

THESIS



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Dennis K. Klipa

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PART I

EXTENDED HÜCKEL MOLECULAR ORBITAL CALCULATIONS OF THE RELATIVE STABILITY OF ISOTRINDENETRIONE

PART II

PREPARATION OF AND ESTIMATION OF THE STRAIN ENERGY IN THE DIELS-ALDER DIMERS OF TWO SIMPLE C-FACE ANNULATED CYCLOPENTADIENONES

By

Dennis K. Klipa

A DISSERTATION

Submitted to

Michigan State University

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for the degree of

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Department of Chemistry

ABSTRACT

PART I

EXTENDED HÜCKEL MOLECULAR ORBITAL CALCULATIONS OF THE RELATIVE STABILITY OF ISOTRINDENETRIONE

PART II

PREPARATION OF AND ESTIMATION OF THE STRAIN ENERGY IN THE DIELS-ALDER DIMERS OF TWO SIMPLE C-FACE ANNULATED CYCLOPENTADIENONES

By

Dennis K. Klipa

In this thesis two factors which might influence the stability of the unknown isotrindenetrione $(\frac{\partial g_{e}}{\partial e})$ were studied.

In the first part of this thesis Extended Hückel Molecular Orbital Theory was used to predict whether $\frac{\partial e}{\partial c}$ would be stabilized electronically as a result of electron delocalization in the central six-membered ring. A comparison of the calculated pi orbital energies of a series of structures including cyclopentadienone ($\frac{1}{12}$), $\frac{\partial e}{\partial c}$, benzene ($\frac{2}{32}$) and triphenylene ($\frac{\partial e}{\partial c}$) with the pi orbital energies of a second series of <u>acyclic</u> structures possessing the corresponding number of double bonds (all trans) showed that although $\frac{\partial e}{\partial c}$

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is predicted to be antiaromatic there does appear to be some relative electronic stabilization.

A second comparison was made in which the pi orbital energy per "unit" was compared for a series of structures consisting of a single unit (e.g., benzene), two units (e.g., biphenylene) and three units (e.g., triphenylene). The comparison was made for the benzene, thiophene, furan and cyclopentadienone systems with the latter three units being coupled across their C-faces. This comparison showed that for the benzene, thiophene and furan systems there is essentially no net increase in stabilization per unit for triphenylene (2a), benzo[1,2-C:3,4-C':5,6-C"]trithiophene (2b) and benzo[1,2-C:3,4-C':5,6-C"]trifuran (2d). This comparison does, however, predict an increase in stabilization for 2e relative to 11 of 12 Kcal per mole per unit.

In the second part of this thesis a new method for retarding cyclopentadienone dimerization was explored. The strain which might develop upon Diels-Alder dimerization of \Re due to the presence of the C-face bridge was examined by studying model dimers (*endo*-pentacyclo-[9.6.1.0²,¹⁰.0⁵,¹⁰.0¹²,¹⁷]octadeca-4,12(17)-diene-3,18dione (\Re) and *endo*-pentacyclo[8.5.1.0²,⁹.0⁵,⁹.0^{11,15}] hexadeca-4,11(15)-diene-3,16-dione (\Re)). These are dimers of two simple C-face annulated cyclopentadienones (4,5,6,7tetrahydro-2-indenone (\Re) and 5,6-dihydro-2(4H)-pentalenone (\Re), respectively).

Cyclopentadienone 18 was prepared by the bromination

of 1,4,5,6,7,7a-hexahydro-2-indenone $\begin{pmatrix} 40\\ 120 \end{pmatrix}$ with N-bromosuccinimide (NBS) followed by dehydrobromination with potassium <u>tert</u>-butoxide in tetrahydrofuran (THF) at -78°C. Monomeric $\frac{18}{100}$ could not be observed or trapped but was isolated as the dimer 20.

Cyclopentadienone 12 was prepared via 4,5,6,7a-tetrahydro-2(1H)-pentalenone (78). Enone 78 was prepared by the following route. Alkylation of 2-carboethoxycyclopentanone with probargyl bromide gave ethyl 1-(2-propynyl)-2-oxocyclopentanecarboxylate (86). Mercuric ion catalyzed hydration of the triple bond gave ethyl 1-acetonyl-2-oxocyclopentanecarboxylate (84). Intramolecular aldol condensation using sodium hydride in refluxing toluene gave 2,3,4,5-tetrahydro-5-oxo-3a(1H)-pentalenecarboxylate (72). Saponification and decarboxylation of the resulting acid gave 78. Bromination of 78 with NBS followed by dehydrobromination with potassium <u>tert</u>-butoxide in THF at -78°C presumably gave 19 which was not directly observed but isolated as the dimer 21.

The kinetics of decarbonylation of 20 and 21 in deuterated benzene were measured at three elevated temperatures. Decarbonylation of 20 at 150 to 173°C gave a complex mixture of products which when heated to 195°C was converted nearly quantitatively to 1,2,5,6,7,8-hexahydrospiro[benz[f]indene-3,1'-cyclopentane]-1-one (22). Decarbonylation of 21 at 82 to 109° gave tetracyclo-[10.3.0.0^{1,9}.0^{3,7}]-pentadeca-2,7,11-trien-10-one (20).

The first order rate constants for the thermal

decarbonylation of 20 and 21 at 109°C are 1.2 x 10^{-6} sec⁻¹ (extrapolated) and 2050 x 10^{-6} sec⁻¹, respectively. The activation parameters for the decarbonylation of 20 and 21 are $\Delta H^{\neq} = 35.5 \pm 1.2$ Kcal/mole (20), 23.5 \pm 0.5 Kcal/mole (21); $\Delta S^{\neq} = 6.3 \pm 2.7$ e.u. (20), -9.8 \pm 1.4 e.u. (21). The $\Delta \Delta H^{\neq}$ indicates that 21 is more strained than 20 by a minimum of 12 Kcal/mole.

The single crystal X-ray structures of 20 and 21 were determined and the strain in 21 is discussed in terms of bond distortions.

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Finally and mostly, I thank my wife, Jackie, for her patience, understanding and continued support in spite of the innumerable sacrifices she has made these past few years. TABLE OF CONTENTS

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INTRODUCTION

Radialenes are carbocyclic compounds per-substituted with exocyclic carbon-carbon double bonds. Although pentaradialene (3) remains unknown, triradialene¹ (1), tetraradialene² (2) and hexaradialene³ (4) have been prepared and found to be quite reactive hydrocarbons. Hexaradialene, for example, is only stable in dilute solution, and is oxidized rapidly on exposure to air.



Alkyl and aryl substituents stabilize radialenes. Thus hexamethyltriradialene⁴ (ξ), heptaphenyltetraradialene⁵ (ξ), hexamethylhexaradialene⁶ (χ) and hexaethylhexaradialene⁷ (ξ) are all stable crystalline compounds.



Another way to stabilize hexaradialenes is to introduce a bridging group, X, (9) between the termini of the exocyclic double bonds. This permits electronic interaction of the π orbitals at both ends of the double bonds. The oldest and most stable exemplification of this concept



9



92

a, x = -CH=CHb, x = S c, x = Se d, x = O e, x = C=O f, x = N-R

is triphenylene (2a) in which the exocyclic double bonds have been incorporated into three benzenoid rings. Recently the trisbenzothiophene⁸ (2b), trisbenzoselenophene^{9a} (2c), trisbenzofuran (2d)^{9b} and trisbenzopyrrole^{9c} (2f, R = benzyl) have been prepared and shown to be quite stable crystalline compounds. The sulfur-containing compound (2b) undergoes normal electrophilic aromatic substitution reactions.

Whereas X bridges with unshared electron pairs (such as sulfur, selenium or oxygen) result in the formation of conjugated aromatic rings (9b, 9c and 9d, respectively), the introduction of carbonyl bridges would give the unknown isotrindenetrione (9e) which would consist of three linked <u>anti</u>aromatic cyclopentadienone rings. The goal of this research was to investigate whether cyclopentadienones linked in this way would possess greater stability than three separate cyclopentadienone moieties. Two factors might work to enhance the stability of such a system.

The first factor involves electronic stabilization. Would the arrangement of the six p-type atomic orbitals of the six central carbon atoms result in any electronic "benzenoid" resonance stabilization? One resonance contributor which can be drawn is the tris-oxyallyl structure (10) in which the central ring is benzenoid.



This question has been considered previously¹⁰ for the parent radialenes 1, 2, 3 and 4. If such delocalization were to occur in hexaradialene $(\frac{\mu}{\lambda})$, a shortening of the ring carbon-carbon bond lengths relative to the corresponding bond lengths in tri-, tetra-, and pentaradialene would be expected. Pariser-Parr-Pople SCF calculations, which determine minimum energy geometries, show (Figure 1) no significant difference in the bond lengths throughout the parent radialene series, suggesting that "benzenoid" resonance is not important in hexaradialene.¹⁰ But since the introduction of bridging groups alters the chemistry of hexaradialene, perhaps "benzenoid" resonance stabilization is significant in these bridged radialenes. In the first part of this thesis Extended Hückel M.O. theory is used to determine whether any electronic stabilization



Figure 1. Calculated ring carbon-carbon bond lengths (Å) for the parent radialenes.10

of this type is predicted for isotrindentrione (9g).

The second factor is steric in nature and involves the well known cyclopentadienone dimerization. Cyclopentadienones, being <u>anti</u>-aromatic, are highly reactive.¹¹ Many cyclopentadienones, in the absence of other reagents, undergo a facile $[4\pi s + 2\pi s]$ dimerization due to their high energy and cisoid diene structure. For example, even though the parent cyclopentadienone (LL) has been detected by low temperature matrix infrared spectroscopy¹² and by microwave spectroscopy¹³ using flash vacuum pyrolysis, it has never been isolated as the monomer.



Most cyclopentadienones which are monomeric, such as 12, 14 13, 14b , 14 18 and 15, 19 owe their stability to bulky



substituents which hinder dimerization.¹⁶ <u>C</u>-face annulated cyclopentadienones (l_{ϵ}) may possess additional stabilization if the bridging group (x) is short or is constrained to be coplanar with the cyclopentadienone ring, because ring strain may develop upon dimerization. The strain in l_{ϵ} results from distortion of optimum bond lengths and bond angles due to geometrical constraints of the x' bridge.



This strain may contribute to the stability of 14 and 15 but more importantly it may also contribute to the stability of ge. Unfortunately, the magnitude of this effect in known systems is masked by additional steric and electronic effects. In the second part of this thesis the magnitude of this strain, in the absence of any special electronic or steric effects, has been approximated by preparing and estimating the strain energy in the dimers (2Q and 21) of the cyclopentadienones 18 and 19 (respectively).









RESULTS AND DISCUSSION

PART I

EXTENDED HÜCKEL MOLECULAR ORBITAL CALCULATIONS OF THE RELATIVE STABILITY OF ISOTRINDENETRIONE

Hückel Molecular Orbital (HMO) theory has been used to explain and oredict the stabilities, physical properties and chemical reactivities of organic π -systems,²¹ but has been limited to homoatomic, planar structures. HMO theory was extended (EHMO) in 1963 by Hoffmann²² to include non-planar structures, differential overlap and, most importantly for this study, heteroatoms. Despite these improvements the EHMO method still has limitations and shortcomings. In order to put the results of these calculations into proper perspective, several aspects of the EHMO method should be clarified.

The EHMO method does not calculate absolute molecular energies because it fails to include several factors. Among these factors are non-valence shell electrons, nuclear-nuclear repulsion and electron-electron repulsion. In addition, the EHMO method is known to overemphasize

"steric" interactions and to inaccurately estimate ring strain.²² Despite these limitations the EHMO method has been quite successful at determining relative stabilities. Thus while the absolute energy values and even the differences in energies between structures may not be accurate, the relative stabilities of closely related structures are generally in accord with experimental observations. In other words, the stability of a given structure can be estimated by the EHMO method but only in reference to another structure. This is the approach used here to determine whether EHMO theory predicts any stabilization for $\frac{9}{6}$.



One other aspect must be considered before discussing the calculations. Since we are interested only in the π resonance stabilization of 9e, we will compare only the

relative π orbital energies of these systems. Since all structures considered in this study are planar and the π molecular orbitals are orthogonal to all σ molecular orbitals, this restriction will not introduce significant errors. In fact this condition is necessary in order to make a valid comparison because while the number of π bonds is constant or an integral multiple, the number of σ C-C bonds and σ C-H bonds is not. This is illustrated in the comparison of <u>trans</u>-1,3,5-hexatriene (22) and benzene (23). Triene 22 has eight C-H bonds and five σ C-C



bonds while benzene has only six C-H bonds and six σ C-C bonds. Thus a comparison of the σ orbital energies would be meaningless in the context of this study.

The EHMO calculations were carried out using a computer program written by Professor J. F. Harrison²³ of Michigan State University. The program is fairly simple to use as the only inputs necessary are:

- 1. Accurate atomic coordinates.
- 2. Energy values of valence shell atomic orbitals. (α -Values)

Accurate atomic coordinates for known structures were taken from x-ray or microwave data. The coordinates for unknown structures were estimated based on similar structures in the literature. The dimensions of the structures used in this study are given in Table I. The energy values of valence shell atomic orbitals were kindly provided by Professor Harrison or were taken from the literature²⁹ and are listed in Table II. The molecular orbital energy values are calculated before the electrons are entered into the calculations. Therefore, the orbital energies were multiplied by a factor of 2 to obtain the energies of the doubly occupied orbitals.

To determine whether EHMO theory predicts any electronic stabilization for $g_{\mathcal{C}}$, as a result of possible π electron delocalization in the central ring (10), two separate comparisons were made.



Method.
EHMO
the
bγ
Examined
Structures
of
Geometries
Molecular
able I.
Н

CMPD		Bot	nd Lengtł	1 (Å)*		BC	nd Angl	e (°)**			Ref.
No.	ರ	Ą	ల	q	e	ಶ	ß	٢	Ş	Э	
9a	1.440	1.410	1.420	1.380	1.420	120	120	121	119	1	24
9b	1.440	1.440	1.369	1.711		120	112	111	92	1 1 1	28
9d	1.440	1.440	1.354	1.371		120	106	111	106	f 1 1	27
9e	1.440	1.440	1.350	1.440	1.240	120	109	108	106	127	ł
11	1.240	1.440	1.350	1.440		127	106	108	109	 	ł
22	1.350	1.440	1.350			**					, (
23	1.397					120	 	1	1	 	26
24	1.350	1.440	1.350	1.440		**					ł
25	1.350	1.440	1.350	1.440		***					ŀ
26	1.350	1.440	1.240			**					ļ
27	1.350	1.440	1.240	1.350	1.440	***					ł
28	1.350	1.440	1.240	1.350	1.440	***					ł
29	1.514	1.426	1.372	1.423	1.385	06	122.6	115.2	122.2	 	20 20
30	1.714	1.370	1.423			92	111	112			28
31	1.514	1.440	1.369	1.711		90	112	111	92		28
32	1.371	1.354	1.440			106	111	106		 	27
33	1.514	1.440	1.354	1.371		90	106	111	106		27
34	1.514	1.440	1.350	1.440	1.240	90	109	108	106	127	1 1
TTA*	C-H poi	nd lengtl	hs are l.	.08 Å.							
**All	C-H poi	nds bised	ot the ar	ngle dete	ermined 1	oy the	carbon	they are	attached	to an	d the
				þ		2		>			

2 two atoms bonded to that carbon.

*****All** bond angles in acyclic structures are 120°.









































d



9e

Atom	Orbital	α Value
Н	ls	-13.6
C	2s	-21.4
С	2p	-11.4
0	2s	- 35.57
0	2p	-18.03
S	3s	-21.13
S	gb	-13.31
	·····	

Table II. α Values of EHMO Calculations.

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The first comparison was made between cyclic structures containing 1, 2 and 3 "units" (35, 36 and 2) and acyclic structures containing the same number of double bonds in the all <u>trans</u> configuration (37, 38 and 32, respectively). The EHMO calculations were performed on



the benzene series (23, 22, 2a) and the cyclopentadienone series (11, 34, 2e). The results of these comparisons are shown in Figure 2. An energy value of zero has been assigned to the acyclic structures. The energy difference between the acyclic and corresponding cyclic structures is listed below each cyclic structure.



24

+ 23.6







22

+ 14.4





Figure 2. Comparison of $\Sigma \Xi \pi$ between cyclic and acyclic structures (Kcal/mole).

If a π system is stabilized in going from an acyclic to a cyclic array, then the total π energy decreases (- sign). If there is a net <u>de</u>stabilization, the total π energy increases (+ sign). In the benzene series (23, 29, 9a) a decrease in energy is observed for each case as expected for this well known aromatic series. In the cyclopentadienone series (11, 3⁴/₂, 9e) an increase in energy is observed in each case. Thus EHMO theory predicts not only that 11 is antiaromatic as expected but also that 3⁴/₂ and 9e are also antiaromatic.

Although EHMO theory predicts that $\Re e$ will be antiaromatic, closer examination of the data shows that $\Re e$ possesses some intrinsic stabilization. In the benzene series (23, 29, 9a) there is a steady increase in the stabilization energy (-18.0, -22.2, -30.0). Conversely, if there were no additional resonance stabilization in $\Re e$ a steady increase in the destabilization energy for the cyclopentadienone series (11, 34, 9e) would be expected. There is an increase in destabilization energy when going from 11 to 34 (+14.4 to +23.6) but there is no further increase in destabilization energy when going from 34 to 9e(+23.6 to +22.8). This result suggests that the three cyclopentadienone units linked in this way (9e) are stabilized by π electron resonance stabilization.

The second comparison was made by setting the total π energy for 35 (x = -CH=CH-, S, O, C=O) equal to zero



and observing how the total π energy per ring varies when

two units are brought together to form 36 and when three units are combined to form 9. The results of these EHMO calculations are shown in Figure 3.

If there were no additional π resonance stabilization in 9 as a result of linking three units of 35 in this way, then the difference in ΣE_{π} per ring for 9 relative to 35 should be zero. This is approximately what is seen for the benzene, thiophene and furan systems. The cyclopentadienone system, however, shows a significant stabilization for 9e (12.2 kcal/mole/ring) relative to an isolated cyclopentadienone unit (11). Although the absolute value of this stabilization cannot be known with high accuracy, there is little doubt that EHMO theory does predict significant π electron resonance stabilization for 9e.

One may ask why 9e is predicted to have additional resonance stabilization, while 9a, 9b and 9d are not.

0









+3.8

+3.4



- 0.4



0

0

30



+0.4



- 1.2



Figure 3. Comparison of $\Sigma \Xi \pi$ (Kcal/mole) per ring for cyclic structures 35, 36 and 9 where x = -CH=CH-, S, O, C=O.

