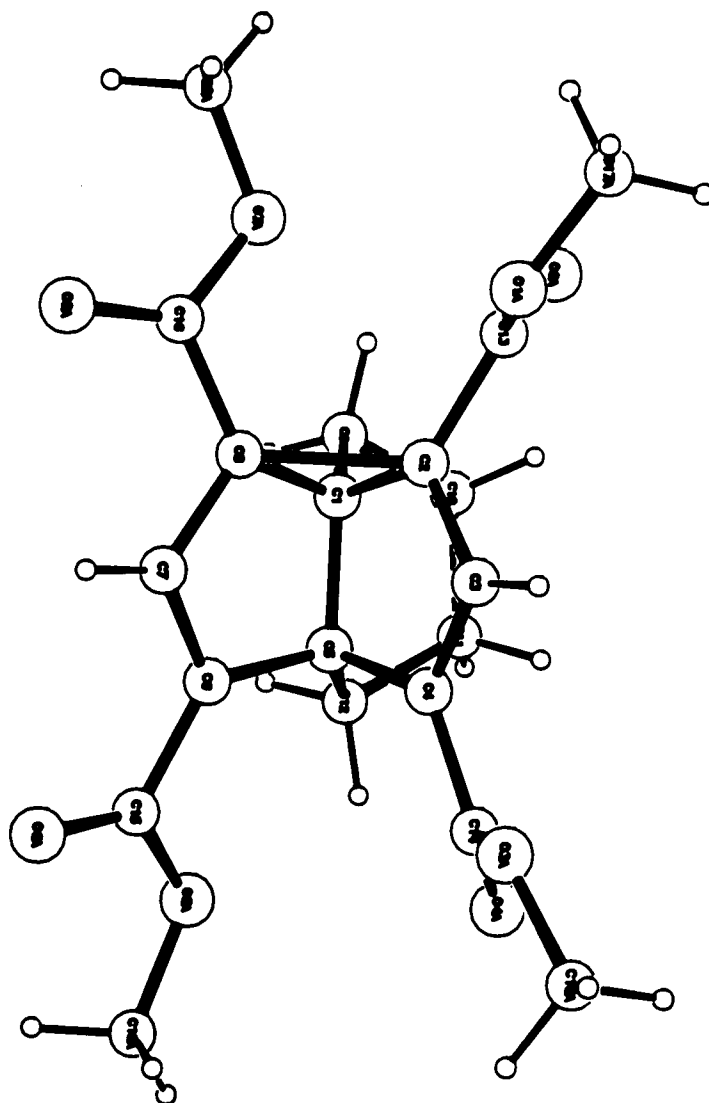


Figure 8. X-ray crystallographic structure of:  
1,5-cyclohexano-2,4,6,8- tetrakis (carbomethoxy)  
semibullvalene

Table 13. Selected Geometric Features of  
1,5-cyclohexano-2,4,6,8- tetrakis (carbomethoxy)  
semibullvalene

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Distance A

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C1 - C5	1.565	C6 - C7	1.363
C1 - C2	1.484	C4 - C5	1.518
C1 - C8	1.510	C5 - C6	1.517
C2 - C8	1.828	C1 - C9	1.512
C2 - C3	1.413	C5 - C12	1.524
C7 - C8	1.426	C4 - C6	2.195
C3 - C4	1.364		

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Angle, deg.

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C2-C1-C8	75.23	C1-C8-C7	108.77
C1-C8-C2	51.75	C5-C4-C3	111.26
C8-C2-C1	53.02	C5-C6-C7	111.09
C4-C5-C6	92.62	C2-C3-C4	110.16
C1-C2-C3	110.80	C6-C7-C8	111.25

---

The resultant transfer of electron density from the cyclopropane to the  $\pi$ -electron acceptor system weakens those bonds for 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. 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 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 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 (95). 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 (96,97), there are very few in which the bond distance is greater than 1.6 Å (94). 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 12b does not increase the C4-C6 distance with respect to the unsubstituted compounds (29,94).

X-ray structure determination of 1,5-cyclooctano-2,4,6,8-tetrakis (carbomethoxy) semibullvalene

Crystals of the yellow 1,5-cyclooctano-2,4,6,8-tetrakis (carbomethoxy) semibullvalene 12d suitable for X-ray crystallography were obtained by recrystallisation from methanol. The X-ray structure determination of 1,5-cyclooctano-2,4,6,8-tetrakis (carbomethoxy) semibullvalene was carried out on a single crystal measuring 0.8 x 0.25 x 0.4 on a Nicolet R3m diffractometer. The crystals were monoclinic, space group P2<sub>1</sub>/C with a = 10.615(2) , b = 14.909(3) , c = 14.224(2) Å,  $\beta = 109.69(1)^\circ$ ,  $d_{\text{calc}} 1.31 \text{ g/cm}^3$ , for Z = 4. The intensity data were measured with graphite monochromated Cu K $\alpha$  radiation using  $\omega$ -scan (3.91-29.30 scans/min). A total of 2860 reflections were measured of which 2371 were considered to be observed ( $I > 3\sigma(I)$ ). The structure was solved by a direct methods using the SHELXTL software and was refined by blocked cascade least squares. In the final refinement anisotropic thermal parameters were used for the nonhydrogen atoms and the isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations.

but their parameters are not refined. The final discrepancy indexes are  $R = 0.051$  and  $wR = 0.059$ . The final difference map has no peaks greater than 0.24.

The crystal structure of 12d is shown in Figure 9. Pertinent structural parameters are summarised in Table 14. The atomic position and thermal parameters appear in Appendix A (Table 4).

The most striking feature is the coplanarity of the four carbomethoxy groups, lying within  $20^\circ$  about a plane. The C2-C8 distance equals the C4-C6 distance which is equal to 1.99 Å. The C2-C3, C3-C4, C6-C7, C7-C8 are all equal to 1.385 Å. The molecule shows a high degree of symmetry. The cyclooctane ring exists in a pseudo chair form. The X-ray structure confirms the CPDAS  $^{13}\text{C}$  NMR spectrum of 12d.

The symmetrical structure could arise from a crystallographic averaging due to disordered packing in the crystal of a true semibullvalene structure. However, one would then expect to see disorder positions of C2, C4, C6, and C8 possibly reflected in large thermal factors at these positions or residual electron density in a difference Fourier map. This is not observed and therefore an averaged structure is unlikely.

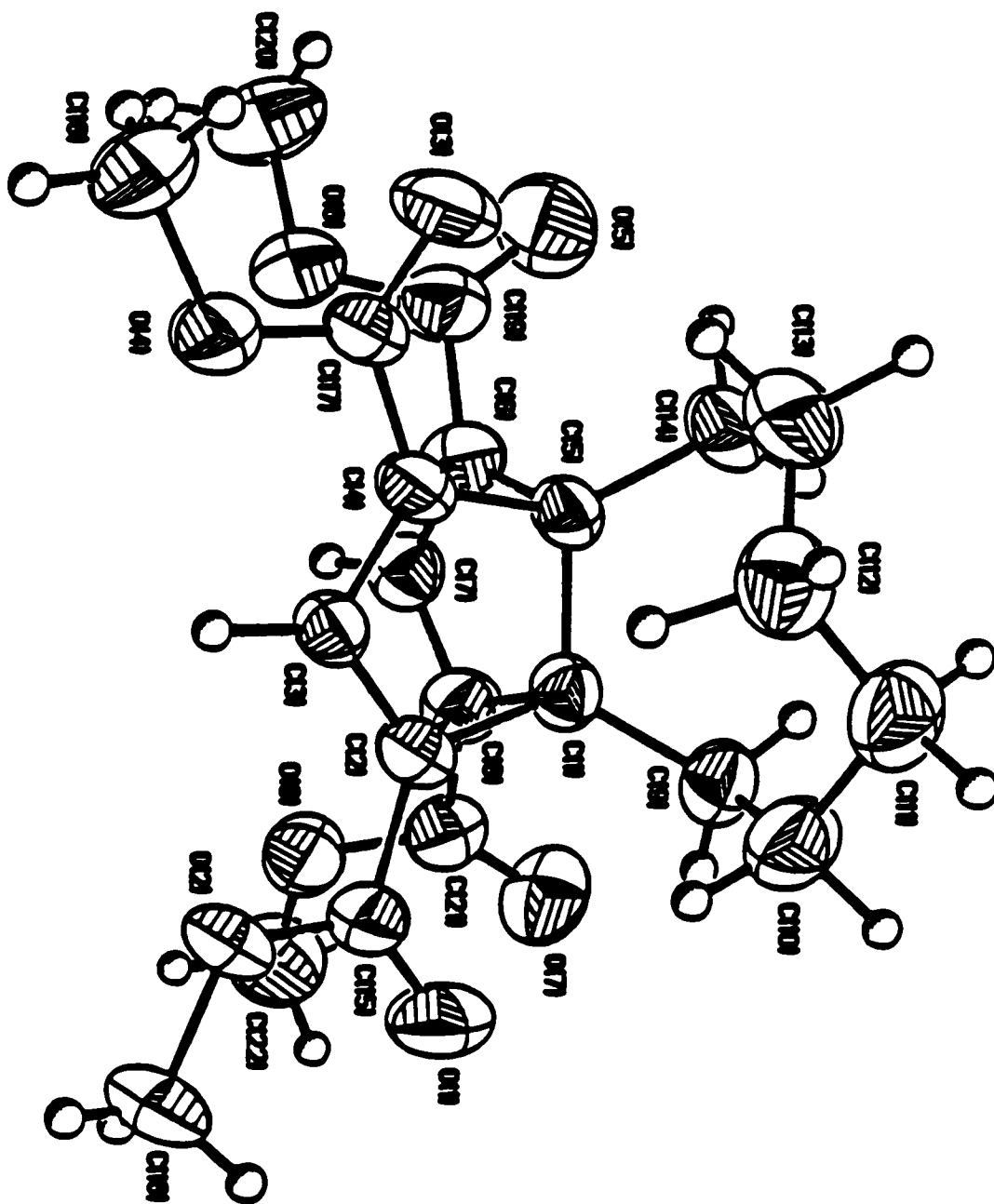


Figure 9. X-ray crystallographic structure of  
1,5-cyclooctano-2,4,6,8-tetrakis (carbomethoxy)  
semibullvalene

Table 14. Selected Geometric Features of  
1,5-cyclooctano-2,4,6,8-tetrakis (carbomethoxy)  
semibullvalene

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Distance A			
C1 - C5	1.592(3)	C6 - C7	1.382(4)
C1 - C2	1.514(4)	C4 - C5	1.514(4)
C1 - C8	1.496(4)	C5 - C6	1.495(4)
C2 - C8	1.990(4)	C1 - C9	1.525(3)
C2 - C3	1.388(3)	C5 - C12	1.521(4)
C7 - C8	1.392(3)	C4 - C6	1.993(4)
C3 - C4	1.385(4)		

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Angle, deg.			
C2-C1-C8	82.8(2)	C1-C8-C7	111.7(2)
C1-C8-C2	49.0(2)	C5-C4-C3	111.6(2)
C8-C2-C1	48.2(2)	C5-C6-C7	112.3(2)
C4-C5-C6	82.9(2)	C2-C3-C4	110.9(2)
C1-C2-C3	111.1(2)	C6-C7-C8	109.9(2)

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To rule out the possibility of any crystal packing effect, a comparison is drawn between the carbon resonances in the solid and solution phases. Table 15 summarizes this information.

Table 15. Comparison of solid and solution C-13 NMR of  
1,5 cyclooctano-2,4,6,8-tetrakis (carbomethoxy)  
semibullvalene

Phase	C=O of ester	C 3,7 vinylic	C 2,4,6,8	C 1,5	OMe	Cyclo- alkane
Solid	165.06	128.44	104.72	72.58	53.19	24.53
Soln.	165.75	130.90	104.32	73.64	52.29	25.75

The maximum difference in the respective chemical shift is observed in the C 3,7 resonance (1.5 ppm) while the other resonances compare very well. This excludes the possibility of crystal packing effects that might have needed consideration otherwise, in interpreting the X-ray structure of 1,5-cyclooctano-2,4,6,8-tetrakis (carbomethoxy) semibullvalene. The interpretation involving a dynamic behaviour in the solid phase cannot be completely ruled out at this point. Dynamic behaviour is observed in the solid phase of bullvalene, (98).

An alternative to the low temperature solid state NMR experiments to resolve the question of dynamic behaviour,

would be to carry out low temperature X-ray studies. A variation in the bond lengths at lower temperature would suggest dynamic behaviour in the solid state.

It is very interesting to compare the geometry of semibullvalenes 6, 12b, 12d. The varied chemical behavior can be attributed completely to these minor geometric differences. Table 16 summarizes a comparison of selected geometric features.

Based on reactivities, NMR, and X-ray studies, it can be concluded that in 6, the allyl radicals formed (by rupture of the 2-8 bond), are so far apart that it rearranges to cyclooctatetraene very easily.

Annulation of five and six membered rings do not allow this transformation; on the other hand there is an apparent lowering of the energy of the triplet diradical leading to endoperoxide formation. In the 1,5-cyclooctano compound, however, the two allyl moieties are closer and probably interact strongly.

Table 16: Comparison of selected geometric features in 6, 12b, and 12d. Distances are measured in Å and angles in °.

Compound	C2-C8	C4-C6	C2-C3	C3-C4	C6-C7	C7-C8
6	1.78	2.21	1.43	1.34	1.35	1.41
12b	1.83	2.195	1.41	1.36	1.36	1.426
12d	1.99	1.99	1.39	1.385	1.38	1.39

Compound	C4-C5-C6	C2-C1-C8
6	93.1	72.5
12b	92.62	75.2
12d	82.9	82.8

In conclusion, it can be stated that, the goal of lowering the activation energy for the Cope rearrangement in semibullvalenes has clearly been achieved; for example, 1,5-cyclohexano-2,4,6,8-tetrakis (carbomethoxy) has a value lower than  $3.8 \pm 0.5$  Kcal/mole based on low temperature dynamic solution C-13 NMR studies. This value is in accord with the theories presented in the thesis. The X-ray structure corresponded very well the low

activation energy for the Cope rearrangement in this molecule.

## CHAPTER 4

## TOWARDS THE SYNTHESIS OF 1,5 CYCLOPROPA SEMIBULLVALENE

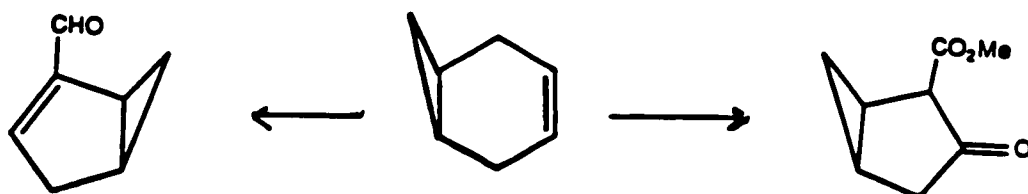
**INTRODUCTION**

The attachment of a ring at positions 1 and 5 in the semibullvalene system was predicted to have a pronounced effect on the activation energy for the Cope rearrangement (33, 93, 34). The most interesting in the series of 1,5 annulated semibullvalenes are clearly the cyclopropa-compound and the cyclobuta-compound (33, 93), refer to Table 4. It may be recalled that the difference in energy between the delocalized and localized structure in case of 1,5-cyclopropa semibullvalene was been calculated to be 9.1 Kcal/mole (93). Our attention was therefore focussed towards the synthesis and investigations of 1,5-cyclopropasemibullvalene and/or its derivatives.

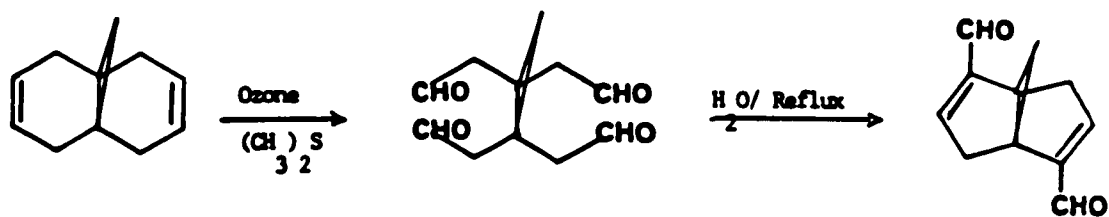
**SYNTHETIC SCHEMES:**

The synthesis of 1,5-cyclopropa semibullvalene and 1,5-cyclobuta semibullvalene cannot be executed via the

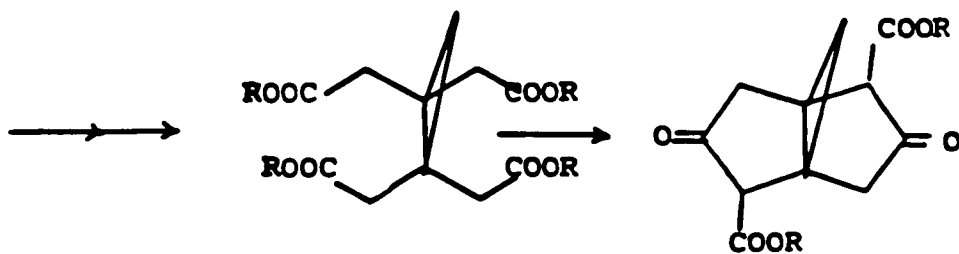
corresponding Weiss reaction (50) since cyclopropanedione and 1,2-cyclobutanedione are not stable under the conditions of the reaction. We propose a new, very general route to substituted and annulated semibullvalenes, based on the known conversion of cyclohexenes into either cyclopentene aldehydes (99) or cyclopentanone-2- carboxylic esters (100) as shown below.



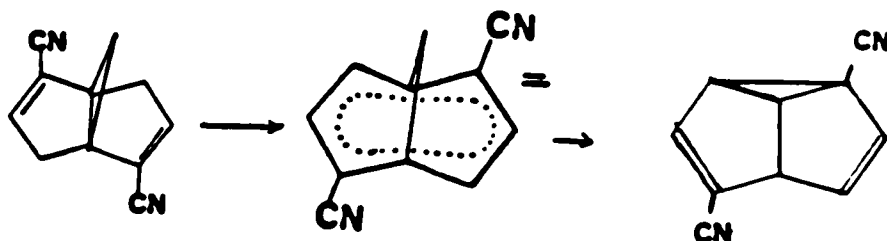
For the proposed 1,5-cyclopropasemibullvalene and its 2,6-dicyano derivative, the selected precursor is the known tricycloundecadiene, 20, available in three steps from naphthalene (101).



Reductive work up of the ozonide of tricycloundecadiene, 20, and subsequent aldol condensation of the intermediate tetraldehyde would lead to two isomeric dialdehydes. Alternatively, oxidative work-up of the ozonide, would lead to the tetraacid which on treatment with diazomethane would lead to the tetraester. Dieckmann condensation of this compound is expected to form the isomeric diesters.



