#### PART I

THE PHOTOREARRANGEMENT OF 1,3,3,4,5,6 · HEXAMETHYLBICYCLO[2,2,2] OCT · 5 · ENE · 2,7 · AND · 2,8 · DIONE

#### PART II

THE SYNTHESIS AND LOW TEMPERATURE NMR SPECTRUM OF 1,4-DIETHYL-2,3,5,6,7,8-HEXAMETHYLNAPHTHALENE

> Thesis for the Degree of Ph. D. MICHIGAN STATE UNIVERSITY MICHAEL PETSCHEL, JR. 1969

THESIS

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This is to certify that the

#### thesis entitled

PART I. The Photorearrangement of 1,3,3,4,5,6-Hexamethylbicyclo[2.2.2]oct-5-ene-2,7- and -2,8-dione.

PART II. The Synthesis and Low Temperature Nmr Spectrum of 1,4-Diethy1-2,3,4,5,6,7-hexamethylnaphthalene.

presented by

Michael Petschel, Jr.

has been accepted towards fulfillment of the requirements for

Ph.D. Chemistry

Major professor

9/22/69 Date\_\_\_\_\_

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#### ABSTRACT

#### PART I

THE PHOTOREARRANGEMENT OF 1,3,3,4,5,6-HEXAMETHYLBICYCLO[2.2.2]OCT-5-ENE-2,7- AND -2,8-DIONE

### PART II

THE SYNTHESIS AND LOW TEMPERATURE NMR SPECTRUM OF 1,4-DIETHYL-2,3,5,6,7,8-HEXAMETHYLNAPHTHALENE

By

Michael Petschel, Jr.

In the first part of this thesis the photochemistry of 1,3,3,4,5,6hexamethylbicyclo[2.2.2]oct-5-ene-2,7- and 2,8-dione (39 and 40) was investigated.



Irradiation of ether solutions of 39 provided only one product, while similar irradiation of ether solutions of 40 gave rise to five products. The single product arising from 39 has been identified as 1,2,4,4,5,8-hexamethyltricyclo[3.3.0<sup>2</sup>,<sup>8</sup>]octane-3,7-dione (48). The photoproduct 48 is most probably formed via a 1,2-acyl migration from 39.

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The five products obtained by irradiation of 40 were identified as 1,2,4,4,5,8-hexamethyltricyclo[3.3.0.0<sup>2,8</sup>]octane-3,6-dione (71), 1,2,4,6,7,7-hexamethyltricyclo[4.2.0.0<sup>2,4</sup>]octane-5,8-dione (73), 1,2,3,3,4,6-hexamethyltricyclo[4.2.0.0<sup>2,4</sup>]octane-5,8-dione (74), 1,3,3,4,7,8-hexamethylbicyclo[4.2.0]oct-7-ene-2,5-dione (62) and 1,4,6,6,7,8-hexamethylbicyclo[4.2.0]oct-7-ene-2,5-dione (70).

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Photoproducts 69 and 70 are primary photoproducts derived via a 1,3-acyl migration from 40 and are involved in a photostationary state with 40. Products 73 and 74 are secondary photoproducts derived via a 1,2-acyl migration from 69 and 70 respectively. The tricyclic 71 may arise as a primary photoproduct from 40 or a secondary photoproduct from 69 or both.

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The same products are obtained whether or not each photorearrangement is sensitized with acetone; also, both reactions are quenched by piperylene. This requires that the photoisomerizations of both 32 and 40 occur from the triplet state.

The second part of this thesis describes the synthesis of 1,4diethyl-2,3,5,6,7,8-hexamethylnaphthalene 130 and suggests an explanation for the appearance of its low temperature nmr spectrum.



At ambient temperature, the nmr spectrum of 130 contained a triplet and a quartet which indicates that the peri-interactions are not sufficient to sterically hinder rotation in the ethyl group. The time averaged equivalence of environments disappeared as the temperature was lowered and a coalescence temperature was observed at -70°. At -85° two well resolved but overlapping triplets appeared with an area ratio between 3:1 and 3:2.

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According to the nmr data, the spatial arrangement of the substituents in 130 is similar to that of octamethylnaphthalene. Based on this similarity, three conformations are considered which may give rise to the observed low temperature spectrum.

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## PART I

# THE PHOTOREARRANGEMENT OF 1,3,3,4,5,6-HEXAMETHYLBICYCLO[2.2.2]OCT-5-ENE-2,7- AND -2,8-DIONE

## PART II

# THE SYNTHESIS AND LOW TEMPERATURE NMR SPECTRUM OF 1,4-DIETHYL-2,3,5,6,7,8-HEXAMETHYLNAPHTHALENE

By

Michael Petschel, Jr.

## A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

#### DOCTOR OF PHILOSOPHY

Department of Chemistry

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1969 and June

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December, 1968



#### ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Professor Harold Hart for his enthusiasm, encouragement and guidance throughout the course of this study.

Appreciation is extended to the National Science Foundation for a pre-doctoral fellowship from December 16, 1968 to March 15, 1969 and June 16, 1969 to September 15, 1969.

Appreciation is also extended to Michigan State University for a Graduate Teaching Assistantship from September, 1966 through December, 1968 and from April, 1969 through June, 1969. TO

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# PART II

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PART I

THE PHOTOREARRANGEMENT OF

1,3,3,4,5,6-HEXAMETHYLBICYCLO[2.2.2]OCT-5-ENE-2,7- AND -2,8-DIONE

#### INTRODUCTION

 $\beta$ , $\gamma$ -Unsaturated ketones have received attention as representatives of a class of compounds in which two chromophores interact although they are not formally conjugated. Initial investigations were aimed at understanding the nature of this interaction by theoretical treatment<sup>1</sup> and by measurement of uv spectra<sup>2</sup>, circular dichroism<sup>3</sup> and optical rotatory dispersion curves<sup>4</sup> of representative compounds.

The ultraviolet spectra of  $\beta$ ,  $\gamma$ -unsaturated ketones in hexane show an enhanced n, $\pi$ \* absorption near 300 nm and a relatively intense band between 200 and 210 nm.<sup>5</sup> The transition at 210 nm is shifted toward longer wavelength in a polar solvent such as ethanol and has been identified as a charge transfer band.<sup>1</sup> In the case of  $\alpha$ , $\beta$ -unsaturated ketones this band appears around 250 nm with a somewhat greater intensity.<sup>6</sup>

The view is generally accepted<sup>7</sup> that the enhanced  $n,\pi^*$  transition is due to interaction between the  $\pi$  electrons of the carbon-carbon double bond and the non-bonding p-orbital of the carbonyl oxygen. This overlap can only take place when the  $\pi$  and lone-pair electrons have a common component in space;  $\beta,\gamma$ -unsaturated carbonyl compounds in which the lone-pair electrons and  $\pi$  electrons are orthogonal exhibit only normal absorptions.<sup>4</sup>

The charge transfer bands, according to the view of Labhart and Wagnière<sup>1</sup>, are due to the excitation of an electron from a molecular orbital resembling the bonding olefinic molecular orbital to one resembling the anti-bonding carbonyl molecular orbital. One may and does at times observe charge transfer bands without at the same time finding  $n,\pi^*$  enhancement. The 7-norbornenone  $\frac{1}{4}$  and the <u>endo-exo</u> fused ketone  $\frac{2}{4}$  are examples studied by Winstein<sup>8</sup>. In both cases the carbon-carbon double bond and the carbonyl lone-pair electrons are orthogonal and no  $n,\pi^*$  enhancement is observed; both do however show charge transfer  $\pi,\pi^*$  bands.



Recently the photochemistry of  $\beta$ ,  $\gamma$ -unsaturated ketones has been studied intensively and three rearrangement pathways have been observed. The most common of these is 1,3-acyl migration, first observed by Büchi and Burgess<sup>9</sup> during the irradiation of 1,4,4trimethylbicyclo[3.2.0]hept-6-ene-2-one,  $\beta$ . Other examples include the rearrangement of  $\xi^{10}$ ,  $\zeta^{11}$  and  $\xi^{12}$ .









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The mechanism has generally been described as a Norrish Type I cleavage to give an allyl-acyl diradical which then recombines to give either the  $\beta$ , $\gamma$ -unsaturated product or starting ketone. Recently this  $\alpha$ -fission mechanism has been questioned in an investigation of the photochemistry of 3-acetyl-1,2,3-trimethylcyclopent-1-ene  $\mathcal{H}$  by Schaffner and co-workers<sup>13</sup>. Their results suggest that the reaction proceeds in a concerted manner and they point out that the over-all reaction (for both 1,2- and 1,3-acyl migration) is a  $\sigma^2 + \pi^2$  process which is photochemically allowed<sup>14</sup>. Thus the mechanistic description of the 1,3-acyl migration is still subject to further modification.

Since the product in each case is an isomeric  $\beta$ ,  $\gamma$ -unsaturated ketone and therefore photochemcially labile, a photostationary state is attained. The equilibrium position is determined by the relative photochemical reactivity of the isomers at the incident wavelength and does not reflect the thermodynamic stability of these systems<sup>9</sup>. If a competing reaction is introduced, the photostationary state may never be seen. Such is the case with dehydronorcamphor  $\frac{12^{15}}{12^{15}}$ where further elimination of ketene leads to secondary photoproducts. Bornenones  $\frac{14a}{144}$  are converted to substituted pentadienes via bicyclo[3.2.0]hept-2-ene-7-ones which then eliminate ketene<sup>16</sup>.