There is one simple and perhaps naive explanation. Structures \Re , $\frac{9b}{20}$ and $\frac{9d}{20}$ are made up of three units which are already aromatic. In order for them to participate in central ring "benzenoid" type resonance each individual unit would have to be disturbed. This would result in the loss of some of that aromaticity with a resultant increase in total energy. On the other hand \Re is made up of three <u>antiaromatic</u> cyclopentadienone rings and thus would lose no individual ring stabilization by participation in a resonance structure such as 10.

Conclusions

Both comparisons made in this study indicate that EHMO theory does predict significant stabilization for \Re relative to three isolated cyclopentadienone moieties. Although confidence in the prediction of stabilization is high, the accuracy of the magnitude of that stabilization is not as high. This is an intrinsic characteristic of EHMO calculations. Finally, \Re , although stabilized somewhat over its "monomeric" units, is still predicted to be antiaromatic.

PART II

PREPARATION OF AND ESTIMATION OF THE STRAIN ENERGY IN THE DIELS-ALDER DIMERS OF TWO SIMPLE C-FACE ANNULATED CYCLOPENTADIENONES

Section A. Preparation of endo-pentacyclo-[9.6.1.0^{2,10}.0^{5,10}.0^{12,17}]octadeca-4,12(17)-diene-3,18-dieone (20) via 4,5,6,7-tetrahydro-2-indenone 1&

The most reasonable approach to 1% was from the known bicyclic enone 4%. Enone 4% has the desired carbon frame-work and most of the functionality, and requires only the



introduction of a second carbon-carbon double bond to give the desired 18. Excluding aldol type condensations, most methods of introducing unsaturation α,β to existing carbonyls involve introduction of a functional group X either α or β to the carbonyl and subsequent elimination of HX. If 40 were functionalized β to the carbonyl (41) elimination



could occur either to give the desired dienone 1% or to give the more thermodynamically stable dienone 4%. On the other hand if 4% were functionalized α to the carbonyl (4%) elimination of HX should initially lead only to the desired dienone 1%. Thus hoping to avoid 4% the initial strategy was to functionalize 4% α to the carbonyl.

Attempts Using *a*-Functionalization

The hexahydroinden-2-one (40) was prepared according to procedures of Dauben³⁰ and Raphael.³¹ Treatment of

2-carboethoxycyclohexanone $(\frac{44}{\sqrt{2}})$ with potassium t-butoxide in



refluxing t-butyl alcohol followed by addition of propargyl bromide gave 45. Hydration of the triple bond was accomplished by treating 45 with a catalytic amount of Hg⁺⁺ on Dowex-50 resin and a trace of H₂SO₄ in aqueous methanol. The method is very mild and gives 46 in nearly quantitative yield. Intramolecular aldol condensation using 5% KOH gave 40 in 56% overall yield.

Bromination of ketones α to the carbonyl followed by dehydrobromination has been used successfully to prepare α,β -unsaturated ketones.³² The α bromination of ketones has been accomplished using two different strategies.³⁹

One method uses acid catalysis, 33 and presumably involves attack of Br_2 or Br^+ on the enol form of the ketone. The



acid-catalysed reaction is slow and it was feared that bromination of the double bond in 40 might be competitive under these conditions. Another method for preparing α -bromoketones involves the bromination of enolate anions.³⁴,³⁹ This reaction is very fast even at -78°C and it was hoped



that bromination of the double bond in 40 would be much slower. Thus treatment of 40 with lithium diisopropylamide (LDA) in THF at -78°C, which is known to generate kinetic enolates,³⁵ presumably gave 47. Treatment of this solution with Br_2 was expected to give $48.^{32b}$ In addition to unreacted 40, a dark orange liquid was isolated after column



chromatography. The HMR spectrum of this liquid showed the expected vinyl proton resonance at $\delta 5.80$ and a doublet at $\delta 3.83$ (J = 2.5 Hz) which might correspond to the proton attached to the carbon bearing the bromine atom. The low coupling constant suggests that this proton is probably trans to the bridgehead proton. Unfortunately, even if this were the correct structure, the product was only 60% pure (<30% yield by NMR) and decomposed rapidly on standing. Others^{40b} have also reported α -bromoketones to be quite unstable. Although this result was disappointing, it should be pointed out that this bromination method was introduced originally for saturated or mono-aryl ketones,³⁶ not for enones.

Another popular method for generating α,β unsaturated ketones involves the thermal elimination of α -phenylselen-oxides.³⁷ While α -phenyl- and α -methylsulfoxides³⁸

undergo the same reaction, the phenylselenoxide elimination occurs at lower temperatures, by 100-150°C. In view of the high energy of the expected cyclopentadienones, the phenylselenoxide elimination was preferred. After treatment of 4Q with LDA in THF at -78°C followed by addition of ϕ SeBr, an established procedure for generating α -ketoselenides,³⁷ only a small amount of crude material could be isolated which had the expected vinyl resonance at δ 5.70 and methine doublet δ 3.40 (J = 2.0 Hz) for the methine proton geminal to the phenylselenide. The expected product could not be



isolated and the reaction was not reproducible.

There are many possible explanations for the failure of these reactions. One possibility is that the expected kinetic enolate $(\frac{47}{\sqrt{2}})$ was not being generated. At least two other enolates could be formed (50 and 51). To test this possibility, 40 was treated with LDA and the enolate was quenched with trimethylsilyl chloride (TMSC). After work up, mass spectral analysis of the product showed that

a silyldienol ether had been formed (M/e M^+ = 208), and



in high yield. The ¹³CMR showed only ten unique carbon atoms (the three silyl methyls are magnetically equivalent by rapid rotation) indicating that only one of the three possible isomers (52, 53 or 54) was present. The ¹HMR showed two vinyl protons of equal area at δ 5.58 and 4.98, thus eliminating isomer 53 which has only one vinyl proton.

Of the remaining two isomers (52 and 54) only 52 can undergo a Diels-Alder cycloaddition reaction with dienophiles. Therefore, 52 and 54 should be distinguishable on this basis, keeping in mind that a lack of reaction would be inconclusive. Treatment of a methylene chloride



52

solution of 52/54 with a methylene chloride solution of 4-phenyl-1,2,4-triazoline-3,5-dione $(55)^{41}$, a potent dienophile, gave an immediate reaction as indicated by the rapid loss of the red color as 55 was slowly added. This is taken as an indication that the isomer in hand was indeed the expected isomer 52. Thin layer chromatography $(CHCl_3/SG)$ of the crude product gave 57 in 50% yield. The expected Diels-Alder adduct (56) is presumably hydrolysed to ketone 57 by the silica gel during chromatography.



Other data also suggest that 52 is the correct structure for the silyldienol ether. When attempting to purify the silyldienol ether by preparative V.P.C. (10% FFAP on ChromG/180°C) the more thermodynamically stable isomer (53) was obtained in essentially quantitative yield. The GC-MS spectrum was practically identical with that of 52 but the ¹HMR showed only one vinyl proton at $\delta5.02$ and a greater symmetry in the methylene region. The silyl dienol ether 53 is readily accessible from 52 by a 1,5 prototropic shift. It is conceivable that 53 could have been formed from 54,



by a 1,3-H shift. This is not a thermally allowed reaction



in a concerted manner, however, and the migrating hydrogen is not especially acidic, making an ionic rearrangement mechanism unlikely under these conditions.

Although not conclusive, the spectral data, the Diels-Alder reaction with 55, and the facile conversion to 53

strongly suggest that the silyl dienol isomer 52 had been formed. Therefore, the desired kinetic enolate (47) had been prepared with LDA as expected. This being the case there must be some other explanation for the failure of the bromination and phenylselenation reactions of 40.

One unexplored possibility is that after product formation is achieved rearrangement or decomposition occurs. It is known that the α -hydrogen geminal to the ϕ Se group in α -ketophenylselenides is very acidic. Under the basic conditions of the reaction and work-up, including chromatography, a sizeable portion of 42 may be in equilibrium with its enol 58. Enol 58, like 52, may undergo 1,5-H shifts to give a variety of products (52, 60, 61), among which 59 would be the most likely. The bromoenone 48 may have suffered a similar fate before decomposing to intractable tars.



Although these attempts to functionalize $40^{\circ} \alpha$ - to the carbonyl had not met with the intended success, the α -carbon in 40° had been functionalized as the silyl enol double bond in 52. Perhaps a way could be found to utilize this functionality. In fact Jung and Rathke⁴² have converted silylenol ethers to α,β -unsaturated ketones via β -hydride abstraction with trityl cation or DDQ followed



by loss of Me_3Si^+ . To test this approach, 52 was treated with triphenylmethyl tetrafluoborate under prescribed



conditions. It did not give the expected dienone (18) $\overset{18}{\sim}$



or its dimer (20), but rather the tritylated enone (62) in about 40% yield. Rathke and Jung⁴² found that when there were no β -hydrogens, nucleophilic attack of the enol electrons on the trityl cations became the predominant reaction, as in the case of 63 reacting to give 64, but they



further state that when β -hydrogens are available "nucleophilic attack is less favored than hydride abstraction, and oxidation is the dominant reaction". The reason that nucleophilic attack predominates in the case of 52 in spite of the presence of a β -allylic hydrogen may be that hydride



abstraction would lead to the antiaromatic cyclopentadienyl cation $\ensuremath{ 65} \ensuremath{ .}$



If the energetically unfavorable intermediate 65 was an obstacle to the formation of 18, then perhaps the stability of the cyclopentadienyl anion (66) could be used in some way to facilitate the formation of 18. This leads to the following proposal. Cyclopentadienone





derivative of cyclopentadienone which shows no tendency



to dimerize or react with dienophiles.⁴³ This is probably due in part to the resonance contributor $\xi \zeta'$, as suggested by the molecule's 3.3D dipole moment. Hydrazone $\xi \zeta$ is prepared from $\xi \xi$ and cyclopentadienyl sodium,⁴³ and can



be hydrolyzed to cyclopentadienone $l_{\rm L}$ with ${\rm H_2SO_4}$.⁴³ Unfortunately the requisite cyclopentadienyl anion 62, which would lead to $l_{\rm L}^8$, is not readily available nor could the necessary regiochemistry be predicted <u>a priori</u>.



However, the thermodynamic stability of $\gtrsim 0$ might provide



a sufficient driving force to permit its formation by the oxidation of 71 in much the same way as 2b is prepared



from the tri-sulfide $72.^8$ To test this possibility, the



dimethylhydrazone 71 was prepared as a mixture of Z and E isomers, according to the procedure of Fishel,⁴⁴ in about 90% yield. While the conversion of 72 to 25 with



DDQ required extended reflux at 130°C, 71 underwent an immediate reaction with DDQ at 25°C in benzene as indicated

by the formation of an intensely dark color upon addition of the first drop of the DDQ solution. The only isolable product from the tarry residue of the reaction was the DDQ-hydroquinone (73). It is suspected that initial oxidation occurs by electron transfer from one of the nitrogens, leading to polymerization instead of hydride abstraction from the five membered ring as anticipated.

At this point, after exploring the possibilities of α -functionalization without success, it was decided that perhaps the original strategy (α -functionalization) may have been a tactical error and that β -functionalization might be more successful.

Use of *β*-Functionalization

DePuy⁴⁵ has successfully used this strategy to prepare cyclopentadienone (LL) itself, although in this case there was no opportunity for elimination exocyclic to the cyclopentenone ring. Bromination of cyclopentenone with N-bromosuccinimide (NBS) gave 4-bromocyclopentenone ($7\frac{4}{2}$) in good yield. Treatment of $7\frac{4}{2}$ with Et₃N in ether gave cyclopentadienone dimer ($7\frac{5}{2}$) in nearly quantitative yield.



A similar reaction sequence should also lead to 1%from 4%. Free radical bromination of 4% should give the requisite bromoenone 7% as a result of attack at the more stable tertiary allylic site as opposed to the secondary radical site which would give the unwanted bromoenone (77). Although base promoted dehydrohalogenation of 7\% could lead either to 1% or to the more thermodynamically stable 4%, the methylene protons α to the carbonyl (7\%) are



kinetically the most acidic and therefore the initially formed product could be the desired dienone 1.8.

Treatment of $\frac{4}{3}$ with NBS in refluxing carbon tetrachloride gave the unstable bromoenone (76), which decomposed rapidly when neat but could be kept for a few hours in dilute solution. The yields were as high as 90%. The site of bromination is clear from the ¹HMR spectrum which shows the α -methylene protons as two doublets at δ 3.25 (H₁) and 2.78 (H₂) with a geminal coupling constant of 19.3 Hz. The downfield proton is assigned as H₁ based on its proximity to the bromine atom.



The reaction is interesting because it is a self indicating reaction when a slight excess of enone $\begin{pmatrix} 40\\ \\ \infty \end{pmatrix}$ is used. Initially the reaction mixture is water white. As the reaction mixture is brought to reflux, a light tan color develops and deepens as the refluxing continues. After about 5 minutes (under conditions reported in the experimental section) the solution turns almost instantaneously from brown to water white. Work up at this point shows complete reaction. If the reaction mixture is refluxed much longer noticeable decomposition occurs. If an excess of NBS is used the brown color persists even after 20 minutes at reflux.

Unlike the conversion of 74 to 11, treatment of 76with triethylamine gave back approximately 80% unreacted bromoenone. Being confident of the correct structure assignment of 76 it was felt that a stronger base was needed to effect the elimination. Thus treatment of 76 with potassium <u>tert</u>-butoxide in THF at 0°C gave 20, presumably via l_{8}^{0} , in 29% yield. It was later found that treating 76 with neat Et_{3}^{N} gave 20 in 49% yield. The best yield (60%) was achieved by simultaneous addition of THF solutions of potassium t-butoxide and 76 to a flask kept at -78°C. Attempts to trap l_{8}^{0} with N-phenylmaleimide, dimethyl acetylenedicarboxylate and cyclopentadiene failed.

45

The spectral data were consistent with <u>endo</u> geometry for the dimer 20. Compound 20 gave the correct elemental analysis and showed the correct exact mass to .001 AMU. The IR (KBr) showed a carbonyl stretch at 1765 cm⁻¹ which is in the range of norbornenone carbonyls. The IR also showed the α,β -unsaturated ketone chromophore stretching frequencies at 1690 cm⁻¹ (C=O) and 1615 cm⁻¹ (C=C). The ¹³CMR showed the requisite 18 carbons with the carbonyl resonances at 205.53 and 198.76 ppm (relative to TMS). Despite the complexity of the ¹HMR spectrum the one vinyl



and three methine protons are clearly discernible. The vinyl proton (δ 5.99, H₃) and one methine proton (δ 2.95, H₄) were both singlets. The remaining methine protons (H₁, H₂) appeared as two doublets (δ 3.09, 2.40) with a coupling constant $\underline{J} = 4.7$ Hz which is consistent with <u>endo-20</u>.⁴⁶

Section B. Preparation of endo-pentacyclo-[$8.5.1.0^{2,9}.0^{5,9}.0^{11,15}$]hexadeca-4,11(15)-diene-3,16dione (21) via 5,6-dihydro-2(4H)-pentalenone (12)

Having successfully prepared 20 from 40 it seemed reasonable to prepare 21 from 78 by a similar sequence. Unfortunately, 78 was unknown despite several attempts at its



synthesis 47 and despite the successful synthesis of several of its simple derivatives $72, ^{48}$ $80, ^{48}$ $81, ^{47a}$ $82. ^{47a}$ Attempts to prepare 78 by the standard aqueous



81

82

base-promoted intramolecular aldol condensation of 83 lead to a complex mixture of products. 47



A synthesis of 78 was planned via 79 which was first reported by Becker⁴⁸ in 1978 and more recently by Trost.⁴⁹ Hydrolysis of the ester under mild conditions followed by decarboxylation under neutral conditions should lead to 78.

Becker prepared 79 from the diketoester 84 which he prepared in 33% yield by alkylation of 85 with chloro-acetone according to Herz's procedure.⁵⁰.



In the present work a two step procedure increased the yield of \$4 to \$1%. Thus treatment of \$5 with potassium <u>t</u>-butoxide in refluxing <u>t</u>-butyl alcohol followed by the addition of propargyl bromide gave the alkyne \$6 in \$1% yield. The structure of \$6 was clear from its spectral data (see experimental). Hydration of the triple bond⁵¹ with Hg⁺⁺-Dowex 50 resin in aqueous MeOH and a trace of H₂SO₄ gave \$4 quantitatively. Following Becker's procedure \$4 was



treated with NaH in refluxing toluene to give 72. Although small quantities of 72 could be separated by gas-liquid chromatography, 72 could not be readily purified in synthetically useful quantities. Therefore, crude 72, after bulb-to-bulb distillation, was used in subsequent reactions.

Hydrolysis of 79 was achieved using a slight excess of 1% NaOH at 0-10°C for 1.5 hours. Extraction of the nonhydrolyzable impurities with chloroform, acidification with dilute hydrochloric acid and extraction with chloroform gave crude $\frac{87}{2}$. Heating neat crude $\frac{87}{2}$ (100°C, 15 min) was



accompanied by vigorous gas evolution. After dilution with chloroform, extraction of the remaining acids with dilute sodium hydroxide gave 78 (90% pure by GC, ¹HMR) in 38% yield from $^{84}_{NN}$ as a mobile liquid with an exceptionally sweet aroma.

Following the same procedure used for 40, 78 was brominated with NBS in refluxing CCl_{μ} to give the unstable

bromoenone (§§). Simultaneous addition of THF solutions of §§ and potassium tert-butoxide at -78° C gave 21, presumably via 19, in 50% yield from 78. In addition an isomer of 18 was isolated in up to 10% yield from the reaction mixture and was assigned structure §9 on the basis of its spectral data.



The spectral data for 21 are consistent with the expected endo geometry. The key datum is the coupling constant $\underline{J}_{H_1H_2}$. The observed $\underline{J}_{H_1H_2}$ for 21 is 5.2 Hz which is consistent with the endo geometry.⁴⁶ A coupling constant $\underline{J}_{H_1H_2} \sim 0$ would be expected for the expected for the Both H₃ and H₄ appear as singlets as would be anticipated for



either isomer. The 13 CMR of 21 showed the requisite number of carbons with the carbonyl resonances at 207.42 and 196.08 ppm (relative to TMS). The IR spectrum showed the norbornenone carbonyl stretch at 1768 cm⁻¹ and the enone carbonyl and carbon-carbon double bond stretches at 1690 and 1622 cm⁻¹ respectively.