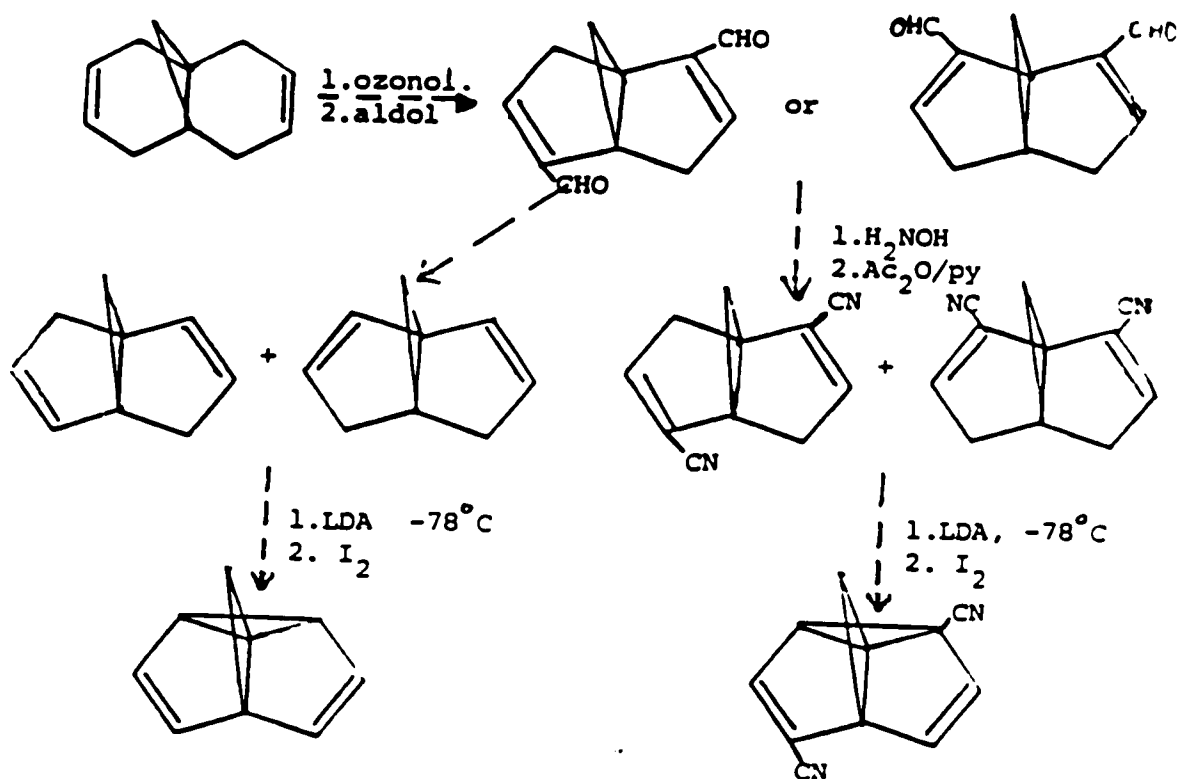
The dialdehydes could then be converted to isomeric dinitriles via their oximes. Treatment of the dinitriles with a strong base should give the dianion. Oxidation of the latter at low temperatures is expected to yield 2,6-dicyano-1,5-cyclopropano semibullvalene.



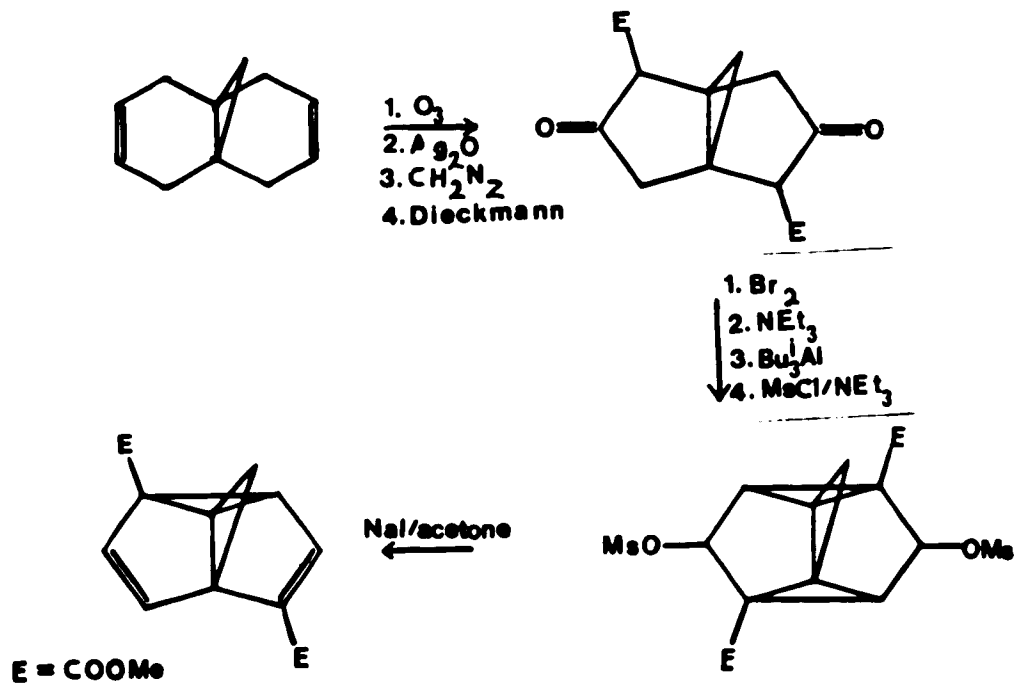
The method of oxidizing the dianion has the advantage of providing very mild conditions for the generation of the extremely strained cyclopropa semibullvalene which contains a spiro-pentane moiety.

### SYNTHESIS

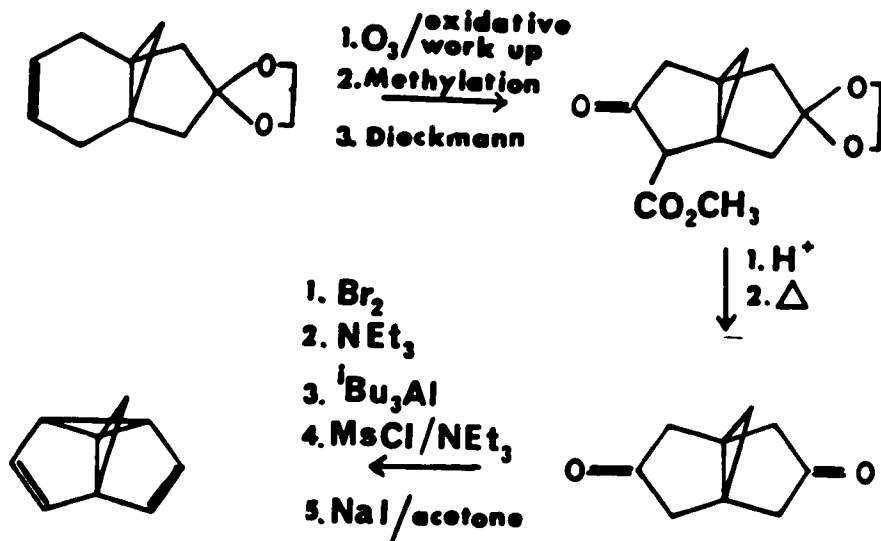
Three possible synthetic schemes towards the synthesis of 1,5-cyclopropa semibullvalene are outlined below.



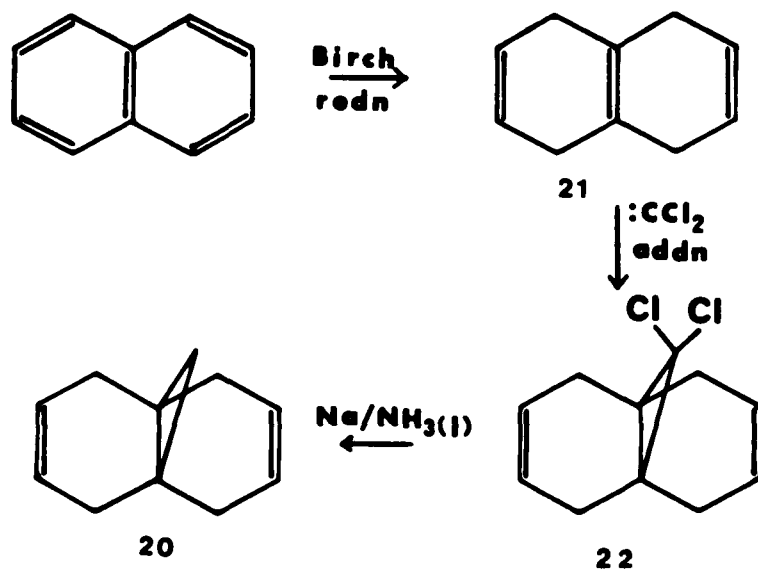
Scheme 5



Scheme 6



The required tricylcoundecadiene, 20, was obtained in the following manner (102):

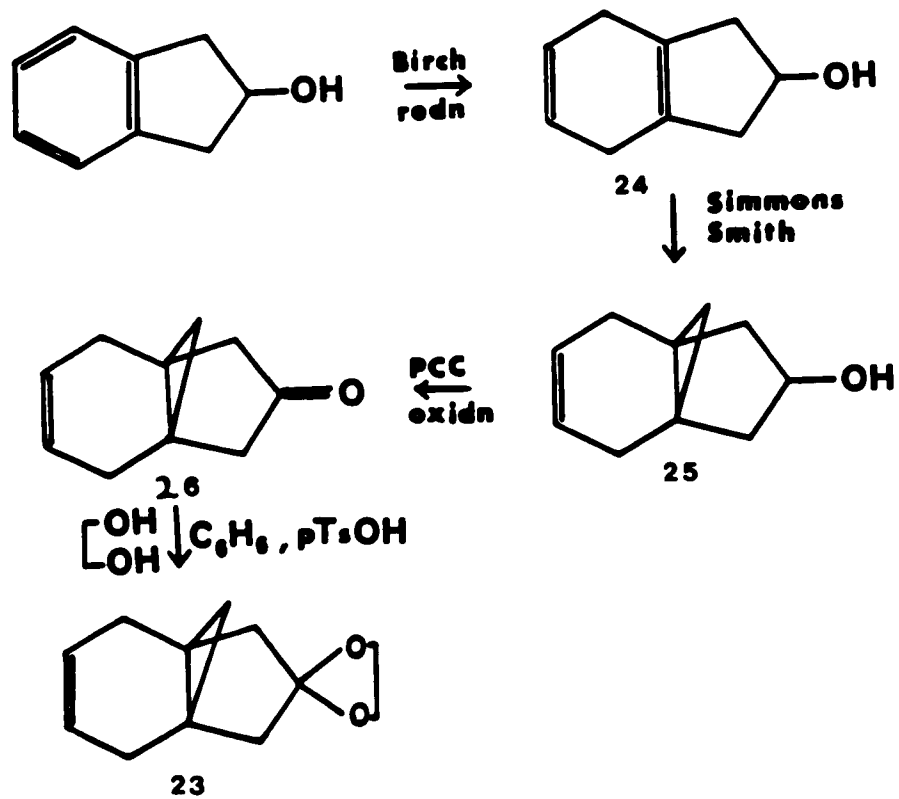


Isotetralin, 21, was obtained by the Birch reduction of naphthalene in 72% yield (mp 50-52°C) (lit mp 52-53°C., yield 75-80%). Dichlorocarbene ( $\text{CHCl}_2/\text{KOBU}^0$ ) addition to the isotetralin led to mono, 22, bis and tris addition products. The reported separation of the mono and bis addition products using fractional distillation proved tedious due to crystallization of the products in the condenser. We therefore introduced the following modification; the mono and the bis adducts were separated after the reductive dechlorination with  $\text{Na}/\text{NH}_3$ , using a spinning band column. Using benzyl triethyl ammonium chloride during the dichlorocarbene addition led to a higher percentage of the undesired bis product.

In a parallel approach we investigated a route involving 23 as the starting material. The literature procedure (103) for this compound presented considerable difficulties, the main problem being the preparation of a Zn/Cu couple of consistent activity required for the Simmons-Smith reaction.

The synthesis of 23 is outlined below:

Synthesis of 23



Birch reduction of 2-indanol led to an 85% yield of 4,7-dihydroindan-2-ol, 24. 24 was converted to [4.3.1]-tricyclo-deca-8-ol-3-ene, 25, in a 73% yield using the Simmons-Smith procedure (103). Several variations on the Simmons-Smith reaction were attempted:

1. Filtering off the Zn/Cu couple before addition of acid during the work-up (this led to a lot of mechanical losses).
2. Continuous extraction of Zn/Cu couple with ether.
3. Addition of pyridine (104) to the reaction.

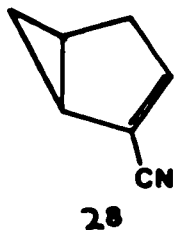
None of the above variations increased the yield noticeably. Success of the Simmons-Smith reaction depends on the quality of the Zn/Cu couple. We changed our procedure for making the Zn/Cu couple using freshly prepared cuprous chloride (105). The yield dropped to 40%. Apparently freshly prepared Zn/Cu couple is too reactive; high yields (106) can be obtained by using commercially (Alfa Chemicals) available Zn/Cu couple.

The [4.3.1]-tricyclo-deca-8-ol-3-ene, 25 (crystallized from hexane), was then oxidised by pyridinium chlorochromate to give [4.3.1]-deca-7-ene-one, 26, (107) in an 84% yield (bp 67°C, 1 mm Hg). The semicarbazone of

26 had a melting point 238-242°C. The ketone, 26, was ketalised by the standard procedure using ethylene glycol and p-TsOH in dry distilled benzene with a Dean-Stark apparatus. The ketal, 23, was obtained in 77% yield (bp 71°C, 1.5 mm Hg).

#### Model Studies

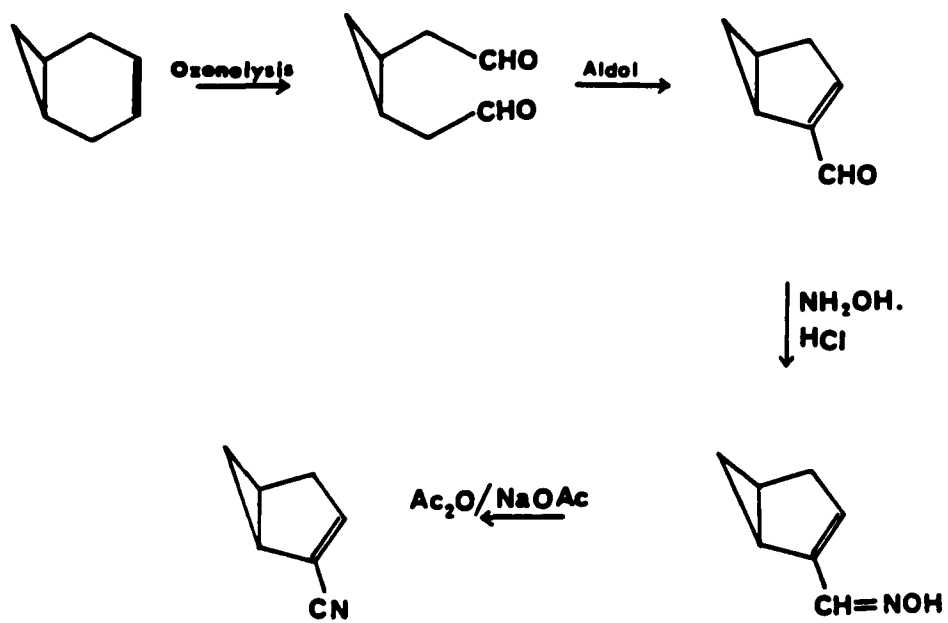
Before using 21 and 23 in the schemes outlined above, we investigated the sequence in Scheme 7 using norcarene, 27 as the starting material. The molecule we chose for model studies was [3.1.0]-bicyclo-hex-2- cyano-2-ene, 28.



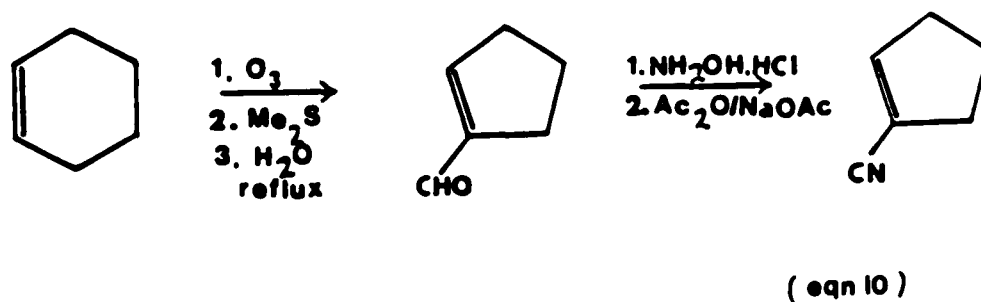
The sequence of steps leading to the molecule shown above is outlined in Scheme 7. The starting material, 27, for Scheme 7 was synthesized in the following manner: a chloroform solution containing the 1,4 cyclohexadiene was added to a mechanically stirred NaOH solution containing benzyl triethyl ammonium chloride (the phase transfer catalyst) dropwise rather than all at once. The reaction was worked up after stirring for one hour. 7,7-dichloro norcarene was obtained in a 50% yield (bp 88°C, 1.5 mm Hg). Norcarene, 27, was then obtained by reductive

dechlorination of the dichloro adduct in a 70% yield (bp 80°C).

Scheme 7



In a further model study we investigated the ozonolysis of cyclohexene and subsequent aldol condensation leading to cyclopentene aldehyde (109). Use of KOH as the base in the aldolization of the dialdehyde obtained from the reductive work-up of the ozonide of cyclohexene led to excessive polymerisation. However, boiling the dialdehyde with water overnight, led to the isolation of cyclopentene aldehyde (eqn 10). This sequence was attempted to qualitatively test its feasibility.



The structure of the cyclopentene aldehyde was confirmed on the basis of its nmr which consisted of a sharp 1H singlet at 9.55 ppm, the aldehydic proton and a 1H triplet at 6.75 ppm corresponding to the olefinic proton. The cyclopentene aldehyde was converted to the cyclopentene nitrile (liquid), ir absorption at  $2240\text{ cm}^{-1}$ , nmr: 6.55 (1H, triplet vinylic H's), 2.0 (6H, multiplet remaining H's) via dehydration ( $\text{Ac}_2\text{O}$ ) of the oxime (liquid). The nmr

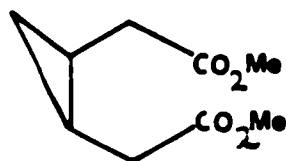
of the oxime in  $D_2O$  showed three signals in the vinylic region; a 1H triplet at 7.2 ppm, a 1H triplet at 6.5 ppm and a broad 2H singlet at 5.9 ppm indicating the presence of syn and anti oximes (110). Since the elimination of water from oxime (by refluxing with  $Ac_2O/NaOAc$ ) occurs only from the anti isomer, we thought longer reflux times would convert the syn to anti thereby increasing the yield of the nitrile.

The same sequence was carried out on norcarene. Reductive work up of the ozonide was followed by an aldol similar to that used in Equation 10. The  $\alpha,\beta$  unsaturated aldehyde, 29 (Scheme 7), was steam volatile and hence purified by steam distillation leading 20% yield. Oxime (30, Scheme 7) formation proceeded in 44% yield. The oxime was converted to the nitrile, 28, ir absorption at  $2200\text{ cm}^{-1}$  by refluxing it with  $Ac_2O$  and  $NaOAc$  overnight.

In attempts to improve the yield in the step leading to the  $\alpha,\beta$  unsaturated aldehyde, we investigated a number of modifications on the aldol condensation. The product obtained from the reductive work up of the ozonide of 27 (Scheme 7) was dissolved in benzene and treated with a few drops of  $AcOH$  in piperidine (111). No cyclopentene aldehyde was obtained from the reaction. A few drops of aqueous sulfuric acid did prove to be an effective catalyst for the aldol. The success of an aldol

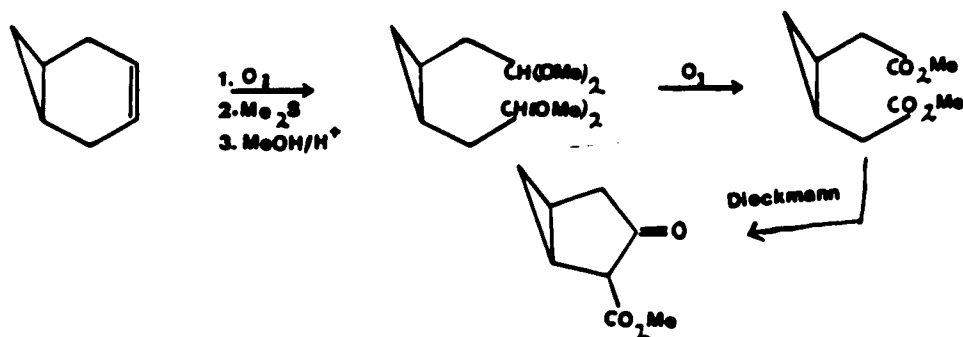
condensation clearly depends on the choice of the catalyst, as is well exemplified by Steve Burke's work (112) in the area of quadrone synthesis.

Since we encountered difficulties with the aldol condensation, we attempted the Dieckmann condensation of the dimethyl ester, 31, shown below (113)



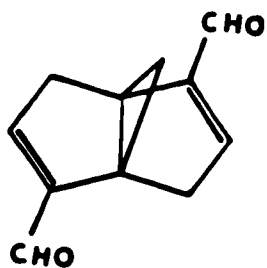
31

The dimethyl ester, 31, was obtained by the reductive work up of the ozonide of norcarene which on treatment with trimethyl orthoformate and methanol solution containing pTsOH (113) led to a 35% yield of the tetraacetal 32, (bp 85-88°C, 1.5 mm Hg). The tetraacetal, 32, on ozonolysis in EtOAc (114) led to a 25% yield of the dimethyl ester, 31. Dieckmann condensation of this diester proceeded smoothly in a 60% yield.