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1,2-Acyl migration was first observed by Tenney and co-workers<sup>17</sup> in the acyclic  $\beta$ , $\gamma$ -unsaturated ketone 15. They observed the formation of the cyclopropyl ketone 16 in 7% yield and suggested a bicyclic oxetane intermediate to explain its formation.



When Williams and Ziffer<sup>18</sup> irradiated ketone 18 and the steroidal ketone 20 (which contains the same chromophore) they observed the first 1,2-acyl migration in a cyclic system. The multiplicity of this Particular rearrangement has not been determined but in other examples 1t has been shown by sensitization studies that the n, $\pi$ \* triplet state 1s involved<sup>19</sup>.





It has been shown that factors such as ring size, substitution, solvent or sensitization may determine the reaction pathway. From a knowledge of the photolytic behavior of 22 one may, for example, predict a similar 1,3 rearrangement for 24. This cycloheptadienone, however, shows only products resulting from a 1,2-acyl migration<sup>19</sup>. The reinvestigation of the photochemistry of dehydronorcamphor  $12_{1/2}$ shows that although the unsensitized reaction proceeds by the 1,3-acyl migration, acetone sensitization gives only the 1,2-acyl migration product<sup>20</sup>. At the present time, therefore, predictions about the preferred rearrangement pathway in any particular system under specific conditions are still difficult to make.





Decarbonylation, the third mode of reaction, has been observed in systems such as  $27^{21}$  and  $29^{22}$ . There are indications that  $\alpha$ -alkyl substitution and  $\beta$ , $\gamma$ -unsaturation facilitate ketone decarbonylation because of their ability to stabilize a biradical intermediate such as 32. Systems which are not  $\beta$ , $\gamma$ -unsaturated or  $\alpha$ -substituted, such as 33, give various rearrangement products derived from hydrogen abstraction<sup>22</sup>.



Ketones in which two  $\beta,\gamma$  double bonds may interact with the carbonyl group have been studied. Compound 34 is at once an  $\alpha,\beta$ -unsaturated and a  $\beta,\gamma$ -unsaturated ketone. Kende and co-workers<sup>23</sup> found that photolysis of 34 gives 35 which rearranges during work-up to the isolated product 36. Irradiation of 37 gives 38 directly<sup>24</sup>. In both cases the preferred path involves 1,3-acyl migration.





The bicyclic[2.2.2]oct-5-ene systems 39 and 40 provide a rigid framework in which two carbonyls can interact with one  $\beta,\gamma$ -carbon-carbon double bond and a system in which the two carbonyl groups can be related 1,3- or 1,4- to each other. These two systems thus provide an opportunity to examine the interaction of one  $\beta,\gamma$ -bond with two carbonyl groups in two geometric and bonding arrangements and their effect on the photochemistry of  $\beta$ , $\gamma$ -unsaturated ketones. As expected, the ultraviolet spectra of both compounds exhibit enhanced  $n,\pi^*$  absorption. Part I of this thesis describes the synthesis and photochemical behavior of these compounds.



#### **RESULTS AND DISCUSSION**

The Synthesis and Characterization of 1,3,3,4,5,6-Hexamethylbicyclo-A. [2.2.2]oct-5-ene-2,7-dione (39) and 1,3,3,4,5,6-Hexamethylbicyclo-[2.2.2]oct-5-ene-2,8-dione (40).

The synthetic route to the compounds 32 and 40 parallels that of Curtin and Frazer<sup>25</sup> for the formation of 1,3,3-trimethylbicyclo[2.2.2]oct-5-ene-2,7- and 2,8-dione. As outlined below, it utilizes the Diels-Alder addition of vinyl acetate to 2,3,4,5,6,6-hexamethyl-2,4cyclohexadienone 41<sup>26</sup>, alkaline hydrolysis of the acetates obtained and oxidation of the resulting keto-alcohols to diketones.



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Vinyl acetate and cyclohexadienone 41 were heated at 200° for 24 hours in a steel bomb or sealed tube to give a mixture of the four possible isomeric acetates which were purified by vacuum distillation. The mixture was analyzed by vpc and showed only two peaks in the ratio of 7:5. The infrared spectrum of the mixture showed principal bands at 1240, 1720 and 1740 cm<sup>-1</sup> indicative of the ester and ketone carbonyl functions. No further attempt was made to characterize the four possible components of the mixture. The yield of the isomers was 81%.

Hydrolysis of the acetate mixture in refluxing 10% methanolic potassium hydroxide for 5 hours gave a mixture of the isomeric alcohols 43a and 43b which were purified by distillation. The mixture showed two peaks on a vpc trace in the ratio of 8:3. The infrared spectrum of the mixture showed absorptions at 1710 and 3500 cm<sup>-1</sup> for the carbonyl and the alcohol functions. The yield of both isomers was 61.5%. No further attempt was made at the full characterization of the components. Unlike the 7-acetoxy-1,3,3-trimethylbicyclo[2.2.2]oct-5-ene-2-one, 44, reported by Curtin and Frazer<sup>25</sup> the analogous 44 does not rearrange in this step. This may be attributed in part to some stabilizing effect of the methyl substituents at C<sub>5</sub> and C<sub>6</sub> especially since the hydrogenated counterpart of 44 is stable to basic hydrolysis.



The mixture of keto-alcohols was dissolved in acetone and titrated with Jones' reagent<sup>27</sup> to effect oxidation to the diketones. Vacuum distillation, column chromatography and vapor phase chromatography were used to purify and separate the two isomers. The yield of the two isomers was 70% with the diketone 39 predominating 6:1 over 40.

The two isomers 32 and 40 were easily distinguished by their spectral characteristics. As noted by Curtin and Frazer<sup>25</sup> the -2,7-dione, being fully substituted in the C<sub>1</sub> position, shows two carbonyl frequencies characteristic of such systems<sup>28</sup>. In 32, these appeared at 1700 and 1725 cm<sup>-1</sup>. The -2,8-dione possessed only one slightly broadened band in the carbonyl region, at 1718 cm<sup>-1</sup>.

The 60 MHz nmr spectrum (CCl<sub>4</sub>) of 32 showed three-proton singlets at  $\tau$  9.10, 8.95, 8.87 and 8.78, three-proton quartets (J = 1 Hz) at  $\tau$  8.38 and 8.18 as well as one proton singlets at  $\tau$  7.87 and 7.82. A 100 MHz nmr spectrum (CCl<sub>4</sub>) showed the latter to be the main peaks of two doublets with a coupling constant J = 16.5 Hz.

The 60 MHz nmr spectrum (CCl<sub>4</sub>) of 40 showed three-proton singlets at  $\tau$  9.10, 9.02, 8.85 and 8.79, a six-proton singlet at  $\tau$  8.27 and a twoproton singlet at  $\tau$  7.90. The 100 MHz spectrum (CCl<sub>4</sub>) showed the latter singlet to be composed of two peaks with a chemical shift difference of only 0.02 ppm (250 Hz sweep width). When the spectrum was run with a sweep width of 100 Hz, splitting was observed for the two peaks with a coupling constant of 18.6 Hz. It has been pointed out<sup>29,30</sup> that maximum geminal coupling of protons  $\alpha$  to an unsaturated center occurs when the plane of the carbonyl bisects the CH<sub>2</sub> angle. This arrangement allows optimum hyperconjugation and the large coupling constant can be explained on

that basis. The fact that the allylic methyl groups have essentially the same chemical shift even in the 100 MHz spectrum may be due to the pseudosymmetry of the molecule (" $C_2$ " axis, except for the gem-dimethyl groups, bisecting the double bond and an imaginary line connecting the bridgehead carbons) which makes them appear enantiotopically related.

The uv spectrum of 39 in 95% ethanol showed absorption maxima at 290 nm ( $\varepsilon$  = 455), 230 nm ( $\varepsilon$  = 2530) and 204 nm ( $\varepsilon$  = 4450). Its isomer 40 showed uv maxima in 95% ethanol at 304 nm ( $\varepsilon$  = 294), 248 nm ( $\varepsilon$  = 132) and 236 nm ( $\varepsilon$  = 161). In cyclohexane these compounds feature the same intense quadruplet near 288, 297, 307 and 317 nm which has been recognized as characteristic of the enhanced n,  $\pi$ \* transition in  $\beta$ ,  $\gamma$ -benzoketones<sup>3</sup>. The uv spectrum of 39 in cyclohexane had a maximum at 270 nm ( $\varepsilon$  = 380) with shoulders at 284 nm ( $\varepsilon$  = 290), 296 nm ( $\varepsilon$  = 160) and 312 nm ( $\varepsilon$  = 80). The uv spectrum of 40 in cyclohexane showed a maximum at 307 nm ( $\varepsilon$  = 600) with shoulders at 284 nm ( $\varepsilon$  = 370), 298 nm ( $\varepsilon$  = 450) and 319 nm ( $\varepsilon$  = 330).

The correct nmr assignments for 39 and 40 can be made if the synthetic sequence is followed using the readily available hexadienone  $45^{26}$ . Since the allylic methyl groups of 39 and 40 are already rather well defined by their chemical shift and coupling constant, there is no problem identifying these in the final products even though the doubly labeled dienone is used.