Dimers 20 and 21 are quite similar in terms of crystallinity, spectral properties and even solubilities. The most striking difference between 20 and 21 is that whereas 20 melts with decomposition at 190-2°C, 21 melts with decomposition at 135-40°C and crystal fracturing was observed as low as 95°C. This dramatic difference in decomposition points is ascribed to an increase in the strain energy in 21 relative to 20. This effect is quantified in the next section by studying the decarbonylation kinetics for 20 and 21. <u>Section C</u>. Decarbonylation Activation Enthalpy as a Measure of the Relative Strain in endo-pentacyclo- $[9.6.1.0^{2,10}.0^{5,10}.0^{12,17}]$ octadeca-4,12(17)diene-3,16-dione (20) and endo-pentacyclo- $[8.5.1.0^{2,9}.0^{5,9}.0^{11,15}]$ hexadeca-4,11(15)-diene-3,16-dione (21)

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Decarbonylation of endo-pentacyclo[9.6.1.0<sup>2,10</sup>.0<sup>5,10</sup>.0<sup>12,17</sup>]-

octadeca-4,12(17)-diene-3,16-dione (22) and endo-pentacyclo-

8.5.1.0^{2,9}.0^{5,9}.0^{11,15}]hexadeca-4,11(15)-diene-3,16-dione (21)
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It was noticed that the decomposition point for 21 (135-140°C) was much lower than that of 20 (190-2°C) and 75 (197-8°C).⁵² Actually 21 exhibits crystal fracturing



at temperatures as low as 95° C. It was felt that perhaps this decrease in the decomposition point was a consequence of the increased strain in 21 due to shortening of the X' bridge (see structure 17, page 7). If this were true then the strain energy should be reflected in the activation enthalpies of decarbonylation (the normal mode of thermal decomposition of non-dissociating cyclopentadienone dimers¹¹) of 22 and 22. More accurately, only that strain energy which is relieved in the transition state would be
reflected in the ΔH^{\neq} . Thus a kinetic study of the decarbonylation of 20 and 21 was undertaken to determine their activation parameters.

The decarbonylations of 20 and 21 were carried out in $\sim 0.2 \ \overline{M} \ C_6 D_6$ solutions which were sealed in 5 mm NMR tubes. The NMR tubes were heated in a constant temperature bath (Figure 4) for a desired length of time, then removed and immediately cooled to room temperature, thus stopping the reaction. The temperature of the bath was determined by the reflux temperature of the solvent placed in the bottom flask. The solvents used and the temperatures achieved are listed in Table III. Since the sealed tubes were less

Table III. Solvents and Temperatures Used in the Constant Temperature Bath for Decarbonylation Reactions.

Reflux Solvent	Temperature (±0.5°C)
l,2-dichloroethane	82°C
l-propanol	97°C
toluene	109°C
anisole	150.5°C
1,3,5-trimethylbenzene	162°C
1,2,3-trimethylbenzene (Tech.)	173°C

dense than the bath medium (ethylene glycol) a holder was



Figure 4. Two schematic views of the constant temperature bath for decarbonylation reactions.

fashioned from nichrome wire, which not only held the NMR tube completely submerged in the bath, but also allowed rapid removal and cooling of the tubes. The entire bath was insulated to ensure uniform heating and to limit the exposure of the samples to light.

At the temperatures used for the decarbonylation of 21 (82, 97, 109°C) only one product (20) was formed. This conclusion is based on the observation that no vinyl



or aromatic proton resonances (¹HMR) were observed other than those assignable to 21 or 20. Trienone 20 is the expected product and exhibits vinyl resonances at $\delta 6.01$, 5.78 and 5.20 and a methine signal at $\delta 2.82$ (Figure 5). The ¹³CMR shows the requisite 15 carbon atoms. The IR spectrum shows the loss of the bridging carbonyl group (no stretch above 1750 cm⁻¹) and retention of the



Figure 5. Partial 250 MHz ¹HMR spectra of 20, 21 and their decarbonylation products.

conjugated enone (1690 and 1620 cm⁻¹). Compound 90 also exhibits the correct parent ion (M⁺ = 212) in the mass spectrum.

In the case of 20 the decarbonylations were carried out at 150.5 to 173°C. At those temperatures 20 gave a mixture of products which appeared to contain some 91, based on the similarity of some of the peaks of the mixture to those in the spectrum of 90 (see Figure 5). When the mixture was heated at 195°C or alternatively when crystalline 20 was heated just above its melting point (\sim 200°C) the sole product formed was 92. It was noticed that the aromatic protons of 92 could also be observed in the mixture of decarbonylation products before heating to 195°C (Figure 5).



Although a multi-step ionic mechanism for the conversion $21 \rightarrow 22$ might be written, enolization of 21 gives a system (21') with the proper orbital overlap to undergo a 6 electron thermally allowed (1,5)-sigmatropic shift which aromatizes the central ring (22'). If the other two double bonds were involved a perhaps indistinguishable 10 electron (1,9)-sigmatropic shift could accomplish the same result.



The decarbonylation of β, γ -cyclopentenones is a well

known cheletropic reaction.^{11,52-54} Although the rearrangement of 21 to 22 has much precedent¹¹ this appears to be the first example of the formation of a spiro compound from the decarbonylation of a cyclopentadienone dimer.¹¹ When 20 was heated to 195°C a complex mixture of products was formed which was not analyzed.

In the kinetic experiments, the extent of reaction was determined by analyzing the 250 MHz ¹HMR spectrum. For 20 the extent of reaction was calculated from the areas of protons 1, 3 and 4 (δ 3.09, 2.95 and 5.99, respectively)



relative to the residual protons in deuterated benzene. This was necessary because of the complex mixture of products formed. However, since 21 gave only one product upon decarbonylation at the temperatures used, the extent of reaction was calculated from the areas of protons 1, 3 and 4 (21) (δ 3.45, 5.86 and 3.01, respectively), and three of the product (90) protons (δ 6.01, 5.20 and 2.82) which have not been uniquely assigned

The decarbonylation of 20 and 21 followed first order kinetics. The extent of reaction (X) as a function of time and temperature is listed in Table IV. The data are plotted in Figures 6 and 7 as L $A_0/(A_0-X)$ versus time, where A_0 is the initial concentration (arbitrary units). A least squares linear regression analysis of the combined data of two runs at each temperature gave the first order rate constants k which are listed in Table V along with the calculated correlation coefficients.

In order to obtain the most accurate results the activation enthalpies of decarbonylation for 20 and 21 were calculated using a multiple data set KINFIT4⁵⁵ computer program which gave a least squares best fit of the entire data set for each compound (Table IV) to the following equations provided by Professor J. L. Dye.⁵⁶ The second equation

$$\frac{k}{k_{ref}} = \frac{T}{T_{ref}} e^{-\underline{\Delta H}^{\neq}} \left(\frac{1}{T} - \frac{1}{T}\right)$$

and

$$Ln \frac{A_{O}}{A_{O}-X} = k t$$

is simply the first order reaction rate law.

The first equation is simply derived by dividing the

Comp.	Temp. (±0.5°C)	Time (sec)	Extent of Rea Run #1	Run #2
ଟୁରୁ	150.5	600 3600 7200 10800 12600 14400	0.038 0.205 0.365 0.467 0.499 0.534 A _o ^{b,c} =0.660	0.059 0.209 0.359 0.452 0.486 0.523 0.654
20	162.0	900 1800 2700 3600 4600	0.151 0.278 0.378 0.438 0.438 A _o ^{b,c} =0.628	0.152 0.281 0.381 0.443 0.513 0.639
£2	173.0	120 360 720 1080 1440 1800	0.082 0.190 0.321 0.419 0.500 0.540 A _o ^{b,c} =0.697	0.064 0.193 0.321 0.435 0.511 0.545 0.705
21	82.0	3600 4800 6000 7200 8400 9600 10800	0.429 0.513 0.594 0.643 0.692 0.734 0.767 A _o ^{b,c} =0.925	0.423 0.515 0.592 0.651 0.699 0.734 0.768 0.927
21	97.0	300 600 900 1200 1500 1800 2100	0.039 0.080 0.120 0.152 0.163 0.185 0.206 A_b,c=0.297	0.036 0.076 0.101 0.116 0.147 0.162 d 0.262

Table IV. Extent of Decarbonylation (X) of 20 and 21.

	Temp	 ∏ime	Extent of Reaction ^{a,c}	
Comp.	(±0.5°C)	(sec)	Run #1	Run #2
21	109.0	120 240 360 480 600 720 840	0.205 0.364 0.473 0.576 0.655 0.709 A ₀ ^b , ^c =0.929	0.184 0.359 0.496 0.597 0.669 0.723 0.761 0.929

^aAmount of starting material which has undergone decarbonylation.

^bInitial concentration.

^CArbitrary units.

^dTube broke after removing from bath.

Table IV. Continued.









Compound	Temp. (±0.5°C)	k (x10 ⁻⁶ sec ⁻¹)	Corr. Coef.
20	173.0	844	0.9969
zq	162.0	342	0.9972
zr	150.5	112	0.9983
ĘQ	109.0 ^a	1.2	
£2	109.0	2050	0.9983
21	97.0	542	0.9927
રી	82.0	163	0.9992

Table V. First Order Decarbonylation Rate Constants for 20 and 21.

^aExtrapolated value.

absolute rate expression for any temperature T

$$k = \frac{k_{\rm B}T}{h} e^{\frac{\Delta H^{\neq}}{RT}} \cdot e^{\frac{\Delta S^{\neq}}{R}}$$

by the expression for a reference temperature ${\rm T}_{\rm ref}$ with a known rate constant ${\rm k}_{\rm ref}.$ The entropy term and all constants

$$k_{ref} = \frac{k_B T_{ref}}{h} e^{-\frac{\Delta H^{\neq}}{RT}} e^{\frac{\Delta S^{\neq}}{R}}$$

except R drop out leaving the first equation. The error limits (one standard deviation) for the enthalpies are

generated by KINFIT4 based on estimates of the error in the input data (time, ± 3 sec; extent of reaction, $\pm 2\%$) and the "degree of fit" of the data.

The activation entropy was calculated manually from the expression:

$$\Delta S^{\neq} = R Ln \left(\frac{k_{ref}}{k_{B}T_{ref}}\right) + \frac{\Delta H^{\neq}}{T_{ref}}$$

where $k_B = Boltzmann's constant$. The square of the standard deviation of the entropy is given by:

$$\delta^{2}(\Delta S^{\neq}) = \frac{R^{2}}{k_{ref}^{2}} (\delta k_{ref})^{2} + (\frac{1}{T_{ref}})^{2} (\delta \Delta H^{\neq})^{2} + 2 \frac{R}{k_{ref}^{T} ref} (\sigma k_{ref}^{\Delta} H^{\neq})$$

where $\sigma k_{ref} \Delta H^{\neq}$ is the covariance of k_{ref} and ΔH^{\neq} and like δk_{ref} is also calculated by KINFIT4. The activation parameters for 20 and 21 as well as comparative data from the literature are listed in Table VI. The activation parameter ΔH^{\neq} shows that the tetramethylene bridge in 20 (ΔH^{\neq} = 35.5 Kcal/mole) introduces little if any measurable strain into the dicyclopentadiene-1,8-dione (75) framework (ΔH^{\neq} = 34.5 Kcal/mole). The trimethylene bridge in 21 (ΔH^{\neq} = 23.5 Kcal/mole), however, introduces a minimum of 12 Kcal/mole of strain energy relative to 20.

Compound	ΔH^{\neq} (Kcal/mole)	∆S [≠] (e.u.)	Ref.
ୡୄୡ	35.5 ± 1.2	6.3 ± 2.7	
21	23.5 ± 0.5	-9.8 ± 1.4	
ZZ	34.5 ± 0.8	9.8 ± 2.3	52
9.3 9.3	25.5 ± 0.7	6.0 ± 2.4	54c
94 20 20 20 20 20 20 20 20 20 20 20 20 20	31.6 ± 1.9	-3.6 ± 4.6	54c
95	27.9 ± 1.0	4.0 <u>+</u> 2.9	53a
27	25.5	1.1	57

Table VI. Decarbonylation Parameters for 7-Norbornenone Derivatives.

Discussion of the Kinetic Results

Three explanations have been offered previously to rationalize observed decreases in ΔH^{\neq} for other 7-nor-bornenone decarbonylations. The first is "steric compression" at the norbornenone double bond as in 25.53^{53a} The



authors claim that the methylene bridge is compressed against the norbornenone double bond and that this tends to flatten the six carbon ring in the norbornenone skeleton. This results in the increase in the overlap of the orbitals of the carbonyl bridge with the double bond. Thus the decreased ΔH^{\neq} (27.9 Kcal/mole) is directly attributed to this increased orbital overlap in the ground state which is a consequence of "steric compression".

Inspection of models of 20 and 21 shows that there is

no increased compression at the corresponding double bond when changing from a six- to a five-membered fused ring. Therefore "steric compression" cannot be used to rationalize the $\Delta\Delta H^{\neq}$ for 20 and 21.

The second rationalization has been used to explain the large $\Delta \Delta H^{\neq}$ (6 Kcal/mole) between 23 and 24. The authors claim^{54a,c} that in 23 there is an increase in the orbital overlap of the carbonyl bridging orbitals and the saturated ethylene bridge. This is a result of the cyclopropane



"banana" bonds which overlap favorably in 23 but not in 24. The observed product in the decarbonyl of 23 and 24



93







is cycloheptatriene 26.



The second rationalization has also been used to explain the low ΔH^{\neq} for 27^{53c} (28.5 Kcal/mole). In this case the edge of the cyclobutene ring participates in the

decarbonylation to give $cyclo_0ctatetraene$ 28. This explanation has also been used to rationalize the fact that



whereas 99 decarbonylates smoothly in refluxing xylene, 100 remains unchanged. $^{54\rm e}$



100

Since both 20 and 21 have the same <u>endo</u>-cyclopentenone ring at the saturated ethylene bridge it is unlikely that 21 has significantly more "edge" overlap than 20. Therefore this second rationalization also does not explain the large $\Delta \Delta H^{\neq}$ between 20 and 21.

The third explanation^{54b} is that the stability of the decarbonylation product provides the driving force for the reaction as in the case of 101. Although there is



some evidence⁵⁷ that 101 may be a fleeting transient, it has never been isolated. Since the initial decarbonylation products from 20 and 21 do not possess any special stability, this third rationalization must also be abandoned.

Actually this third case may be an extreme example of the second case where instead of a cyclopropyl "banana" bond or the cyclobutyl "edge" a second π bond overlaps with the bridging carbonyl orbitals.

Since none of the previously proposed rationalizations for decarbonylation rate enhancement can explain the large $\Delta\Delta H^{\neq}$ there must be some other explanation. Furthermore, since the results of this study are in accord with the predictions proposed earlier in this thesis, it is reasonable to assume that the large $\Delta\Delta H^{\neq}$ may be due to the relief of ring strain in the decarbonylation transition state of 22. The strain energy in 22 relative to 20 may be more than 12 Kcal/mole since only the ring strain which is relieved in the transition state is manifested in the ΔH^{\neq} .

Finally these results show that monomeric <u>C</u>-face annulated cyclopentadienones may be stabilized relative to their [4+2] dimers by increasing the dimer strain energy if the <u>C</u>-face bridging group is short enough. It also suggests that this same conclusion may be true if the bridging group is constrained to be coplanar with the cyclopentadienone ring, as in 9e and 15.

In the last section of this discussion the single crystal X-ray structures of 20 and 21 are examined to determine what structural changes occur in the dicyclopentadienone framework as a result of the strain in 21.

Crystal Data

Single crystals of 2Q and 21 were grown from methylene chloride-methanol solutions by slow evaporation. The X-ray structures were determined by Dr. D. L. Ward whose efforts are gratefully acknowledged.

Crystals of 20, $C_{18}H_{18}O_2$ are orthorhombic; space group $P_{2_12_1^2_1}$; a = 9.170(3), b = 14.622(4), c = 10.273(4)Å; Z = 4; M = 266.34; ρ_C = 1.284 g cm⁻³. Crystals of 21, $C_{16}H_{16}O_2$, are monoclinic, space group $P_{2_{1/n}}$; a = 13.220(4), b = 10.600 (5), c = 8.876(4)Å, α = 99.54(3)°; Z = 4; M = 240.30; ρ_c = 1.301. Lattice dimensions were determined using a Picker F FACS-I diffractometer and $M_{0}K_{\alpha_1}$ (λ = 0.70926Å) radiation.

The intensity data were measured using $M_{0}K_{\alpha}$ radiation $(20_{max} = 50^{\circ} (20); 20_{max} = 55^{\circ} (21))$ yielding 1417 (20) and 2380 (21) total unique data, and based on I > $2\sigma(I)$, 1067 (20) and 1240 (21) observed data. The data were reduced; 5^{8} the structures were solved by direct methods; 5^{9} and the refinement was by full matrix least squares techniques. 60 The final R values were 0.043 (20) and 0.065 (21). The final difference Fourier maps showed densities ranging from +.26 to -.21 (20) and from +.46 to -.46 (21)

with no indication of misplaced or missing atoms.

Positional parameters, bond lengths and bond angles for 2Q and 21 are listed in Appendix 1.

Discussion of X-ray Structures

The structures of 20 and 21 are shown in Figure 8 with the bond lengths indicated. The bond angles for 20 and 21 are shown in Figure 9 and ORTEP stereoscopic views of 20 and 21 are shown in Figure 10.

Structure 21 was solved and refined without difficulty. However, $20_{0,0}$ exhibited two anomalies one of which is easily rationalized. The first anomaly was that the six-membered ring containing C(14) and C(15) was flat and the C(14)-C(15) bond length was $\sim 1.34 \text{\AA}$ indicating that it was a double bond (Figure 11). This was chemically unreasonable. Inspection of a model of $20_{\rm VV}$ showed that there were two possible orientations for this four carbon bridge as shown in 20A and 20B (Figure 11). This difficulty was overcome by assigning half atoms to C(14) and C(15) (as well as their respective hydrogens) and allowing these 4 half carbons to occupy the positions indicated in 20A and 20B. Since this is a crystal phenomenon and 20A and 20B are certainly interconverting rapidly in solution and since this portion of the molecule is not expected to contribute significantly to the relative strain in 20 and 21, the



^aThe hydrogen atoms are omitted for clarity.
^bBond lengths associated with C(14) and C(15) have been omitted due to disorder at these positions.

Figure 8. Bond Lengths^a for 20^{b} and 21.



^aThe hydrogen atoms are omitted for clarity.

^bBond angles associated with C(14) and C(15) have been omitted due to disorder at these positions.

Figure 9. Bond angles a for 20^{b} and 21.





Figure 10. ORTEP stereoscopic views of 20 and 21.



Figure 11. Disordered orientations of C(14) and (15) in crystals of 20.

observed disorder should not affect the interpretation of the important structural changes between 22 and 21.

The second anomaly in 20 is the unexpectedly short C(7)-C(8) bond (1.50 Å instead of ~ 1.54 Å) in the other fourcarbon bridge (Figure 8). At present there is no explanation for this short bond. It is a curious coincidence that the bonds which are involved in these anomalies are essentially the bonds which have been "removed" in 21.