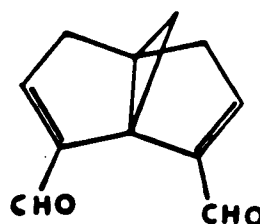


### Synthesis

After experimenting with the aldol condensation, aldehyde-oxime-nitrile conversion, and Dieckmann condensation using norcarene as the model, we undertook the ozonolysis of 20. Reductive work up of the ozonide of 20, followed by aldol condensation using water as the catalyst led to a mixture of dialdehydes 33 and 34 (based on nmr) shown below.



33



34

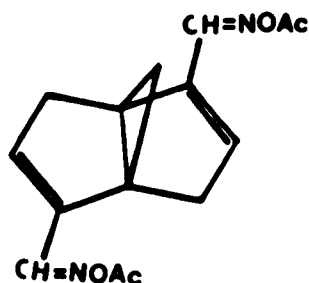
33 was separated from 34 by crystallisation from ether; the first fraction of crystals corresponded to 33. Thus the dialdehyde, 33, was obtained in a 20% yield. The structure of the dialdehyde, 33, was confirmed on the basis of its nmr which exhibited peaks at 1 ppm (2H singlet), 2.9 ppm (4H multiplet), 6.54 ppm (2H triplet) 9.75 ppm (2H singlet). The IR consists of the doublet at 2820  $\text{cm}^{-1}$  (strongly suggestive of an aldehydic group), a peak at 1600  $\text{cm}^{-1}$  (C=C) and a broad carbonyl peak at 1680  $\text{cm}^{-1}$ . The dialdehyde is a colorless solid (mp (crude) 98-100°C).

The most commonly used catalyst for an aldol of this type seemed to be the piperidine acetate procedure (116, 117). In our case this method led to no aldol condensation. The main problem being polymerisation. A variety of conditions which included dil KOH, few drops conc H<sub>2</sub>SO<sub>4</sub>; few crystals of oxalic acid, and NaHCO<sub>3</sub> were among the catalysts used for the condensation. The highest possible yield for the condensation remained at 20%; water being the best catalyst.

Alternative ways to generate the tetraldehyde from 20 were investigated. However, experimental difficulties in the epoxidation and hydrolysis of the epoxide led us to abandon the scheme.

The dialdehyde was converted to the dioxime (115) in 76% yield (mp (MeOH) 246-248°C with decomposition). The dioxime was insoluble in all solvents including MeOH, the solvent it was recrystallised from. However an NMR was obtained from a dilute solution of the oxime in CD<sub>2</sub>COCD<sub>2</sub>. The nmr consists of peaks at -0.05 ppm (1H singlet, one of the cyclopropyl), 0.94 ppm (1H singlet, the other cyclopropyl), AA'BB' system at 2.4-2.67 ppm (the four allylic protons), 5.69 ppm (2H triplet, the two vinylic H's in the ring), 7.88 ppm (2H singlet, the remaining vinylic H's), 8.43 ppm (2H broad singlet) (OH peak). The dioxime when refluxed with Ac<sub>2</sub>O for 20 minutes leading to

the formation of the diacetate. The IR consists of a peak at  $1775\text{ cm}^{-1}$  and a peak at  $1615\text{ cm}^{-1}$  (for the C=N) in agreement with the following structure.



This was confirmed by its nmr which exhibited peaks at 1.08 ppm (2H singlet, cyclopropane H's), 2.2 ppm (6H singlet, OMe), 2.84-2.91 ppm AA'BB' system (the four allylic protons), 6 ppm (2H triplet, vinylic H's in the ring), 8.1 ppm (2H singlet, the remaining vinylic H's).

However refluxing the oxime with anhydrous NaOAc and  $\text{Ac}_2\text{O}$  overnight led to 52% of the desired dinitrile mp  $139\text{--}139.25^\circ\text{C}$  (sublimed at  $105^\circ\text{C}$  0.05 mm Hg). The IR shows the presence of nitrile ( $2200\text{ cm}^{-1}$ ) and double bond ( $1580\text{ cm}^{-1}$ ). The peak at  $2200\text{ cm}^{-1}$  is a doublet. Quast (42) et al., observe a doublet for the 2,6-dicyano-1,5-dimethyl semibullvalene and attributed it to the fact that the molecule does not possess a  $C_2$ -symmetry in the infrared time scale, thus providing a probe for homoaromaticity. However, our observation of a doublet for the cyano group contradicts Quast's interpretation. The explanation of the doublet nature of the cyano peak needs further

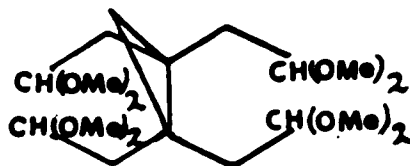
investigation. The nmr confirmed the structure of the dinitrile - 6.34 ppm (2H singlet), 2.68-2.97 ppm AA'BB' system (for the four allylic protons), 1.25 (1H singlet, one cyclopropyl proton), 0.04 ppm (1H singlet, the other cyclopropyl proton). <sup>13</sup>C spectrum consists of peaks at 31.4 ppm (the cyclopropyl carbon at the junction of 1,5), 36.8 ppm (the two allylic carbons), 43.1 ppm (the carbons at 1,5), 115.1 ppm (the cyano carbons), 118.3 ppm (the vinylic carbon bearing the cyano groups), 148.4 ppm (the vinylic carbons bearing the hydrogens).

A major problem with the ozonolysis of 20 was associated with its solubility - it was not completely soluble in MeOH which is the solvent of choice for ozonolysis. CH<sub>2</sub>Cl<sub>2</sub>, Et<sub>2</sub>O, EtOAc and different mixtures of these solvents were used in an attempt to solubilize the olefin (triundecadiene), 20. The solubility might be also be related to the low yield in the aldol condensation.

To investigate the cause of low yields in the aldol condensation, we examined the NMR of the solution obtained after reductive work up of 20 and after rotary evaporation of the solvent. NMR indicated a complete absence of the aldehydic peak; a strong acetal peak was observed however. It is reasonable to assume that the low yields in the aldol is due to strong acetal bonds which are difficult to cleave completely, or due to the strain in the tricyclic

system.

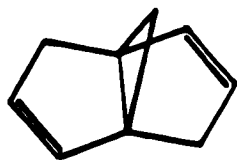
One final attempt to obtain high yields of the tricyclo [3.3.0] non-2,6-diene- 2,6-dialdehyde, 33, was based on the method developed by Frickel (113). The method involved conversion of the tetra aldehyde, obtained from the reductive work up of the ozonide of 20, to the octa acetal, 35, shown below, and acid hydrolysis of the octa acetal to the tetra aldehyde at the time of aldol condensation. The octaacetal was obtained, albeit in very low yields.



35

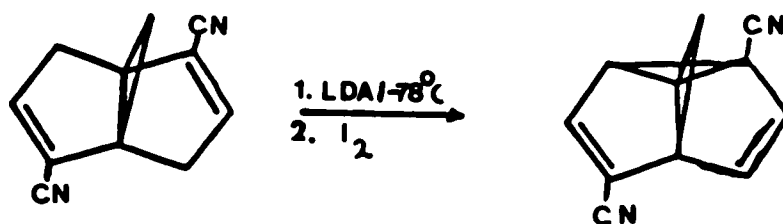
At that point we had 120 mg of tricyclo [3.3.1.0<sup>1,8</sup>] non-2,6-diene- 2,6-dinitrile, 37. Scheme 4 summarizes the sequence of reactions used to synthesize 37 successfully.

The tricyclo [3.3.1.0<sup>1,9</sup>] nonadiene shown below



and its dicyano isomer are formally dihydromopentalenes. Therefore they might react with strong bases to form homopentalene dianion (the same can be expected for the dicyano isomers). These dianions, interesting as such, were expected to undergo oxidation to the cyclopropa semibullvalene or its dicyano isomer. The homopentalene dianion would be the smallest methano-bridged  $10\pi$ -system. The question as to whether the pentalene dianion can be bridged and still maintain its aromatic character, is fascinating (118). Detailed study of the acidity of 37 and of the dianion should prove interesting. That in turn leads to another possible structure for the cyclopropa semibullvalene, namely, the homopentalene structure. The synthesis and detailed investigation of this interesting system was therefore expected to provide some answers and of course raise new questions (119).

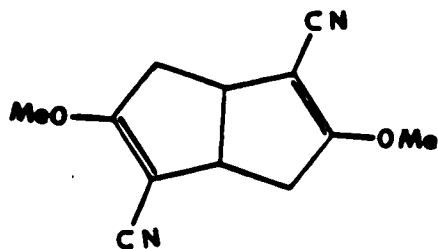
The next step in the synthesis is summarized below. To study the acidity of the protons in the model compound we used at first BuLi as the base.



BuLi added to the nitrile group to give the C-butyl compound, 38, as was evident from nmr. Attempts to trap the anion with dimethyl sulfate and benzyl chloride did not lead to any identifiable products. Usually there were a number of products with very close R<sub>f</sub> values in these reactions. The compounds were separated using a chromatotron. The LDA/I<sub>2</sub> reaction on 37 apparently led to ring opening. Along these lines we carried out a benzylation reaction on 1-cyanocyclohexene and obtained mainly the 1-benzyl-2-cyclohexene carbonitrile (see below).



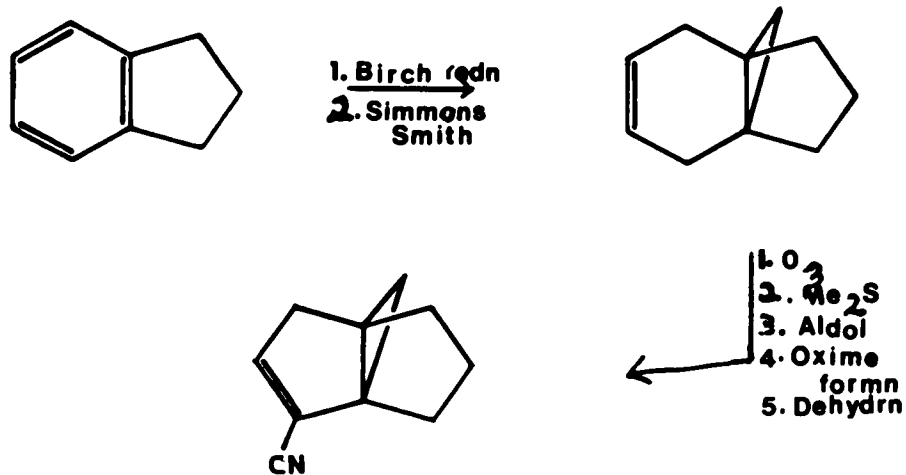
Due to the limited amount of the model compound we carried further studies on the cyano methyl ether, 39, shown below.



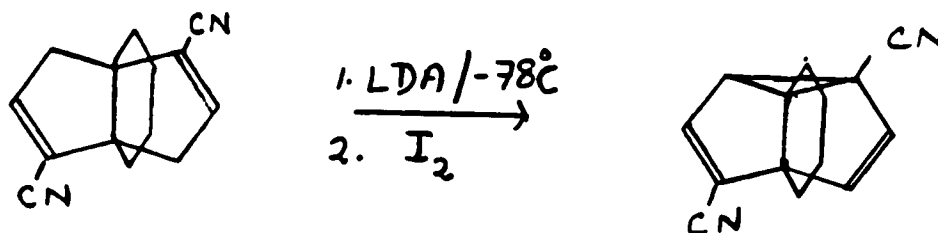
39

Preliminary studies on previously available cyano methyl ethers suggested that the LDA/I<sub>2</sub> reaction caused ring opening of the compound. We needed a compound that is clamped at the 1, 5 position by a cyclopropane. The ideal model compound would therefore be tricyclo[3.3.1]non-2-ene-2-nitrile, 40. Scheme 8 was intended for its synthesis.

Scheme 8



At that point however, instead of embarking on another model study we decided to investigate the reaction of 37 with LDA. The LDA was made by adding BuLi to a THF solution of diisopropylamine at  $-30^{\circ}\text{C}$  (under Argon). On adding the dicyano compound, 37, in THF to the LDA solution at  $-78^{\circ}\text{C}$  the solution turned deep red. However, oxidation of the above solution with oxygen led to products whose structures could not be assigned on the basis of high field proton nmr. This seemed to be the case even when the oxidising agent was changed to iodine. Quast et. al. (120) faced a similar problem in the attempted reaction shown below.



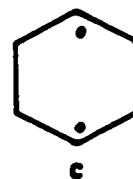
It therefore still remains to successfully synthesize the 1,5-cyclopropa-2,6-dicyanosemibullvalene.

## CHAPTER 5

## MNDO STUDY OF THE COPE REARRANGEMENT IN SEMIBULLVALENES

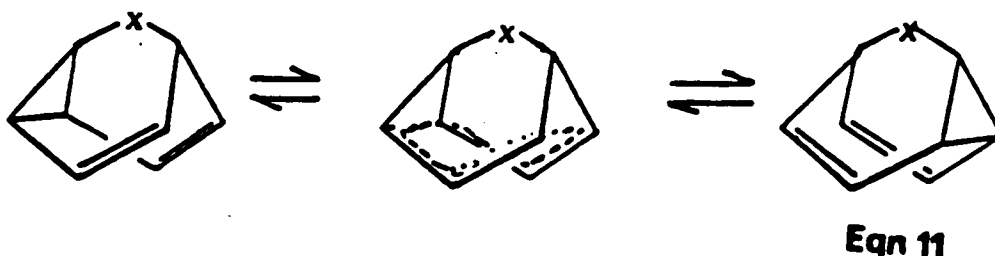
**BACKGROUND**

To gain further insight into the nature of transition states in Cope rearrangements we carried out some theoretical studies using the MNDO approximation. As pointed out in Chapter 1, the transition state for the Cope rearrangement of a series of related compounds is dependent on the type and position of substituents (121, 122, 123). Consider, for example, the simplest molecule 1,5 hexadiene. 2-phenyl and 2,5-diphenyl 1,5-hexadienes undergo Cope rearrangement 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 (124). MINDO/2 calculations for the degenerate Cope rearrangement of 1,5 hexadiene and related compounds by Dewar and coworkers predicted the transition state to resemble the 1,4-diyli transition state (c).



Similar conclusions were arrived at by studies on 2,5 dicyano 1,5 hexadiene (123). The  $\alpha$  secondary deuterium isotope effect on methyl substituted 1,5 hexadienes was studied by Gajewski. The experiment was designed to test the importance of bond making versus bond breaking. If bond breaking was important, the transition state should resemble the bisallyl transition state (a) and if bond making was important the transition state would resemble 1,4 diyl transition state (c). The studies concluded in the same note as the others did. Bond making proved to be more important.

The Cope rearrangement in bullvalene, barbaralene, semibullvalene series (Equation 11) was for the first time studied theoretically by Dewar and Schoeler in 1971 (126). They used MINDO/2 to calculate the geometries and energies for the ground states and transition states for these compounds.



A detailed analysis of the same series was carried out

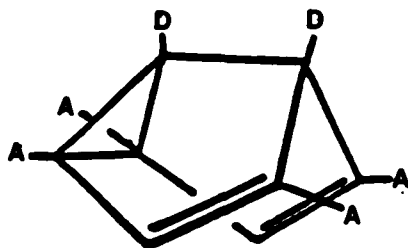
shortly thereafter by Dewar and Lo using MINDO/2 and applying an energy partitioning technique (127). They concluded that the transition state for the Cope rearrangement becomes more like a pair of allyl radicals and is stabilized by a drift in charge from the rest of the molecule to the six atoms involved as the bridge in the series decreases. Electron withdrawing groups at the ends of the allyl radical were predicted to lower the activation energy for the Cope rearrangement by stabilizing the transition state.

Based on the conclusions of their energy partitioning studies, Dewar and co-workers used MINDO/2 to study 3,7 diazasemibullvalene (128). Each iteration changed the bond lengths and bond angles till the final structure was identical to the delocalized one.



A systematic study of the effects of substituents on the Cope rearrangements in semibullvalene was undertaken by Hoffman and Stohrer (22). EHMO theory was used for the study. They 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.



D =  $\pi$ -electron donor

A =  $\pi$ -electron acceptor

#### PREVIOUS WORK IN OUR LABORATORIES

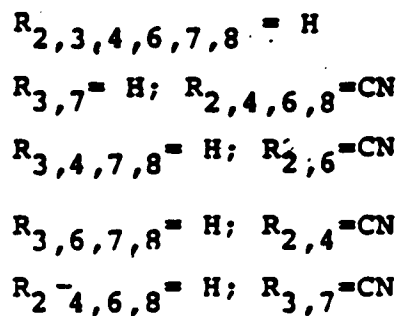
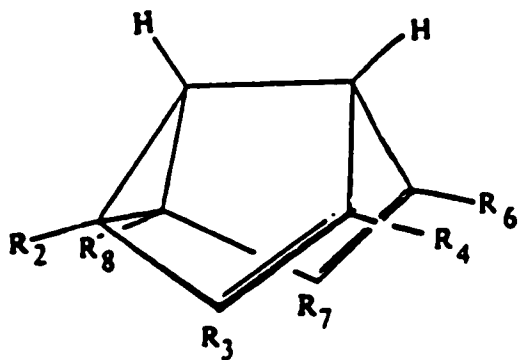
In order to determine what type of alterations (substituent patterns, geometry changes) in semibullvalene nucleus would have the best chance of lowering the activation energy for the Cope rearrangement so that the homoconjugated structure (129) would become the preferred species at room temperature; a theoretical study of some substituted semibullvalenes was carried out by L. Miller in our group (93, 33). Several groups have studied the Cope rearrangement of semibullvalenes using MINDO/2 and extended Huckel method of calculation. The EH method is not sufficiently accurate to be used for calculations of energies or geometries; only relative energies can be

predicted.

It was intended to assess the effects of  $\pi$  electron acceptor at various positions on the semibullvalene. A series of cyano substituted semibullvalenes and the parent semibullvalene (for comparison) was used for the study. The cyano group was chosen because

1. It is a perfect example of electron withdrawing group.
2. It is linear.
3. It has fewer atoms (than for example carbomethoxy) and hence the cost and time of the calculations could be cut down.
4. Cyano groups are synthetically feasible.

The series of compounds chosen for the MNDO study is listed below.



A second series of compounds was chosen on the basis of the results of the first study.

Several semi-empirical methods have been used to study molecular geometries and reaction paths with varying degrees of success. MINDO/1,2,3 utilizes a modification of INDO (intermediate neglect of differential overlap) method for simplification of the Roothan-Hall-SCF LCAO MO method. The MNDO method uses NDDO (neglect of diatomic differential overlap) (130). In the MINDO treatments many of the energy terms were set equal to parametric functions which contained adjustable parameters (131).

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 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 parameterize a semiempirical method using this approximation. Dewar and Thiel used a procedure for estimating the NDDO repulsion integrals and were able to reparameterize 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 (14).

A comparison of results for a number of compounds suggests that the absolute error for more 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 an equivalent calculation is only about 20% greater using this method (13)

The thermal decomposition of azoalkanes and 1,1 diazenes was studied using the MNDO method with 2x2 CI (132). The calculated energies of activation and the geometries of the reactants agreed well. Hence the MNDO method seemed perfect for reaction paths involving neutral

diradicals. There are not too many reports on using MNDO for studying reaction paths; however, there is enough support for the contention that the MNDO is particularly useful for the study of reactions involving neutral free radicals and radical pairs.

Thus the semi-empirical method chosen was the MNDO approximation to molecular orbital theory. The Fletcher, Powell, Davidson algorithm was incorporated in the MNDO program to perform geometrical optimization. 2x2 CI was included in the calculation for all diradical-like species. No elements of symmetry were imposed. The two reaction paths studied for each Cope rearrangement was the opening of 2,8 bond and closing of 4,6 distance. The opening of the 2,8 bond was always the lowest energy path in all cases.

The energy and geometry of ground states were calculated using complete geometric optimization. Appropriate reaction paths were studied by stepping through the coordinate without CI while optimizing internal coordinates individually. Once the approximate geometry was obtained, the 2x2 CI was incorporated in case of the unsubstituted semibullvalene. However in the case of cyano compounds the area around the col was flat and could be located only after inclusion of the 2x2 CI. Several calculations were performed varying several of the

internal coordinates at a time until all were considered; this was done to cut down the costs. The cost of MNDO calculations with 2x2 CI varies approximately with the square of the parameters to be optimized. A few points around the col were recalculated using CI to make sure that the energy of the points on either side was decreasing.