Doubly-labeled 3,5-dimethyl-d<sub>3</sub>-2,4,6,6-tetramethyl-2,4-cyclohexadienone  $\frac{45}{2}$  was prepared by refluxing unlabeled  $\frac{41}{2}$  in CH<sub>3</sub>OD with sodium methoxide as the base required for exchange<sup>26</sup>. Integration of the nmr peaks of the labeled product indicated that the C<sub>3</sub> and C<sub>5</sub> methyl groups were 90% exchanged. The nmr spectrum of  $\frac{46}{26}$  obtained from the labeled starting material showed a 90% reduction of the integrated signals at  $\tau$  8.38 and  $\tau$  8.78. The spectrum of  $\frac{47}{26}$  showed a 90% reduction of the signal at  $\tau$  8.85 and a 45% reduction (note that two methyl groups give rise to this signal) for that at  $\tau$  8.27. These results allow assignment of the peaks at  $\tau$  8.38 and 8.27 to the C<sub>6</sub> methyl groups in  $\frac{39}{26}$  and  $\frac{40}{26}$  respectively. The C<sub>4</sub> methyl group gives rise to the peak at  $\tau$  8.78 in the spectrum of  $\frac{32}{26}$ and to the peak at  $\tau$  8.85 in the spectrum of  $\frac{40}{20}$ . The remaining assignments are made on the basis of structural features of the molecule and a complete listing is found in Table I.

Compound	Chemical Shift (J) <sup>b</sup>	Assignments
	9.10 (s)	C-3 methyl over C=C bond
	8.95 (s)	C-3 methyl
0	8.87 (s)	C-1 methyl
3	8.78 (s)	C-4 methyl
TX	8.38 (q, 1)	C-6 methyl
67 17	20 8.18 (q, 1)	C-5 methyl
5 4 8	7.87 (d, 16.5)	C-8 methylene
22	7.82 (d, 16.5)	

Table I. NMR Spectra<sup>a</sup> of 32 and 42



<sup>a</sup>All spectra are in CCl<sub>4</sub>

<sup>b</sup>Shifts are reported in τ values and J's in Hertz. Multiplicity of peaks is shown in brackets: s, singlet; d, doublet; q, quartet.

B. The Direct and Photosensitized Irradiation of 1,3,3,4,5,6-Hexamethylbicyclo[2.2.2]oct-5-ene-2,7-dione (3%).

Irradiation of a 1% solution of 39 in ether through a Vycor filter using a Hanovia-L 450-W lamp, gave, after nine hours and 70% conversion, a single photoproduct. This same product could be obtained quantitatively after three hours when 39 was irradiated as a 1% solution in acetone through a Vycor filter. The same product was also obtained via acetophenone sensitization in ether through Pyrex. When the irradiation was carried out with a 10% solution of piperylene in ether as the solvent no rearrangement occurred. These results indicate that the reaction proceeds via the  $n,\pi^*$ triplet state. An indication of the rate in the sensitized reaction of 39 is given by the graph (Figure I).

The photoproduct was isolated by preparative vpc. It had a mp.  $84-85^{\circ}$ , and showed a slightly broadened carbonyl band in the ir spectrum at 1720 cm<sup>-1</sup>. Its elemental analysis and mass spectrum showed it to be isomeric with the



Photolysis time in minutes

FIGURE 1. Relative percentages of product and starting material in the photolysis of 1,3,3,4,5,6-hexamethylbicyclo-[2.2.2]oct-5-ene-2,7-dione (32). starting material. The nmr spectrum (CCl<sub>4</sub>) had three-proton singlets at  $\tau$  9.15, 8.98, 8.90, 8.85, 8.74 and 8.72 as well as two doublets (J = 16.5 Hz) which integrated for one proton each at  $\tau$  7.74 and 7.67.

Identification follows from the spectral data and from a consideration of the possible rearrangement pathways open to  $\beta$ ,  $\gamma$ -unsaturated ketones (see Figure 2). (The  $\alpha$ -fission mechanism is used as the accepted form although the 1,2-acyl migration products may be derived as in Section D.) Since the compound is isomeric with the starting material, decarbonylation products such as 51 and 52 can be ruled out. The absence of bands in the ir spectrum around 1780 cm<sup>-1</sup> eliminates a 1,3-acyl migration which would lead to cyclobutanones 42 and 50. 1,2-Acyl migration is the only remaining plausible pathway and should give rise to 1,2,4,4,5,6,8-hexamethyltricyclo-[3.3.0.0<sup>2</sup>,<sup>8</sup>]octane-3,7-dione 48, as indicated in Figure 2.

Further evidence supporting the structure could be obtained by the dimethylation of 48 to the symmetrical 1,2,4,4,5,6,6,8-octamethyltricyclo[3.3.0.0<sup>2,8</sup>]octane-3,7-dione 53. Compound 53 has equivalent methyl groups at C<sub>2</sub> and C<sub>8</sub>, at C<sub>4</sub> and C<sub>6</sub> and at C<sub>1</sub> and C<sub>5</sub>. This symmetrical arrangement should give an nmr pattern with areas in the ratio of 2:2:2:1:1.





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FIGURE 2. A mechanistic scheme to derive the possible products in the photorearrangement of 1,3,3,4,5,6-hexamethylbicyclo[2.2.2]oct-5-ene-2,7-dione (39).

Treatment of 48 in ether with sodium hydride and excess methyl iodide gave a product in 70% yield, mp. 174-175°, which showed bands in the ir spectrum at 1720 and 1740 cm<sup>-1</sup>. The nmr spectrum (CCl<sub>4</sub>) consisted of six-proton singlets at  $\tau$  9.08 and 8.98, a nine-proton singlet at  $\tau$  8.82 and a three-proton singlet at  $\tau$  8.73. Certainly this is not the pattern predicted, but it might result from the fortuitous overlap of signals. When the spectrum was taken in CD<sub>3</sub>CN the expected pattern was found, with six-proton singlets at  $\tau$  9.08, 8.93 and 8.82 and three-proton singlets at  $\tau$  8.77 and 8.69.

With the idea in mind that compound 53 should be the photoproduct derived from the fully methylated analog of 39 - 1,3,3,4,5,6,8,8-octamethylbicyclo[2.2.2]oct-5-ene-2,7-dione 54, attempts were made to methylate 39 to give 54. These all failed to give the expected product. An explanation lies in the fact that fully substituted  $\beta$ -diketones are easily rearranged by base. Compound 44 serves as an example<sup>31</sup>.





СH<sub>3</sub>0<sub>2</sub>С(CH<sub>2</sub>)<sub>3</sub>СО-СН-СH<sub>2</sub>С<sub>6</sub>H<sub>5</sub>

It is of interest that the symmetrical ketone 53 showed two carbonyl frequencies, 20 cm<sup>-1</sup> apart. This phenomenon also has been observed in the cyclobutanediones 57 and  $58^{32}$ . It has been extensively studied in



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anhydrides where it has been shown to be due to mechanical coupling<sup>33</sup>. In the 1,4-cyclohexamedione 50 however, two frequencies are not observed since the molecule exists in the boat form. In the various cases where it has been observed, this phenomenon has been attributed to the occurence of (a) an equilibrium between associated and non-associated forms of the same molecule, (b) an equilibrium of conformers, (c) Fermi resonance and (d) mechanical coupling<sup>34</sup>.

The prediction of uv spectra of cyclopropyl conjugated ketones has been facilitated by a set of empirical rules developed by Dauben<sup>35</sup>. The values assigned to certain bicyclic ketones and their methyl derivatives are listed in Table II. Using these values, one calculates a uv maximum for both 48 and 53 of 222 nm (193 + 7 + 3 + 3 + 7 + 5 - 3 = 222). In line with this predicted value, 48 exhibited uv maxima in 95% ethanol at 220 nm ( $\varepsilon = 1770$ ) and at 280 nm ( $\varepsilon = 230$ ), whereas 53 had uv maxima in 95% ethanol at 224 nm ( $\varepsilon = 1770$ ) and 280 nm ( $\varepsilon = 230$ ).

Absorption in Ethano	1 Solvent		-
Rβ' Rβ' O Rα Rβ (GH <sub>2</sub>	) <sub>n</sub>		
Bicyclo[4.1.0]hept-2-one $(n = 1)$	1	.93	nm
Increments for:			
Alkyl groups, a		+7	nm
β		+3	nm
β'		+7	nm
Rigidity		+5	nm
Ring Size, n = 0		-3	nm
n = 2		+3	nm
Solvent correction for water		+7	nm
	Calcd max = tot 95% EtOH	al	

The total absence of any products derived from decarbonylation and especially 1,3-acyl migration is rather striking. It suggests that the latter products, if formed, are further photolyzed at the wavelength employed. It is, however, not possible to observe the cyclobutanones 49 and 50 in either the sensitized or the direct photolysis of 39 through Corex or Pyrex nor are they detected by vpc after a photolysis time of only 15 minutes (~30% conversion).

One reason for the absence of 1,3-acyl migration products may be found in their photolytic instability at the incident wavelength. This instability is most certainly due to the formation of the stabilized diradical intermediates 39a and 39b where an electron can be delocalized over five atoms. A further discussion will be reserved for Section D where the photolysis results will be examined in light of such features.

Table II. Rule for Conjugated Cyclopropane-Carbonyl

One can see from the suggested mechanism in Figure 2 that a 1,2-acyl migration in either 32 or the possible primary photoproducts 42 and 52 can produce 48. However, the same product, 48, would be formed in either case unless the starting material were labeled as shown in 42, below. The different substitution of the labeled groups in the products would permit differentiation between path  $\underline{a}$  and path  $\underline{b}$  by the examination of the nmr spectrum of the product.