Although there are several differences in bond lengths between 2Q and 2l the most striking change in bond lengths involves the carbon-carbon single bonds which are formed during the Diels-Alder dimerization. The single bonds in 2l (C(1)-C(2) and C(9)-C(10)) are longer than the corresponding bonds in 20 by 0.019 and 0.011Å, respectively. Since the standard deviation for these bonds are 0.006 and 0.005Å, respectively (for both 20 and 21), the differences in bond lengths, although small, are probably significant. In other strained cyclopentadienones which exist as dissociating dimers the corresponding bonds are thought to be elongated also.¹¹

Since 22 decarbonylates much more readily than 20 the carbonyl bridging bonds in 21 might be expected to be longer (i.e., weaker) than in 20. This is not the case. In fact, the C(1)-C(16) (21) bond is essentially the same as the corresponding bond in 20 and the C(10)-C(16) (21) bond is even shorter than the corresponding bond in 20. Surprisingly, the carbonyl bridge is more symmetrically disposed in 21 than in 20.

There are several variations in bond and torsion angles between 2Q and 2L. Essentially all of the significant bond angle variations are centered at the termini of the X'(17) bridging group (C(5) and C(9) in 2L). Of course, the bond angles at the termini of the X bridge change in going from 2Q to 2L but are unexceptional.



One of the explanations for decarbonylation rate acceleration discussed in Section C was that there was an increased overlap of the carbonyl bridging orbitals with the pi orbital of the "norbornenone" double bond by decreasing the angle of the bridge relative to the pi orbital. As can be seen in Figure 9 the C(16)-C(1)-C(15)and C(16)-C(10)-C(11) angles (21) are within 1° of the corresponding angles in 2Q. This confirms the conclusion drawn earlier from inspection of models that this type of increased overlap cannot be used to explain the decrease in ΔH^{\neq} for 21 relative to 20.

At the sp² hybridized carbon C(5) two angular distortions occur. The C(4)-C(5)-C(6) angle in 21 is expanded to 136.7 ± 0.5° from 128.5 ± 0.5° for the corresponding

angle in 20 which is already distorted from the ideal 120°. The orientation of the C(5)-C(6) bond not only extends this bond angle but also results in a twisting of the C(4)-C(5) double bond. The ORTEP stereoscopic views (Figure 10) of 20 and 21 have been drawn looking down the C(4)-(5) axis to show the increase in the C(3)-C(4)-C(5)-C(6)torsion angle in going from 20 (3.3°) to 21 (14.4°). This results in decreased pi overlap and an increase in the total energy of the molecule.

At the other end of the X' bridge three of the six bond angles change significantly in going from 20 to 21. The angles which are enclosed in the norbornenone and cyclopentenone rings as well as the C(8)-C(9)-C(10) angle (21) do not change very much. However, the C(2)-C(9)-C(8)(21) angle increases from 115.9° in 20 to 121.6° in 21 and the C(5)-C(9)-C(10) angle (21) decreases from the normal tetrahedral angle of 109.4° in 20 to 101.2° in 21.

The last bond angle change in going from 20 to 21 is a decrease toward the normal tetrahedral angle of 109° . The C(5)-C(9)-C(10) angle (21) decreases from 114.6° in 20 to 111.5° in 21. In other words this end of the cyclopentenone ring is 3° more <u>endo</u> in 21 than in 20. This was unexpected since it was initially felt that the shortened bridge would pull the cyclopentenone ring up (<u>exo</u>). However, this observation, when coupled with the elongation of the sigma bonds formed in the dimerization (<u>vide supra</u>),

can be interpreted as suggesting that $21 \\ \text{C}$ is closer to its transition state for dimerization (in terms of energy or distance along the "reaction coordinate") than 22 is to its transition state.

Any conclusions drawn from the single crystal X-ray structures must be tempered with the fact that the solid state structure and solution state structure may differ significantly due to crystal lattice forces and solvation factors. Nevertheless, the idea that short bridges in \underline{C} face annulated cyclopentadienones results in increased distortions of optimum bond lengths and bond angles in their Diels-Alder dimers seems to be justified based on the X-ray data presented here.

EXPERIMENTAL

General

All melting points were recorded on a Thomas-Hoover melting-point apparatus and are uncorrected. Infrared spectra were recorded either as neat films or as KBr pellets on a Perkin-Elmer 167 Grating Spectrophotometer. ¹HMR spectra were recorded on a Varian T-60, Bruker 180 or Bruker 250 spectrometer and ¹³C NMR spectra were recorded on a Varian CFT-20 or Bruker 250 spectrometer. All spectra were taken at ambient temperatures and are recorded in delta (δ) values relative to TMS. The coupling constants (J) are recorded in Hertz (Hz). All mass spectra were obtained on either a Hitachi RMU-6 or Finnigan-4000 mass spectrometer. Ultraviolet spectra were recorded on a Cary-17 spectrophotometer. Elemental analyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, Michigan. Exact mass determinations were made at the regional NIH facility, Michigan State University. Toluene, tetrahydrofuran, ether, diisopropylamine and hexamethyldisilizane were dried and distilled in glass prior to use. All other commercially available reagents were used as received unless otherwise specified.

Ethyl 1-(2-propynyl)-2-oxocyclohexanecarboxylate (45)

45 was prepared according to Dauben's³⁰ procedure. To a 2-L flask fitted with a magnetic stirrer, 250-mL addition funnel, N2 purge and a reflux condenser was added tert-butanol (1110 mL) and potassium metal (30.5 g, 0.78 mole). The tert-butanol was refluxed until all of the potassium had reacted ($\sqrt{4}$ h). To this solution was slowly added neat 2-carboethoxycyclohexanone (126 g, 0.74 mole) and refluxed for an additional 30 minutes. To this was slowly added propargyl bromide (97.1 g, 0.99 mole). After refluxing for an additional 30 minutes the mixture was dumped onto ice ($\sqrt{500}$ g). After separating the organic layer the aqueous layer was washed with ether (4 x 250 mL). The organic layers were combined, dried $(MgSO_{\mu})$ and filtered. The solvents were removed under reduced pressure and the resulting oil was vacuum distilled giving pure 45 (118 g, .54 mole) in 77% yield (lit. 30 84%). B.p. 108°C at 0.65 torr (lit.³⁰ 134-137°C at 9 torr). ¹HMR (60 MHz, CDC1₃, TMS) $\delta 4.13(2H,q,J = 7 Hz)$, 2.8-1.5 (11H, br m), 1.24(3H,t, J = 7 Hz). IR (neat) cm⁻¹ 3280 (m), 2950(m), 2860(w), 2130(w), 1715(vs), 1450(m), 1370(w), 1315(m), 1200(s), 1130(m), 1090(m), 1060(w), 1025(m), 910(w). ¹³CMR (20 MHz, CDCl₃, TMS) &186.36, 169.96, 79.15, 71.00, 61.26, 59.56, 40.40, 34.95, 26.92, 24.31, 21.96, 13.71. M.S. m/e (rel. int.) 208(6, M^+), 207(28), 162(26), 140(35), 134 (100), 143(33), 113(34), 107(47), 93(26), 92(21), 91(45),

79(51), 78(22), 77(35), 67(37), 65(42), 41(38), 39(67).

Ethyl l-acetonyl-2-oxocyclohexanecarboxylate (46)

46 was prepared according to Dauben's procedure.³⁰ To a three neck flask fitted with a magnetic stirrer was added 45 (117.1 g, 0.563 mole), water (400 mL), methanol (1600 mL), HgO supported on Dowex 50 resin (0.6 g; see Experimental) and sulfuric acid (2 drops). This mixture was stirred at 25°C for 96 hours. The mixture was filtered to remove the resin and neutralized with ammonium hydroxide. The methanol was removed under reduced pressure. The resulting liquid was dissolved in methylene chloride ($_{0.500}$ mL), dried $(MgSO_{J_1})$, and filtered. Evaporation of the methylene chloride under reduced pressure gave essentially pure 46 (126.5 g, 0.560 mole) in 99% yield. This product was used without further purification. ¹HMR (60 MHz, CDCl₃, TMS) δ 4.13(2H, q, J = 7 Hz), 2.80(2H,s), 2.8-1.5(11H,br m; including a sharp singlet at $\delta 2.14$ (3H)), 1.25(3H,t,7 Hz). IR (neat) cm^{-1} 2950(m), 1720(vs), 1450(m), 1370(m), 1320(m), 1265(m), 1200(s), 1175(m), 1140(m), 1090(m), 1030(m). ¹³CMR (20 MHz, CDC1₃, TMS) 207.07, 205.23, 171.84, 61.37, 59.30, 48.03, 40.50, 36.71, 30.29, 29.91, 1401. M.S. m/e (rel. int.) 226(3, M^+), 208(8), 180(56), 153(25), 141 (45), 137(55), 124(31), 123(27), 111(36), 109(52), 71(67) 55(28), 53(20), 43(100), 41(43), 39(28).

1,4,5,6,7,7a-hexahydro-2-indenone (40)

Compound 46 was converted to 40 following Raphael's procedure.³¹ To a 3-L flask fitted with a reflux condenser, magnetic stirrer, heating mantle, and N2 purge was added 46 (125.5 g, 0.555 mole) and an aqueous solution of 5% potassium hydroxide (2500 g, 1.89 mole). The mixture was refluxed for 6 h and cooled to 25°C. The product was extracted with methylene chloride (4 x 250 mL). The methylene chloride solution was dried (MgSO $_{\mu}$) and filtered. The solvent was removed under reduced pressure; the product was isolated by distillation at 100°C and 2.8 torr (lit.³⁰ 91-93°C at 2.8 torr; 88°C at 4 torr³¹) (54.1 g, 0.398 mole) in 73% yield. ¹HMR (60 MHz, CDCl₃, TMS) δ5.68 (lH,s), 3.0-0.9 (llH,br m). IR (neat) cm⁻¹ 2930(s), 2850(m), 1700(vs), 1625(s), 1450(m), 1410(m), 1350(w), 1290(m), 1250(m), 1200(m), 1170(m), 1130(w), 1065(w), 950 (m), 890(w), 850(m), 830(w), 820(w). ¹³CMR (20 MHz, CD₃(N)) δ208.57, 185.51, 126.26, 117.53, 42.31, 41.81, 35.17, 27.26, 25.30. M.S. m/e (rel. int.) 137(11), 136(100,M⁺), 121(36), 108(51), 107(43), (95(53), 94(26), 93(42), 82(28), 80(30), 79(72), 77(32), 66(22), 41(29), 53(39).

Attempted Synthesis of 1-bromo-1,4,5,6,7,7a-hexahydro-2indenone (48)

Following a similar procedure by Smith, 34 to a 100-mL round-bottomed flask fitted with a 10-mL addition funnel,

N₂ purge, magnetic stirrer and a rubber septa were added diisopropylamine (0.391 g, 3.87 mmole) and THF (10 mL). The solution was cooled to 0°C and 1.9 \overline{M} n-BuLi (1.93 mL, 3.67 mmole) was added. The solution was stirred for 5 min at 0° C, cooled to -78° C, and hexamethylphosphoramide (0.646 g, 3.61 mmole) was added. After 30 minutes 1,4,5,6,7,7a-hexahydro-2-indenone (40) (0.509 g, 3.74 mmole) in THF (5 mL) was added dropwise. After an additional 30 minutes a solution of bromine (0.612 g, 3.83 mmole) in THF (5 mL) was added. This resulting solution was stirred for 1 h at -78°C, warmed to 25°C, dumped into saturated ammonium chloride and extracted with ether (2 x 100 mL). The ether layer was dried (MgSO $_4$) and filtered. The ether was removed under reduced pressure to give a dark oil whose ¹HMR spectrum showed, in addition to 40, a new vinyl proton at 5.80(s) and a doublet at $\delta 3.80 \ (J = 2.5 \text{ Hz})$ which is consistent with $\frac{48}{22}$. Attempted purification of $\frac{48}{\sqrt{2}}$ by column chromatography (SG/ CH_2Cl_2) gave an orange oil (0.52 g) which had the same vinyl proton at $\delta 5.80$ and doublet at $\delta 3.80$ but, assuming the correct assignment to 48, the product was only 60% pure for a yield of only 39%. Attempts to further purify $\frac{48}{\sqrt{3}}$ were unsuccessful as the product decomposed.
Attempted Synthesis of 1-phenylseleno-1,4,5,6,7,7a-hexahydro-2-indenone (42).

To a 100-mL round-bottomed flask fitted with a N_{2} purge, magnetic stirrer and a 10-mL addition funnel, was added freshly distilled THF (15 mL). The flask was cooled to 0°C with an ice bath and diisopropylamine (0.366 g, 3.63 mmole) was added followed by the addition of 1.9 \overline{M} n-BuLi (1.94 mL, 3.69 mmole). After 5 min at 0°C the flask was cooled to -78° C and hexamethylphosphoramide (0.643 g, 3.60 mmole) was added. After 20 minutes at -78°C a solution of 1,4,5,6,7,7a-hexahydro-2-indenone (40) (0.504 g, 3.71 mmole) in THF (10 mL) was added dropwise. After stirring for an additional 0.5 h, a THF solution of phenylselenyl bromide (ϕ SeBr, 3.70 mmole; prepared³⁷ by the addition of bromine (0.326 g, 2.04 mmole) to a THF solution (10 mL) of diphenyl diselenide (0.578 g, 1.85 mmole)) was added rapidly. Immediate decoloration of the ϕ SeBr was observed. The cold solution was dumped into 10% HCl (100 mL) and the mixture was extracted with ether (2 x 100 mL). The ether extract was washed with 10% NaHCO₃ (1 x 25 mL), H_2O (1 x 25 mL), and saturated NaCl, dried (MgSO₄) and filtered. The ether was removed under reduced pressure to give a light yellow oil (0.9 g). The ¹HMR showed a singlet at $\delta 5.70$ and a doublet at $\delta 3.40$ (J=2 Hz), which was consistent with 49; however, the product was only 50% pure by [⊥]HMR. Attempts to purify this product lead to decomposition

and no 49 could be isolated.

2-Trimethylsilyloxy-4,5,6,7-tetrahydro[3aH]-indene (52)

To a magnetically stirred 100-mL flask fitted with N_2 purge, addition funnel and cooled to -78°C was added n-BuLi (10.51 mL, 2.1 m, 22.6 mmoles) and THF (25 mL) followed by diisopropylamine (2.30 g, 22.8 mmole). After the mixture was stirred for 15 minutes at -78°C a solution of 1,4,5,6,7,7a-hexahydro-2-indenone (40) (3.0 g, 22.06 mmoles in 15 mL of THF) was added dropwise over a 15-minute period and stirred for an additional 15 minutes when a solution of trimethylchlorosilane (4.0 g, 36.8 mmoles), THF (25 mL) and diisopropylamine (0.5 mL) was added rapidly via a stainless steel canula. The resulting clear solution was stirred for an additional 15 minutes and then partitioned between cold ($\sqrt{5}^{\circ}$ C) pentane (200 mL) and sat'd NaHCO₃ and filtered and the solvent was removed at room temperature under reduced pressure until the odor of diisopropylamine was no longer detectable to give a pale yellow liquid (4.41 g, 96% crude) which by 1 HMR and 13 CMR was greater than 90% pure. Attempted distillation of the product failed due to severe foaming. The following data was obtained using the crude product.

¹HMR (60 MHz, CDCl₃, TMS) δ5.57 (1H,br s); 4.97 (1H,br s); 2.8-0.8(9H,m), 0.23(9H,s). ¹³CMR (20 MHz,

CDC1₃, TMS) 156.03, 153.6, 122.16, 108.31, 49.46, 33.45, 29.40, 29.90, 25.80, 0.50. M.S. m/e (rel. int.) 209(15), 208(67,M⁺), 207(22), 181(11), 180(64), 165(11), 91(13), 75(37), 73(100), 45(22). IR (Film, neat) cm⁻¹ 3070(w), 2930(s), 2850(m), 1625(m), 1565(m), 1442(w), 1355(m), 1332(m), 1304(m), 1253(s), 1213(m), 1194(m), 1144(m), 962(m), 931(w), 870(vs), 850(vs), 755(m).

2-Trimethylsilyloxy-4,5,6,7-tetrahydro-[1H]-indene (53)

When 2-trimethylsilyloxy-4,5,6,7-tetrahydro-[3aH]indene (52) was passed through a preparative scale vapor phase chromatograph (10% SE-30 on Chrom W, 3/8 in. by 6 ft., 180°C), in addition to approximately 3% of 4Q which was present in 52, a new silyldienol ether (52) was obtained pure as a water white liquid as the only other product. No trace of 52 could be detected by NMR. Although the IR spectrum of 53 was very similar to 52 and the mass spectra were indistinguishable, the 13 CMR and particularly the ¹HMR were distinctly different. ¹HMR (60 MHz, CDCl₃, TMS) δ 5.02(1H,s), 2.69(2H,m), 2.09(4H,m), 1.63(4H,m), 0.24(9H,s). ¹³CMR (20 MHz, CDCl₃, TMS) δ 159.00, 136.74, 125.81, 107.83, 43.48, 24.79(2C), 23.37, 23.12, -0.05.

Anal. Calcd for C₁₂H₂₀OSi: C, 69.17; H, 9.67. Found: C, 69.33; H, 9.65.

2,4,6-Triaza-3,5,13-trioxo-4-phenyltetracyclo[5.5.2.0^{1,8}.0^{2,6}]tetradecane (57)

To a magnetically stirred 50-mL flask containing methylene chloride (20 mL) and 2-trimethylsilyloxy-4,5,6,7tetrahydro-[3aH]-indene (52) (200 mg, 0.96 mmole) at 25°C was slowly added a dark red solution of 4-phenyl-1,2,4triazoline-3,5-dione (PTAD)(0.168 mg, 0.96 mmoles) in methylene chloride. A fast reaction was observed by the rapid disappearance of the dark red color until the last few drops were added when the red color of PTAD persisted. The solvent was removed under reduced pressure. The crude product was purified by preparative thin layer chromatography (SG-ether) to give the desilylated Diels-Alder adduct (57) (150 mg, 50%). ¹HMR (60 MHz, CDC1₃, TMS) δ7.30(5H,brs), 5.90(1H,m), 4.9-4.3(2H,brm), 3.0-0.8(9H, br m). IR (KBr) cm⁻¹ 3070(w), 2940(m), 1777(s), 1705(vs), 1605(s), 1502(s), 1430(s), 760(m), 700(m). M.S. m/e (rel. int.) 312(5), 311(22,m⁺), 177(39), 136(35), 135(100), 134(35), 119(62), 107(32), 93(48), 91(75), 86(42), 84(68), 79(38), 77(51), 44(89), 41(48), 39(47). Exact Mass. Calcd. for C₁₇H₁₇N₃O₃: 311.12698. Found: 311.12540.