The results of the above study include:

1. Although no symmetry elements 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 differing by no more than 0.01 Å.
2. The orbitals of the homoconjugated structure resemble two interacting allyl systems. In the 2,4 dicyanosemibullvalene, the delocalised structure where the allyl group that has both the CN's on the same allyl group is significantly lower in energy than the other allyl group allowing less interactive stabilisation.
3. The distance between the ends of the allyl systems (C2-C8 and C4-C6) varies for the homoconjugated structures, while in the ground states the non-bonded distance (C4-C6) is fairly constant (2.43-2.45 Å).

The 2,4 and 3,7 dicyano semibullvalenes have non-bonded distances of 2.36 and 2.37 Å in the homoconjugated states while the 2,6 dicyano and 2,4,6,8 tetracyano compounds have distances 2.50 and 2.52 Å respectively. In the unsubstituted compound the distance is almost the same for both states. The bond angle (C4-C5-C6) varies in the same way; it is largest for the 2,6 dicyano and tetracyano compounds (123, 133). The C3-C7 move apart as do ends of the allyl system. The homoconjugated ground state did not resemble the 1,4 diyl structure in any of the systems studied.

4. The activation energy for the Cope rearrangement is lowered if the cyano groups are in the 2,4,6,8 and 2,6 positions. However, the 3,7 and 2,4 substitution pattern raises the activation energy.

Going back to the geometries of the homoconjugated structures of the 2,6 and 2,4,6,8 compounds one observes that the farther the allyl groups move the lower the activation energy. The ring system tends to flatten. However, the angle strain resulting from large distortions seem to impede further reductions in energy. Hence, molecules free of such strain were devised by introducing N instead of C at positions 1 and 5. Annulating a small

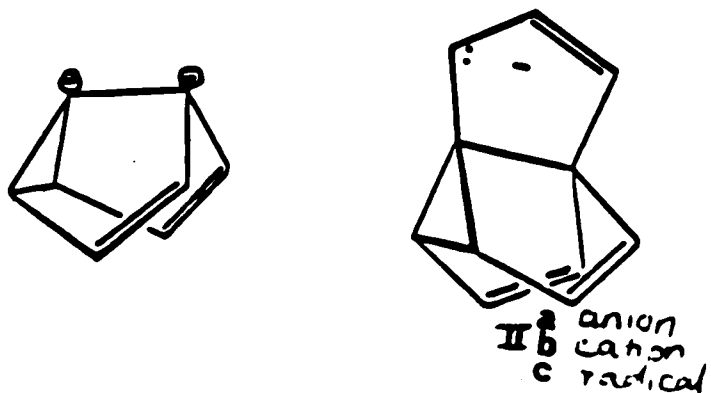
ring to 1,5 positions too would cause the C4-C5-C6 angle to open up.

In an attempt to test the above hypothesis the energies and geometries of the localized and homoconjugated structures of 1,5 diazasemibullvalene, 1,5 methylene (cyclopropa) semibullvalene, 1,5 dimethylene (cyclobuta) semibullvalene were calculated. As predicted, 1,5 diazasemibullvalene and 1,5 methylene semibullvalene have lower activation energies for the Cope rearrangement.

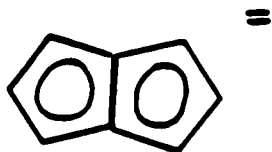
#### RECENT WORK

In continuation of the above studies we investigated the effects of two negative charges at positions 1,5, i.e., the 1,5 dianion of semibullvalene, I.

An intriguing line of thought occurs when we consider the effect of annullating an allyl moiety (cation, anion or radical) at the 1,5 junction in semibullvalene, II. While the 1,5 allyl anion semibullvalene is certainly a 1,5 donor substituted semibullvalene its donor negative charge is located in two  $\pi$  orbitals orthogonal to the symmetry plane bisecting the semibullvalene structure. Tables 17, 18 and 19 summarize the results. Appendix B lists the optimized geometries in complete detail.



The pentalene structure shown below is preferred over the 1,5 dianion semibullvalene structure by 131.2 Kcals/mole.



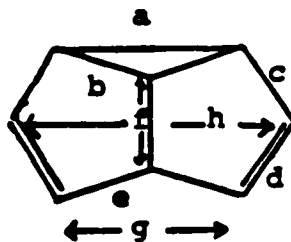
In spite of the negative charge, II a, the allyl anion apparently does not behave as an electron donor. This is evident from the positive value for the activation energy. This could be a result of the negative charges being present in a plane orthogonal to the semibullvalene

structure. The homoconjugated structures of the allyl cation and radical are currently under study.

Table 17. Heats of Formation and Activation Energies of I, IIa,b, and c.

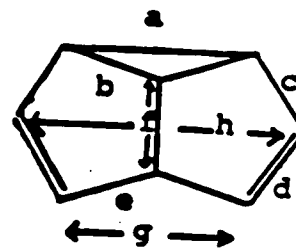
Compound	H local- ized	H homo- conjugated	E
I	273.70	155.06	-117.6
IIa	101.68	130.83	+29.15
IIb	291.74	-----	----
IIc	129.42	-----	----

Table 18. Geometries for the Localized Structures.



Compound	a	b	c	d	e	f	g	h
I	1.57	1.50	1.50	1.37	1.46	1.56	2.42	3.26
IIa	1.57	1.55	1.50	1.36	1.53	1.61	2.42	3.14
IIb	2.46	1.50	1.40	1.40	1.50	1.63	2.46	3.76
IIc	1.58	1.47	1.53	1.37	1.48	1.63	2.43	3.20

Table 19. Geometries for the Delocalized  
(Homoconjugated) Structures.



Compound	a	b	c	d	e	f	g	h
I	2.73	1.42	1.42	1.42	1.43	1.47	2.72	4.35
IIa	2.10	1.52	1.41	1.41	1.52	1.62	2.10	3.25
IIb			-----					
IIc			-----					

CHAPTER 6  
CONCLUSIONS

SUMMARY

The degenerate Cope rearrangement in semibullvalene is characterized by a small  $E_{act}$  (5.1 Kcal/mole). The idea of stabilizing the transition state for the rearrangement to such an extent it became the ground state of the molecule has fascinated many chemists (14).

L. Miller from our laboratory reported the synthesis and X-ray structure of 1,5-dimethyl-2,4,6,8-tetrakis (caromethoxy) semibullvalene in 1981 (34). In 1983 L. Miller and J. Dannenberg (93) carried out a detailed study of the substituent effect on the Cope rearrangement in semibullvalene. Upon examination of the transition state geometry it was found that the lowering of transition state geometry was in most cases accompanied by the widening of the C2-C1-C8 angle greater than the  $T_s$ . Though these deviations are small ( $<4^\circ$ ), the authors felt that the angle strain resulting from larger distortions of this angle could be impediment to further reductions in the energy of the transition state. In order to test the hypothesis, 1,5-cyclopropa semibullvalene and 1,5-cyclobuta semibullvalene were studied using the MNDO approximation. The study revealed that the difference in

the heat of formation of the delocalized and localized structure was negative in the case of the cyclopropa compound and positive in case of the cyclobuta compound. This observation led us to synthesize and investigate 1,5-annulated semibullvalenes.

The synthesis of these annulated semibullvalenes has led to the development of a general flexible synthetic scheme (refer Chapter 2, Scheme 2) starting with the Weiss product of the corresponding alkane dione and 1,3-dimethyl acetone dicarboxylate.

The chemical reactivity of these annulated semibullvalenes showed remarkable differences depending on the ring size attached to positions 1 and 5. We investigated the thermal rearrangement and reaction with oxygen. The results are summarized in Table 20. The activation energy involved in the conversion of the 1,5-dimethyl compound to the corresponding cyclooctatetraene was determined to be 25.6 Kcal/mole compared to a value of 39 Kcal/mole for the parent semibullvalene (78). The rate of oxygen uptake by the 1,5-cyclopentano compound was found to be approximately thirty times faster than the uptake by the 1,5-cyclohexano compound.

Table 20 Chemical reactivities of the 2,4,6,8-tetrakis  
(carbomethoxy) 1,5-annulated semibullvalenes

Semibullvalenes	Rearrangement to corresponding COT's	Reaction with oxygen to form peroxides
1,5-Dimethyl	+	-
1,5-cyclopentano	-	+ *
1,5-cyclohexano	-	+
1,5-cycloheptano	- **	-
1,5-cyclooctano	- **	-

\* Two different peroxides were obtained

\*\* The compounds decompose at 200°C

The  $^{13}\text{C}$  NMR of all the annulated semibullvalenes in solution at room temperature, indicate a rapid Cope rearrangement. As the temperature was lowered the carbon resonances for C2,4,6,8 shorten (sharp) in the case of 1,5-cyclohexano compound. In case of the dimethyl compound the resonance for C2,4,6,8 just begin to broaden at  $-160^\circ\text{C}$ . This along with the CPMAS C-13 spectrum sets the upper limit for the free energy of activation to be 4.3 Kcal/mole. Since the peak for the 1,5-cyclohexano compound is still sharp at  $-160^\circ\text{C}$  the free energy of

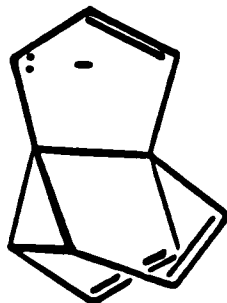
activation is a lot lower than  $3.8 \pm 0.5$  Kcal/mole. In the CPMAS  $^{13}\text{C}$  NMR spectrum of the 1,5-cyclooctano compound, 12d, the cyclopropyl carbons and the carbons of the double bond i.e, carbons 2,4,6, and 8 appear at an averaged position. The signal for C2,4,6,8 appears to be broad.

Table 16 in Chapter 3 summarizes a comparison of the significant geometric features in these annulated semibullvalenes. The most striking feature was observed in the case of the 1,5-cyclooctano compound. The open end (C4-C6) is equal in length to the C2-C8 bond (1.99 Å). The other bonds (C2-C3, C3-C4, C6-C7, C7-C8) measure 1.39 Å. The thermal parameters are very sharp. Thus the structure does not represent two Cope structures rapidly rearranging at room temperature. It therefore appears to resemble two allyl radicals interacting at a distance 1.99 Å apart - a neutral homoaromatic molecule.

A new route to the synthesis of 1,5-cyclopropa-2,6-dicyano semibullvalene was developed. The scheme progressed upto the point of synthesizing bicyclo [3.3.1]-nona-2,6- diene-2,6- dicarbonitrile 37. Naphthalene was Birch reduced followed by dichlorocarbene addition which on removal of chlorines led to the formation of tricyclo[4.4.1.0<sup>1,4</sup>] undeca-3,8-diene. Ozonolysis of the diene followed by aldol condensation led to the dialdehyde 33. Dioxime formation followed by

dehydration led to the dinitrile 37. Detailed study of the acidity of the dicyano compound and of the dianion was expected to prove interesting. The homopentalene dianion would have been the smallest homopentalene dianion. The dianion formation followed by oxidation did not lead to any identifiable product.

Finally MNDO calculations were performed to study 1,5-dianion and 1,5-allyl (anion, cation, radical) semibullvalenes. The pentalene structure was preferred over the 1,5 dianion semibullvalene structure by 131.2 Kcal/mole.



The difference in the heat of formation between the delocalized and localized structures was found to 29 Kcal/mole, using the MNDO approximation and incorporating 2x2 CI in the optimization of the delocalized structure.

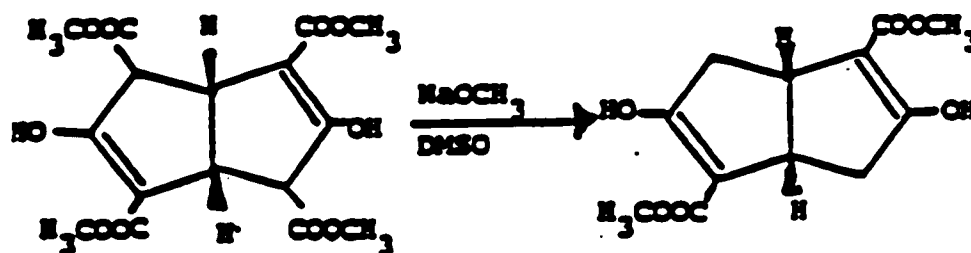
### SUGGESTIONS FOR SPECTRAL WORK

1. In order to understand the low temperature nmr of 12d a more complete nmr study involving line shape analysis varying the temperature from  $-70^{\circ}$  to  $-160^{\circ}\text{C}$  should be carried out and the pattern of broadening as well as any subtle changes in chemical shift studied.
2. The best method for the study of rapidly equilibrating species having low activation energies is variable temperature, high resolution solid state  $^{13}\text{C}$  nmr (134). The 1,5-cyclooctano-2,4,6,8-tetrakis (carbomethoxy) semibullvalene is an excellent candidate for such an experiment. Lack of change in the variable temperature CPMAS  $^{13}\text{C}$  NMR would strongly support the symmetrical structure and argue against the possibility of equilibrating species.
3. The doublet nature of the nitrile peak at  $2200\text{ cm}^{-1}$  in the IR of tricyclo[3.3.1]non-2,6-2,6-diene has to be further investigated. High resolution FTIR studies need to be carried out in order to determine the number of equivalent ester groups.
4. It still remains to obtain low temperature UV/visible spectra of the semibullvalenes; which might provide

useful information regarding the thermochromicity of the compound. 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 phenomenon would be of value. A preliminary study of the solid state UV/visible spectra of the compound was inconclusive (135).

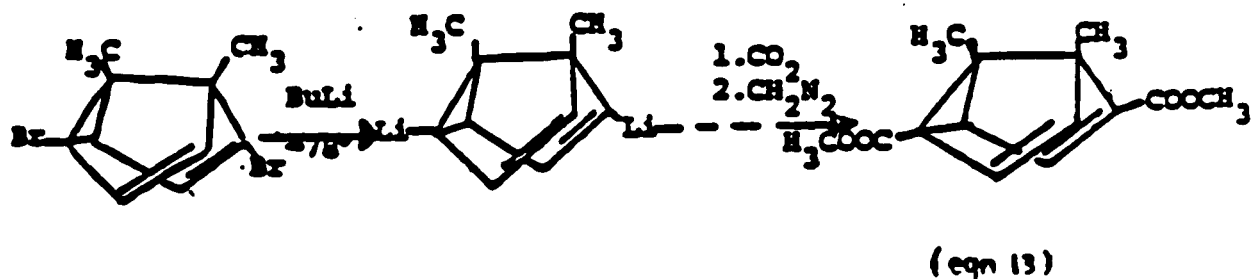
#### SUGGESTIONS FOR EXPERIMENTAL AND THEORETICAL WORK:

1. Apparently four carbomethoxy groups are too bulky, so one should consider having just two carbomethoxy groups instead. One method of synthesizing these compounds utilizes existing precursor molecules. The enol ester, 41, can be converted to the diester in 90% yield (eqn 12) (136).



(eqn 12)

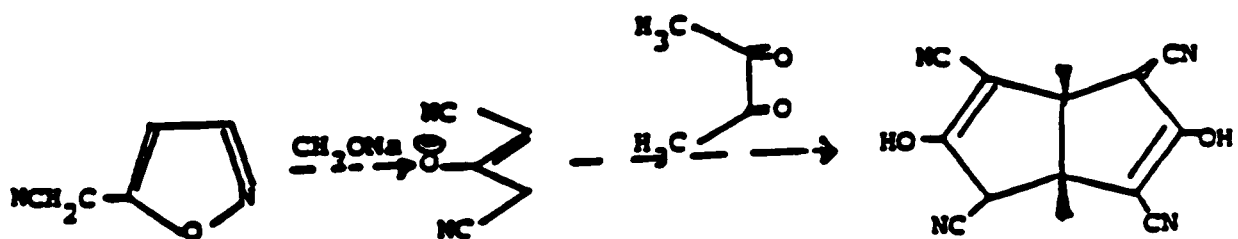
Another alternative is to use the 1,5-dimethyl-2,6-dibromosemibullvalene which was made earlier by L. Miller at our laboratories. It should be possible to make the dilithium compound by treating it with BuLi at  $-78^{\circ}\text{C}$ . Addition of  $\text{CO}_2$  followed by  $\text{CH}_2\text{N}_2$  should produce the dicarbomethoxy derivative (eqn 13).



2. The nitrile group is a far better choice as an electron withdrawing group because it is smaller and linear. The dibromo starting material is already available in our laboratories. It can be converted to the dinitrile semibullvalene as shown below. It is important to protect the carbonyl group before the CuCN reaction because the sequence apparently did not work well when carried out in the absence of the protection. A lot of decomposition products was observed in a preliminary study by L. Miller.

3. Since a variety of methods to convert the tetraester compounds at different stages to the tetracyano compounds proved to be difficult, direct synthetic route to incorporate the cyano groups at an early phase are proposed.

One route involves the in situ trapping of 1,3-dicyanoacetone by 2,3-butanedione. The 1,3-dicyanoacetone could be generated from 5-cyanomethylisooxazole and  $\text{CH}_2\text{ONa}$  in the presence of the dione (137). If conditions are optimum, the enol would be formed (eqn 14) and could be transformed into the desired semibullvalene following the route used for the 1,5-dimethyl-2,4,6,8-tetrakis (carbomethoxy) semibullvalene and the annulated semibullvalenes.

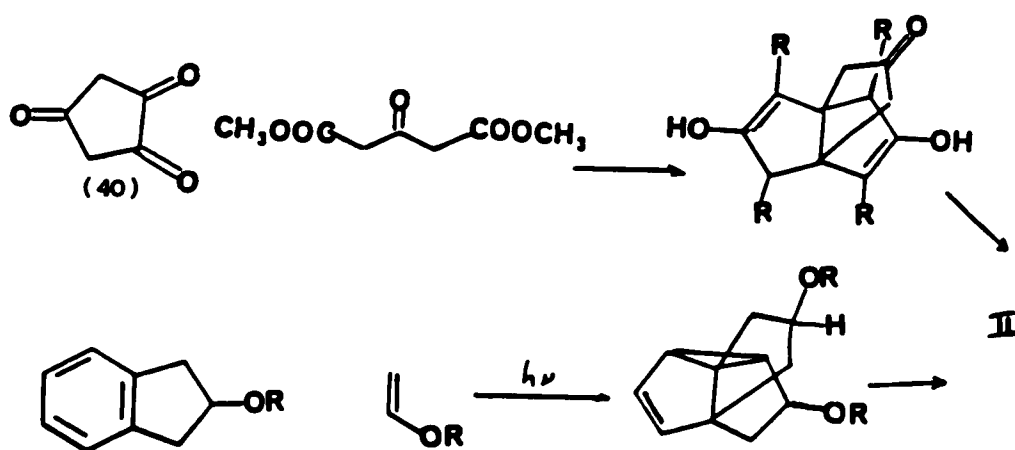


4. Since the annulation of a cyclopropane at positions 1,5 has been predicted to have a dramatic effect on

the Cope rearrangement, it is important to pursue the synthesis of 1,5-cyclopropa-2,6-dicyano semibullvalene. Along these lines it is important to synthesize tricyclo [3.3.1] non-2-ene-2-nitrile (Scheme 8, Chapter 4). The LDA/I<sub>2</sub> reaction on the above molecule should be studied in every detail before using the actual precursor, bicyclo[3.3.1]non-2,6-dicyano-2,6-diene. Attention should be directed to the dianion which would be the smallest methano bridged cyclooctatetraene dianion.

5. It is equally important to make the semibullvalene with a cyclobutane annulated at positions 1,5.
6. It is also important to obtain the 1,5 annulated cyclooctatetraenes. It is therefore crucial to identify the products obtained on decomposition of the cycloheptano and cyclooctano compounds. Since we failed to make cyclooctatetraenes from 12a - 12d, and we have the best chance with 12d; the ester groups in the semibullvalene 12d should be reduced to methyls (138) thereby changing the substitution pattern in the semibullvalene. This semibullvalene could then rearrange to the annulated cyclooctatetraene.
7. Two routes are proposed for the annulation of the allyl/cation/anion/radical (139). The second route is

based on the elegant synthesis of modephene by P.Wender (140) involving the meta-photocycloaddition of vinyl acetate to 2-indanol acetate. Several possibilities exist for the conversion of the compound obtained from the above schemes to the respective cation, anion, and radical.