Photolysis of 61 labeled with a deuterated methyl group at  $C_6$  would give a photoproduct 62 in which the  $C_2$  methyl group would be labeled if only path <u>a</u> were operative. Alternatively, product 63 would be obtained, in which the  $C_8$  methyl group would be labeled, if only path <u>b</u> were operative. If the rearrangement goes via both pathways then the methyl signals for both the  $C_2$  and  $C_8$  substituents should be effected. They should be reduced in integrated area and any predominance of either path would be reflected in the relative reduction for the corresponding methyl signals.

When 61 having the methyl group at C<sub>6</sub> 60% exchanged with deuterium  $^{Was}$  photolyzed, a product was obtained whose nmr spectrum (CCl<sub>4</sub>) was

identical to that of 48 except that the signals at  $\tau$  8.90 and 8.85 showed an equal 30% reduction in integrated areas. Since the reduction in areas was equal, there must be no preference for migration of either carbonyl function.

The nmr signals in the spectra of 48 and 53 can be assigned from the results of the dimethylation of 48 and from a further photolysis and dimethylation in which the groups at C<sub>4</sub> and C<sub>6</sub> are both labeled by incorporation of deuterium as in 46. Photolysis should produce the mixture of 64 and 65 which would be dimethylated to 66 and 67.



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Photolysis of 46, 90% exchanged at  $C_4$  and  $C_6$ , gave a photoproduct whose nmr spectrum was identical to that of 48 except that the signal at  $\tau$  8.72 had essentially disappeared and those at  $\tau$  8.90 and 8.85 showed 45% reduction in area. Dimethylation of the product in ether with NaH and excess methyl iodide gave a product whose nmr spectrum (CD<sub>3</sub>CN) was identical to that of 53 except that the signal at  $\tau$  8.82 had been reduced to only one methyl group while that at  $\tau$  8.69 had disappeared.

From these and the previous results, the signals at  $\tau$  8.90 and 8.85 in the spectrum of 48 can be assigned to the C<sub>2</sub> and C<sub>8</sub> methyl groups respectively. The signals at  $\tau$  8.72 and 8.74 belong to the C<sub>5</sub> and C<sub>1</sub> methyl groups respectively and the two remaining signals at  $\tau$  9.08 and 8.98 must be due to the geminal methyl groups at C<sub>4</sub>.



Since dimethylation of 48 gave 53 in which the nmr signals  $(CD_3CN)$ at  $\tau$  9.08, 8.93 and 8.82 contain six protons, these signals must belong to the methyl groups at  $C_2$  and  $C_8$  and to those  $\alpha$  and  $\beta$  at  $C_4$  and  $C_6$ . Since the signal at  $\tau$  8.82 was reduced when 46 was photolyzed, it follows that this signal is due to the  $C_2$  and  $C_8$  methyl groups. (This is as expected since the dimethylation created identical environments at  $C_2$ and  $C_8$ , and allows the assignment of the peak at  $\tau$  8.85 to the  $C_2$  methyl group in the spectrum of 48.) The signal at  $\tau$  8.69, which has disappeared

in the nmr spectrum of 66 and 67 can only belong to the  $C_5$  methyl group. The signal at  $\tau$  8.74 must be the result of the C<sub>1</sub> methyl group. The signals at  $\tau$  9.08 and 8.93 in the spectrum of 53 must be due to the geminal methyl groups at  $C_4$  and  $C_6$  but their unequivocal assignment is not possible since the difference in chemical shift may be the result of their different relationship to the cyclopropane ring or simply a difference which seems to be a general phenomenon for geminal methyl groups. The assignments for both the tricyclic compounds are shown in Table III.

Table III	$\frac{1}{2}$	
Compound	Chemical Shift (J) <sup>b</sup>	Assignments <sup>C</sup>
	9.15 (s)	$\alpha$ -methyl at C-4 (?)
α_β	8.98 (s)	$\beta$ -methyl at C-4 (?)
	8.90 (s)	C-8 methyl
4 6	8.84 (s)	C-2 methyl
$0 = (3 + 1)^{3} = 7 = 0$	8.74 (s)	C-1 methyl
	8.72 (s)	C-5 methyl
	7.74 (d. 16.5)	
4.0	7.67 (d, 16.5)	C-6 methylene
40 ~~		
	9.08 (s)	$\alpha$ -methyls at C-4 and C-6 (
	8.98 (s)	$\beta$ -methyls at C-4 and C-6 (
βαβ	8.82 (s)	?
	8.73 (s)	?
$0 = 3^{4} + 5^{6} = 0$	spectrum in CD <sub>3</sub> CN	
2-8	9.08 (s)	$\alpha$ -methyls at C-4 and C-6 (
	8.93 (s)	$\beta$ -methyls at C-4 and C-6 (
• •	8.82 (s)	C-2 and C-8 methyls
रुरु	8.77 (s)	C-1 methyl
	8.69 (s)	C-5 methyl

<sup>a</sup>All spectra are in CC1<sub>4</sub> except as noted

<sup>b</sup>Shifts are reported in  $\tau$  values and J's in Hertz. Multiplicity of peaks is shown in brackets: s, singlet; d, doublet; q, quartet.

<sup>C</sup>A question mark indicates that the assignment is tentative.

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C. The Direct and Photosensitized Irradiation of 1,3,3,4,5,6-Hexamethylbicyclo[2.2.2]oct-5-ene-2,8-dione (40).

When a 1% solution of 40 in ether was photolyzed through Corex using a Hanovia-L 450-W lamp for two hours a mixture of five products was obtained. This is in sharp contrast with the isomer 32 which, as described in Section B, gave a single photoproduct. The relative ratios of the products from 40 continued to change for 38 hours until the starting material and two of the photoproducts were consumed. Irradiation of a 1% solution in acetone of 40 under the same conditions for 9 hours resulted in a mixture of products with vpc retention times which matched those of the unsensitized reaction. Photolysis of a 1% solution of 40 in ether containing 10% by volume of piperylene resulted only in the recovery of unchanged starting material. Since the reaction is quenched and sensitized, the  $n,\pi^*$  triplet state must be involved. Graphs which show the relative percentages of the products are given in Figure 3 for the sensitized rearrangement.

Since the product ratios varied with time it was clear that the initial photoproducts were also labile under the photolysis conditions. The three common photorearrangement pathways predicted the structures shown in Figure 4 as possible photoproducts. (The  $\alpha$ -fission mechanism is used in drawing this scheme although the 1,2-acyl migration products may be arrived at as shown in Section D.) Since six of these are themselves  $\beta$ , $\gamma$ -unsaturated ketones, they might well be expected to react further, thus accounting for the observed change in product ratios.

The five products were trapped after vpc separation and were characterized by spectroscopic methods. Under conditions which permitted



photolysis time in hours

- FIGURE 3. A graphical display of the relative percentages of products and reactant as a function of time.
  - a. Starting material 1,3,3,4,5,6-hexamethylbicyclo-[2.2.2]oct-5-ene-2,8-dione (40) and 1,2,4,4,5,8hexamethyltricyclo[3.3.0.0<sup>2</sup>,<sup>8</sup>]octane-3,6-dione (71).



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FIGURE 3. (Continued)

b. 1,2,4,6,7,7- and 1,2,3,3,4,6-hexamethyltricyclo-[4.2.0.0<sup>2</sup>,<sup>4</sup>]octane-5,8-dione (73 and 74).



FIGURE 3. (Continued)

c. 1,3,3,4,7,8- and 1,4,6,6,7,8-hexamethyltricyclo-[4.2.0]octane-2,5-dione (69 and 70).



their separation, the products had retention times of 16.2, 21.8, 24, 28.6 and 34 minutes, with the starting material coming off last at 39 minutes. The mass spectrum of each of the products had a parent peak at m/e = 220. Therefore they are all isomeric with the starting material. This eliminates all decarbonylation products such as structures 75 and 76.

The ir spectra of four products (all except that with a retention time of 34 minutes) showed carbonyl absorptions at 1770 cm<sup>-1</sup>, characteristic of cyclobutanones; thus presumably four of the six possible cyclobutanones were obtained. Since these come in three sets (62-72, 12-74, 12-78) which can be differentiated by the presence or absence of allylic methyl groups or vinyl hydrogens, a distinction seemed possible on the basis of their nmr spectra.





The products with retention times 21.8 and 24 minutes are assigned structures 69 and 70 respectively. They are the only products with two adjacent allylic methyls, as deduced from their nmr spectra. The ir spectrum of 69 showed carbonyl bands at 1705 and 1770 cm<sup>-1</sup>. The absorption at 1770 cm<sup>-1</sup> is characteristic of a cyclobutanone and the 1705 cm<sup>-1</sup> band may be due to a 6-membered ring ketone (1715 cm<sup>-1</sup>) shifted by conjugation with unsaturated groups. The nmr spectrum (CCl<sub>4</sub>) showed three-proton singlets at  $\tau$  9.22, 8.98, 8.93 and 8.78, two three-proton quartets (J = 1 Hz) at  $\tau$  8.45 and 8.42 and a two-proton singlet at  $\tau$  7.33. The quartets in the nmr spectrum indicated the presence of two adjacent allylic methyl groups. These spectral characteristics are consistent with the proposed structure as 1,3,3,4,7,8-hexamethylbicyclo[4.2.0]oct-7-ene-2,5-dione.