3,3a,4,5,6,7-Hexahydro-3-(1,1,1-triphenylmethyl)-2-indenone (62)

To a magnetically stirred 50-mL round-bottomed flask purged with N_2 was added triphenylmethyl tetrafluoborate

(1.59 g, 4.80 mmoles), collidine (0.59 g, 4.80 mmoles) and methylene chloride (10 mL, distilled from CaH₂). When everything had dissolved a solution of 2-trimethylsilyloxy-4,5,6,7-tetrahydro-[3aH]-indene (52) (0.5 g, 2.40 mmoles) in methylene chloride (10 mL) was slowly added (5 min) at 25°C and allowed to stir for 2 h. The reaction mixture was dumped into H₂O (50 mL). The organic layer was separated and washed successively with H₂O (50 mL), 10% HCl (50 mL), saturated NaHCO₃ (50 mL), H₂O (50 mL), dried (MgSO₄), filtered and the solvent removed under reduced pressure to give a dark yellow solid (1.624 g). TLC (SG/ CH₂Cl₂) showed two spots. Trituration with ether gave a white solid (0.351 g). Preparative TLC (SG/CHCl₃) of 75 mg of this solid gave 72 mg (96%) of (62) as a white solid with m.p. 218°C (39% total yield).

¹HMR (60 MHz, CDCl₃, TMS) 67.07(15H,m), 5.23(1H,s), 3.80(1H,s) 2.8 to 0.8(9H,m). ¹³CMR (20 MHz, CDCl₃, TMS) 6205.73, 180.17, 127.81, 125.79, 125.31, 123.89, 55.29, 45.82, 34.40, 28.90, 25.45, 23.53. IR (KBr) cm⁻¹ 3110(w), 3090(w), 3060(m), 3040(m), 3020(w), 3000(w), 2965(m), 2935(m), 2885(w), 2860(w), 2843(m), 1690(s), 1630(s), 1595(w), 1495(m), 1450(m), 1440(m), 1358(w), 1342(w), 1330(w), 1315(w), 1305(w), 1292(w), 1270(w), 1248(w), 1195(w), 1185(m), 1160(w), 1080(w), 1077(w), 1040(m), 1000(w), 960(w), 950(m), 930(w), 910(w), 885(w), 868(m), 838(m), 792(m), 770(m), 740(s), 720(m), 710(s), 695(m), 662(w),

635(m), 615(m). M.S. m/e (rel. int.) 378(3,M⁺), 244(21) 243(100), 165(23).

Exact Mass. Calcd. for C₂₈H₂₆O: 378.19836. Found: 378.19678.

3,3a,4,5,6,7-Hexahydro-2-indenone dimethylhydrazone (71)

To a magnetically stirred 25-mL flask fitted with a reflux condenser and N_{2} purge was added 3,3a,4,5,6,7hexahydroinden-2-one (40) (1.00 g, 7.35 mmoles), EtOH (7.5 mL) and <u>unsym-N,N-dimethylhydrazine</u> (7.5 g, 125 mmoles). The solution was refluxed for 22 h, cooled to 25°C, and the solvent and excess N,N-dimethylhydrazine were removed under reduced pressure to give a mixture of the \underline{Z} and \underline{E} isomers (30/70) of the expected dimethylhydrazone (71) as a dark red oil (1.2 g, 92% crude yield) containing less than 2% starting material (by V.P.C.). A sample of the pure hydrazones was obtained by preparative scale V.P.C. (5% SE-30 on Chrom W, 1/4 in. x 6 ft.) as a colorless liquid which rapidly turned dark red upon exposure to air. ¹HMR (60 MHz, $CDCl_3$) $\delta6.23$, 5.80(1H, singlets, vinyl protons from Z and E isomers); 3.2 - 0.8 (17H, br m, including a sharp singlet at 4.2, $N(CH_3)_2$). ¹³CMR (20 MHz, CDCl₃, TMS) 8174.67, 172.91, 168.72, 166.25, 123.69, 118.14, 47.91, 47.44, 47.13, 43.77, 42.36, 37.19, 35.28, 34.69, 30.33, 29.99, 27.20, 25.59. IR (thin film) cm⁻¹ 2980(m), 2930(s),

2855(s), 2815(m), 2770(m), 1625(s), 1470(m), 1448(m), 1355(w), 1255(w), 1200(w), 1162(w), 1025(m), 976(s), 952(m), 940(w), 860(m), 848(w), 820(w), 767(w), 712(w). M.S. m/e (rel. int.) 179(14), 178(100,M⁺), 177(16), 163(11), 136(13), 134(14), 132(18), 118(10), 107(23), 106(15), 105(14), 94(17), 93(31), 92(20), 91(38), 79(42), 78(11), 77(24), 67(12), 65(17), 53(12), 53(10), 46(16), 45(25), 44(42), 43(89), 42(26), 41(22), 39(12). Exact Mass. Calcd for $C_{11}H_{18}N_2$: 178.14700.

Found: 178.14702.

Reaction of 3,3a,4,5,6,7-hexahydro-2-indenone dimethyl hydrazone (71) with dichlorodicyanoquinone (DDQ)

To a magnetically stirred solution of the hydrazone (71) (0.340 g, 1.91 mmoles) dissolved in benzene (10 mL) in a 50-mL flask protected with a N₂ purge was added dropwise (10 min) a solution of DDQ (0.478 g, 2.11 mmole) in benzene (10 mL). The initially light tan solution of the hydrazone (71) darkened immediately upon addition of the first drop of the DDQ solution and had become opaque at the end of the addition. After stirring the mixture for an additional 50 minutes a ball of black solid material had encased the teflon coated magnetic stirring bar. The dark benzene solution was decanted off and the benzene was removed under reduced pressure leaving a small amount of un-identifiable black tar-like material. The black ball of material was dissolved in methanol, the magnet was removed and the methanol was evaporated leaving a dark solid. The solid was practically insoluble in carbontetrachloride, ether, and chloroform. When it was dissolved in methylene chloride only a small amount of black residue remained which was removed by decantation. Evaporation of the methylene chloride gave a fluffy tan solid. The spectral data for this solid was consistent with the hydroquinone of DDQ but gave no indication of the presence of ZQ. The ¹HMR (CDCl₃, TMS) showed only one peak at $\delta 2.76$. The IR (KBr) showed a broad phenolic absorption at 3400 cm⁻¹. The mass spectrum showed the parent peaks at m/e 228, 230 and 232 in the expected ratio for two chlorine atoms.

<u>7a-Bromo-1,4,5,6,7,7a-hexahydro-2-indenone (76)</u>

To a 50-mL bear-shaped flask fitted with heating mantle, magnetic stirrer, reflux condenser and N₂ purge was added 1,4,5,6,7,7a-hexahydro-2-indenone (40) (1.00 g, 7.35 mmole), N-bromosuccinimide (1.20 g, 7.32 mmole) and carbon tetrachloride (30 mL). As the reaction mixture was refluxed it became light brown until after about 4 minutes when the mixture suddenly became water white. The heating mantle was replaced with an ice bath and the reaction mixture was cooled to 5 to 10°C, filtered and the solvent removed under reduced pressure to give a light tan liquid which would darken rapidly if left undiluted

and thus was not stable enough to permit either elemental analysis or exact mass determination. Its NMR (¹H and ¹³C) and IR spectra, however, were consistent with 00%pure 7a-bromo-1,4,5,6,7,7a-hexahydro-2-indenone which was used without further purification. ¹HMR (180 MHz, CDCl₃) 5.912 (1H,d,<u>J</u> = 1.5 Hz), 3.246(1H,d, <u>J</u> = 19.3 Hz), 2.776 (1H,d, <u>J</u> = 19.3 Hz), 2.77-1.0 (8H,m); ¹³CMR (20 MHz, CDCl₃, TMS) δ 203.00, 180.26, 127.39, 66.17, 55.11, 43.26, 27.49, 26.52, 22.48; IR (neat) cm⁻¹. 3080(w), 2940(s), 2880(m), 1708(vs), 1610(s), 1450(m), 1438(m), 1408(m), 1350(w), 1322(m), 1278(w), 1256(w), 1244(w), 1220(m), 1180(w), 1140(w), 1070(m), 958(m), 938(m), 860(m), 835(w), 820(m), 760(w), 680(m).

<u>endo-Pentacyclo[9.6.1.0^{2,10}.0^{5,10}.0^{12,17}]octadeca-4,12(17)-</u> <u>diene-3,18-dione (20)</u>

To 50-mL of THF cooled to -78° C in a 250-mL flask with magnetic stirring and under a N₂ purge was added slowly (15 min) and concomitantly THF solutions of KOtBu (0.71 g, 7.39 mmoles in 50 mL of THF) and crude 7a-bromo-1,4,5,6,7,7ahexahydro-2-indenone (prepared from NBS and 7.35 mmoles of 1,4,5,6,7,7a-hexahydro-2-indenone in 50 mL of THF) as described above. The dark red reaction mixture was stirred for an additional 30 minutes, and allowed to warm to 0°C, when water (7 mL) was added and most of the THF was removed under reduced pressure. The residue was

taken up in chloroform (100 mL) and water (50 mL). The aqueous layer was separated and washed with chloroform (1 x 50 mL). The combined organic layers were dried $(MgSO_{ll})$, filtered and the solvent was removed under reduced pressure to give a dark red residue which when triturated with ether gave light tan crystals of endo-pentacyclo[9.6.1.0^{2,10}.0^{5,10}.0^{12,17}]octadeca-4,12(17)-diene-3,18dione (0.587 g, 60% yield). Alternatively, flash chroma $tography^{61}$ (5% EtOAc/CHCl₃) effectively isolates this product from the reaction mixture. Recrystallization from MeOH-CH₂Cl₂ gave white crystals, m.p. 190-2°C (dec). ¹HMR $(180 \text{ MHz}, \text{CDCl}_3, \text{TMS}) \delta 5.99(1\text{H}, \text{s}), 3.09(1\text{H}, \text{d}, \text{J} = 4.7 \text{ Hz}),$ 2.95(1H,s), 2.77(1H,m), 2.40(1H,d), J = 4.7 Hz), 1.39-2.23(15H,m). ¹³CMR (20 MHz, CDCl₃, TMS) &205.53, 198.76, 181.52, 135.61, 134.89, 132.16, 56.46, 53.45, 52.11, 51.73, 34.48, 30.00, 27.16, 25.07, 24.74, 22.86, 22.70, 22.65(sh); IR (KBr) cm⁻¹ 3000(m), 2944(s), 2964(s), 2840(m), 1765(vs), 1690(vs), 1615(s), 1450(m), 1430(m), 1355(m), 1323(w), 1315(w), 1288(m), 1272(m), 1262(w), 1247(m), 1214(m), 1196(m), 1190(w), 1169(m), 1149(w), 1090(w), 1040(w), 976(w), 942(w), 922(w), 899(m), 869(s), 855(w), 842(w), 830(w), 817(w), 807(w), 777(w), 685(w), 670(w), 652(w), 638(w), 612(w); M.S. m/e (rel. int.) 268(3,M⁺), 241(21), 240(100), 212(41), 211(52), 198(19), 197(18), 183(21), 141(27), 134(48), 129(17), 128(21), 115(20), 91(21), 77(17), 44(48); UV (CH₃CN) λ_{max} (ε) 231 nm (10,650), 320(44), 332(40), 348(19).

Anal. Calcd. for C₁₈H₂₀O₂: C, 80.56; H, 7.51. Found: C, 80.42; H, 7.49. Exact Mass. Calcd. for C₁₈H₂₀O₂: 268.14630. Found: 268.14621.

Reaction of 7a-bromo-1,4,5,6,7,7a-hexahydro-2-indenone (76) with triethylamine in ether

Fresh crude 76 (36.8 mmole), prepared as described above, was dissolved in ether (60 mL) and transferred to a 100-mL addition funnel which was attached to a 250-mL round-bottomed flask containing triethylamine (4.10 g, 40.6 mmole) and ether (40 mL) cooled to -20°C. The bromoenone (76) solution was slowly added (alo min) to the magnetically stirred amine solution. While the mixture was stirred an additional 0.5 h at -20°C a white precipitate began to form. The mixture was allowed to warm to 25°C (0.5 h) and was dumped into 5% NaHCO₂ (50 mL) and ether (100 mL). The ether layer was separated and the aqueous layer was extracted with ether (1 x 100 mL). The combined ether layers were washed with 5% hydrochloric acid (1 x 25 mL), saturated sodium chloride (1 x 25 mL), and water $(1 \times 25 \text{ mL})$, dried $(MgSO_4)$ and filtered. The ether was removed under reduced pressure to give a light brown oil (8.3 g) whose IR and ¹HMR spectra were nearly identical with the crude $\chi \xi$ (>80% recovery based on ¹HMR).

Reaction of 7a-bromo-1,4,5,6,7,7a-hexahydro-2-indenone (76) with neat triethylamine

Fresh crude χ_{0}^{c} (7.35 mmole), prepared as described above, was treated with triethylamine (5 mL, 36.0 mmole) in the absence of solvent and cooling. After the mixture was stirred magnetically for 1 h the tan slush was diluted with water (30 mL) and the product was extracted with chloroform (1 x 100 mL plus 1 x 50 mL). The combined organic layers were washed with 5% hydrochloric acid (1 x 25 mL - washing was acidic to litmus), saturated sodium bicarbonate (1 x 25 mL) and water (2 x 25 mL), dried (MgSO₄) and filtered. The chloroform was removed under reduced pressure to give a nearly completely crystalline mass which when triturated with ether and filtered gave 2Q (0.483 g, 49%). The melting point and spectral data were identical with those of 2Q prepared with potassium tert-butoxide in THF at -78°C (vide supra).

Reaction of 7a-bromo-1,4,5,6,7,7a-hexahydro-2-indenone (76) with potassium tert-butoxide at 0°C

Fresh crude χ_{6}^{6} (34.7 mmoles), prepared as described above), was dissolved in dry THF and placed in a 50-mL addition funnel attached to a 250-mL round-bottomed flask containing THF (100 mL) and fitted with a N₂ purge, magnetic stirrer and a second 50-mL addition funnel. To

the second addition funnel was added potassium tertbutoxide (3.33 g, 34.7 mmole) dissolved in THF (50 mL). The flask was cooled to 0°C and the two reactants were added simultaneously over a period of about 5 min and stirred for an additional 0.5 h. The mixture was dumped into a mixture of ether (200 mL), pentane (100 mL) and water (200 mL) and shaken in a separatory funnel. A large "rag" layer was formed which was broken by filtration and the layers were separated. The aqueous layer was washed with ether (1 x 200 mL) and the combined organic layers were washed with 5% hydrochloric acid (1 x 25 mL, washing was acidic to litmus), saturated sodium bicarbonate (1 x 25 mL) and water (3 x 25 mL), dried (MgSO $_4$) and filtered. The solvents were removed under reduced pressure to give a dark brown, partially crystalline residue. Crystallization from methanol/pentane and flash chromatographic separation (SG/5% EtOAc/CHCl₃) of the mother liquor gave crystalline 20 (1.34 g, 29%). The melting point and spectral data were identical with those of 20 prepared with potassium tert-butoxide in THF at -78°C (vide supra).

Reaction of 7a-bromo-1,4,5,6,7,7a-hexahydro-2-indenone (76) with lithium hexamethyldisilazide in ether/hexane (1:1)

Fresh crude 76 (7.35 mmole), prepared as described above, was dissolved in a mixture (1:1) of ether and hexane (100 mL) and put in a 250-mL round-bottomed flask fitted with a N_2 purge, magnetic stirrer and addition funnel, and cooled to -78° C. To this solution was slowly added lithium hexamethyldisilazide (prepared in the addition funnel from hexamethyldisilazane (1.18 g, 7.35 mmole)) and 2.1 \overline{M} n-BuLi (3.5 mL, 7.35 mmole) which were magnetically stirred for 0.5 h and diluted with hexane to 50 mL) over a 10 min period. The contents of the flask were allowed to warm to 25°C and the solvent was removed under reduced pressure. The residue was taken up in chloroform (200 mL) and water (50 mL). The organic layer was separated, washed with water (2 x 50 mL), 5% hydrochloric acid (1 x 25 mL), saturated sodium bicarbonate (1 x 25 mL) and water (1 x 25 mL), dried (MgSO_{μ}), and filtered. The solvent was removed under reduced pressure to give a dark brown oil. Flash chromatography (SG/3% EtOAc/CHCl₃) gave 20 (0.272 g, 28% yield) the melting point and spectral data of which were identical to those of 20 prepared with potassium tert-butoxide in THF at -78°C (vide supra).

Reaction of 7a-bromo-1,4,5,6,7,7a-hexahydro-2-indenone (76) with lithium hexamethyldisilazide in THF

Fresh crude 76, prepared as described above, was treated with lithium hexamethyldisilazide under the same conditions as described in the immediately preceding reaction except that THF was used as the solvent and only 50 mL was placed in the reaction flask. Flash chromatography (SG/4% EtOAc/CHCl₃) of the crude product gave 2Q (0.417 g, 42% yield), the melting point and spectral data of which were identical to those of 20 prepared with potassium <u>tert</u>-butoxide in THF at -78° C (vide supra).

Attempted trapping of 18 with N-phenylmaleimide

Fresh crude χ_{6}^{c} (3.0 mmoles), prepared as described above, was dissolved in ether (15 mL) and placed in a 25mL addition funnel which was fitted to a 100-mL round-bottomed flask. To this flask, also fitted with a magnetic stirrer and a N₂ purge, was added ether (75 mL), N-phenylmaleimide (1.04 g, 6.0 mmoles) and triethylamine (0.61 g, 6.0 mmoles). The stirred contents were cooled to -20°C and the solution of χ_{6}^{c} was added over a 5 min period, stirred for an additional 15 min, and dumped into a mixture of saturated sodium bicarbonate (50 mL) and ether (100 mL). The mixture was shaken and the ether layer was separated, washed with water (1 x 25 mL), 5% hydrochloric acid (1 x 25 mL) and water (1 x 25 mL), dried (MgSO₄) and filtered. The ether was removed under reduced pressure. Although flash chromatography (SG/30% EtOAc, petroleum ether 30-60) of the residue gave back 50% of χ_{6} , and an unquantified amount of N-phenylmaleimide the ¹HMR spectra of all fractions showed no indication of an adduct between 18 and N-phenylmaleimide.

Attempted trapping of 18 with dimethylacetylene dicarboxylate (DMAD)

To a 250-mL round-bottomed flask fitted with a N_2 purge, magnetic stirrer and two 50-mL addition funnels was added DMAD (1.05 g, 7.35 mmoles) and THF (50 mL). To one funnel was added potassium <u>tert</u>-butoxide (0.706 g, 7.35 mmole) dissolved THF (50 mL) and to the other was added fresh crude 76 (7.35 mmole), prepared as described above, dissolved in THF (50 mL). The contents of the funnels were added slowly (15 min) and concomitantly to the stirred solution of DMAD cooled to -78° C. The mixture was allowed to warm to 25°C and stirred for 14 h. The mixture was partitioned between methylene chloride (100 mL) and water (100 mL). The aqueous layer was washed with methylene chloride (1 x 25 mL) and the combined organic layers were washed with water (2 x 25 mL), 5% hydrochloric acid (1 x 15 mL), water (1 x 25 mL), saturated sodium bicarbonate (1 x 25 mL) and water (1 x 25 mL), dried (MgSO $_4$) and

filtered. Flash chromatography of the products gave 22 in 62% yield but no indication (¹HMR) of an adduct of 1.8 and DMAD.