8. In order to separate the 1,5 donor effects from the 2,4,6,8 acceptor effect a detailed theoretical study of 1,5 dimethyl semibullvalene should be carried out. Discussions with other workers in this area suggest that 1,5 donor substitution on semibullvalene apparently stabilizes the transition state to a greater extent than previously assumed.

CHAPTER 7  
EXPERIMENTAL

All solvents and reagents were purified by literature procedures. IR spectra were obtained on a Perkin-Elmer 1310 spectrophotometer (KBr pellet, unless indicated otherwise). UV-Visible spectra were run on a Beckmann DU B spectrophotometer in absolute ethanol solution. Routine H-1 NMR spectra were recorded at 60 MHz on a Varian EM360 or a QE 300 (General Electric) spectrometer in CDCl<sub>3</sub>, (unless otherwise stated) using TMS as an internal standard. High field H-1 and C-13 NMR's were obtained on Jeol GX 400 Mhz. and Bruker WH-400 and WH-500 spectrometers. Elemental analyses were performed by Dr. Franz Scheidl, Microlit laboratories, New Jersey. Melting points were determined on a Buchi meltemp apparatus and are uncorrected.

"Usual" or "standard" work-up refers to the following procedure. The reaction mixture was poured onto ice-water (containing NaHSO<sub>3</sub> for I<sub>2</sub> and Br<sub>2</sub> producing reactions) extracted 3 times with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were washed with dilute HCl, followed by a washing with a saturated NaCl solution, and a final wash with a saturated NaHCO<sub>3</sub> solution and dried over anhydrous MgSO<sub>4</sub>. After filtration of the drying agent (MgSO<sub>4</sub>) the organic

solvent was evaporated in vacuo using a Buchi Rotavapor-R.

### 1,5 RING ANNULATION

#### Preparation of 2-cyclopentylidene cyclopentanone (141):

This was carried out according to the procedure reported by Mayer (141). To 400 g of cyclopentanone, a solution of 30 g of sodium in 450 mL absolute ethanol was added with stirring and ice cooling. The mixture was left for two days at  $-2^{\circ}\text{C}$ , then concentrated on a rotary evaporator. The mixture was partitioned between water and ether, and the ethereal extract was dried and concentrated leaving behind the 2-cyclopentylidene cyclopentanone. 164.3 g, 46% (lit (141) 50-52%) of the pure product was obtained by high vacuum distillation of the crude oil ( $72^{\circ}\text{C}$ , 1 mm Hg). NMR 1.8-2.4 (two multiplets), it is identical to the spectrum in the Aldrich catalog (2nd Edn., Vol 1, #414A).

#### Ozonolysis of 2-cyclopentylidene cyclopentanone:

The ozonolysis was carried out following Cook's procedure (61). Distilled 2-cyclopentylidene cyclopentanone (60.0g, 0.40 mol) was dissolved in methanol (600 mL) and ozone was passed through the solution until the reaction was complete (generally 6 to 8 hours), i.e., until the appearance of a blue green color showed the presence of

excess ozone. Dimethyl sulfide (35 g, 0.60 mol) was then added to the ozonide at dry ice-acetone temperature and the solution was allowed to warm to room temperature. The mixture was stirred overnight, then methanol was removed under reduced pressure (water aspirator). Cyclopentanone was removed from the medium using a high vacuum pump. The procedure so far is similar to that reported by Cook (61). Cook (personal communication) suggested distillation of the crude dione, to avoid the chromatography at this point. However in our hands attempted distillations of the crude brown oil led to extensive decomposition. The material was chromatographed using a silica gel column (EtOAc, 600 g silica gel) to provide 37.6 g (95%) of cyclopentane-1,2-dione. The material stains skin on contact. It slowly decomposes in air, and should be stored in the freezer. The compound exists in the enol form as is evident from its nmr  $\delta$  2.5 (4H br peak), 5.7 (1H br singlet), 6.5 (1H triplet) and compares well with the NMR reported earlier (142).

Preparation of tetramethyl[3.3.3]propellane-8,11-dione-7,9,10,12-tetracarboxylate, 7a (62(a))

The procedure developed by Weiss (62(a)) was followed. Dimethyl 3-ketoglutarate (86.75 g, 0.47 mol) was dissolved in citrate-phosphate buffer (3000 mL, pH 6.6) and cyclopentane-1,2-dione (23 g, 0.285 mol) was added to the

solution at room temperature in four gram portions over a two-week period. The aqueous buffer was prepared by dissolving dibasic sodium phosphate (163.8 mL, 0.2M) and citric acid (61.2 mL, 0.1M) in tap water (1274 mL). The white precipitate was filtered and triturated with MeOH, leaving 19.3 g (20%) of 7a mp (MeOH) 156-8°C (lit. (62(a)) 150-2) ir 3215 cm<sup>-1</sup> (OH of enol) broad peak, 2940 cm<sup>-1</sup> (C-H), 1730 cm<sup>-1</sup> (ester carbonyl), 1660 cm<sup>-1</sup> (C=C of the enol); the ir was in complete agreement with spectra obtained from Cook's laboratories; nmr  $\delta$  1.30 (6H multiplet cyclopentane H's), 3.75 (6H, singlet OMe), 3.88 (6H singlet OMe), 3.92 (2H singlet 4,8), 10.80 (1H br singlet).

Preparation of 2,4,6,8-tetrakis (carbomethoxy) pentacyclo [3.3.3.0<sup>1,3</sup>.0<sup>2,4</sup>.0<sup>5,6</sup>] undeca-3,7-dione, 9a.

The pentacyclic ketone was prepared from 7a by a two step reaction. A solution of 2.7 mL (8.2 g, .051 mol) of Br<sub>2</sub> in 20 mL was added to a solution of 10 g (0.023 mol) of 7a in 150 mL CHCl<sub>3</sub>, over a period of one hour, then the solution was stirred at room temperature overnight. Excess bromine was removed by washing with saturated NaHSO<sub>3</sub>. The organic layer was then washed with saturated NaCl and dried over MgSO<sub>4</sub>. The CHCl<sub>3</sub> solution containing the dibromo adduct 8a, was chilled and a solution of 8.8 mL (6.4 g, 0.06mol) triethyl amine in 50 mL of CHCl<sub>3</sub>, was added to it over a

period of 30 minutes. After stirring for two hours the solution was worked in the usual way. The crude product was triturated with ether; shiny colorless crystals appeared and were identified to be the dibromo compound 8a, m.p 196-197°C (dec.) (MeOH). Two fractions of 8a were obtained. The mother liquor contained mainly 2,4,6,8-tetrakis (carbomethoxy) pentacyclo [3.3.3.0<sup>1,5</sup>.0<sup>2,6</sup>.0<sup>3,7</sup>]undeca-3,7-dione (9a), based on NMR data. The dione was difficult to crystallize from MeOH, EtOAc, EtOAc-hexane mixtures, ether, or CCl<sub>4</sub>. A few crystals were obtained from EtOAc, mp 169-172°C; ir 2950 cm<sup>-1</sup> 1770 and 1745 cm<sup>-1</sup>, 1720 cm<sup>-1</sup>; nmr δ 2.2 (2H, quintet, middle H's in cyclopentane), 2.47 (4H triplet, middle H's in cyclopentane), 3.77 (12H, singlet OMe); C-13 nmr δ 24.85 and 28.62 (t, cyclopentane carbons), 48.59 (s, C 1,5), 53.21 (s, C 2,4,6,8), 54.68 (q, OMe), 162.06 (s, ester carbonyls), 189.9 (s, carbonyl carbons). The dione was carried over to the next step in the crude form.

Preparation of 1,5-dimethyl-2,4,6,8-tetracarboethoxy pentacyclo [3.3.3.0<sup>1,5</sup>.0<sup>2,6</sup>.0<sup>3,7</sup>] undeca-diexo-3,7-diol, 10a.

An ice-cooled suspension of 4.1 g (10 mmole) of 9a in 50 mL of toluene was stirred under argon, and 50 mL of a solution of (i-Bu)<sub>2</sub>Al in toluene (25% soln 1.6M, 80 mmol) was added (67). The clear yellow solution was stirred at

room temperature for one hour. After cooling the reaction with ice, 25 mL of ice-cold 3M HCl solution was added cautiously. The reaction mixture was then poured into ice-water, diluted with HCl and extracted with EtOAc. The organic layers were washed in the usual way. The crude diol was recrystallised from ethyl acetate, giving 2.65g (65%) of pure diol, mp 199-202°C; ir 3490  $\text{cm}^{-1}$  (O-H), 2980 and 2960  $\text{cm}^{-1}$  (C-H), 1730 and 1700  $\text{cm}^{-1}$  (C=O of ester); nmr  $\delta$  2.25 (2H quintet, the middle H's of cyclopentane), 2.35 (4H triplet, the four outer H's of cyclopentane), 3.57 (2H doublet, OH), 3.7 (12H singlet, OMe), 4.84 (2H doublet, H 3,7).

Preparation of the dimethansulfonyl derivative of 10a, 11a.

A solution of 3 g (7.1 mmol) of the alcohol 10a and 5.4 mL of distilled triethylamine (3.9 g, 38.7 mmol) in 100 mL of distilled  $\text{CH}_2\text{Cl}_2$  was cooled in an ice-bath, and a solution of 3.2 mL (4.65 g, 40.62 mmol) of distilled methanesulfonyl chloride in 10 mL of  $\text{CH}_2\text{Cl}_2$  was added over a period of 30 minutes. The solution was stirred for an additional 2 hours without removing the ice-bath (allowing the temperature of the ice bath to rise slowly to the room temperature). The product was isolated by dilution with ice water, acidification with HCl, followed by extraction with ether. After the standard work up, trituration of the

residue with EtOAc led to 2.7 gms (66%) of the dimesylate as a white solid, mp (EtOAc) 136-7°C (dec.); ir 2960  $\text{cm}^{-1}$  (C-H), 1740-1725  $\text{cm}^{-1}$  (doublet ester carbonyls); nmr  $\delta$  2.26 (2H quintet, the two middle H's in the cyclopentane ring), 2.42 (4H triplet, the four outer H's in cyclopentane), 3.04 (6H singlet, S-Me), 3.67 (12H singlet, OMe), 5.73 (2H singlet, H 3,7).

Preparation of 1,5-cyclopentano-2,4,6,8-tetracarboxymethoxy semibullvalene, 12a.

To a refluxing solution of 4 g of oven dried NaI in 20 mL of acetone degassed with argon and under a blanket of argon, 0.5 g (1 mmol) of 11a was added. The oil bath temperature was maintained at 67°C and the blanket of argon was maintained during the overnight reflux period. Argon was bubbled through the  $\text{NaHSO}_3$ , saturated NaCl, and the  $\text{NaHCO}_3$  solutions before use. The separatory funnel always contained a piece of solid  $\text{CO}_2$  (dry ice) during the work up in order to maintain an inert atmosphere; in short, extreme care was taken to exclude air to prevent the conversion of the semibullvalene to the endoperoxide. Standard (oxygen free) work up provided 0.215 gms (64%) of the semibullvalene as a yellow solid, mp 105-7 (crude); uv 243.92 nm ( $\epsilon = 8343.6$ ); ir 2950  $\text{cm}^{-1}$  (C-H), 1710  $\text{cm}^{-1}$  (ester carbonyl), 1590  $\text{cm}^{-1}$  (C=C); nmr  $\delta$  1.66 (2H quintet, the two middle H's of the cyclopentane ring),

2.22 (4H triplet, the four outer H's of the cyclopentane ring), 3.77 (12H singlet, OMe), 6.43 (2H, singlet H 3,7); C-13 nmr  $\delta$  27.99 and 28.57 (t, cyclopentane carbons), 52.12 (q, OMe), 76.8 (s, C 1,5), 103.91 (s, C 2,4,6,8), 132.41 (d, C 3,7), 165.36 (C=O).

Preparation of cyclohexane-1,2-dione:

This was carried out according to the procedure reported in Organic Synthesis (collected vol 4, pp 229). To 170 g (1.74 mol) of cyclohexanone maintained at 10°C, a solution of 39 g of SeO<sub>2</sub> (0.3 mol) in 50 mL of dioxane and 10 mL of water was added dropwise while the solution was stirred mechanically, over a period of 3 h. The solution was stirred 5 h at 15°C. Stirring was continued at room temperature for 6 h. The red colored selenium was filtered off using a Buchner funnel. The selenium thus collected was washed with 30 mL of boiling 95% ethanol and the ethanol solution was decanted and combined with the filtrate. Distillation under reduced pressure gave two fractions:

1. 25-60°C at 16 mm Hg ( EtOH, water, dioxane, cyclohexanone) and 60-90°C at 16 mm Hg containing cyclohexanone, cyclohexane-1,2-dione, water, dioxane.
2. 60-90°C at 16 mm Hg (cyclohexanone, cyclohexane 1,2-

dione, water and dioxane).

The second fraction on redistillation gives the two fractions:

1. 25-75/16 mm

2. 75-79/16 mm

The second fraction weighing 125 g (60% yield) crystallized, and was identified as cyclohexane-1,2-dione; mp 35-38 (°C); nmr  $\delta$  (deuterated DMSO) 2.1 (6H multiplet), 6 (1H triplet, vinylic H of enol), 8 (1H broad singlet, OH).

Preparation of tetramethyl[4.3.3]propellane-8,11-dione-7,9,10,12-tetracarboxylate, 7b (50)

This was done according to the procedure reported by Weber and Cook (50). Cyclohexane-1,2-dione (Aldrich, not distilled) (10g, 0.09 mol) was dissolved in citrate-phosphate buffer (500 mL, pH = 5.6) and dimethyl 1,3-acetonedicarboxylate (31 g, 0.18 mol) was added. The citrate-phosphate buffer was made by dissolving hepta hydrate sodium hydrogen phosphate (11.67g, 43.5 mmol) and citric acid (3.68g, 17.5mmol) in water (900 mL). After the solution was stirred at room temperature for 2 h a

white precipitate began to form. The mixture was stirred for an additional two weeks and then the solid was filtered from the reaction to provide 7b (12.25 g, 40% yield; the yield was 66% when freshly prepared cyclohexane-1,2-dione was used); mp 154-6°C (lit. (50) 171-5). The mp of the compound triturated with methanol is 164-8°C; the mother liquor afforded crystals, mp 155-168°C. The mp of 154-6°C was obtained by recrystallizing the mixture melting at 155-168°C. All the above products had identical NMR's. Products from the Weiss reaction in general had a wide range of melting points. IR 2940  $\text{cm}^{-1}$  (C-H), 1730  $\text{cm}^{-1}$  (ester carbonyl), 1660  $\text{cm}^{-1}$  (C=C enol double bond); lit. (62(a)) 2940  $\text{cm}^{-1}$  1730  $\text{cm}^{-1}$  1650  $\text{cm}^{-1}$ ; nmr  $\delta$  1.5 (4H multiplet, cyclohexane H's), 1.95 (4H multiplet, cyclohexane H's), 3.7 (15H overlapping singlets OMe), 10.95 (1H singlet, OH).

Preparation of 2,4,6,8-tetrakis (carbomethoxy) pentacyclo [4.3.3.0<sup>1,4</sup>.0<sup>2,5</sup>.0<sup>6,7</sup>] dodeca-8,11-dione, 9b.

The pentacyclic ketone 9b was prepared from 7b by a two step reaction. A solution of 2.7 mL (8.2 g, .051 mol) of  $\text{Br}_2$  in 20 mL of  $\text{CHCl}_3$  was added to a solution of 10 g (0.023 mol) of 7b in 150 mL of  $\text{CHCl}_3$  over a period of one hour. The bromine did not completely react. The solution was stirred at room temperature overnight, then washed with saturated  $\text{NaHSO}_3$  to remove the excess bromine. The

organic layer was then washed with saturated NaCl and dried over MgSO<sub>4</sub>. The CHCl<sub>3</sub> solution, containing the dibromo adduct 8b, was chilled and a solution of 8.8 mL (6.4 g, 0.06mol) of triethyl amine in 20 mL of CHCl<sub>3</sub>, was added to it over a period of 30 minutes. After stirring for two hours the solution was worked up in the usual way. The crude product was triturated with ether. 4 g (39% yield) of the dione (shiny colorless crystals) were obtained, mp 170-172°C (MeOH), ir 2950 cm<sup>-1</sup> (C-H), 1770 and 1740 cm<sup>-1</sup> (doublet ester carbonyl), 1715 cm<sup>-1</sup> (C=O); nmr δ 1.85 (4H triplet, cyclohexane H's), 2.2 (4H triplet, cyclohexane H's), 3.8 (12H singlet, OMe). C-13 nmr δ 18.2 and 19.7 (t, cyclohexane C's), 49.1 (s, C 1,5), 49.6 (s, C 2,4,6,8), 53.3 (q, OMe), 162.0 (s, ester carbonyls), 189.9 (s, carbonyl). An analytical sample was prepared by recrystallization of the dione from methanol. Anal. Calc. for C<sub>20</sub>H<sub>20</sub>O<sub>10</sub>: C, 57.15; H 4.79. Found: C, 56.93; H, 4.74.

Preparation of 2,4,6,8- tetrakis (carbomethoxy) pentacyclo [4.3.3.0<sup>1,4</sup>.0<sup>2,7</sup>.0<sup>5,8</sup>.0<sup>6,7</sup>] dodeca-diexo-3,7-diol, 10b.

An ice-cooled suspension of 4.24 g (10 mmol) of 9b in 50 mL of toluene was stirred under argon and 50 mL of a solution of (i-Bu)<sub>3</sub>Al in toluene (25% solution, 1.6 M, 80 mmol) was added (67). The clear solution was stirred at room temperature for one hour. After cooling the reaction in an ice-bath, 25 mL of 3M HCl was added cautiously. The

reaction mixture was then poured into ice water, which was diluted with HCl, and extracted with EtOAc. The organic layer was washed in the usual way. This step led to 2.7 g of the diol (63% yield); mp 213-215.5°C; ir 3420  $\text{cm}^{-1}$  (OH), 2920  $\text{cm}^{-1}$  (C-H), 1720  $\text{cm}^{-1}$  (C=O); nmr  $\delta$  1.8 and 2.2 (8H multiplet, cyclohexane H's), 3.7 (12H singlet, OMe), 4.6 (2H doublet, H 3,7). An analytical sample of the diol was prepared by recrystallization from EtOAc. Anal: Calc for  $\text{C}_{22}\text{H}_{34}\text{O}_4$ : C, 56.60; H 5.70; Found: C, 56.70; H 5.80.

Preparation of the dimethansulfonyl Derivative of 10b, 11b.

A solution of 3 g (7.142 mmol) of the diol 10b, and 5.35 mL of distilled triethylamine (3.91 g, 38.67 mmol) in 100 mL  $\text{CH}_2\text{Cl}_2$  was chilled in an ice bath. A solution of 3.143 mL (4.65 g, 40.62 mmol) of distilled methanesulfonyl chloride in 10 mL  $\text{CH}_2\text{Cl}_2$  was then added slowly. The reaction mixture was stirred for two hours while the temperature slowly rose to room temperature. After the standard workup, the oil produced was triturated with EtOAc, giving 2.6 g of the dimesylate (63%); mp 111-112°C (dec); ir 2960  $\text{cm}^{-1}$  (C-H), 1720  $\text{cm}^{-1}$  (broad peak ester carbonyls); nmr  $\delta$  1.8 and 2.3 (cyclohexane H's), 3 (6H singlet, S-Me), 3.65 (12H singlet, OMe), 5.7 (2H singlet, H 3,7). An analytical sample was prepared by recrystallization from EtOAc. Anal. Calc for  $\text{C}_{22}\text{H}_{30}\text{O}_4\text{S}_2$ :

C, 45.51; H, 4.86; S, 11.04; Found: C, 45.52; H 4.81; S, 10.98.

Preparation of 1,5-cyclohexano-2,4,6,8-tetracarbomethoxy semibullvalene, 12b.