The product  $\chi_{0}$ , 1,4,6,6,7,8-hexamethylbicyclo[4.2.0]oct-7-ene-2,5dione, was assigned this structure on the basis of the absorptions in the ir spectrum at 1700 and 1770 cm<sup>-1</sup> and an nmr spectrum (CCl<sub>4</sub>) which showed three-proton singlets at  $\tau$  8.86, 8.82, 8.78 and 8.66, a six-proton singlet at  $\tau$  8.32 and two one-proton doublets centered at  $\tau$  7.46 and 6.61 (J = 16 Hz). Compound  $\chi_{2}^{0}$ , which may serve as a model for the cyclobutanone CH<sub>2</sub> splitting, was characterized by Erman<sup>36</sup>. Its spectrum contains four peaks centered at  $\tau$  6.98 (J = 17.5 Hz). The four peaks of  $\chi_{0}^{0}$  are centered at  $\tau$  7.04. Cookson<sup>37</sup> cites a range of 15.3 to 18.0 Hz for the geminal coupling constants in  $\alpha$ -methylene groups of structures containing the moiety  $\xi_{0}^{0}$ . Compound  $\xi_{1}^{1}$  prepared by House<sup>38</sup> shows doublets for H<sub>2</sub> and H<sub>3</sub> at  $\tau$  7.38 and 6.88 respectively with a coupling constant J = 17.1 Hz.



Structures 69 and 70 are readily distinguished by the difference in appearance and chemical shift of the methylene protons. In 69, the methylene protons are in similar environments and appear as a singlet. In 70, on the other hand, one of the methylene protons extends over the carbonyl of the six-membered ring and will therefore be in a quite different environment than the other. Thus the two have grossly different chemical shifts, and split each other by 16 Hz. The appearance of a high field methyl group at  $\tau$  9.22 in 62 but not in 70 also supports the structural assignment. Presumably this is the methyl which extends over the six-membered ring, in 62.



Structures 77 and 78 can be ruled out for the remaining cyclobutanones since there is no product which shows either three allylic methyl groups or any vinylic hydrogens in its nmr spectrum. Therefore the remaining two cyclobutanones should presumably have structures 73 and 74 (the geometries will be discussed later).



The photoproduct with the shortest retention time, 16.2 minutes, is identified as 1,2,4,6,7,7-hexamethylbicyclo[4.2.0.0<sup>2,4</sup>]octane-5,8dione,  $\chi_3^2$ . It had carbonyl absorptions in the ir spectrum at 1718 and 1770 cm<sup>-1</sup> and an nmr spectrum (CCl<sub>4</sub>) which showed three-proton singlets at  $\tau$  9.08, 8.95, 8.92 and 8.83, a six-proton singlet at  $\tau$  8.78 and a twoproton singlet at  $\tau$  9.33. The 1718 cm<sup>-1</sup> absorption indicates the presence of a five-membered ring ketone conjugated with a cyclopropane ring<sup>39</sup> and the 1770 cm<sup>-1</sup> absorption is characteristic of a cyclobutanon e. The high-field appearance of the two methylene hydrogens is consistent with their being on a three-membered ring. The appearance of both protons with the same chemical shift seems fortuitous and may be a consequence of the geometry, as discussed below. The cyclopropyl protons in  $82^{40}$  appear at  $\tau$  9.57 and 9.43 (J = 5.5 Hz) but their position in the unsubstituted framework 83 is at  $\tau$  8.9<sup>41</sup>. The spectral data appear consistent with structure Z3.



Compound  $\chi_4^4$  (retention time 28.6 minutes) showed carbonyl absorptions at 1718 and 1770 cm<sup>-1</sup>, exactly the same as  $\chi_3^3$ . Its nmr spectrum (CCl<sub>4</sub>), however, was grossly different. It showed three-proton singlets at  $\tau$  9.07 and 8.87, six-proton singlets at  $\tau$  8.94 and 8.82 and two one-proton doublets (J = 17.5 Hz) centered at  $\tau$  7.32 and 7.13. The ir absorptions again indicate the presence of a cyclobutanone and of a cyclopentanone conjugated with a cyclopropane ring. The coupling of the low-field doublets in the nmr spectrum is also consistent with the geminal coupling of a cyclobutanone methylene. These spectral data are consistent with the structure 1,2,3,3,4,6-hexamethyltricyclo[4.2.0.0<sup>2,4</sup>]octane-5,8-dione,  $\chi_4^4$ .

The photolysis of the doubly labeled 47 led to doubly labeled 84 and 85 and allowed the assignment of two peaks in the nmr spectrum of these compounds.



Compound 84 was trapped by vpc from a photolysis of 47. Its nmr spectrum was the same as that of 73 except that the signal at  $\tau$  8.95 had disappeared and that at  $\tau$  8.78 had been reduced to one methyl group. This simply allows the statement that these signals are due to the methyl groups at C<sub>1</sub> and C<sub>5</sub> in this system. 85 obtained in the same manner had an nmr spectrum in which the signals corresponded to those in the spectrum of 74 with the exception that the signal at  $\tau$  8.87 had disappeared and that at  $\tau$  8.82 had been reduced by one methyl group. Again, it is only possible to say that these signals are due to the methyl substituents at C<sub>2</sub> and C<sub>7</sub> but no definite assignment can be made. A change in the substituents on the cyclopropane ring or on the cyclobutanone changes the spectrum of the two isomers enough so that no correlation between the two spectra can be made which would allow definite assignments.

The geometric relationship between the cyclopropane and cyclobutane rings in 73 and 74 can be varied to give 86, 87, 88 and 89. Definite





87



identification of the particular geometric arrangement would require extensive degradative and spectroscopic study. On the basis of the chemical shift of the cyclopropane protons, the more likely arrangement for 73 is 86, not 87. Here the cyclopropyl protons would be removed from the influence of the carbonyl groups. They would thus be more likely to show the same chemical shift. The possibilities for 74 cannot be distinguished by a similarly simple approach, although the trans geometries are probably the least sterically hindered.

It is interesting that the six-membered fused systems 62 and 70 do not behave like the five-membered ring fused systems 20 and 21 studied by Cookson<sup>15</sup>. The latter lose ketene whereas the former do not. Presumably the conversion to 62 and 70 and 73 and 74 (and tricyclic product; see below) is a lower energy process than is ketene formation. The products of such ketene formation would be quite stable (2,3,4,5-tetramethylphenol via aromatization of the dienone first formed, from 62, and hexamethyl-2,4cyclohexadienone from 70).





The most probable structures for the fifth photoproduct (retention time 34 minutes) would be  $\chi_{1}^{2}$  and  $\chi_{2}^{2}$ , formed either directly from 40, or indirectly via the cyclobutanones 62 and  $\chi_{2}^{0}$  (see Figure 4). The product showed two carbonyl absorptions in the ir spectrum, at 1720 and 1738 cm<sup>-1</sup> and a maximum uv absorption (95% ethanol) at 267 nm ( $\varepsilon$  = 25). In accord with either  $\chi_{1}^{2}$  and  $\chi_{2}^{2}$ , the ir absorption at 1720 cm<sup>-1</sup> is indicative of a cyclopentanone conjugated with a cyclopropane ring whereas the 1738 cm<sup>-1</sup> absorption is characteristic of an ordinary cyclopentanone. The nmr spectrum (CCl<sub>4</sub>) showed three-proton singlets at  $\tau$  9.37, 9.09, 8.99 and 8.79, a six-proton singlet at  $\tau$  8.83 and a two-proton singlet at  $\tau$  7.83. Thus there are no allylic mathyls and presumably no carbon-carbon double bonds in the molecule. It is difficult to distinguish between  $\chi_{1}^{2}$  and  $\chi_{2}^{2}$ on the basis of the nmr spectrum, which is reasonably consistent with both structures.

Identification was attempted by lithium in liquid ammonia reduction to give 92 or 93. Nmr spectroscopy presumably would allow a distinction to be drawn between 92 and 93 from the coupling pattern of the methylene protons  $\alpha$  to the carbonyl function. Unfortunately, the reduction did not proceed in a straightforward manner but gave at least six products, according to a vpc trace.





An alternative method which should distinguish between structures  $\chi_1^2$  and  $\chi_2^2$  would be the selective reduction of the less hindered ketone to give the keto-alcohol  $\chi_4^2$  or  $\chi_5^2$ . Compound  $\chi_4^2$  would retain the cyclo-propyl-cyclopentanone conjugation to give an ir absorption at 1718 cm<sup>-1</sup>. Compound  $\chi_5^2$ , on the other hand, would only show the 1740 cm<sup>-1</sup> absorption for a simple cyclopentanone.



In general, the stereochemical outcome of metal hydride reductions of cyclic ketones is difficult to predict. Dauben<sup>42</sup>, in studies of hindered ketone systems, developed the idea of steric approach control: steric hindrance to the approach of the metal hydride ion to the carbonyl function. A similar rationalization applied in this situation would predict the selective reduction of the C<sub>6</sub> carbonyl of  $\chi_{L}$  and the C<sub>3</sub> carbonyl of  $\chi_{L}$ . These positions are less hindered by the methyl substituents than the alternative positions which have geminal methyl groups a to the carbonyl.