Attempted trapping of 18 with cyclopentadiene

To a 50-mL flask fitted with a magnetic stirrer was added triethylamine (10 g, 100 mmole) and cyclopentadiene (7.1 g, 108 mmole). To this solution was slowly added (0.5 h) a solution of fresh crude χ_{ξ} (7.35 mmole), prepared as described above. The resulting mixture was stirred at 25°C for 60 h, washed with water (3 x 25 mL), dried (MgSO₄) and filtered. The ether and cyclopentadiene were removed under reduced pressure. Flash chromatography of the residue gave χ_{χ} (41%) and a small amount of dicyclopentadiene but no indication (¹HMR) of any adduct of 18 and cyclopentadiene.

Ethyl 1-(2-propynyl)-2-oxocyclopentanecarboxylate (86)

t-Butyl alcohol (850 mL) and potassium metal (26.2 g, 0.670 moles) were heated at reflux in a 2-L, 3-necked, round-bottomed flask fitted with a heating mantle, N_2 purge, 250-mL addition funnel and tempered water (\sim 40°C) reflux condenser until all of the potassium metal had disappeared. Then neat 2-oxocarboethoxycyclopentane (95 g, 0.609 moles) was added to this solution in a slow stream

(10 min) and refluxed for 15 min. To this refluxing solution was slowly added propargyl bromide (90.6 g of an 80% solution in toluene, 0.609 moles) over a 45-min period (Caution: Rapid addition can cause the reaction mixture to boil out the condenser since the alkylation is quite fast and very exothermic). After the addition was complete t-butanol (~ 600 mL) was removed by distillation. The reaction mixture was cooled to room temperature and poured onto ice (500 g). The organic layer was separated and washed with water (3 x 200 mL) and the combined organic layers were evaporated under reduced pressure to remove the t-BuOH, taken up in chloroform (750 mL), dried (MgSO_{μ}), filtered, evaporated under reduced pressure and distilled (107°C at 4.00 Torr) to yield pure ethyl 1-(2-propynyl)-2-oxocyclopentanecarboxylate as a colorless liquid (95.6 g, 81% yield) ¹H NMR (250 MHz, CDCl₃) δ4.158 (2H, q, <u>J</u>=7.3 Hz), 2.687, 2.680 (2H, d, AB, \underline{J}_{d} =2.7 Hz \underline{J}_{AB} =17 Hz), 2.60-2.06(m,6H), 2.046(1H,t,J=2.7 Hz), 1.247(3H,t,J=7.3 Hz). ¹³CMR (20 MHz, CDCl₃, TMS) δ213.11, 170.23, 79.97, 70.99, 61.64, 58.75, 38.20, 32.57, 23.13, 19.79, 14.04; IR(neat) cm⁻¹ 3280(m), 2980(m), 1750(vs), 1725(vs), 1470(w), 1450(w), 1425(w), 1405(w), 1330(m), 1015(m), 930(w), 860(w), 810(w); M.S., m/e (rel. int.) 194(5, M^+), 166(38), 149(26), 138(53), 121(79), 120(28), 111(54), 110(31), 109(37), 93(92), 92(44), 91(96), 79(74), 78(30), 77(95), 67(40), 65(84), 64(23), 53(32), 51(22), 43(27), 41(37), 39(100).

Ethyl 1-acetonyl-2-oxocyclopentanecarboxylate (84)

A mixture of ethyl 1-(2-propynyl)-2-oxocyclopentanecarboxylate (86.0 g, 0.443 moles), MeOH (600 mL), H₂O (150 mL), HgO impregnated Dowex 50 H^+ resin⁵¹ (200-400 mesh) (2.0 g) and conc. H_2SO_{\perp} (4 drops) was magnetically stirred in a 1-L, round-bottomed flask for 60 h at room temperature, filtered to remove the resin and evaporated under reduced pressure to remove MeOH. This mixture was taken up in chloroform (400 mL) and the aqueous layer was separated and washed with chloroform (1 x 100 mL). The combined organic layers were dried (MgSO_{μ}), filtered and the solvent was removed under reduced pressure to yield pure ethyl l-acetonyl-2-oxocyclopentanecarboxylate (93.0 g, 0.439 moles, 99% yield) as a colorless liquid. 1 HMR (250 MHz, CDCl₃) δ4.141 (2H,q,J=7.3 Hz), 3.184, 2.099 (AB,2H, J=18.3 Hz), 1.95-2.65(6H,m), 2.147(3H,s), 1.237(3H,t,J=7.3 Hz); ¹³CMR (20 MHz, CDCl₃, TMS) 6214.26, 205.14, 170.45, 61.44, 57.44, 47.42, 37.55, 33.24, 29.86, 19.79, 13.97; $IR(neat) \text{ cm}^{-1} 2945(m), 2910(m), 1750(vs), 1720(vs), 1420(m),$ 1450(m), 1405(s), 1368(s), 1325(m), 1282(m), 1255(m), 1230(s), 1168(s), 1148(s), 1110(m), 1050(w), 1030(m), 970(w), 940(w), 920(w), 858(w); M.S., m/e (rel. int.) 212(0.4, M⁺), 167(12), 166(34), 141(7), 139(15), 138(7),

124(21), 123(26), 113(13), 111(32), 110(8), 97(17), 95(28), 71(8), 68(8), 67(20), 55(13), 43(100), 41(13), 40(10), 39(7).

<u>Anal</u>. Calcd. for C₁₁H₁₆O₄: C, 62.25; H, 7.60 Found: C, 62.14; H, 7.70.

Hg⁺⁺ catalyst on Dowex-50 H⁺ Resin

Using a procedure similar to Newman's⁵¹ Dowex-50 $^{\rm R}$ H⁺ resin (1.0 g) was washed with dilute sulfuric acid and was air dried overnight. The resin was suspended in 200 mL of dilute sulfuric acid to which was added mercuric oxide (0.10 g). The suspension was stirred magnetically for 24 h and filtered. The resin was washed with dilute sulfuric acid, air dried for 1 h and stored in a vial until needed.

4,5,6,6a-Tetrahydro-2(1H)-pentalenone (78)

To a 1-L round-bottomed flask fitted with a reflux condenser, 250-mL addition funnel, nitrogen purge, magnetic stirrer and heating mantle was added NaH (4.0 g, 0.167 moles) and dry (from K/benzophenone) toluene (300 mL) which was then brought to reflux. To the refluxing mixture was slowly added a toluene solution (200 mL) of ethyl 1-acetonyl-2-oxocyclopentanecarboxylate (8.0 g, 0.039 moles) over a 2-h period and the mixture was refluxed for 18 hrs. The reaction mixture was cooled to 10°C and carefully acidified with 10% HCl (90 mL, 0.25 moles). The aqueous layer was separated and washed with ether (3 x 50 mL). The organic layers were combined, washed with saturated brine (1 x 50 mL), dried (MgSO_{μ}) and filtered. After removing the solvent under reduced pressure, bulb-to-bulb distillation (100°C at 0.1 Torr) gave a colorless liquid (4.44 g) containing the desired ethyl 2,3,4,5-tetrahydro-5-oxo-3a(1H)-pentalenecarboxylate (72) which was not readily isolated on a preparative scale. Therefore the impure product was treated with 1% NaOH (100 mL) for 1.5 h at 0-10°C. The resulting mixture was washed with chloroform (1 x 50 mL) acidified (10% HCl), and extracted with chloroform (3 x 50 mL). The chloroform extract was dried $(MgSO_{ll})$ and the solvent removed under reduced pressure to give a clear oil which was heated on a steam bath for 10 min (gas evolution was observed), diluted with chloroform (100 mL), washed with 5% NaOH (1 x 25 mL), dried (MgSO_{μ}), filtered and the solvent removed under reduced pressure to give 1.75 g (38% yield) of > 95% pure (by NMR and VPC) 4,5,6,6a-tetrahydro-2(1H)pentalene 78. Preparative scale VPC (5% FFAP on Chrom W AWDMCS, 1/4 in. x 6 ft., 160° C) gave pure 78. IR(neat) cm⁻¹ 2968(s), 2875(m), 1705(vs), 1625(s), 1452(m), 1375(w), 1315(m), 1258(w), 1176(m), 1158(m), 1108(w), 1082(w), 1028(w), 932(w), 872(m), 835(w), 819(w); UV λ_{max} (MeOH) 228 nm (ϵ =12,200), 293(62); M.S. m/e (rel. int.) 122(100,M⁺),

123(8.5), 121(31), 107(22), 95(5), 94(72), 93(11), 91(13), 81(5), 80(16), 79(52), 77(25), 66(39), 65(13); ¹HMR(60 MHz, CDCl₃) δ5.86(1H,br s), 1.7-3.0(9H,m); ¹³CMR(20 MHz, CDCl₃, TMS) δ210.93, 191.41, 124.79, 46.74, 42.36, 31.16, 26.30, 25.55.

Exact Mass Calcd. for C₈H₁₀O: 122.07260. Found: 122.07317.

Attempts to improve the yield of 4,5,6,6a-tetrahydro-2(1H)pentalenone (78)

The following five experiments were performed in an attempt to improve the yield of 7.8. In each case only the conditions of the aldol condensation of the diketoester 8.4 were altered. The rest of the procedure was the same as that described in the preceding experiment.

Potassium hydride in refluxing toluene

To a 1-L round-bottomed flask fitted with a magnetic stirrer, 250-mL addition funnel, heating mantle, reflux condenser and N₂ purge was added toluene (300 mL) and potassium hydride (6.7 g, 167 mmoles; the dispersion oil was removed with pentane). There was slowly added a toluene (200 mL) solution of $\overset{84}{\sim}$ (8.0 g, 38.7 mmole) at 25°C. The mixture was stirred at 25°C for 16 h. VPC analysis (3% UCW/98 on Chrom W, 1/8 in. x 18 in.) of a small sample indicated that no reaction had occurred. The mixture was refluxed and the reaction was monitored by VPC. After 6 h most of 84 had been consumed but no product peaks had appeared. Standard workup, hydrolysis and decarboxylation procedures failed to give any trace of 78.

Potassium tert-butoxide in refluxing toluene

To a 1-L round-bottomed flask fitted with a reflux condenser, 250-mL addition funnel, magnetic stirrer, N₂ purge and heating mantle was added potassium <u>tert</u>-butoxide (4.0 g, 41.6 mmole) and toluene (300 mL) which was brought to reflux. To this mixture was added dropwise (2 h) a toluene (200 mL) solution of $\frac{84}{\sqrt{2}}$ (8.0 g, 38.7 mmole). The mixture was refluxed for an additional 18 h. Standard work-up, hydrolysis and decarboxylation procedures gave $\frac{78}{\sqrt{2}}$ (0.990 g, 8.11 mmoles) in 21% yield and greater than 90% purity.

Potassium tert-butoxide in refluxing THF

To a 1-L round-bottomed flask fitted with a reflux condenser, 250-mL addition funnel, magnetic stirrer, N_2 purge and heating mantle was added potassium <u>tert</u>-butoxide (3.84 g, 40.0 mmole) and THF (300 mL) which was brought to reflux. To this was added dropwise (2 h) a THF (200 mL) solution of &4 (8.0 g, 38.7 mmole). The mixture was refluxed for an additional 18 h. Standard work-up, hydrolysis

and decarboxylation procedures gave 7% (0.548 g, 4.49 mmole) in 12% yield and greater than 90% purity. (Note: After quenching the base, most of the THF was removed under reduced pressure and the residue was taken up in chloroform (100 mL) before continuing the standard work-up.)

Potassium tert-butoxide in refluxing THF (inverse addition

To a 1-L round-bottomed flask fitted with a reflux condenser, 250-mL addition funnel, magnetic stirrer, N₂ purge and heating mantle was added &4 (8.0 g, 38.7 mmole) and THF (300 mL) which was brought to reflux. To this was added dropwise (2 h) a THF (200 mL)solution of potassium <u>tert</u>-butoxide (4.0 g, 41.6 mmole). The mixture was refluxed for an additional 18 h. Standard work-up, hydrolysis and decarboxylation procedures gave 7& (0.895 g, 7.34 mmole) in 19% yield and greater than 90% purity. (Note: After quenching the base, most of the THF was removed under reduced pressure and the residue was taken up in chloroform (100 mL) before continuing the standard work-up.)

Potassium tert-butoxide in refluxing ether

To a 1-L round-bottomed flask fitted with a reflux condenser, 250-mL addition funnel, magnetic stirrer, N_2 purge and heating mantle was added potassium <u>tert</u>-butoxide (4.0 g, 41.6 mmole) and ether (300 mL) which was brought

to reflux. To this was added dropwise (2 h) an ether (200 mL) solution of 84 (8.0 g, 38.7 mmole). The mixture was refluxed for an additional 18 h. Standard work-up, hydrolysis and decarboxylation procedures gave 78 (0.887 g, 7.27 mmole) in 19% yield and greater than 95% purity. (Note: After quenching the base, most of the ether was removed under reduced pressure and the residue was taken up in chloroform (100 mL) before continuing the standard work-up.)

<u>endo-Pentacyclo[8.5.1.0^{2,9}.0^{5,9}.0^{11,15}]hexadeca-4,11(15)-</u> <u>diene-3,16-dione (21)</u>

To a 50-mL pear-shaped flask, fitted with a magnetic stirrer, reflux condenser, N₂ purge and heating mantle was added 4,5,6,6a-tetrahydro-2(lH)-pentalenenone (0.97 g, 7.95 mmoles), N-bromsuccinimide (1.30 g, 7.90 mmole) and carbon tetrachloride (30 mL). As the reaction mixture was refluxed, it became light brown until after about 4 minutes when the mixture suddenly became water white again. The heating mantle was quickly replaced with an ice bath and the mixture was cooled to 5 to 10°C. The reaction mixture was filtered and the solvent removed under reduced pressure (\sim 20 Torr) without heating. As soon as the solvent stopped distilling the flask was evacuated to 10⁻¹ Torr for 2 minutes to remove as much solvent as possible. The resultant bromoenone, which rapidly decomposes when

concentrated, was neither purified nor characterized but immediately dissolved in dry THF (50 mL) and transferred to an addition funnel. The bromoenone solution was added dropwise and concomitantly with a solution of t-BuOK (0.84 g, 8.75 mmoles, in 50 mL of THF) over a 20-minute period to a 250-mL, 3-necked round-bottomed flask containing THF (50 mL) at -78°C and protected by an N_2 purge. The dark red reaction mixture was stirred an additional 20 minutes and allowed to warm to just above 0°C when water (5 mL) was added and most of the THF was removed under reduced pressure. The residue was taken up in chloroform (100 mL) the organic layer separated, dried (MgSO $_{\rm L}$), filtered and the solvent removed under reduced pressure. Flash chromatography (10% acetone/CHCl₃) of the residue gave endo-pentacyclo[8.5.1.0^{2,9}.0^{5,9}.0^{11,15}]hexadeca-4,11(15)diene-3,16-dione (0.46 g, 49% yield) which is readily recrystallized from CH₂Cl₂/MeOH, m.p. 135-140°C (dec). ¹HMR (250 MHz, CDCl₃) δ 5.858(1H,s), 3.455(1H,d,<u>J</u>=5.2 Hz), 3.005 (1H,s), 2.672(1H,d,J=5.2 Hz), 2.65-1.60(12H,m); ¹³CMR (20 MHz, CDCl₃, TMS) 6207.42, 196.08, 187.91, 142.38, 140.87, 129.04, 58.60, 56.19, 52.01, 50.56, 31.61, 31.21, 31.12, 26.02, 23.87, 23.66; IR (KBr) cm⁻¹ 3025(w), 2950(m), 2875(w), 2855(w), 1768(vs), 1690(vs), 1622(s), 1449(w), 1425(w), 1331(w), 1328(w), 1315(w), 1250(m), 1200(w), 1190(m), 1175(m), 1150(w), 1132(w), 1058(w), 1018(w), 978(w), 959(w), 938(w), 903(w), 889(m), 870(m), 854(w), 818(w), 788(w),

735(w), 710(w); M.S. m/e (rel. int.) 240(1.5,M⁺), 213(15), 212(42), 184(76), 183(21), 171(17), 170(60), 169(33), 168(25), 156(44), 155(45), 142(19), 141(50), 129(26), 128(46), 127(14), 120(43), 117(29), 116(18), 115(68), 91(56), 78(21), 77(48), 65(27), 64(21), 63(36), 53(24), 52(17), 51(45), 50(16), 41(26), 39(100,B): UV (MeOH) $\lambda_{max}(\epsilon)$ 229 nm (10,500), 317(79), 327(69).

Anal. Calcd for C₁₆H₁₆O₂: C, 79.97; H, 6.71. Found: C, 80.08; H, 6.72.

Also isolated by flash chromatography was 4,5-dihydro-2(1H)-pentalenone (δθ) (92 mg, 10%) m.p. 35°C; ¹HMR (60 MHz, CDCl₃) δ6.03(1H,s), 5.77(1H,s), 2.83(6H,s); ¹³CMR (20 MHz, CDCl₃, TMS) δ208.39, 187.44, 145.79, 131.68, 121.06, 36.00, 25.71; IR cm⁻¹ 3078(w), 2958(m), 2925(m), 2875(w), 2835(w), 1700(vs), 1595(s), 1448(m), 1418(m), 1395(m), 1357(w), 1301(w), 1266(m), 1252(m), 1210(m), 1178(m), 1148(m), 1058(w), 1003(w), 988(m), 938(m), 866(w), 841(m), 800(m), 780(m); M.S. m/e (rel. int.) 121(8), 120(52,M⁺), 92(21), 91(100), 65(17), 63(11), 51(16), 50(10), 40(70), 39(35); UV (MeOH) λ_{max}(ε) 282 nm (16,300). Anal. Calcd. for C₈H₈O: C, 79.97; H, 6.71.

Found: C, 80.08; H, 6.72.

Attempted trapping of 19 with cyclopentene

To a 250-mL round-bottomed flask fitted with a N_2 purge, magnetic stirrer and two 50-mL addition funnels was

added cyclopentene (22 g, 0.32 moles). To one funnel was added a THF (50 mL) solution of potassium tert-butoxide and to the other was added a THF (50 mL) solution of the bromoenone 88 (8.20 mmoles), prepared as described in the preceding experiment. The contents of the two funnels were added slowly (~ 0.5 h) and concomitantly to the stirred cyclopentene which was cooled to -78°C. The reaction mixture was allowed to warm to 25°C overnight, and was treated with water (10 mL). Most of the THF was removed under reduced pressure and the residue was taken up in chloroform (100 mL) and washed with water (2 x 50 mL). The chloroform solution was dried (MgSO $_{\mu}$) and filtered. The chloroform was removed under reduced pressure. Flash chromatography (8% EtOAc (CHCl₃) of the residue (0.62 g) gave 21 (15%), pentalenone $\frac{78}{28}$ (2%) and pentalenone $\frac{89}{28}$ (2%) but no indication (1 HMR) of any adduct of 19 and cyclopentene.