To a solution of 4g (0.027 mmol) of NaI (under Argon) in 20 mL of acetone degassed with argon, 0.5g (0.8 mmol) of 11b was added. The mixture was refluxed overnight under a blanket of argon. Argon was bubbled through the solutions of NaHSO<sub>3</sub>, saturated NaCl solution, and saturated NaHCO<sub>3</sub>, used for extraction. The separatory funnel always contained a piece of solid carbon dioxide (dry ice) to exclude oxygen. All possibilities of oxygen conversion of semibullvalene to its endoperoxide were minimized. After the usual work up, followed by crystallization (MeOH) 0.215 g (64%) of bright, shiny, golden yellow crystals of 12b were obtained, mp 123-124°C (MeOH); uv 242.25 nm ( $\epsilon = 8879.8$ ); ir 2940 cm<sup>-1</sup> (C-H), 1720 cm<sup>-1</sup> (ester carbonyls), 1590 cm<sup>-1</sup> (C=C); nmr  $\delta$  1.45 and 2.05 (cyclohexane H's), 3.75 (12H singlet, OMe), 6.42 (2H singlet, H 3,7); C-13 nmr  $\delta$  18 (t, cyclohexane C's), 52 (q, OMe), 70 (s, C 1,5), 106.5 (s, C 2,4,6,8), 132.5 (d, C 3,7), 165 (C=O). X-ray structure: C2-C8=1.83, C4-C6=2.195, C2-C3=1.41, C3-C4=1.36, C6-C7=1.36, C7-C8=1.43, C1-C5=1.57 Å; C2-C1-C8=75.23°, C4-C5-C6=92.62°. Anal Calc for C<sub>20</sub>H<sub>22</sub>O<sub>6</sub>; C, 61.53; H, 5.68; Found; C, 61.44; H, 5.62.

Isolation of the iodomesylate during the synthesis of 12b

To 1.482 g (27 mmol) of NaI in 5.3 mL of distilled acetone, 0.2 g (0.345 mmol) of the dimesylate 11b was added. The reaction mixture was refluxed for 6 h. The usual work up followed by recrystallization from EtOAc led to 0.12 g (57%) of the iodomesylate; nmr  $\delta$  1.8 (8H m, cyclohexane H's), 3.8 (12H s, OMe), 5.2 (1H s, the H on the carbon bearing the mesyl group), 6.45 (1H s, the H on the carbon bearing the iodine).

Preparation of the endoperoxide of semibullvalene 12b:

1. A 1g (2.5 mmol) sample of pure semibullvalene 12b was stored in a sample vial with a "press on" of a lid at room temperature in the dark. After a period of six months 923 mg (85%) mp 151.5-153°C of endoperoxide was obtained from the semibullvalene.
2. 57 mg (0.015 mmol) of the semibullvalene 12b was dissolved in 20 mL of distilled acetone and a slow stream of oxygen was bubbled through it for 48 h. 60 mg (quantitative conversion) of endoperoxide was obtained from the semibullvalene, mp 151.5-153°C.
3. The endoperoxide was also obtained during the

preparation of 12b if the reaction was not carried out under argon, or air was let in during any stage of the work up.

The semibullvalene 12b is more soluble than the endoperoxide in MeOH. TLC: (9:1 ether/CH<sub>2</sub>Cl<sub>2</sub> on silica gel), R<sub>f</sub> of (12b) 0.4, R<sub>f</sub> (19) 0.5. Mp 151.5-153°C, nmr δ 1.1 (2H, t), 1.25 (2H, t), 1.4 (2H, distorted triplet), 2.3 (2H, br doublet), 3.75 (12H d, OMe), 7.0 (2H s, vinylic H's). An analytical sample was prepared by recrystallization from methanol. Anal: Calculated for C<sub>20</sub>H<sub>22</sub>O<sub>10</sub>; C, 56.87; H, 5.25; Found; C, 56.89; H, 5.33.

Reaction of semibullvalene 12b with Dimethyl acetylene dicarboxylate

Semibullvalene 12b (92 mg, 2.4 mmol) was dissolved in about 10 ml of distilled toluene and 0.03 mL of DMAD (distilled) was added. It was refluxed for 24 h, then discarded when it was discovered (TLC) that 12b was unchanged.

Sublimation of the endoperoxide 19

In an attempt to convert the endoperoxide to the semibullvalene 12b by heating (by loss of oxygen) the endoperoxide was sublimed at 150°C and 0.5 mm of Hg. This

led to two products (NMR) different from semibullvalene and endoperoxide which were not further identified.

Thermolysis of 1,5 cyclohexano 2,4,6,8 tetrakis (carbomethoxy) semibullvalene 12b:

A solution of 26.9 mg of 12b under argon in 25 mL of xylene was refluxed for 24 hours. The semibullvalene remained unchanged (by 400 MHz  $H^1$  NMR).

## KINETICS

### Kinetics of the conversion of 1,5-dimethyl 2,4,6,8-tetrakis (carbomethoxy) semibullvalene to the corresponding cyclooctatetraene

#### (a) Determination of rate constant at 65°C

A scrupulously clean 25 mL two-necked round bottomed flask was charged with 100 mg (0.3 mmol) of 1,5-dimethyl 2,4,6,8-tetrakis (carbomethoxy) semibullvalene **6** in 18 mL of CCl<sub>4</sub> (freshly distilled). The mixture was heated at 65°C under nitrogen, and 400 MHz <sup>1</sup>H NMR's were obtained every hour.

A plot of  $\ln(c_0/c)$  vs  $t$ , where  $c_0$  is the concentration of semibullvalene **6** at time zero and  $c$  is the concentration of the semibullvalene at time  $t$ , should be a straight line the slope of which would give the value of  $k$ . The kinetics were determined by integrating peaks at 6.2 ppm (semibullvalene vinylic H) and 7.2 ppm (cyclooctatetraene vinylic H).

Tabulation:

t in hours	% of SB left	ln c <sub>0</sub> /c
1	91.84	0.085
2	89.08	0.12
3	84.37	0.17
4	81.20	0.21
6	76.16	0.27
8	65.95	0.42

Slope =  $0.046 \text{ hr}^{-1} = 1.28 \times 10^{-5} \text{ sec}^{-1}$

$k = 1.28 \times 10^{-5} \text{ sec}^{-1}$  at  $65^{\circ}\text{C}$ .

(b) Determination of rate constant at  $73^{\circ}\text{C}$

The same procedure was repeated at  $73^{\circ}\text{C}$ , leading to the following results:

t in hours	% of SB left	ln c <sub>0</sub> /c
1	85.29	0.152
2	75.39	0.282
3	64.29	0.442
4	56.77	0.566
5	51.89	0.656

$$\text{Slope} = 0.1292 \text{ hr}^{-1} = 3.59 \times 10^{-5} \text{ sec}^{-1}$$

$$k = 3.59 \times 10^{-5} \text{ sec}^{-1} \text{ at } 73^\circ\text{C}.$$

(c) Determination of rate constant at  $85^\circ\text{C}$  The procedure was repeated at  $85^\circ\text{C}$ .

t in hours	% of SB left	$\ln c_0/c$
2	54.2	0.612
4	25.2	1.38
6	12.6	2.07

$$\text{Slope} = 0.365 \text{ hr}^{-1} = 1.014 \times 10^{-4} \text{ sec}^{-1}$$

$$k = 1.014 \times 10^{-4} \text{ sec}^{-1} \text{ at } 85^\circ\text{C}..$$

(d) The reaction exhibited first order kinetics through half lives of 15 h, 5.4 h, 1.9 h at  $65^\circ\text{C}$ ,  $73^\circ\text{C}$  and  $85^\circ\text{C}$  respectively. Determination of the activation energy using the Arrhenius equation and by graphing the above results, gave a value of 25.6 Kcal/mole for the  $E_a$ ,  $A = 1.98 \times 10^{11}$ . These values can also be obtained by solving the equations simultaneously.

Determination of k for 12b to 13.

Oxygen was bubbled through a solution of semibullvalene 12b (75 mg, 0.19 mmol) in 18 mL  $\text{CCl}_4$  at  $26^\circ\text{C}$  and 758.2 mm Hg, contained in a clean, dry, 3-neck flask fitted with a condenser and drying tube. A portion of this solution (0.5 mL) was transferred every hour to an NMR tube and 0.05 mL of acetone  $d_6$  was added to it.  $^1\text{H}$  NMR spectra were then obtained at 400 MHz.

The slope of a plot of  $\ln c_0/c$  vs  $t$  gives the value of  $k$ . The kinetics were determined by integrating peaks at 6.42 (semibullvalene vinylic H) and 7 ppm (endoperoxide vinylic H).

$t$	% of SB left	$\ln c_0/c$
0	93.41	0.00
1	87.87	0.06
2	83.21	0.12
3	80.08	0.15
4	77.24	0.19
5	74.33	0.23
7	60.72	0.43

$$\text{Slope} = 0.058 \text{ hr}^{-1} = 1.6 \times 10^{-8} \text{ sec}^{-1}$$

Thus  $k = 1.6 \times 10^{-3} \text{ sec}^{-1}$  at  $26^\circ\text{C}$ , 758.2 mm Hg, and an oxygen flow rate of 16 mL/min.

Kinetics for the absorption of oxygen by semibullvalene 12a.

Using the same procedure as for the above experiment and starting with 41.1 mg (0.1 mmol) of the semibullvalene in 18 mL of  $\text{CCl}_4$ , at  $24^\circ\text{C}$  and 759 mm of Hg a plot of  $\ln c_0/c$  versus  $t$  gave the value for  $k$ . The rate of oxygen flow was 16 mL/min.

$t$	% of SB left	$\ln c_0/c$
0	100.00	0.00
1	34.00	1.08
2	1.00	4.60

This led to a value of  $k = 4.7 \times 10^{-4} \text{ sec}^{-1}$ .

Bubbling oxygen through a solution of semibullvalene 12a.

From NMR of the solution used for the kinetics experiment described above it was evident that two compounds were being formed. Separation of two compounds on the chromatotron using a 10% EtOAc/hexane mixture led to the isolation of two peroxides assigned structures 17 and 18.

TOWARDS THE SYNTHESIS OF 1,5 CYCLOPROPA SEMIBULLVALENEPreparation of Isotetralin, 21, (101):

This was done according to the procedure described in Organic Synthesis (101). In a 5-l, three necked, round bottomed flask, immersed in a dry ice-acetone bath and fitted with a dry ice condenser, a tube-sealed stirrer with a strong motor, a drying tube (KOH), and a gas delivery tube running to the bottom of the flask, 2.5 L of ammonia was condensed. The ammonia tank was heated with a hot air gun during condensation, and the ammonia was dried by means of the drying tower (KOH) between the cylinder and the flask. The gas delivery tube was removed and 110g (0.86 mol) of naphthalene in 440 mL of ether and 330 mL of ethanol was added all at once. 70g (3 mol) of sodium was added in small pieces over a period of 20 minutes. Another 20 g of sodium was added after a period of 3 hours. The cooling bath was removed, and the ammonia was allowed to evaporate overnight (hood). The remaining white solid was ice cooled and stirred under nitrogen during slow addition of 60 mL of methanol to destroy unreacted sodium, followed by the addition of 2 - 2.5 L of ice water to dissolve salts. The white solid should be worked up as soon as possible since the residue turns brown-red on standing due to formation of decomposition products; isolation of isotetralin then becomes difficult and the yield may drop sharply. The reaction mixture was

extracted with 500 mL of ether (alternatively the remaining ether from the reaction flask can be evaporated at reduced pressure and the water slurry filtered to give the same yield after crystallization). Evaporation of the ether extract under reduced pressure gave a coarse, white solid which was collected on a Buchner funnel and washed with water. Crystallization from methanol gave two crops of crystals, 64.56 g (59-62°C) and 18.30 g (52-56°C), a total of 73% yield. Authors (101) reported a yield of 75-80%, mp 52-53°C, purity about 98%; pure isotetralin has a mp 58°C. Isotetralin should not be kept under low pressure (oil pump) for drying longer than is necessary since the compound has relatively high vapor pressure. NMR  $\delta$  2.5 (8H br singlet, allylic H's), 5.7 (4H br singlet, vinylic H's).

Preparation of 11,11-Dichloro[4.4.2.0<sup>1,6</sup>]undeca-3,8-diene, 22, (101):

This was done according to the procedure described in Organic Synthesis (101). The method of purification suggested by the authors did not work well in our hands. A 3L, three necked, round-bottomed flask was fitted with a tube sealed stirrer, a pressure equalizing dropping funnel, and a Claisen-adaptor that bore an inlet tube for argon and a low temperature thermometer. In the flask was placed a solution of 132.2 g (1 mole) of 1,4,5,8

tetrahydronaphthalene, 21, in 1.3 L of anhydrous ether. To this solution was added 150 g (1.33 mole) of potassium t-butoxide under an argon atmosphere, and the resulting suspension is cooled to  $-30 \pm 5^\circ\text{C}$  with a dry ice-acetone bath and stirred efficiently. While these conditions were maintained, a solution of 119.5 g (1 mole) of chloroform in 150 mL of ether was added dropwise during 90 minutes. Temperatures above  $-30^\circ\text{C}$  reduce the stereoselectivity of the addition; isotetralin partially crystallizes at temperatures lower than  $-30^\circ\text{C}$ , reducing the yield. The mixture was stirred for another 30 minutes at  $-30^\circ\text{C}$ , and the temperature was then raised above  $0^\circ\text{C}$ , then 300-350 mL of ice water was added to dissolve the salts. The two layers which formed were separated. Addition of dilute sulfuric acid aided separation when the phase boundary was obscured by dark colors. The organic layer was washed with two 300 mL portions of water, while the aqueous layer was extracted with two 200 mL portions of ether. The ether phases are combined and dried over magnesium sulfate. After filtration of the drying agent the ether was removed on a rotary evaporator, and the residual oil was distilled under reduced pressure.

The distillation was expediently carried out in a set-up which consisted of a 500 mL, round-bottomed flask, an electrically heated 1.5 x 30 cm Vigreux column, a short air-cooled condenser, and an ice-cooled receiver

flask. During the distillation the liquid was stirred magnetically and heated by an oil bath on a hot plate. The first fraction was all isotetralin bp 55-58°C. More of the material distilled when the column was heated to about 100°C. The products then started to crystallize in the column thereby posing problems. All attempts to separate the mono and bis adducts failed; separation after the removal of chlorines worked better. After collection of the isotetralin, a fraction of bp 95-102 (1 mm), which consisted mainly of 1:1 adduct was collected. The residue consisted mainly of 2:1 adduct. The fraction 95-102°C (1 mm) was used for the next step.

Preparation of Tricyclo[4.4.1.0<sup>1,6</sup>] undeca-3,8-diene, 20,  
(101)

This was done according to the procedure described in Organic Synthesis (101). We used spinning band distillation instead of the method described in the above procedure. In a 2L, three-necked, round-bottomed flask, immersed in a dry ice-acetone bath, and fitted with a dry ice condenser, a tube-sealed stirrer, a drying tube, and a gas delivery tube running to the bottom of the flask, 800 mL of ammonia was condensed. The gas delivery tube was removed and with vigorous stirring, 56 g (2.45 g-atoms) of sodium was added in small portions over a period of 1/2 hour. The flask was then fitted with a dropping funnel

through which a solution of 81.4 g (0.386 mol) of mainly 11,11-dichlorotricyclo[4.4.1.0<sup>1,6</sup>]undeca-3,8-diene (the mixture obtained from the above reaction) in 500 mL of anhydrous ether was added during an hour, while cooling and stirring was maintained. After the addition was complete, the dry ice-acetone bath was removed, and the ammonia was allowed to evaporate overnight. The flask was placed in a dry ice-acetone bath again, and a gentle stream of N<sub>2</sub> was passed continuously through the system. With stirring, a mixture of 90 mL of methanol and 90 mL of ether was then added dropwise. Following that, the bath temperature was allowed to rise slowly to 0°C and, with continued stirring, 500 mL of ice water was added slowly. The reaction mixture was transferred to a 2-L separatory funnel, and the two layers were separated. The organic layer was washed with 200 mL of water, while the aqueous layer was extracted with three 150 mL portions of pentane. When emulsions occurred acidification aided separation of the two layers. The combined ether-pentane phases were dried over MgSO<sub>4</sub>, then filtered. The drying agent was washed well with pentane and the combined organic layers were concentrated by distillation through a 30-cm Vigreux column. The liquid that remained was transferred to a 250 mL, round bottomed flask and distilled (spinning band) under reduced pressure, giving tricyclo[4.4.1.0<sup>1,6</sup>]undeca-3,8-diene as a colorless liquid at 80-81°C (11mm Hg). NMR  $\delta$  0.5 (2H s, cyclopropyl H's), 2.1 (8H br s,

allylic H's), 5.3 (4H br s, vinylic H's).

Preparation of 4,7-dihydroindan-2-ol, 24, (103):

This was done according to the procedure reported in Kohn's thesis (103). To a solution of 40 g indan-2-ol, 130 mL absolute ethanol, 200 mL of THF in liquid ammonia (400 mL), 35 g (1.52 mol) of sodium was added gradually over a period of 45 minutes. After 2 hours, 10 g of additional sodium was added. The ammonia was left to evaporate overnight, then about 300 mL of methanol was added to remove excess sodium. After rotary evaporation of the mixture, 300 mL of water was added. The mixture was extracted with three 200 mL portions of ether; the combined etherial extracts were washed with dil HCl and saturated NaHCO<sub>3</sub> solution, dried over MgSO<sub>4</sub>, and concentrated in vacuo. The residue was distilled giving 34.3 g (84.5%) of 4,7-dihydroindan-2-ol, bp liquid at 70°C (1 mm Hg). NMR  $\delta$  2.6 (9H multiplet, allylic H's and the H on the carbon bearing the OH), 4.4 (1H br s, OH), 5.7 (4H br s, vinylic H).

Simmons-Smith reaction of 4,7-dihydroindan-2-ol, 25, (103):

50 g (0.19 mol) diiodomethane was refluxed with 166 g of Zn/Cu couple (the couple was made by the procedure of

E. Legoff, J. Org. Chem., 1964, 29, 2048) in 300 mL of ether for 30 minutes. To the boiling solution was added a solution of 40.8 g (0.3 mole) of 4,7-dihydroindan-2-ol, 23, and 110g (0.8 mol) of diiodomethane was added. The mixture was refluxed for 72 hours, then cooled in an ice bath with stirring, while 50 mL of methanol was slowly added, followed by 50 mL of ice water. The mixture was acidified with dil sulfuric acid and extracted with ether. The ethereal extract was washed with saturated NaHCO<sub>3</sub>, dried (MgSO<sub>4</sub>), and concentrated in vacuo. The residue was distilled, giving 32.56 g of the desired product as a colorless liquid, bp 80° (1 mm Hg). NMR  $\delta$  0.6 (1H d, one of the cyclopropyl), 0.8 (1H d, the other cyclopropyl), 1.9 (8H d, allylic H's and the H's  $\beta$  to the OH), 4.4 (1H d, OH), 5.4 (2H t, vinylic H's).

Jones oxidation of 25, 26:

The Jones reagent used in this experiment was made by dissolving 35 g (0.23 mol) of CrO<sub>3</sub> in 250 mL of water containing 31 mL of concentrated sulfuric acid. To 12 g (0.08 mole) of the alcohol 25, in 50 mL of distilled acetone was added dropwise 40 mL of the Jones reagent, while the solution was stirred magnetically and chilled in an ice-bath. The mixture was stirred for 30 minutes, 10 mL of isopropanol was added and stirring was continued for an additional 10 minutes. The reaction mixture was extracted

with ether. The ethereal layer was washed in saturated  $\text{NaHCO}_3$ , dried ( $\text{MgSO}_4$ ), and concentrated in vacuo. Distillation of the residue afforded 7 g (80%) of the ketone, bp  $67^\circ\text{C}$  (1 mm Hg). NMR  $\delta$  0.2 (1H d, one of the cyclopropyl H's), 0.8 (1H d, the other cyclopropyl H's), 2.5 (8H br s, allylic H's and the H's  $\beta$  to the carbonyl), 5.55 (2H br s, vinylic H's).

Ketalization of ketone 26 to 23:

8.4 g (0.06 mole) of the ketone 26, 50 mg of p-toluenesulfonic acid, 250 mL of dry benzene, and 12 mL (13.4g, 0.215 mol) of ethylene glycol were refluxed for 5 hours in a Dean Stark apparatus. The mixture was washed with ice cold saturated  $\text{NaHCO}_3$ , dried over  $\text{MgSO}_4$ , and concentrated in vacuo. The residue was distilled affording 7.7 g (77%) of the desired ketal, bp  $72^\circ\text{C}$  (1 mm Hg). NMR  $\delta$  0.5 (1H d, one of the cyclopropyl H's), 0.8 (1H d, the other cyclopropyl H), 2.0 (4H br s, allylic H's), 2.25 (4H br s, the H's of the saturated ring), 3.8 (4H t, the ketal H's), 5.5 (2H br s, vinylic H's).