When the reduction was carried out in ether  $(0-5^{\circ})$  using lithium aluminum hydride, a product was obtained which had two OH absorptions in the ir spectrum at 3450 and 3610 cm<sup>-1</sup> but no absorptions in the carbonyl region. Obviously the reduction had taken place at both carbonyl positions.

The use of the more bulky lithium tri-tertiarybutoxyaluminum hydride resulted in the isolation of unreacted starting material if the reaction was run for only 30 minutes. After 10 hours a rearranged product was isolated. The ir spectrum of this material showed absorptions at 1620, 1700 and 1738 cm<sup>-1</sup> but no bands were found in the OH region. The use of lithium tri-tertiarybutoxyaluminum hydride has been found to complicate the reduction of enolizable 1,3-diketones because of its basicity<sup>43</sup>. In a similar manner the reagent may cause the rearrangement of the enolizable  $\chi$ . Compound  $\chi$ , once enolized, has no rearrangement pathway open to it. Two possible products for the rearrangement of  $\chi$  are shown.





**?**7,7 77,7 The carbonyl and carbon-carbon double bond frequencies at 1738, 1700 and 1620 cm<sup>-1</sup> suggest a cyclopentanone and a cyclopentenone moiety as in 27. Since the intermediate anion in the rearrangement could be stabilized as in 27a, the formation of 27 is more likely than formation of 26 where no such stabilization can occur. Regardless of the product formed, the occurence of the rearrangement indicates that the fifth photoproduct probably has structure 71 rather than 72.

The reduction proceeded in the desired fashion when the compound was treated with sodium borohydride in 95% ethanol for 12 hours. The reduction product had absorption bands in the ir spectrum at 1718 cm<sup>-1</sup> for a carbonyl function and at 3200 cm<sup>-1</sup> for the OH group. The position of the remaining carbonyl frequency suggests that the carbonyl which was not reduced is still conjugated with the three-membered ring. The low frequency **e** the OH absorption is explained by strong intramolecular hydrogen bonding between the carbonyl and alcohol functions<sup>46</sup>. The nmr spectrum showed peaks at  $\tau$  9.18, 9.04, 8.95, 8.92, 8.86 and 8.74. Neither the methylene splitting nor the OH signal could be seen. This is not surprising since the non-equivalence of the methylene hydrogens would require that they give an eight line pattern. The nmr spectrum was different from that of the starting material and the totality of the evidence supports the assignment of the fifth product as  $\chi$  rather than  $\chi$ ?

Further evidence to support this assignment is obtained by relating the nmr spectrum of 48 to that of 71.



The common features of 48 and 71 are the  $C_2$  methyl group  $\alpha$  to a carbonyl and the geminal methyl groups at  $C_4$ . In 72 the  $C_2$  methyl group and the methylene hydrogens are disposed as in 48. If it is possible to argue from analogy in these isomers it is possible to make some predictions concerning the chemical shifts of these substituents. The  $C_2$  methyl group should appear at  $\tau$  8.85 in 71 and at  $\tau$  8.90 in 72. In both 71 and 72 the methyl group at  $C_5$  is now  $\alpha$  to a carbonyl and a methyl group in this position and spatial arrangement appears at  $\tau$  8.98 in both 48 and 53. In structure 72 the methylene protons should appear as doublets around  $\tau$  7.7 as they do in 48. The absence of this pattern is the first indication from the nmr spectrum that 71 rather than 72 is the correct structure of the fifth photoproduct. The other predictions may be tested by the photolysis of the doubly labeled 47. The results of such labeling on the mar spectrum of the photoproduct are shown below.



If the product in question has structure 71 then the methyl groups at C<sub>2</sub> and C<sub>5</sub> will be labeled and affected in the nmr spectrum. From the above analogy this would involve signals at  $\tau$  8.85 and 8.98. If, on the other hand, the product has structure 72 then the nmr signals at  $\tau$  8.82 or 8.74 should be effected. These two values are suggested since both the C<sub>1</sub> and C<sub>8</sub> methyl groups are on a quaternary carbon and removed from the carbonyl groups. The value of  $\tau$  8.74 corresponds to the signal for the C<sub>1</sub> methyl group in 48. The value of  $\tau$  8.82 is found as a general value and is cited for compound 100 by Williams and Ziffer<sup>47</sup>.



Compound  $\frac{47}{2}$  labeled at methyl groups C<sub>4</sub> and C<sub>6</sub> to the extent of 90% with deuterium, as shown by nmr, was photolyzed and the product with the structure in question was collected by vpc. The nmr spectrum (CCl<sub>4</sub>) showed three-proton singlets at  $\tau$  9.37, 9.10 and 8.97 as well as a three-proton singlet at  $\tau$  8.83 and a two-proton singlet at  $\tau$  7.83. The peak at  $\tau$  8.99 was virtually absent and the signal at  $\tau$  8.83 was reduced in area to three protons. Thus the labeling results once again appear to be support structure  $\frac{71}{2}$  rather than  $\frac{72}{2}$ .

D. Mechanistic Considerations in the Photolysis of 39 and 40.

The mechanistic schemes in Figures 2 and 4 account for the photoproducts derived from 32 and 40 via the intermediate acyl-allyl diradicals 32a, 32b, 68a and 68b. Although this  $\alpha$ -fission mechanism has been generally accepted<sup>48</sup>, the products may arise in a concerted fashion from a  $\sigma^2 - \pi^2$  photochemically allowed process (see Introduction). A further possibility for the formation of the 1,2-acyl migration products by a di- $\pi$ -methane rearrangement is shown below for 32. This mechanism was detected by Givens and Oettle in the sensitized photolysis of benzobicyclo[2.2.2]octadienone,  $101^{49}$ .



The results of this present study do not allow any differentiation between these mechanistic possibilities.

The most obvious difference between the photolytic behavior of 32 and 40 is the absence of any detectable cyclobutanone products for the rearrangement of 32. If the diradical mechanism is accepted, this difference seems to be a function of the stability of the intermediate diradicals shown below.




The intermediates 392 and 395 are more stable than 682 and 685 because an electron can be delocalized over five atoms in the former while in the latter the stabilization is simply that of an allylic radical. This difference in stability would tend to lower the energy of the excited state for 39 relative to 40. The photoreactivity of the intermediate cyclobutanones formed would also be greater for those derived from 39. If a mechanism in which a photostationary state which is continuously depleted by the formation of photochemically inert products exists, the diradical from which these inert products are derived is produced at a faster rate in the case of 39 than of 40.

Although the photolysis of 32 gives only one product, this product may be formed via two different paths: (a) by a direct 1,2-acyl migration from 32 or (b) a 1,2-acyl migration from 42 or 50 which would be formed by a 1,3-acyl migration from 32. Because neither 42 nor 50 could be trapped or detected even at short photolysis times, one must conclude that most probably 48 is formed directly from 32.

An unequivocal determination of the mechanism for the photorearrangement of 40 is not possible from the present data. In this rearrangement, the products which have a bearing on the mechanism can also be formed by routes similar to (a) and (b) above. In this case both cyclobutanones 69

and 20 were observed, so that a 1,3-acyl migration is indicated as a reaction mode for 42. Furthermore, the presence of a photostationary state is suggested by the initial, rapid build-up and subsequent decline in the concentration of these products. The photostationary state is destroyed by the formation of the secondary photoproducts 73 and 74 and possibly The absence of the tricyclic product 72, which could be a primary な・ photoproduct formed by 1,2-acyl migration from 42 or a secondary photoproduct formed by 1,2-acyl migration from ZQ, is puzzling. The presence of 71 which would be derived from either 40 or 69 by a 1,2-acyl migration only adds to the paradox. Since 72 is not present, neither 40 nor 70 undergoes a 1,2-acyl migration to give this product. This conclusion requires that one carbonyl group of 40 can take part in a 1,2 migration while the other cannot and it also seems to require that two similar carbonyl groups (as in 62 and 72) are not involved in the same type of rearrangement.

The present problem may be the result of subtle electronic differences which are as yet not understood. These differences cannot simply result from the stability of intermediates since similar diradicals are involved for the formation of both 71 and 72. The difference may depend upon subtle changes in substitution and geometry. A phenomenon which may bear a relationship to this problem is that of the photostationary state.







In each of the three instances shown above from the work of Paquette<sup>10</sup> as well as the initial observations of Büchi and Burgess<sup>9</sup>, the photostationary state has a different composition but the intermediate diradical stability is essentially the same for all compounds. Thus if the stability of the diradical were the determining factor, a 50:50 mixture should be obtained in all cases. However, the photostationary state is achieved after different irradiation times and with different compositions for each case. It is not necessary to point out subtle substitution differences and possible geometric modifications arising from these which might effect the process. Suffice it to say that the subtle differences operating in the 1,3-acyl migration may also determine whether a 1,2-acyl migration takes place involving one carbonyl group and not another. E. An Attempted Synthesis of 1,2,2,3,3,4,5,5,6,6-Decamethylbicyclo[2.2.2]hexane (119) and 1,2,2,3,4,5-Hexamethylbicyclo[2.2.0]hexane (122).

The photochemical literature contains a number of examples of decarbonylation reactions in which the irradiation of a cyclic ketone leads to a cycloalkane. Some examples, of which the most pertinent is 116, are shown below<sup>50</sup>,<sup>51</sup>,<sup>52</sup>,<sup>53</sup>.