Kinetic measurement of the decarbonylation of endo-pentacyclo[9.6.1.0^{2,10}.0^{5,10}.0^{12,17}]octadeca-4,12(17)-diene-3,18-dione (20) and endo-pentacyclo[8.5.1.0^{2,9}.0^{5,9}.0^{11,15}]hexadeca-4,11(15)-diene-3,16-dione (21)

Sealed 5 mm NMR tubes containing ~ 0.2 M solutions of dimer (20) or (21) in deuterated benzene were heated at the desired temperature (151, 162, 173°C for 20 and 82, 97, 109°C for 21) in a constant temp bath (see Figure 4). The

tubes were periodically removed from the constant temperature bath, and immediately cooled to 25°C and analyzed by 250 MHz NMR. Six to eight analyses were made between 0 and 85% reaction. The first order rate constant calculations were performed by a least squares analysis of the data from duplicate runs and were based on the amount of starting material plus product formed for dimer 21. Due to the complexity of the isomeric product mixture from dimer (20), however, its first order decarbonylation rate constant calculations were based on remaining starting material relative to the residual protons in the deuterated benzene. The kinetic parameters for dimers (20) and (21) can be found in Tables (4) and (5).

Thermolysis of endo-pentacyclo[9.6.1. $0^{2,10}$. $0^{5,10}$. $0^{12,17}$]octadeca-4,12(17)-diene-3,18-dione (20)

A. Endo-pentacyclo[9.6.1.0^{2,10}.0^{5,10}.0^{12,17}]octadeca-4,12(17)-diene-3,18-dione (20) (0.212 g, 0.791 mmole) was placed in a 25-mL flask and heated at 205°C where it melted and evolved a gas. After 5 minutes gas evolution had ceased and the product was cooled. IR and NMR analysis of the light yellow oil showed no starting material. Purification by flash chromatography (CHCl₃) gave 1,2,5,6,7,8-hexahydrospiro[benz[f]indene-3,1'-cyclopentane]-1-one (92) (0.187 g, 93% yield) as a clear viscous oil. ¹HMR (180 MHz, CDCl₃, TMS) $\delta7.41(1H,s)$, 7.17(1H,s), 2.83(4H,m), 2.53(2H,s), 1.81(12H,m). ¹³CMR(20 MHz, CDCl₃, TMS) δ 186.45, 159.28, 145.66, 136.98, 134.34, 123.95, 123.26, 52.56, 49.46, 41.95, 30.58, 29.38, 25.02, 22.99, 22.89; IR(neat) cm⁻¹ 3015(m), 3940(s), 2870(m), 1712(vs), 1619(s), 1578(w), 1485(w), 1455(m), 1438(m), 1410(w), 1336(w), 1320(m), 1288(w), 1258(m), 1230(w), 1195(w), 1162(w), 1113(m), 1062(w), 978(w), 950(w), 928(m), 875(w), 822(w), 757(m); M.S. (C.I.) m/e (rel. int.) 241(100,M⁺+1), 240(52,M⁺), 212(43), 211(20), 199(55), 198(87), 183(29), 170(35), 169(20), 155(33), 153(23), 152(22), 142(31), 141(92), 129(39), 128(61), 115(70), 91(25), 42(39), 41(63), 39(53); UV (CH₃CN) $\lambda_{max}(\epsilon)$ 254 nm (11,400), 300(3,380), 330(225).

<u>Anal</u>. Calcd. for C₁₇H₂₀O: C, 84.95; H, 8.39 Found: C, 85.04; H, 8.39.

B. A sealed 5-mm NMR tube containing a ~ 0.2 M solution of 20_{Λ} in C_6D_6 was heated at 173°C during a kinetic run. After about 80% conversion there were an additional nine peaks in the region $\delta 6.0$ to 8.0 of the 250 MHz ¹HMR spectrum; $\delta 7.70$, 7.00, 6.75, 6.10, 5.94, 5.81 (20, vinyl proton), 5.74, 5.66, 5.61 and 5.48. The peaks at $\delta 5.94$, 5.74 and 5.61 are similar in shape to the vinyl proton peaks in the 250 MHz ¹HMR of 20 (derived from 21) at $\delta 6.12$, 5.89 and 5.31, suggesting the presence of the expected 21 (see Figure 5). When the same solution was heated to 195°C for 12 h only two peaks remained in that region other than C_6D_5H ($\delta 7.70$ and 7.00). These peaks were also observed in mixture before heating at 195°C. When the deuterated benzene was replaced with deuteriochloroform a 1 HMR spectrum was obtained which was identical to that obtained for 22 above.

Thermolysis of endo-pentacyclo[$8.5.1.0^2, 9.0^5, 9.0^{11,15}$]hexadeca-4,11(15)-diene-3,16-dione (21)

The sealed 5 mm NMR tubes containing v0.2 M solution of 21 in $C_6 D_6$ used for the decarbonylation kinetic studies were heated at the temperatures at which the kinetic measurements were made until no trace of starting material could be observed by NMR. The resulting 250 MHz ¹HMR was consistent in all cases with a quantitative conversion to the expected tetracyclo[10.3.0.0^{1,9}.0^{3,7}]-pentadeca-2,7,11trien-10-one (90). The contents of the tubes were combined, the solvent was removed under reduced pressure and the light yellow oil was characterized after passing through a short column (SG/CHCl₃). ¹HMR (250 MHz, C₆D₆) δ6.12(1H,m), 5.89(1H,s), 5.29(1H,s), 2.91(1H,m), 2.60-0.9 12H,m). ¹³CMR (20 MHz, CDC1₃, TMS) 212.46, 192.63, 139.69, 124.69, 118.24, 114.62, 56.51, 56.13, 39.81, 31.45, 31.12, 25.23, 24.86, 22.49. IR (thin film) cm⁻¹ 2940(s), 2860 (m,sh), 1690(vs), 1620(s), 1425(m), 1368(w), 1300(m), 1237(m), 1205(w), 1148(m), 1047(w), 896(w), 843(m), 830(sh), 783(m). M.S. m/e (rel. int.) 213(9), 212(40), 211(13), 184(90), 183(26), 171(21), 170(66), 169(43), 168(27),

155(64), 153(22), 142(25), 141(73), 129(41), 128(63), 128(21), 117(75), 116(32), 115(100), 91(62), 78(22), 77(51), 67(22), 65(20), 53(21), 41(26), 39(38).

Exact Mass. Calcd for C₁₅H₁₆O: 212.12012. Found: 212.11998.

APPENDIX

APPENDIX 1

Single Crystal X-ray Bond Lengths, Bond Angles and Positional Parameters for 20 and 21

Fractional Atomic Coordinates for 20 $_{\rm VV}$

Atom	Х	Y	Z
C(1) C(2) C(3) C(4) C(5) C(6) C(7) C(8) C(9) C(10) C(11) C(12) C(12) C(13) C(14A) C(14B) C(15A) C(15B) C(15	.209045 .084618 058502 163796 101006 170266 136739 .023697 .086741 .059051 .165376 .126755 .060778 .067060 007979 .091185 .030546 .118774 .153356 .295018 078578 .417588 .25279 .102115 263396 268485 169842 169842 159895 .022930 .077477 .026455 203291	.746024 .746225 .780163 .705689 .630417 .539880 .516378 .519890 .615572 .643522 .594025 .615228 .550126 .596724 .601066 .671918 .698922 .750961 .704170 .662213 .855429 .651893 .794750 .774480 .712321 .542310 .495828 .549235 .451856 .508482 .477050 .658392 .619025	.237258 .136984 .192610 .183528 .136510 .105229 037431 065560 036203 .104635 .199793 .339011 .435775 .571624 .550303 .599398 .567817 .487339 .362506 .189955 .239193 .154935 .262383 .065696 .208444 .121122 .168105 0883533 060296 156001 .004418 092366 071503
H(11) H(131) H(132)	.176150 .137339 050539	.526755 .504228 .517332	.183785 .455041 .392599

Atom	Х	Y	Z
H(161) H(162) H(14A1) H(14A2) H(14B1) H(14B2) H(15A1) H(15A2) H(15B1) H(15B2)	.028889 .200596 .169038 001740 024632 103031 .182200 .040706 .028278 075914	.787736 .772877 .590605 .564046 .557161 .628321 .645702 .703389 .726065 .705358	.480116 .511231 .608247 .632751 .624658 .524100 .622804 .673541 .656574 .531077

Fractional Atomic Coordinates for 20 - Continued.

Atoms	Distance S.D.	Atoms	Distance S.D.
$\begin{array}{ccccc} C(1) & C(1) \\ C(17) & C(1) \\ C(18) & C(1) \\ H(1) & C(1) \\ C(3) & C(2) \\ C(10) & C(2) \\ H(2) & C(2) \\ C(4) & C(3) \\ O(19) & C(3) \\ C(5) & C(4) \\ H(4) & C(4) \\ C(6) & C(5) \\ C(10) & C(5) \\ C(10) & C(5) \\ C(7) & C(6) \\ H(61) & C(6) \\ H(61) & C(6) \\ H(62) & C(6) \\ C(8) & C(7) \\ H(71) & C(7) \\ H(72) & C(7) \\ C(9) & C(8) \\ H(81) & C(8) \\ H(81) & C(8) \\ H(82) & C(8) \\ C(10) & C(9) \\ H(91) & C(9) \\ H(92) & C(9) \\ C(11) & C(10) \\ C(12) & C(11) \\ C(12) & C(11) \\ C(12) & C(11) \\ C(13) & C(12) \\ C(14B) & C(13) \\ H(131) & C(13) \\ H(132) & C(14A) \\ C(15A) & C(14A) \\ C(15B) & C(14A) \\ H(14B1) & C(14A) \\ H(14B1) & C(14A) \\ H(14B2) & C(14A) \\ H(14B1) & C(14B) \\ H(14B1) & C(14$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(15B) C(14B) H(14A1) C(14B) H(14A2) C(14B) H(14B1) C(14B) H(14B2) C(14B) H(14B2) C(14B) C(15B) C(15A) C(16) C(15A) H(15A1) C(15A) H(15A1) C(15A) H(15B1) C(15A) H(15B1) C(15A) H(15B2) C(15A) H(15B2) C(15B) H(15A1) C(15B) H(15A1) C(15B) H(15B1) C(15B) H(15B1) C(15B) H(15B2) C(15B) H(15B2) C(15B) H(15B2) C(15B) H(15B2) C(15B) H(15B2) C(15B) H(161) C(16) H(162) C(16) H(162) C(16) H(162) H(161) H(162) H(161) H(122) H(161) H(15A2) H(161) H(15A2) H(161) H(15A2) H(14A1) H(14B2) H(14A1) H(14B2) H(14A2) H(14B2) H(14B1) H(14B2) H(14B1) H(15B2) H(14B2) H(15B2) H(14B2) H(15B2) H(15A1) H(15B2) H(15B1) H(15B2) H(15B1) H(15B2) H(15B1) H(15B2) H(15B1)	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
Bond Angles for 20

Bond Angles for 20 - Continued.

Atom 1	Atom 2	Atom 3	Angle	S.D.
Atom 1 C(15A) C(15A) C(15B) C(15B) C(15B) C(15B) C(15B) C(15B) H(14A1) H(14A1) H(14A1) H(14A1) H(14A1) H(14A2) H(14A2) H(14A2) H(14A2) H(14A2) H(14B1) H(14B1) H(14B1) H(14B2) C(13) C(13) C(13) C(13) C(13) C(13) C(13) C(13) C(13) C(13) C(13) C(13) C(13) C(13) C(13) C(13) C(14A) C(14A) C(14A) C(14A) C(14A) C(15A)	Atom 2 C(14A) C(14A) C(14A) C(14A) C(14A) C(14A) C(14A) C(14A) C(14A) C(14A) C(14A) C(14A) C(14A) C(14A) C(14A) C(14A) C(14A) C(14B)	Atom 3 H(14B2) H(15A1) H(15A1) H(14A1 H(14A2) H(14B1) H(14B2) H(15A1) H(14B2) H(14B2) H(14B2) H(14B2) H(14B2) H(14B2) H(14B2) H(15A1) H(15A1) H(15A1) H(15A1) C(15A) C(15B) H(14A1) H(14B2) H(15A1) H(14B2) H(Angle 89.31 42.84 107.32 109.92 109.93 61.74 70.77 107.71 116.89 168.40 36.60 10.56 66.67 129.51 132.15 78.37 110.66 117.69 80.52 111.23 109.57 110.37 120.74 50.95 79.74 2.47 69.19 81.91 161.42 118.22 29.63 50.58	S.D. .01 .01 .00 .01 .00 .01 .00 .02 .02 .02 .02 .02 .02 .02
C(15A) C(15A) C(15A) C(15A) C(15B) C(15B)	C(14B) C(14B) C(14B) C(14B) C(14B) C(14B) C(14B)	H(14A2) H(14B1) H(14B2) H(15B2) H(14A1) H(14A2)	93.16 106.41 110.66 67.96 79.68 113.74	.02 .02 .02 .02 .02 .01
C(15B) C(15B) C(15B) H(14A1) H(14A1)	C(14B) C(14B) C(14B) C(14B) C(14B) C(14B)	H(14B1) H(14B2) H(15B2) H(14A2) H(14B1	123.86 81.68 38.56 67.11 79.97	.02 .01 .01 .01 .01

Bond Angles for 20 - Continued.

Atom 1	Atom 2	Atom 3	Angle	S.D.
Atom 1 H(14A1) H(14A1) H(14A2) H(14A2) H(14A2) H(14B1) H(14B1) H(14B1) H(14B1) H(14B1) H(14B2) C(14A) C(14A) C(14A) C(14A) C(14A) C(14A) C(14A) C(14A) C(14A) C(14B) C(14B) C(14B) C(14B) C(14B) C(14B) C(14B) C(14B) C(14B) C(14B) C(14B) C(14B) C(15B) C(15B) C(15B) C(15B) C(15B) C(15B)	Atom 2 C(14B) C(14B) C(14B) C(14B) C(14B) C(14B) C(14B) C(14B) C(14B) C(15A)	Atom 3 H(14B2) H(15B2) H(14B1) H(14B2) H(15B2) H(15B2) H(15B2) H(15B2) C(14B) C(15B) C(16) H(14A1) H(15A2) H(15B1) H(15A2) H(15B1) H(15A2) H(15A1) H(15A2) H(15B1) H(15A1) H(15A1) H(15A2) H(15B1) H(15B1) H(15B1) H(15B1) H(15B2)	Angle 161.24 118.23 14.08 119.50 128.00 109.07 128.16 43.20 29.11 104.48 121.50 45.70 81.19 122.33 133.54 89.95 76.42 110.46 74.75 110.28 107.39 110.67 61.20 56.44 148.60 165.28 75.32 59.11 16.18	S.D. .01 .01 .00 .01 .01 .01 .01 .0
C(16) C(16) C(16) C(16) C(16)	C(15A) C(15A) C(15A) C(15A) C(15A)	H(14A1) H(15A1) H(15A2) H(15B1) H(15B2)	124.46 108.94 106.20 87.17	.01 .01 .02 .02
H(14A1) H(14A1) H(14A1) H(14A1) H(15A1) H(15A1) H(15A1) H(15A2) H(15A2) H(15B1)	C(15A) C(15A) C(15A) C(15A) C(15A) C(15A) C(15A) C(15A) C(15A) C(15A) C(15A)	H(15A1) H(15A2) H(15B1) H(15B2) H(15B2) H(15B1) H(15B2) H(15B1) H(15B2) H(15B2)	35.55 125.44 144.96 135.48 113.49 126.41 168.93 19.69 76.88 64.63	.00 .01 .01 .02 .01 .00 .00 .02 .02

Bond Angles for 20 - Continued.

Atom 1	Atom 2	Atom 3	Angle	S.D.
C(14A) $C(14A)$ $C(14A)$ $C(14A)$ $C(14A)$ $C(14A)$ $C(14A)$ $C(14A)$ $C(14B)$ $C(15A)$ $C(15A)$ $C(15A)$ $C(16)$ $C(16)$ $C(16)$ $C(16)$ $C(16)$ $H(161)$ $H(161)$ $H(161)$ $H(161)$ $H(161)$ $H(14B2)$ $H(14B2)$ $H(14B2)$ $H(14B2)$ $H(14B2)$ $H(15A1)$ $H(15$	C(15B) C(15	C(14B) C(15A) C(16) H(161) H(15A1) H(15A1) H(15B2) C(15A) C(16) H(161) H(15B2) C(16) H(15B1)	27.75 47.01 115.06 144.90 64.06 50.41 90.82 11.74 107.43 73.94 126.60 136.09 36.30 78.03 101.45 19.38 79.73 96.52 132.96 109.49 8.20 62.69 80.22 152.26 38.16 127.59 88.39 120.74 109.90 106.21 125.20 101.42 102.42 121.24 101.21 73.31 114.22 115.66 43.50 67.98 82.95 157.71 20.97	.61 .93 .88 2.55 .02 .00 .00 .01 .00 1.05 .78 2.31 .01 .01 .00 .01 .01 .01 .01 .02 .02 .01 .02 .02 .01 .02 .02 .02 .02 .02 .02 .02 .02 .02 .02

Bond Angles for 20 - Continued.