Preparation of 7,7 dichloro norcarene (10B)

To 77.5 mL of water, 77.5 g of NaOH was added. The solution was stirred mechanically, using an all glass mechanical stirrer. After cooling it to 0°C, 1 g of benzyl triethyl ammonium chloride was added. From a dropping funnel, a mixture of 45 mL of cyclohexa-1,4-diene (38.25 g, 0.7 mole) and 112 mL (167g, 1.4 mol) of CHCl<sub>3</sub> mixture, was added to the basic solution dropwise immediately after addition of the catalyst. Two layers were separated, and the aqueous layer was extracted with three 100 mL portions of CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases were dried (MgSO<sub>4</sub>), concentrated in vacuo and the residue was distilled to give 23.33 g (50%) of 7,7dichloro norcarene, bp 88°C (15 mm Hg) NMR ( $\delta$ ) 1.8 (2H t, cyclopropyl H's), 2.3 (4H br singlet, allylic H's), 5.9 (2H br peak, vinylic H's).

Preparation of norcarene 27:

In a 1 L, three necked round bottomed flask was fitted with an all glass mechanical stirrer, an inlet and a dry ice condenser, 300 mL of ammonia was condensed. 21 g (0.9 g-atoms) of sodium was added in small portions over a period of 30 minutes, followed by 23.3g (0.14 mol) of 7,7-dichloronorcarene in 200 mL of anhydrous ether added dropwise over a period of one hour. The dry ice-acetone bath was removed and ammonia was allowed to evaporate

overnight. The flask was then placed in a dry ice-acetone bath again and a gentle stream of  $N_2$  was passed through the flask while, with stirring, a mixture of 45 mL methanol and 45 mL ether was added dropwise. The bath temperature was then allowed to rise slowly to  $0^\circ C$ , and with continued stirring, 250 mL of ice water was added slowly. Two layers were separated. The organic layer was washed with 100 mL of water, while the aqueous layer was extracted with three 75 mL portions of pentane. The ether and pentane phases were combined and dried ( $MgSO_4$ ), then slowly evaporated through a one foot Vigreux column. The residue was distilled giving 9.3 g (70% yield) of norcarene as a colorless liquid, bp  $80^\circ C$ . NMR  $\delta$  0.3 (2H t, two cyclopropyl H's), 0.9 (2H t, the cyclopropyl H's at the junction of the two rings), 2.4 (4H br s, allylic H's), 5.3 (2H br s, vinylic H's).

Ozonolysis of norcarene 27 followed by aldol condensation,  
29:

Ozone was passed through a solution of 9.4 g (0.1 mole) of norcarene, 27, in 100 mL of methanol, until the solution turned blue. 12 mL (0.16 mole) of dimethyl sulfide was then added, and the mixture was stirred overnight. 200 mL of water was then added and methanol was slowly distilled off. The methanol solution was concentrated; it left no residue behind. 100 mL of water was added to the aqueous

residue, the mixture was refluxed for 3 hours, then distilled. The distillate, which contained water and the  $\alpha,\beta$  unsaturated aldehyde, was saturated with salt and extracted with ether. The ether solution was concentrated on a rotary evaporator leaving behind 2 g (20%) of the  $\alpha,\beta$  unsaturated aldehyde. NMR  $\delta$  0.1 (1H m, one of the cyclopropyl H's), 1.1 (1H m, another cyclopropyl H), 1.9 (1H m, another cyclopropyl H), 2.3 (1H m, cyclopropyl H), 2.85 (2H d, allylic H's), 6.5 (1H br s, vinylic H), 9.8 (1H s, CHO).

Oxime formation of 29, 30, followed by its dehydration to 28:

5g (0.07 mol) of hydroxylamine hydrochloride was dissolved in 30 mL of water. 20 mL of 10% NaOH solution was added, followed by the 2g (0.02 mol) of the  $\alpha,\beta$  unsaturated aldehyde, 29, obtained above. Ether extraction of the mixture yielded 1 g (44%) of oxime, 30. This was refluxed with 4 g of acetic acid and 1 g of NaOAc, for two hours. The usual workup gave 0.2 g (10%) of the desired nitrile, 28. NMR of the oxime:  $\delta$  -0.1 (1H m, one of the cyclopropyl H's), 0.8 (1H m, another cyclopropyl H), 1.5 (1H m, another cyclopropyl H), 2.1 (1H m, cyclopropyl H), 2.45 (2H t, allylic H's), 5.5 (1H br s, vinylic ring H), 7.8 (1H s, the other vinylic H), 8.7-8.9 (1H br s, OH). NMR of the nitrile  $\delta$  0.2 (1H m, one of the cyclopropyl

H's), 1.1 (1H m, the other cyclopropyl H), 2.0 (2H m, cyclopropyl H), 2.6 (2H t, allylic H's), 6.2 (1H br s, vinylic H).

Ozonolysis of norcarene, 27, followed by methyl acetal, 32, formation (113):

Ozonolysis of 9.4 g (0.1 mole) of norcarene, 27, as above, was followed by addition of 12 mL (0.16 mole) dimethyl sulfide. To this, 120 mL of trimethyl orthoformate and 0.1 g of p-toluenesulfonic acid in 1 mL of MeOH was added. The mixture was stirred overnight, and then concentrated in vacuo. The residue was extracted with ether, which was washed with saturated NaHCO<sub>3</sub> solution, dried (MgSO<sub>4</sub>) and concentrated in vacuo. The residue was distilled and gave 6.77 g (35%) of the desired acetal, 32, bp 85-88 (1.5 mm Hg). NMR  $\delta$  0.8 (2H m, two of the cyclopropyl H's), 1.6 (2H m, the H's at the substituted carbons of cyclopropane), 3.3 (16H br s, OMe's and the CH<sub>2</sub>'s), 4.4 (2H t, CH's).

Ozonolysis of the tetra acetal, 32 to the diester, 31:

Ozone was passed through a solution of 6.77g (0.03 mol) the acetal, 32, in 100 mL of ethyl acetate for 8 hours. The solvent was removed by evaporation and the residue was dissolved in ether. This solution was washed with aqueous

sodium carbonate and water, dried and concentrated in vacuo. The resulting residue was distilled, giving 1.44 g of the diester, 31, bp 80°C (1 mm Hg). NMR  $\delta$  0.1 (1H m, one of the cyclopropyl H's), 1.2 (3H m, the remaining cyclopropyl H's), 2.4 (2H distorted t, H's  $\beta$  to the ester), 3.65 (6H s, OMe).

Deickmann condensation of the diester 31:

The diester (1.44 g, 0.007 mole) was dissolved in toluene (50 mL) and 0.4 g sodium (0.002 mole) was added all at once. Approximately 5 mL of MeOH was added to get the reaction started. The mixture was refluxed for 1/2 hour at 120°C. Excess sodium was reacted with absolute ethanol, and the reaction mixture was diluted with 100 mL of ice-cold 10% acetic acid. The aqueous layer was extracted twice with pentane, then toluene and ether. The organic layers were combined, washed with 5% NaHCO<sub>3</sub> solution, water and concentrated in vacuo. The resulting residue was distilled to give 60% yield of the  $\beta$  ketoester, bp 88°C at 1.5 mm Hg). NMR  $\delta$  0.1 (1H m, one of the cyclopropyl H's), 1.1 (3H m, cyclopropyl H's), 2.3 (2H d, the H's  $\beta$  to the C=O), 3.6 (1H distorted t, the H  $\alpha$  to the ester).

Preparation of bicyclo[3.3.0]deca-2,6-dialdehyde-2,6-diene, 33:

10 g (66.66 mmol) of 20 was ozonized in 200 mL of methanol. 24 mL (0.32 mol) of dimethyl sulfide was then added and the solution was stirred overnight. 200 mL of water was added, MeOH was distilled off, and 200ml additional water was added. From the residue remaining after the steam distillation of the mixture 2.65 g (20%) of solid dialdehyde 33, mp 98-100°C (crude) was isolated by extraction with ether followed by usual workup. IR 2820  $\text{cm}^{-1}$  (doublet, CHO), 1680  $\text{cm}^{-1}$  (broad C=O peak), 1600  $\text{cm}^{-1}$  (C=C); nmr  $\delta$  1.0 (2H singlet, cyclopropane H's), 2.9 (4H multiplet, allylic H's), 6.54 (2H triplet, vinylic H's), 9.75 (2H singlet, CHO).

Footnote:

Attempted oxidation of the dialdehyde to the diacid using  $\text{Ag}_2\text{O}$  and subsequent esterification did not yield the desired diester.

Preparation of the dioxime of the dialdehyde 33, 36:

0.5 g (7 mmol) of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  was dissolved in 3 mL of water. 2 mL of 10% NaOH were added, followed by 0.1 g (0.5 mmol) of the dialdehyde, 33. A little ethanol was

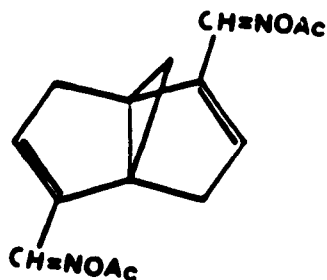
used to homogenize the mixture. The mixture was boiled for 30 minutes on a steam bath, then concentrated on a rotary evaporator. The residue was extracted with ether, which yielded 0.9 g (76%) of dioxime, 36, mp 246-248°C. NMR  $\delta$  (deuterated acetone) -0.05 (1H singlet, one of the cyclopropyl H's), 0.94 (1H singlet, the other cyclopropyl H), AA'BB' system at 2.4 to 2.67 (the four allylic H's), 5.69 (2H triplet, vinylic H's in the ring), 7.8 (2H singlet, the remaining vinylic H's), 8.43 (2H broad singlet, OH).

Dehydration of the dioxime 36 to the dinitrile 37:

A mixture of 0.4g (2 mmol) of the oxime 36, along with 0.7 g of anhydrous sodium acetate and 5.5 mL of  $\text{Ac}_2\text{O}$  was refluxed for 12 hours, then poured into an ice-cold solution of NaOH (4.25 g, 0.106 moles in 125 mL water). Extraction with ether, which was washed with  $\text{NaHCO}_3$  solution, dried and evaporated, yielded 168.6 mg (51.6 %) of the dinitrile 37, mp 139-139.5°C. IR  $2200\text{ cm}^{-1}$  (nitrile),  $1580\text{ cm}^{-1}$  (C=C); nmr  $\delta$  0.04 (1H singlet, one of the cyclopropyl H's), 1.25 (the other cyclopropyl H's), 2.68 to 2.97 AA'BB' system (the four allylic H's), 6.34 (2H singlet, the vinylic H's); C-13 nmr 31.4 (s, the carbon connecting 1 and 5), 36.8 (d, the two allylic C's), 43.1 (s, C 1,5), 115.1 (s, nitrile), 118.3 (s, the vinylic carbon bearing the nitriles), 148.4 (s, vinylic C's).

Footnotes:

A reflux period of 20 m led to the formation of the acetate of the oxime. IR  $1775\text{ cm}^{-1}$  (anhydride),  $1615\text{ cm}^{-1}$  (C=N); nmr  $\delta$  1.08 (2H s, cyclopropyl H's), 2.2 (6H s, OMe), 2.84-2.91 (AA'BB' system of the four allylic H's), 6 (2H t, the ring vinylic H's), 8.1 (2H s, vinylic H's).



Dibenzylidene derivative of bicyclo[3.3.0]deca-1,5-dimethyl-3,7-dione:

At least three different compounds were obtained (based on mp) from a mixture of benzaldehyde and bicyclo[3.3.0]deca-1,5-dimethyl-3,7-dione in refluxing ethanolic sodium ethoxide.

## Attempted Syntheses

### Synthesis of 2-chloro cyclopentanone:

This was done according to the procedure reported by Hesse (143). A one litre three necked flask fitted with a thermometer gas inlet and reflux condenser was charged with 84 grams (1 mol) of cyclopentanone, 300 mL of MeOH and a few crystals of iodine. Good stirring was maintained magnetically. A 140 watt lamp irradiated the reaction mixture. Chlorine was passed into the mixture as soon as the reaction started (indicated by the disappearance of the  $I_2$  color and a rise in temperature), while the reaction mixture was maintained at 0-5°C. Note: The reaction was never too cold, as evidenced by the green color of accumulated chlorine. As soon as the calculated amount of chlorine (71 g, 1 mol) was added, the flask was fitted with a distillation apparatus and MeOH was distilled off under vacuum (water aspirator). The whole work up was done in one stretch to avoid condensation reactions. During the first distillation the fraction between 70-85°C was collected. The distillate was redistilled and the fraction between 78-80°C was collected. The NMR of this product matched the nmr for 2-chlorocyclopentanone in the Aldrich catalog (2nd Edn. Vol 1, #394B) except for an additional peak at 3 ppm. The singlet at 3 ppm appeared in spite of changing the solvent

from MeOH to CCl<sub>4</sub>.

Synthesis of cyclopentane-1,2-dione:

This was done according to the procedure by Inhoffen (60). A 500 mL three necked flask fitted with stirrer dropping funnel, and reflux condenser was charged with 20 grams of 2-Chlorocyclopentanone as obtained above and of 200 mL water and heated to 100°C. While the mixture was stirred 83.3 g (0.3 mol) FeCl<sub>3</sub>·6H<sub>2</sub>O in 41.7 mL water was added. The reaction mixture was cooled to 40°C. 60 g of ammonium sulfate was added, and it was extracted continuously for three hours with ether. The solution of the compound in ether was dried and concentrated and the residue was purified by vacuum distillation (83-86°C at 14 mm Hg) leading to 3 g (20%) of cyclopentane-1,2-dione. However, the reaction failed consistently thereafter. There were considerable difficulties in obtaining reproducible results in this reaction.

Footnote: 2-bromocyclopentanone was made the reaction of cyclopentanone with Cupric bromide. There were two attempts to convert it to cyclopentane-1,2-dione:

1. DMSO oxidation of 2-bromocyclopentanone (&dpbmc.)
2. FeCl<sub>3</sub> hydrolysis of 2-bromocyclopentanone

Both the attempts failed.

## APPENDIX A

Table I. Final Atomic Parameters for SB-C6

Atom	x	y	z	B(A <sup>2</sup> )
C1	0.5004(1)	0.3277(2)	0.39000(6)	2.62(3)
C2	0.5412(2)	0.1429(2)	0.38015(8)	3.31(3)
C3	0.4380(1)	0.0512(2)	0.35233(7)	2.75(3)
C4	0.3390(2)	0.1605(3)	0.34103(9)	3.66(3)
C5	0.3667(1)	0.3395(2)	0.36758(7)	2.83(3)
C6	0.3037(2)	0.2966(3)	0.42220(8)	3.58(3)
C7	0.3872(2)	0.2350(2)	0.46597(7)	3.13(3)
C8	0.5111(2)	0.2435(3)	0.44979(8)	4.09(4)
C9	0.5853(2)	0.4844(2)	0.37683(8)	3.28(3)
C10	0.5651(2)	0.5286(3)	0.31133(8)	4.15(4)
C11	0.4285(2)	0.5210(3)	0.28529(8)	4.19(4)
C12	0.3350(2)	0.5019(2)	0.33094(8)	3.48(3)
C13	0.6704(1)	0.0808(2)	0.37345(7)	3.10(3)
C14	0.2213(2)	0.1081(3)	0.30660(8)	3.73(4)
C15	0.1705(2)	0.3163(3)	0.43059(9)	3.99(4)
C16	0.6151(2)	0.2335(3)	0.49760(7)	3.30(3)
O1A	0.6896(2)	-0.0808(3)	0.39579(9)	2.86(4)
O2A	0.7467(2)	0.1413(4)	0.3515(1)	4.09(5)
O3A	0.1978(2)	-0.0617(4)	0.3150(1)	3.62(5)
O4A	0.1620(2)	0.1989(4)	0.2707(1)	3.91(5)
O5A	0.1076(2)	0.4045(4)	0.3832(1)	3.63(5)
O6A	0.1250(2)	0.2716(4)	0.4746(1)	3.89(5)
O7A	0.7318(2)	0.2518(4)	0.4767(1)	3.38(5)
O8A	0.5944(2)	0.2124(3)	0.54958(9)	3.36(5)
C17A	0.8022(3)	-0.1694(5)	0.3868(2)	3.97(7)
C18A	0.1007(4)	-0.1541(6)	0.2792(2)	5.5(1)
C19A	-0.0270(3)	0.4014(6)	0.3887(2)	4.89(9)
C20A	0.8323(3)	0.2295(6)	0.5213(2)	3.77(7)
O1B	0.6818(4)	-0.0876(7)	0.3796(2)	3.32(8)§
O2B	0.7463(4)	0.1866(6)	0.3510(2)	2.42(6)§
O3B	0.1669(5)	-0.0238(8)	0.3286(2)	4.3(1)§
O4B	0.1811(6)	0.2037(9)	0.2616(3)	4.8(1)§
O5B	0.1091(6)	0.4214(9)	0.3980(3)	4.3(1)§
O6B	0.1141(6)	0.2168(9)	0.4604(3)	4.8(1)§
O7B	0.7231(4)	0.2088(6)	0.4803(2)	2.97(7)§
O8B	0.6021(6)	0.2587(9)	0.5463(3)	5.0(1)§
C17B	0.8197(9)	-0.137(1)	0.3739(4)	5.2(2)§
C18B	0.0695(8)	-0.099(1)	0.2892(4)	4.2(1)§
C19B	-0.0204(7)	0.448(1)	0.4023(3)	3.5(1)§
C20B	0.8177(8)	0.202(1)	0.5310(4)	4.2(1)§

Table I (continued). Final Atomic Parameters for SB-C6

Atom	x	y	z	B(A <sup>2</sup> )
O1C	0.6991(5)	-0.0647(7)	0.4089(2)	3.37(8)§
O2C	0.7381(4)	0.1639(6)	0.3408(2)	2.59(7)§
O3C	0.2193(5)	-0.0749(7)	0.2980(2)	3.53(8)§
O4C	0.1364(6)	0.187(1)	0.2925(3)	5.4(1)§
O5C	0.1042(5)	0.3657(7)	0.3851(2)	4.66(9)§
O6C	0.1399(7)	0.329(1)	0.4824(3)	5.8(1)§
O7C	0.7146(5)	0.2642(7)	0.4827(2)	3.34(8)§
O8C	0.6044(5)	0.1743(7)	0.5446(2)	3.91(9)§
C17C	0.8217(7)	-0.1328(9)	0.3950(3)	3.2(1)§
C18C	0.090(1)	-0.116(1)	0.2671(4)	5.0(2)§
C19C	-0.0190(6)	0.4528(9)	0.3842(3)	3.0(1)§
C20C	0.8355(7)	0.181(1)	0.5189(3)	3.5(1)§
H3	0.437	-0.076	0.343	3.5
H7	0.364	0.189	0.504	3.5
H9A	0.678	0.473	0.383	4
H9B	0.560	0.595	0.395	4
H10A	0.613	0.444	0.290	4.5
H10B	0.596	0.649	0.306	4.5
H11A	0.419	0.418	0.257	4.5
H11B	0.409	0.630	0.262	4.5
H12A	0.340	0.606	0.357	4
H12B	0.249	0.491	0.311	4
H17AA	0.804	-0.288	0.406	4.5
H17AB	0.808	-0.183	0.344	4.5
H17AC	0.874	-0.100	0.405	4.5
H18AA	0.094	-0.277	0.294	6
H18AB	0.015	-0.095	0.289	6
H18AC	0.106	-0.146	0.239	6
H19AA	-0.074	0.461	0.335	5
H19AB	-0.055	0.275	0.389	5
H19AC	-0.043	0.457	0.426	5
H20AA	0.911	0.257	0.505	4.5
H20AB	0.823	0.313	0.556	4.5
H20AC	0.829	0.110	0.536	4.5
H17BA	0.818	-0.271	0.375	4.5

Table I (continued). Final Atomic Parameters for SB-C6

Atom	x	y	z	B(A <sup>2</sup> )
H17BB	0.826	-0.113	0.328	4.5
H17BC	0.873	-0.082	0.397	4.5
H18BA	0.032	-0.199	0.308	4.5
H18BB	0.004	-0.007	0.279	4.5
H18BC	0.104	-0.138	0.232	4.5
H19BA	-0.058	0.535	0.378	4
H19BB	-0.044	0.330	0.396	4
H19BC	-0.033	0.477	0.447	4
H20BA	0.905	0.168	0.518	4.5
H20BB	0.819	0.293	0.556	4.5
H20BC	0.795	0.083	0.553	4.5
H17CA	0.841	-0.237	0.420	4
H17CB	0.816	-0.167	0.352	4
H17CC	0.887	-0.042	0.403	4
H18CA	0.109	-0.260	0.260	4.5
H18CB	0.035	-0.100	0.288	4.5
H18CC	0.096	-0.072	0.226	4.5
H19CA	-0.053	0.468	0.342	4
H19CB	-0.078	0.378	0.404	4
H19CC	-0.007	0.566	0.404	4
H20CA	0.908	0.217	0.492	4
H20CB	0.852	0.230	0.556	4
H20CC	0.836	0.051	0.518	4

Standard deviations are in parentheses.