When 116 was photolyzed in the vapor phase (partial pressure of the ketone was 15 mm, 150 mm of  $CO_2$ ) at 80° with a mercury arc source, the main products were 1,5-hexadiene and bicyclo[2.2.0]hexane. The yield of 117 was small, and a maximum yield of 5% was attained by increasing the wavelength of light or the  $CO_2$  pressure.

Although this example does not foreshadow a good yield, an attempt was made to synthesize 1,2,2,3,3,4,5,5,6,6-decamethylbicyclo[2.2.0]hexane 120, by the bis-decarbonylation of 1,2,2,4,4,5,6,6,8,8-decamethylbicyclo-[3.3.0]octane-3,7-dione, 112. The latter could be derived from 53 by reduction with lithium in liquid ammonia followed by methylation of the intermediate 118.





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The reduction of 53 was unsuccessful due to the lack of solubility of 53 in ether or THF. When a successful run was completed it was found (by vpc) that only about 5% of the starting material had reacted. It was then decided to reduce 48 with lithium in liquid ammonia and to attempt to place four methyl groups on the product 121 to give 112.



Treatment of 48 with lithium in liquid ammonia gave a colorless, solid product, mp. 74-76°, in 82% yield. The nmr spectrum (CCl<sub>4</sub>) of this compound showed peaks at  $\tau$  9.02, 8.97, 8.90 and 8.87 for the methyl substituents and a series of peaks centered at  $\tau$  7.90 with major signals at  $\tau$  7.92 and 7.87. Integration of the hydrogen and methyl signals results in a 1:4.4 ratio of the two areas. The calculated ratio for 121 is 1:4.5.

The ir spectrum of this compound showed a band at 1732 cm<sup>-1</sup> as the only major carbonyl absorption. Thus the cyclopropane ring is no longer present. The uv spectrum consisted of a broad band from 350 to 250 nm with the maximum between 275-300 nm ( $\varepsilon = 180$ ). The carbon-hydrogen analysis was consistent with  $C_{14}H_{22}O_2$  and the mass spectrum had a parent peak at m/e = 222. All of these facts are consistent with the successful reduction of 48 to 121.

The planned sequence could not be followed when the methylation of 121 failed to take place in ether or in refluxing benzene with NaH as the base. An attempt was therefore made to bis-decarbonylate 121 to give 1,2,2,3,4,5-hexamethylbicyclo[2.2.0]hexane 122.



Compound 121 and a catalytic amount of mercury were placed in a quartz vessel which was then flushed with nitrogen, cooled in dry ice and evacuated below  $10^{-2}$  mm of Hg. Photolysis was carried out in a Rayonet apparatus at 85-90° using 2537Å light for 12 hours. Analysis of the recovered material by vpc and nmr showed it to be recovered 121. Extension of the photolysis time to 36 hours effected no change.

Since no definitive studies have been made concerning the requirements for photodecarbonylations of this type, it is difficult to attribute the failure of 121 to decarbonylate to any specific factor. Some possibilities which must of course come to mind are vapor pressure, temperature, wavelength of light and a substitution. To cite the anamolous nature of some other results, a look at a substitution is revealing. The ketone 113 photodecarbonylates in solution while the similarly alkyl-substituted 2,6-dimethylcyclohexane 111 does not. 111 does decarbonylate in the gas phase, however. The result in the case of 121 must be considered as incomplete since a large number of variables are as yet unexplored.

#### **EXPERIMENTAL**

### A. GENERAL PROCEDURES

Nmr spectra were obtained on a Varian A-60 spectrometer in  $CCl_4$ solution (unless otherwise noted) with tetramethylsilane as an internal reference, given the value  $\tau = 10.00$ . The low temperature and 100 MHz spectra were obtained by Mr. E. J. Roach on a Varian HA-100 spectrometer. Infrared spectra were taken with a Unicam SP-200 or a Perkin-Elmer 237-B spectrometer as a neat smear between NaCl plates or in  $CCl_4$  solution. Ultraviolet spectra were obtained with a Unicam SP-800 spectrometer. Mass spectra were determined by the author with a Consolidated Electrodynamics Corporation 21-103C or by Mrs. R. Guile with a Hitachi-Perkin-Elmer RMU-6 mass spectrometer. Varian Aerograph gas chromatographs were used. Melting points were determined with a Gallenkamp Melting Point Apparatus and are uncorrected. Analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Michigan.

### **B. GENERAL PHOTOLYSIS PROCEDURE**

All irradiations were carried out with a 450 watt Hanovia Type L mercury lamp. The solutions to be irradiated were placed in quartz test tubes, sealed and degassed by bubbling purified and deoxygenated nitrogen through them. The test tubes were secured to the outside of a quartz well into which the mercury lamp, surrounded by the appropriate filter, was placed. The temperature was maintained between 18-25° by a water bath.

The reactions were monitored by withdrawing aliquots of the solutions and examining these by vapor phase chromatography (vpc). Vpc calibration curves were obtained by evaporation of the solvent, dilution of the non-volatile materials to achieve a known concentration and comparison by vpc with a standard solution of pure starting material.

For each irradiation a dark reaction was carried out in which part of the initial photolysis solution was stored in a quartz test tube for one week. After this time the solvent was evaporated and spectra were taken. No dark reactions were observed nor is there evidence for thermal rearrangement of any of the starting materials or products on the vpc.

C. Reaction of 2,3,4,5,6,6-Hexamethyl-2,4-cyclohexadienone (41) with

Vinyl Acetate: Synthesis of 7- and 8-Acetoxy-1,3,3,4,5,6-hexamethylbicyclo[2.2.2]oct-5-ene-2-one (42a and 42b).

A mixture of 15 g of dienone 41 and 15 g of vinyl acetate was heated in a sealed tube at 200° for 24 hours. The excess vinyl acetate was removed under reduced pressure and the residue was distilled. The fraction boiling between 110-115° at 0.08 mm of Hg was collected. This fraction showed two peaks on a vpc trace (5' x 1/4", SE-30, 180°, 80 ml/min of He) in the ratio of 7:5. No crystalline product could be obtained from a number of solvent systems. The analytical sample was a mixture of all isomers obtained by vpc trapping.

Anal. Calcd. for C<sub>16</sub>H<sub>24</sub>O<sub>3</sub>: C, 72.7; H, 9.15 Found: C, 73.0; H, 9.2.

The infrared spectrum of the mixture showed bands at 1740, 1720 and 1240 cm<sup>-1</sup>. No further attempt was made to identify the four possible isomers of this addition. The yield based on dienone 41 was 81%.

D. Hydrolysis of a Mixture of 42a and 42b: Synthesis of 7- and 8-Hydroxy-1,3,3,4,5,6-hexamethylbicyclo[2.2.2]oct-5-ene-2-one (43a and 43b).

24.4 g of the acetate mixture (prepared in C above) was dissolved in 65 ml of methanol and to this solution was added 6.3 g of NaOH in 10 ml of water. The reaction mixture was refluxed for 5 hours. Dilution with 200 ml of water was followed by extraction with 3 x 100 ml of ether. After the extract had been dried over  $MgSO_4$  the ether was removed under reduced pressure and the residue was distilled. The fraction boiling between 110-120° at 0.09 mm of Hg was collected. This fraction showed two peaks in the vpc trace with an area ratio of 8:3 (5' x 1/4", SE-30, 170°, 90 ml/min of He). The two components were trapped as a mixture for the analytical sample.

Anal. Calcd. for C<sub>14</sub>H<sub>22</sub>O<sub>2</sub>: C, 75.63; H, 9.97 Found: C, 75.88; H, 10.00

The infrared spectrum of the mixture showed bands at 1710 and 3500  $\rm cm^{-1}$ . No further characterization of the individual isomers was attempted. The yield of 43a and 43b was 61.5%.

E. Oxidation of the Keto-alcohol Mixture 43a and 43b: Synthesis of 1,3,3,4,5,6-Hexamethylbicyclo[2.2.2]oct-5-ene-2,7- and 2,8-dione 32 and 40).

15.4 g of the keto-alcohol mixture (prepared in D above) was dissolved in 100 ml of acetone and cooled to 0-5°. The solution was then titrated with Jones' reagent (prepared according to the literature method<sup>29</sup>) until 15 minutes of stirring failed to discharge the orange-brown color. The reaction mixture was diluted with 400 ml of water and extracted with 3 x 100 ml of ether. The ether extract was washed with 3 x 50 ml of 5% NaHCO<sub>3</sub> solution and then dried over  $MgSO_4$ . The ether was then removed under reduced pressure. The oily residue which remained was vacuum distilled and the fraction boiling between 98-120° at 0.1 mm of Hg was collected and analyzed by vpc (5' x 1/4", SE-30, 170°, 100 ml/min of He). The diketones were present in a ratio of 6:1 with 39 predominating. Under these conditions compound 40 had a retention time of 23 minutes and 39 had a retention time of 27 minutes.

The separation of the two isomers was effected by preparative vpc  $(8' \times 1/2", SE-96, 165^\circ, N_2 \text{ flow of } 0.2 \text{ l/min.})$ , or by column chromatography on silica gel. Hexane, hexane:  $CCl_4$  (4:1, 3:1, 2:1, 1:1),  $CCl_4$ ,  $CCl_4$ :  $CH_2Cl_2$  (1:1, 1:2),  $CH_2Cl_2$  and  $CHCl_3$  were used as eluents. This method had to be followed by further vpc separation since the minor product was still contaminated by the major component. It was nevertheless the more useful method for the separation of larger quantities. The order in which the two isomers were eluted from the column was opposite to that in the vpc trace with 39 being eluted by  $CCl_4$  and 40 starting to come off the column with  $CH_2Cl_2:CCl_4$  in a 2:1 ratio. The analytical sample was a mixture of both peaks trapped after vpc purification.