Atom 1Atom 2Atom 3AngleS.D. $H(15A2)$ $C(15B)$ $H(15B2)$ 115.54 .01 $H(15B1)$ $C(15B)$ $H(15B2)$ 105.91 .01 $C(15A)$ $C(16)$ $C(15B)$ 27.04 .49 $C(15A)$ $C(16)$ $C(17)$ 108.17 .59 $C(15A)$ $C(16)$ $H(161)$ 107.81 3.56 $C(15A)$ $C(16)$ $H(162)$ 101.39 3.24 $C(15B)$ $C(16)$ $H(162)$ 103.99 3.24 $C(15B)$ $C(16)$ $H(161)$ 81.74 3.48 $C(15B)$ $C(16)$ $H(161)$ 81.74 3.48 $C(15B)$ $C(16)$ $H(161)$ 111.33 3.58 $C(17)$ $C(16)$ $H(162)$ 123.52 6.95 $C(17)$ $C(16)$ $H(162)$ 123.52 6.95 $C(1)$ $C(17)$ $C(16)$ 128.23 .39 $C(12)$ $C(17)$ $C(16)$ 128.23 .39 $C(12)$ $C(17)$ $C(16)$ 124.10 .36 $C(1)$ $C(17)$ $C(16)$ 124.10 .36 $C(1)$ $C(18)$ $C(11)$ 95.66 .33 $C(1)$ $C(18)$ $C(20)$ 132.98 .39					
H(15A2) $C(15B)$ $H(15B2)$ 115.54 .01 $H(15B1)$ $C(15B)$ $H(15B2)$ 105.91 .01 $C(15A)$ $C(16)$ $C(15B)$ 27.04 .49 $C(15A)$ $C(16)$ $C(17)$ 108.17 .59 $C(15A)$ $C(16)$ $H(161)$ 107.81 3.56 $C(15A)$ $C(16)$ $H(162)$ 101.39 3.24 $C(15B)$ $C(16)$ $H(162)$ 101.39 3.24 $C(15B)$ $C(16)$ $H(161)$ 81.74 3.48 $C(15B)$ $C(16)$ $H(161)$ 81.74 3.48 $C(15B)$ $C(16)$ $H(162)$ 123.32 3.36 $C(17)$ $C(16)$ $H(162)$ 123.52 6.95 $C(17)$ $C(16)$ $H(162)$ 123.52 6.95 $C(1)$ $C(17)$ $C(12)$ 107.43 .35 $C(1)$ $C(17)$ $C(16)$ 128.23 .39 $C(12)$ $C(17)$ $C(16)$ 124.10 .36 $C(1)$ $C(18)$ $C(11)$ 95.66 .33 $C(1)$ $C(18)$ $O(20)$ 132.98 .39	Atom 1	Atom 2	Atom 3	Angle	S.D.
C(11) C(18) O(20) 131.35 .36	H(15A2) H(15B1) C(15A) C(15A) C(15A) C(15B) C(15B) C(15B) C(15B) C(17) C(17) H(161) C(17) H(161) C(1) C(1) C(1) C(1) C(1) C(1) C(1)	C(15B) C(15B) C(16) C(16) C(16) C(16) C(16) C(16) C(16) C(16) C(16) C(16) C(16) C(17) C(17) C(17) C(17) C(17) C(18) C(18) C(18)	H(15B2) H(15B2) C(15B) C(17) H(161) H(162) C(17) H(161) H(162) H(162) H(162) H(162) C(12) C(12) C(16) C(12) C(16) C(11) O(20) O(20)	115.54 105.91 27.04 108.17 107.81 101.39 112.74 81.74 123.32 111.33 103.51 123.52 107.43 128.23 124.10 95.66 132.98 131.35	.01 .01 .49 .59 3.56 3.24 .66 3.48 3.36 3.58 3.55 3.155 .359 .359 .359 .359 .359 .359 .359 .3

Bond Angles for 20 - Continued.

Atom	Х	Y	Z
C(1) C(2) C(3) C(4) C(5) C(6) C(7) C(8) C(10) C(12) C(12) C(12) C(12) C(12) C(12) C(14) C(15) C(16) C(17) O(18) H(11) H(21) H(41) H(61) H(62) H(71) H(62) H(71) H(72) H(81) H(121) H(121) H(122) H(131) H(142) H(141) H(142) H(141) H(142) H(142) H(141) H(142) H($\begin{array}{c}100286\\051214\\094774\\009805\\ .075384\\ .187340\\ .239306\\ .152887\\ .061803\\ .064732\\011283\\009646\\124239\\186294\\106284\\003760\\183763\\ .013199\\158875\\056250\\017466\\ .208458\\ .201742\\ .277055\\ .281640\\ .134683\\ .166942\\ .129656\\ .027603\\ .024819\\142007\\149617\\236817\\233393\end{array}$.188385 .111577 .144226 .190892 .196401 .210520 .126309 .066798 .157773 .268179 .368169 .498393 .528247 .413295 .323682 .205500 .129768 .178773 .150604 .024197 .203997 .298003 .190851 .051127 .177055 - $.020229$.053306 .295141 .501409 .556222 .547766 .599074 .427456 .379898	.359223 .240417 .074543 .002044 .102268 .098044 .230021 .302103 .259373 .378008 .313898 .252790 .203408 .238515 .305516 .480541 .015659 .612687 .391847 .251683 099571 .121302 .003407 .186700 .316886 .256300 .413412 .428587 .161866 .328687 .098904 .269482 .297943 .153002

Fractional Atomic Coordinates for 22



Bond Lengths for 21

Bond	Angles	for	Zł
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Atom 1	Atom 2	Atom 3	Angle	S.D.
C(2) C(2) C(2) C(15) C(15) C(15) C(11) C(1) C(1) C(1) C(1) C(1) C(1) C(C(1) C(1) C(1) C(1) C(1) C(2) C(3) C(3) C(4) C(5) C(5) C(6) C(6) C(6) C(6) C(7) C(7) C(7) C(7) C(7) C(7) C(7) C(7) C(7) C(7) C(7) C(7) C(8)	C(15) C(16) H(11) C(16) H(11) H(11) C(3) C(9) H(21) C(9) H(21) C(9) H(21) C(4) O(17) C(5) H(41) H(41) C(6) C(9) C(7) H(61) H(62) H(61) H(62) H(62) H(61) H(62) H(62) H(71) H(72) H(71) H(72) H(72) H(72) H(81) H(82) H(106.80 98.36 115.76 95.92 119.32 117.13 113.65 105.24 105.24 103.58 107.76 112.62 107.73 124.67 127.57 110.46 121.51 127.68 136.71 113.43 108.90 103.98 109.76 110.95 108.20 115.55 108.26 106.40 107.80 112.72 110.03 104.75 114.79 104.18 109.85 110.93 105.25 104.33	$\begin{array}{c} .33\\ .31\\ 1.91\\ .32\\ 1.82\\ 1.92\\ 1.82\\ 2.33\\ 2.004\\ 2.33\\ 2.004\\ 2.33\\ 2.004\\ 2.33\\ 2.004\\ 2.33\\ 2.004\\ 2.33\\ 2.004\\ 2.33\\ 2.10\\ .43\\ 2.10\\ .44\\ 2.551\\ 2.5974\\ 0.22\\ 2.5\\ 2.668\\ 4.24\\ 2.08\\ 2.22\\ 2.5\\ 2.668\\ 4.24\\ 2.08\\ 1.83\\ 2.10\\ .44\\ 1.83\\ 2.55\\ 2.26\\ 2.668\\ 4.24\\ 2.08\\ 1.83\\ 2.10\\ .44\\ 1.83\\ 2.55\\ 2.26\\ 2.668\\ 4.24\\ 2.08\\ 1.83\\ 2.10\\ 1.83\\ 2.10\\ 1.83\\ 2.10\\ 1.83\\ 2.10\\ 1.83\\ 2.10\\ 1.83\\ 2.10\\ 1.83\\ 1.83\\ 1.91\\ 1.91\\ 1$
C(2) C(5)	C(9) C(9) C(9)	C(10) C(8)	102.93	• 30 • 31 • 34

Atom l	Atom 2	Atom 3	Angle	S.D.
C(8) C(9) C(9) C(11) C(11) C(11) C(10) C(10) C(10) C(12) C(11) C(11) C(11) C(11) C(11) C(12) C(1	$\begin{array}{c} C(9)\\ C(10)\\ C(10)\\ C(10)\\ C(10)\\ C(10)\\ C(10)\\ C(10)\\ C(11)\\ C(11)\\ C(11)\\ C(12)\\ C(13)\\ C(13)\\ C(13)\\ C(13)\\ C(14)\\ C(14)\\ C(14)\\ C(14)\\ C(14)\\ C(14)\\ C(15)\\ C(15)\\ C(15)\\ C(16)\\ C(1$	$\begin{array}{c} C(10)\\ C(11)\\ C(16)\\ H(101)\\ C(16)\\ H(101)\\ H(101)\\ C(12)\\ C(15)\\ C(15)\\ C(15)\\ C(15)\\ C(15)\\ C(15)\\ H(121)\\ H(122)\\ H(122)\\ H(122)\\ H(122)\\ H(122)\\ H(131)\\ H(132)\\ H(131)\\ H(132)\\ H(14)\\ H(142)\\ H(14)\\ H(142)\\ H(14)\\ H(142)\\ H(14)\\ H(142)\\ H(14)\\ H(14$	111.80 109.29 97.09 117.62 96.10 117.62 115.30 138.01 109.63 112.30 102.83 111.03 111.62 110.62 113.33 107.44 108.31 113.52 112.43 108.73 103.05 110.20 102.87 116.56 115.45 114.26 115.45 114.05 94.30 108.61 137.52 113.70 97.95 131.32 130.73	$\begin{array}{c} .38\\ .31\\ .30\\ 1.64\\ .30\\ 1.63\\ .369\\ 1.63\\ .37\\ .41\\ .379\\ 2.229\\ 2.2222\\ 2.222\\ 2.222\\ 2.2222\\ 2.222\\ 2.222\\ 2.2222\\ 2.222\\ 2.$

Bond Angles for 21 - Continued.

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REFERENCES

REFERENCES

- P. A. Waitkus, E. B. Sanders, L. I. Peterson, and
 G. W. Griffin, J. Amer. Chem. Soc., 89, 6318 (1967).
- 2. G. W. Griffin and L. I. Peterson, <u>ibid.</u>, <u>84</u>, 3398 (1962).
- 3a. A. J. Barkovich, E. S. Strauss and K. P. C. Vollhardt, <u>ibid</u>., 22, 8321 (1977).
- 3b. P. Schiess and M. Heitzmann, <u>Helv. Chim. Acta.</u>, <u>61</u>, 844 (1978).
- 3c. L. G. Haruff, M. Brown and V. Boekelheide, J. Amer. Chem. Soc., 100, 2893 (1978).
- 4. G. Köbrich and E. Heinemann, <u>Angew. Chem. Int. Ed.</u> Engl., 4, 594 (1965).
- 5. Private communication from Professor Fumio Toda, Ehime University, Matsuyama, Japan.
- 6. H. Hopf and A. K. Wick, <u>Helv. Chim. Acta.</u>, 44, 380 (1961).
- 7. H. Hopf and A. Gati, ibid., 48, 1289 (1965).
- 8. M. Sasaoka and H. Hart, <u>J. Amer. Chem. Soc</u>., 100, 4326 (1978).
- 9a. Unreported result of Dr. A. Sy while a postdoctoral student of H. Hart, Michigan State University.
- 9b. M. B. Stringer and D. Wege, <u>Tetrahedron Lett.</u>, 3831 (1980).
- 9c. J. H. Gall, C. J. Gilmore and D. D. MacNicol, <u>J. C. S.</u> Chem. Comm., 927 (1979).
- 10. M. J. S. Dewar and G. J. Gleicher, <u>J. Amer. Chem. Soc.</u>, <u>87</u>, 692 (1965).
- 11. For a review of cyclopentadienones see: M. A. Ogliaruso, M. G. Romanelli and E. I. Becker, Chem. Rev., 65, 261 (1965).

- 12. O. L. Chapman and C. L. McIntosh, <u>Chem. Comm</u>., 770 (1971).
- 13. P. A. Baron and R. D. Brown, <u>Chem. Phys.</u>, 1, 444 (1973).
- 14a. K. Ziegler and B. Schnell, Ann., 445, 266 (1925.
- 14b. G. Maier and S. Pfriem, <u>Angew. Chem. Int. Ed. Engl.</u>, 17, 519 (1978).
- 15. F. R. Japp and C. I. Burton, J. Chem. Soc., 420 (1887).
- 16. C. F. H. Allen and J. A. VanAllan, <u>J. Amer. Chem. Soc.</u>, 72, 5165 (1950).
- 17. G. Maier and F. Bosslet, Tetrahedron Lett., 1025 (1972).
- 18. W. Dilthey, I. terHorst and W. Schommer, <u>J. Prakt</u>. <u>Chem</u>., 143, 189 (1935).
- 19. C. F. H. Allen and J. A. VanAllan, <u>J. Org. Chem</u>., <u>17</u>, 845 (1952).
- 20a. J. M. Holland and D. W. Jones, Chem. Comm., 587 (1969).
- 20b. J. M. Holland and D. W. Jones, <u>J. Chem. Soc. (C)</u>, 608 (1971).
- 20c. A. Hassner and D. J. Anderson, <u>J. Amer. Chem. Soc.</u>, <u>94</u>, 8255 (1972).
- 21. K. Yates, "Hückel Molecular Orbital Theory", Academic Press, New York, 1978, p. 27.
- 22. R. Hoffmann, J. Chem. Phys., 32, 1397 (1963).
- 23. Unpublished computer program.
- 24. F. R. Ahmed and J. Trotter, <u>Acta. Cryst</u>., 16, 503 (1963).
- 25. J. K. Fawcett and J. Trotter; ibid, 20, 87 (1966).
- 26. W. Reusch, "An Introduction to Organic Chemistry", Holden-Day, Inc., San Francisco, 1977, p. 110.
- 27. B. Bak, L. Hansen-Nygaard and J. Rastrup-Andersen, <u>Disc. Far. Soc</u>., 19, 30 (1955).

- B. Bak, D. Christensen, L. Hansen-Nygaard and J. Rastrup-Andersen, <u>J. Molecular Spectroscopy</u>, ζ, 58-63 (1961).
- 29. H. A. Skinner and H. O. Pritchard, <u>Trans. Far. Soc.</u>, 49, 1245 (1953).
- 30. W. G. Dauben, J. W. McFarland and J. B. Rogan, <u>J. Org</u>. <u>Chem</u>., 26, 297 (1961).
- 31. A. M. Islam and R. A. Raphael, <u>J. Chem. Soc</u>., 4086 (1952).
- 32a. R. Joly, J. Warnant, G. Nominé, and D. Bertin, <u>Bull</u>. <u>Soc. Chim. Fr.</u>, 366 (1958).
- 32b. P. L. Stotter and K. A. Hill, <u>J. Org. Chem</u>., <u>38</u>, 2576 (1973).
- 33a. E. W. Garbisch, Jr., <u>J. Org. Chem</u>., <u>30</u>, 2109, 1965.
- 33b. H. M. R. Hoffmann and J. G. Vinter, <u>ibid</u>, 39, 3921 (1974).
- 34. A. B. Smith, Synthetic Communications, 5, 435 (1975).
- 35. H. O. House, L. J. Czuba, M. Gall and H. D. Olmstead, <u>J. Org. Chem</u>., 34, 2324 (1969).
- 36. H. O. House, M. Gall and H. D. Olmstead, <u>ibid</u>, <u>36</u>, 2361 (1971).
- 37. H. J. Reich, J. M. Renga and I. L. Reich, <u>J. Am. Chem.</u> <u>Soc.</u>, <u>97</u>, 5434 (1975).
- 38. B. M. Trost, T. N. Salzmann and K. Hiroi, <u>ibid</u>, 4887 (1976).
- 39. A third technique for preparing α -bromoketones is a base promoted reaction using a quaternary ammonium tribromide salt as the source of Br_2^{40} . This methodology was not investigated in this study.
- 40a. D. V. C. Awang and S. Wolfe, <u>Can. J. Chem</u>., 47, 706 (1969).
- 40b. L. A. Paquette, R. H. Meisinger and R. E. Wingard, Jr., J. Am. Chem. Soc., 95, 2230 (1973).
- 40c. M. Fetlzon, M. Jurion and A. Nguyen Trong, Organic Preparation and Preparations Int., 6, 31 (1974).

- 41. J. C. Stickler and W. H. Pirkle, <u>J. Org. Chem</u>., 31, 3444 (1966).
- 42. M. E. Jung, Y. G. Pan, M. W. Rathke, D. F. Sullivan and R. P. Woodbury, <u>ibid</u>., <u>42</u>, 3961 (1977).
- 43. K. Hafner and K. Wagner, <u>Angew. Chem. Internat. Edit.</u>, 2, 740 (1963).
- 44. G. R. Newkome and D. L. Fishel, <u>J. Org. Chem</u>., <u>31</u>, 677 (1966).
- 45. C. H. DePuy, M. Isaks, K. L. Eilers and G. F. Morris, J. Org. Chem., 3503 (1964).
- 46. P. Laszlo and P. V. R. Schleyer, J. Am. Chem. Soc., §6, 1171 (1964).
- 47a. M. Miyashita, T. Yanami and A. Yoshikoshi, <u>J. Am.</u> <u>Chem. Soc</u>., <u>28</u>, 4679 (1976).
- 47b. Private communication from S. Danishefsky.
- 47c. Private communication from J. A. Berson.
- 48. D. Becker, N. C. Brodsky and J. Kalo, <u>J. Org. Chem.</u>, 43, 2557 (1978).
- 49. B. M. Trost, D. P. Curran, <u>J. Am. Chem. Soc</u>., 102, 5699 (1980).
- 50. W. Herz, <u>J. Am. Chem. Soc</u>., 78, 1485 (1956).
- 51. M. S. Newman, J. Am. Chem. Soc., 75, 4740 (1953).
- 52. J. E. Baldwin, Can. J. Chem., 44, 2051 (1966).
- 53a. R. McCulloch, A. R. Rye and D. Wege, <u>Tetrahedron Lett</u>., 5231 (1969).
- 53b. M. Sakai, ibid., 2297 (1973).
- 53c. A. Diaz, R. Rubio, R. G. Hernandez, J. P. Daudy and R. Cetina, <u>J. Org. Chem</u>., <u>45</u>, 150 (1980).
- 54a. B. Halton, M. A. Battiste, R. Rehberg, C. L. Deyrup and M. E. Brennan, J. Am. Chem. Soc., 89 5964 (1967).
- 54b. J. M. Landesberg and J. Sieczkowski, <u>J. Am. Chem. Soc</u>., 91, 2120 (1969).

- 54c. S. C. Clark and B. L. Johnson, <u>Tetrahedron</u>, 27, 3555 (1971).
- 54d. K. Kurabayashi and T. Mukai, <u>Tetrahedron Lett.</u>, 1049 (1972).
- 54e. G. Kretschmer, I. W. McCay, M. M. Paddon-Row and R. N. Warrener, <u>ibid</u>., 1339 (1975).
- 55. An updated version of a program published by J. L. Dye and V. A. Nicely, <u>J. Chem. Ed.</u>, <u>48</u>, 443 (1971).
- 56. Professor J. L. Dye is a Professor of Physical Chemistry at Michigan State University and is responsible for the development of KINFIT4.55
- 57. S. Yankelevich and B. Fuchs, <u>Tetrahedron Lett.</u>, 4945 (1967).
- 58. K.-T. Wei and D. L. Ward, <u>Acta Crystallographica</u>, <u>B32</u>, 2768 (1976).
- 59. P. Main, "MULTAN78 A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data", Univ. York, England (1978).
- 60. A. Zalkin, Private communication (1974).
- 61. W. C. Still, M. Kahn and A. Mitra, <u>J. Org. Chem</u>., <u>4</u>3, 2923 (1978).