The starred atoms were refined isotropically.

The parameters of the hydrogen atoms were not refined.

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

Table II. General Temperature Factors (U's) for SB-C6

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
C1	0.0328(6)	0.0337(7)	0.0329(6)	-0.0002(6)	0.0035(5)	0.0000(6)
C2	0.0306(7)	0.0353(8)	0.0595(9)	0.0007(6)	0.0025(7)	-0.0040(7)
C3	0.0326(7)	0.0360(7)	0.0359(6)	-0.0001(6)	0.0031(6)	0.0002(6)
C4	0.0361(7)	0.0408(8)	0.060(1)	-0.0029(7)	-0.0077(7)	0.0051(8)
C5	0.0333(7)	0.0373(7)	0.0368(7)	0.0028(6)	0.0039(6)	0.0018(6)
C6	0.0345(7)	0.0509(9)	0.0514(8)	0.0044(7)	0.0095(6)	0.0100(8)
C7	0.0379(7)	0.0455(9)	0.0364(7)	0.0024(7)	0.0077(6)	0.0023(7)
C8	0.0375(8)	0.075(1)	0.0420(8)	-0.0088(8)	-0.0017(7)	0.0196(8)
C9	0.0413(8)	0.0368(8)	0.0468(8)	-0.0054(7)	0.0056(7)	0.0006(7)
C10	0.057(1)	0.053(1)	0.0499(9)	-0.0045(9)	0.0144(8)	0.0124(8)
C11	0.062(1)	0.054(1)	0.0431(8)	-0.0026(9)	0.0040(8)	0.0108(8)
C12	0.0455(8)	0.0401(8)	0.0459(8)	0.0067(7)	0.0019(7)	0.0066(7)
C13	0.0295(7)	0.0418(8)	0.0458(8)	0.0012(6)	0.0010(6)	-0.0057(7)
C14	0.0320(7)	0.053(1)	0.0544(9)	0.0018(7)	-0.0049(7)	-0.0025(8)
C15	0.0345(7)	0.054(1)	0.063(1)	0.0051(8)	0.0103(7)	0.0080(9)
C16	0.0403(7)	0.0482(9)	0.0362(7)	-0.0021(7)	0.0017(6)	0.0026(7)
O1A	0.0326(9)	0.041(1)	0.0349(9)	0.0109(9)	0.0000(8)	-0.0059(9)
O2A	0.049(1)	0.045(1)	0.063(1)	0.005(1)	0.016(1)	0.015(1)
O3A	0.034(1)	0.050(1)	0.052(1)	-0.011(1)	-0.005(1)	-0.007(1)
O4A	0.041(1)	0.063(2)	0.041(1)	0.001(1)	-0.013(1)	0.015(1)
O5A	0.0224(8)	0.060(1)	0.056(1)	0.0149(9)	0.0047(9)	0.010(1)
O6A	0.0264(9)	0.069(2)	0.055(1)	0.001(1)	0.0174(8)	0.003(1)
O7A	0.0266(9)	0.065(1)	0.037(1)	-0.006(1)	0.0023(8)	0.004(1)
O8A	0.052(1)	0.051(1)	0.0245(9)	0.002(1)	0.0040(9)	0.0050(9)
C17A	0.026(1)	0.039(2)	0.087(2)	0.007(1)	0.013(1)	-0.002(2)
C18A	0.048(2)	0.052(2)	0.102(3)	-0.005(2)	-0.035(2)	-0.009(2)
C19A	0.029(1)	0.052(2)	0.104(3)	0.003(2)	0.006(2)	0.003(2)
C20A	0.032(1)	0.065(2)	0.044(2)	0.004(2)	-0.007(1)	0.003(2)

Standard deviations are in parentheses.

The form of the anisotropic thermal parameter is:

$$U = \frac{1}{2} [ a^2 U_{11} + b^2 U_{22} + c^2 U_{33} + 2h_1 abU_{12} + 2h_2 acU_{13} + 2h_3 bcU_{23} ]$$

where a, b, and c are reciprocal lattice constants.

Table III Atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for SB-C8

	x	y	z	U
C(1)	4135(2)	2570(2)	4720(2)	43(1)*
C(2)	4597(3)	2189(2)	3905(2)	56(1)*
C(3)	3519(2)	1890(2)	3105(2)	40(1)*
C(4)	2328(3)	2007(2)	3288(2)	51(1)*
C(5)	2554(2)	2443(2)	4292(2)	43(1)*
C(6)	2090(3)	3265(2)	3669(2)	59(1)*
C(7)	3142(3)	3810(2)	3664(2)	48(1)*
C(8)	4345(3)	3445(2)	4279(2)	53(1)*
C(9)	4915(3)	2381(2)	5816(2)	55(1)*
C(10)	5278(3)	1403(2)	6125(2)	67(1)*
C(11)	4145(5)	817(3)	6265(3)	74(2)*
C(11')	4179(13)	708(8)	5641(10)	71(5)*
C(12)	3064(4)	576(3)	5293(3)	67(2)*
C(12')	3006(14)	867(9)	6066(10)	72(6)*
C(13)	1743(3)	1110(2)	5111(3)	74(1)*
C(14)	1815(3)	2130(2)	4982(2)	60(1)*
C(15)	6005(3)	2057(2)	3984(2)	51(1)*
C(16)	7439(3)	1555(3)	3134(3)	80(2)*
C(17)	1015(3)	1681(2)	2628(2)	49(1)*
C(18)	-187(3)	1080(3)	1055(2)	76(1)*
C(19)	670(3)	3573(2)	3226(2)	60(1)*
C(20)	-1021(4)	3976(4)	1737(3)	106(2)*
C(21)	5592(3)	3990(2)	4582(2)	52(1)*
C(22)	6978(3)	4854(3)	3944(3)	84(2)*
O(1)	6950(2)	2299(2)	4678(2)	76(1)*
O(2)	6102(2)	1651(2)	3185(2)	66(1)*
O(3)	3(2)	1730(2)	2817(2)	81(1)*
O(4)	1081(2)	1334(1)	1788(1)	62(1)*
O(5)	-59(3)	3700(2)	3689(2)	95(1)*
O(6)	350(2)	3721(2)	2260(2)	78(1)*
O(7)	6244(2)	4181(2)	5419(2)	75(1)*
O(8)	5839(2)	4280(1)	3776(1)	65(1)*

\* Equivalent isotropic U defined as one third of the trace of the orthogonalised  $U_{ij}$  tensor

Table IV Anisotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{Sn-C8}$ 

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
C(1)	46(1)	45(1)	39(1)	-3(1)	16(1)	-1(1)
C(2)	37(1)	88(2)	48(1)	-9(1)	18(1)	-5(1)
C(3)	40(1)	43(1)	40(1)	-4(1)	18(1)	-2(1)
C(4)	38(1)	72(2)	47(1)	-12(1)	21(1)	-6(1)
C(5)	42(1)	52(1)	41(1)	-7(1)	21(1)	-1(1)
C(6)	45(2)	72(2)	57(2)	8(1)	13(1)	1(1)
C(7)	52(2)	46(1)	46(1)	-6(1)	18(1)	-0(1)
C(8)	45(2)	58(2)	55(2)	7(1)	16(1)	-4(1)
C(9)	57(2)	66(2)	41(1)	-1(1)	14(1)	-5(1)
C(10)	62(2)	70(2)	63(2)	17(2)	12(1)	0(2)
C(11)	80(3)	75(3)	64(2)	20(2)	28(2)	-9(2)
C(11')	76(8)	52(7)	86(9)	6(6)	29(7)	-1(6)
C(12)	79(3)	57(2)	66(2)	6(2)	27(2)	-9(2)
C(12')	91(9)	63(7)	79(8)	15(6)	51(7)	3(7)
C(13)	65(2)	85(2)	80(2)	20(2)	35(2)	-10(2)
C(14)	55(2)	80(2)	86(2)	-8(1)	31(1)	-3(1)
C(15)	38(1)	68(2)	49(1)	10(1)	16(1)	-1(1)
C(16)	48(2)	120(3)	59(2)	12(2)	41(2)	12(2)
C(17)	36(1)	64(2)	51(1)	-6(1)	20(1)	-6(1)
C(18)	60(2)	97(3)	59(2)	-23(2)	5(1)	-19(2)
C(19)	49(2)	66(2)	65(2)	0(1)	19(1)	7(1)
C(20)	61(2)	143(4)	95(3)	25(3)	2(2)	29(2)
C(21)	51(2)	48(2)	54(2)	4(1)	14(1)	-2(1)
C(22)	73(2)	86(2)	92(2)	11(2)	29(2)	-31(2)
O(1)	39(1)	109(2)	75(1)	-12(1)	11(1)	-3(1)
O(2)	39(1)	104(2)	63(1)	-4(1)	28(1)	3(1)
O(3)	41(1)	132(2)	79(1)	-31(1)	31(1)	-18(1)
O(4)	43(1)	92(2)	50(1)	-20(1)	15(1)	-10(1)
O(5)	84(2)	122(2)	90(2)	7(1)	43(1)	43(2)
O(6)	50(1)	112(2)	67(1)	17(1)	12(1)	17(1)
O(7)	85(1)	71(1)	59(1)	-9(1)	12(1)	-27(1)
O(8)	59(1)	78(1)	57(1)	5(1)	17(1)	-20(1)

The anisotropic temperature exponent takes the form:

$$-2\pi^2(h^2a^*{}^2U_{11} + \dots + 2hka^*b^*U_{12})$$

Table V H-Atom coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for SB-C8

	x	y	z	U
H(3)	3518	1614	2419	44
H(7)	3071	4425	3214	54
H(9A)	5737	2714	5988	64
H(9B)	4389	2599	6200	64
H(10A)	6010	1413	6843	76
H(10B)	5707	1152	5610	76
H(11A)	4642	217	6675	96
H(11B)	3706	1177	6695	96
H(12A)	3422	679	4663	77
H(12B)	2916	-75	5303	77
H(13A)	1223	970	5610	84
H(13B)	1113	841	4406	84
H(14A)	2256	2385	5630	67
H(14B)	915	2353	4721	67
H(16A)	8028	1321	3756	93
H(16B)	7760	2130	3009	93
H(16C)	7414	1150	2604	93
H(18A)	-628	654	1345	85
H(18B)	-34	815	488	85
H(18C)	-740	1602	846	85
H(20A)	-1212	4531	2002	119
H(20B)	-1609	3517	1820	119
H(20C)	-1153	4049	1039	119
H(22A)	7075	5005	3315	93
H(22B)	7768	4551	4357	93
H(22C)	6852	5393	4271	93

## APPENDIX B

SEMI BUL GS

HEAT OF FORMATION 273 70366 KCAL/MOLE

IONIZATION POTENTIAL -4.4142<sup>o</sup> EV

CHARGE -2

ATOM NUMBER	ATOMIC NUMBER	BOND LENGTH (ANGSTROMS)	BOND ANGLE (DEGREES)			TWIST ANGLE (DEGREES)		
			J I	K J I	L K J I	J	K	L
1	6							
2	6	2.4165 *				1		
3	6	1.3744 *	106.531 *			2	1	
4	6	3.2629 *	73.144 *		-1.164 *	3	2	1
5	6	1.4573 *	110.327 *		-37.652 *	1	4	3
6	6	1.5028 *	109.437 *		4.360 *	4	1	5
7	6	1.5742 *	123.022 *		-0.875 *	6	4	3
8	6	1.5588 *	105.638 *		-12.507 *	7	3	2
9	1	1.0875 *	127.095 *		180.233 *	3	2	5
10	1	1.0875 *	127.095 *		177.766 *	4	1	5
11	1	1.0943 *	124.868 *		4.979 *	2	3	9
12	1	1.0943 *	124.868 *		-8.118 *	1	4	10
13	1	1.1009 *	115.814 *		20.025 *	7	3	9
14	1	1.1009 *	115.814 *		-18.345 *	6	4	10

SEPI EUL

HEAT OF FORMATION                    142.42E32 KCAL/MOLE  
 IONIZATION POTENTIAL                -2.2CCCEC EV  
 CHARGE                                -2

ATOM NUMBER	ATOMIC NUMBER	BOND LENGTH (ANGSTROMS)	BOND ANGLE (DEGREES)		TORSION ANGLE (DEGREES)			J	K	L
			K	J	L	K	J			
1	5	1.4260								
2	6	1.4163	107.542				1			
3	6	1.4210	110.101				2			
4	5	1.4276	107.363		0.017		3	1		
5	6	1.4262	144.888		176.698		4	2		
6	6	1.4183	107.146		0.228		5	4		
7	6	1.4227	110.350		-0.227		6	5		
8	6	1.4227	110.350		179.866		7	6		
9	1	1.0145	125.915		179.866		8	7		
10	1	1.0145	124.908		179.866		9	8		
11	1	1.0146	125.788		179.874		10	9		
12	1	1.0146	124.908		179.880		11	10		
13	1	1.0144	125.595		179.891		12	11		
14	1	1.0144	125.707		179.891		13	12		

SEMI-BLA ANION

HEAT OF FORMATION 101.68019 KCAL/MOLE

IONIZATION POTENTIAL 1.41244 EV

CHARGE -1

ATOM NUMBER	ATOMIC NUMBER	BOND LENGTH (ANGSTROMS)	BOND ANGLE (DEGREES)	THIRD ANGLE (DEGREES)	J	K	L
1	6	2.4341			1		
2	6	1.3583	103.209		2		1
3	6	3.1559	74.749	0.004	3		2
4	6	1.3351	111.697	-39.185	1		4
5	6	1.4569	111.689	6.278	4		1
6	6	1.5689	122.015	-0.103	6		4
7	6	1.5479	106.007	-9.509	7		3
8	6	1.4934	107.641	148.429	9		8
9	6	1.3948	109.219	0.319	9		5
10	6	1.4072	113.887	-0.371	10		9
11	6	1.0844	126.634	126.683	3		2
12	1	1.0841	126.827	183.290	4		1
13	1	1.0836	126.785	-0.729	2		3
14	1	1.0839	126.592	0.784	1		4
15	1	1.0934	116.695	29.007	7		3
16	1	1.0932	116.515	-23.012	6		4
17	1	1.0779	123.400	128.769	9		5
18	1	1.0902	123.265	179.742	10		10
19	1	1.0768	127.214	180.094	11		10
20	1						9

## SEMI BUL ANION TS CI

LOWEST EIGENVALUES -- HEATS OF FORMATION IN KCAL/MOLE

1            2  
 130 834    304 375

IONIZATION POTENTIAL            1 37996 EV

CHARGE            -1

ATOM NUMBER	ATOMIC NUMBER	BOND LENGTH (ANGSTROMS)	BOND ANGLE (DEGREES)	TWIST ANGLE (DEGREES)	J	K	L
1	6						
2	6	2 1046 *			1		
3	6	1 4102 *	114 897 *		2	1	
4	6	3 2501 *	65 313 *	0 650 *	3	2	1
5	6	1 5174 *	110 924 *	-49 282 *	1	4	3
6	6	1 4103 *	111 491 *	1 104 *	4	1	5
7	6	2 1046 *	113 174 *	-0 435 *	6	4	3
8	6	1 5170 *	111 015 *	-2 550 *	7	3	2
9	6	1 4793 *	104 194 *	134 730 *	5	8	6
10	6	1 3993 *	108 905 *	-0 094 *	9	5	8
11	6	1 3988 *	113 849 *	0 211 *	10	9	5
12	1	1 0852 *	124 024 *	178 522 *	3	2	5
13	1	1 0855 *	124 359 *	183 349 *	4	1	5
14	1	1 0829 *	124 988 *	-7 933 *	2	3	12
15	1	1 0831 *	125 153 *	7 910 *	1	4	13
16	1	1 0831 *	124 819 *	8 185 *	7	3	12
17	1	1 0825 *	124 943 *	-8 037 *	6	4	13
18	1	1 0776 *	123 659 *	180 155 *	9	5	8
19	1	1 0904 *	123 029 *	180 139 *	10	9	5
20	1	1 0775 *	127 419 *	179 624 *	11	10	9

## SEMI BUL CAT

HEAT OF FORMATION 291 73690 KCAL/MOLE

IONIZATION POTENTIAL 13 94108 EV

CHARGE 1

ATOM NUMBER I	ATOMIC NUMBER	BOND LENGTH (ANGSTROMS)		BOND ANGLE (DEGREES)			TWIST ANGLE (DEGREES)			J	K	L
		J	I	K	J	I	L	K	J			
1	6											
2	6	2 4494 *							1			
3	6	1 3588 *		104 985 *					2	1		
4	6	3 1540 *		79 006 *			-0 017 *		3	2	1	
5	6	1 5309 *		111 029 *			-38 406 *		1	4	3	
6	6	1 5044 *		112 412 *			6 037 *		4	1	5	
7	6	1 5360 *		122 531 *			0 075 *		6	4	3	
8	6	1 5756 *		104 230 *			-10 669 *		7	3	2	
9	6	1 5090 *		102 071 *			149 948 *		5	8	6	
10	6	1 3962 *		110 262 *			-0 070 *		9	5	8	
11	6	1 4298 *		111 335 *			0 103 *		10	9	5	
12	1	1 0850 *		126 863 *			176 087 *		3	2	5	
13	1	1 0848 *		126 915 *			183 789 *		4	1	5	
14	1	1 0833 *		127 638 *			-0 519 *		2	3	12	
15	1	1 0834 *		127 602 *			0 458 *		1	4	13	
16	1	1 0957 *		116 716 *			30 144 *		7	3	12	
17	1	1 0955 *		116 714 *			-30 056 *		6	4	13	
18	1	1 0869 *		123 413 *			179 910 *		9	5	8	
19	1	1 0865 *		125 035 *			179 964 *		10	9	5	
20	1	1 0881 *		125 276 *			179 827 *		11	10	9	

## SEMI BUL RAD

HEAT OF FORMATION                    122.07931 KCAL/MOLE  
 DIPOLE MOMENT                        0.27115 DEBYE  
 MULTIPLICITY                        2  
 ONE ELECTRON IN ORBITAL        27

ATOM NUMBER I	ATOMIC NUMBER	BOND LENGTH (ANGSTROMS) J I	BOND ANGLE (DEGREES)		TWIST ANGLE (DEGREES)			J	K	L
			K	J I	L	K J I				
1	6									
2	6	2.4543 *					1			
3	6	1.3591 *	105.496 *				2	1		
4	6	3.1868 *	74.448 *		-0.212 *		3	2	1	
5	6	1.5326 *	110.960 *		-38.683 *		1	4	3	
6	6	1.5000 *	112.098 *		5.280 *		4	1	5	
7	6	1.5633 *	122.648 *		0.005 *		6	4	3	
8	6	1.5486 *	105.467 *		-10.551 *		7	3	2	
9	6	1.5027 *	101.930 *		148.908 *		5	8	6	
10	6	1.3993 *	110.441 *		0.340 *		9	5	8	
11	6	1.4132 *	112.213 *		-0.444 *		10	9	5	
12	1	1.0833 *	126.800 *		176.688 *		3	2	5	
13	1	1.0836 *	126.743 *		182.974 *		4	1	5	
14	1	1.0822 *	127.502 *		-0.515 *		2	3	12	
15	1	1.0823 *	127.435 *		0.683 *		1	4	13	
16	1	1.0939 *	116.683 *		26.475 *		7	3	12	
17	1	1.0937 *	116.683 *		-26.159 *		6	4	13	
18	1	1.0808 *	123.263 *		180.217 *		9	5	8	
19	1	1.0857 *	124.069 *		180.031 *		10	9	5	
20	1	1.0799 *	126.394 *		180.299 *		11	10	9	

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