Anal. Calcd. for C<sub>14</sub>H<sub>20</sub>O<sub>2</sub>: C, 76.32; H, 9.15

## Found: C, 76.44; H, 9.18.

The infrared spectrum of 32 showed carbonyl absorptions at 1770 and 1725 cm<sup>-1</sup>. The nmr spectrum (CCl<sub>4</sub>) showed three-proton singlets at  $\tau$  9.10, 8.95, 8.87 and 8.78, three-proton quartets (J = 1 Hz) at  $\tau$  8.38 and 8.18 and singlets integrating for one proton each at  $\tau$  7.87 and 7.82

(see Figure 5). A 100 MHz spectrum showed the latter to be the main peaks of two doublets with a coupling constant J = 16.5 Hz. The uv spectrum in 95% ethanol had maxima at 290 nm ( $\varepsilon$  = 455), 230 nm ( $\varepsilon$  = 2530) and 204 nm ( $\varepsilon$  = 4450). In cyclohexane the uv spectrum of 39 showed a maximum at 270 nm ( $\varepsilon$  = 380) with shoulders at 284 nm ( $\varepsilon$  = 290), 296 nm ( $\varepsilon$  = 160) and 312 nm ( $\varepsilon$  = 80).

The infrared spectrum of 40 showed only a broad band in the carbonyl region at 1718 cm<sup>-1</sup>. Its nmr spectrum (CCl<sub>4</sub>) showed three-proton singlets at  $\tau$  9.10, 9.02, 8.85 and 8.79, a six-proton singlet at  $\tau$  8.27 and a two-proton singlet at  $\tau$  7.90 (see Figure 6). The 100 MHz spectrum showed the singlet at  $\tau$  7.90 to be composed of two peaks with a chemial shift difference of 0.02 ppm (250 Hz sweep width). Splitting could be seen if the spectrum was run with a sweep width of 100 Hz; the coupling constant for the two doublets was 18.6 Hz. The uv spectrum of 40 in 95% ethanol showed maxima at 304 nm ( $\epsilon$  = 294), 248 nm ( $\epsilon$  = 132) and 236 nm ( $\epsilon$  = 161). In cyclohexane the uv spectrum of 40 showed a maximum at 307 nm ( $\epsilon$  = 600) with shoulders at 284 nm ( $\epsilon$  = 370), 298 nm ( $\epsilon$  = 450) and 319 nm ( $\epsilon$  = 330).

F. Photolysis of 1,3,3,4,5,6-Hexamethylbicyclo[2.2.2]oct-5-ene-2,7-

dione (32): Isolation of 1,2,4,4,5,8-Hexamethyltricyclo[3.3.0.0<sup>2,8</sup>]octane-3,7-dione (48).

1. A solution of 0.0894 g of 39 in 8 ml of ether was irradiated using a Hanovia-L 450 W lamp with a Vycor filter for 9 hours. A vpc trace (5' x 1/4", SE-30, 175°, 80 ml/min of He; these vpc conditions were used in the remaining experiments in this section) of the reaction mixture showed the formation of one photoproduct





FIGURE 6. Nmr spectrum (CC1<sub>4</sub>) of 1,3,3,4,5,6-hexamethylbicyclo[2.2.2]oct-5-ene-2,8-dione (42).



with a retention time of 24 minutes. The starting material had a retention time of 27 minutes under these conditions. Comparison with a standard solution of 39 showed the starting material to be 70% converted.

2. A solution of 0.1222 g of 39 in 10 ml of acetone was irradiated as above for 4 hours. Conversion was complete after this time and only one photoproduct was observed. This material had the same retention time as the product of the unsensitized reaction. 3. 0.0864 g of 32 were dissolved in 10 ml of a solution containing 10% by volume of piperylene and 90% by volume of ether. This mixture was photolyzed for 2 hours under the same conditions as above. After the solvent had been removed, the remaining non-volatile material was collected on the gas chromatograph and spectra were taken. These spectra were identical to those of the starting material. No other products derived from 32 were observed. 4. A solution of 0.526 g of 32 in 10 ml of acetone was prepared. Individual photolysis solutions were prepared by diluting 1 ml aliquots of this standard solution to 5 ml. The extent of conversion during photolysis through Vycor was determined by removal of the samples at 15, 30, 60, 120 and 180 minutes. A plot of these data is shown in Figure 1. Conversion was complete after 180 minutes; only one product could be detected by vpc.

The solid photoproduct (mp 84-85°, purified by sublimation) formed in both the sensitized and unsensitized photolysis of 39, showed a parent peak in the mass spectrum at m/e = 220. Its infrared spectrum showed bands at 1718 and 1738 cm<sup>-1</sup>. The nmr spectrum (CC1<sub>4</sub>) had three-proton singlets at  $\tau$  9.15, 8.98, 8.90, 8.85, 8.74 and 8.72 as well as two

singlets at  $\tau$  7.87 and 7.80 integrating for one proton each (see Figure 7). A 100 MHz spectrum showed the latter to be two doublets centered at  $\tau$  8.01 and 7.67 with a coupling constant J = 16.5 Hz. The uv spectrum in 95% ethanol had maxima at 280 nm ( $\epsilon$  = 230) and 220 nm ( $\epsilon$  = 1770). An analytical sample was obtained by sublimation at water aspirator pressure with a bath temperature of 65°.

Anal. Calcd. for C<sub>14</sub>H<sub>20</sub>O<sub>2</sub>: C, 76.32; H, 9.15 Found: C, 76.27; H, 9.15.

G. Dimethylation of 48: Synthesis of 1,2,4,4,5,6,6,8-Octamethyltricyclo[3.3.0.0<sup>2</sup>,<sup>8</sup>]octane-3,7-dione (53).

A solution of 0.8 g of the tricyclic dione 4.8 in 15 ml of anhydrous ether was added over a period of 20 minutes to a cooled (0-5°) suspension of 3 g of NaH in 30 ml of anhydrous ether. The reaction flask was continuously flushed with nitrogen. The yellowish slurry was stirred for 0.5 hours before adding a solution of 1 g of methyl iodide in 10 ml of anhydrous ether. After being stirred for another hour, the reaction mixture was added dropwise to 250 ml of ice water. The product was extracted with 3 x 50 ml of ether and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure and white crystals were obtained. Recrystallization from ether-petroleum ether mixtures gave a white solid melting at 174-175°. The yield was 70% of theoretical.

Anal. Calcd. for  $C_{16}H_{24}O_2$ : C, 77.37; H, 9.74

Found: C, 77.31; H, 9.75.

The infrared spectrum showed bands at 1720 and 1740 cm<sup>-1</sup>. The nmr spectrum (CCl<sub>4</sub>) consisted of six-proton singlets at  $\tau$  9.08 and 8.98, a nine-proton singlet at  $\tau$  8.82 and a three-proton singlet at  $\tau$  8.73





(see Figure 8). An nmr spectrum in  $CD_3CN$  showed six-proton singlets at  $\tau$  9.08, 8.93 and 8.82 and three-proton singlets at  $\tau$  8.77 and 8.69 (see Figures 8 and 9).

# H. Preparation of 3-Methyl-d<sub>3</sub>-2,4,5,6,6-pentamethyl-2,4-cyclohexadienone (60).

20 g of dienone 41 was added to 50 ml of methanol-d in which 0.5 g of sodium had been dissolved. The reaction was monitored by nmr until the signal at  $\tau$  7.95 for the C<sub>3</sub> methyl group had essentially disappeared. The labeled dienone was isolated by pouring the solution into 200 ml of methylene chloride and washing with 4 x 50 ml of water. Any base remaining was destroyed with solid CO<sub>2</sub>. After drying the solution over MgSO<sub>4</sub>, the solvent was removed under reduced pressure. Distillation gave the dienone as a straw-yellow liquid, bp. 100-102° at 1.8 mm of Hg.

The nmr spectrum of  $\oint Q$  showed an integrated area of one hydrogen for the signal at  $\tau$  7.95 whereas the integrated areas of the other signals were not reduced. Deuterium incorporation to the extent of 60% had been achieved at the C<sub>3</sub> methyl group.

I. Preparation of 3,5-Dimethyl-d<sub>3</sub>-2,4,6,6-tetramethyl-2,4-cyclohexadienone (45).

20 g of unlabeled dienone 41 was refluxed in 50 ml of methanol-d in which 0.5 g of sodium had been dissolved. After 8 hours an additional 20 ml of methanol-d containing 0.5 g of dissolved sodium was added and reflux was continued for another 24 hours. The crude product mixture had an nmr spectrum in which the signal at  $\tau$  7.95 showed only a weak septet and the signal at  $\tau$  8.14 (containing the C<sub>5</sub> methyl group) had



FIGURE 9. Nmr spectrum (CD<sub>3</sub>CN) of 1,2,4,4,5,6,6,8-octamethyltricyclo[3.3.0.0<sup>2,8</sup>]octane-3,7-dione (53).

split into a doublet. This doublet integrated for 6.5 hydrogens indicating that about 90% deuterium exchange had taken place in the methyl group at  $C_5$ .

Work-up as in Section H above gave pure dienone which had an nmr spectrum in which the signal at  $\tau$  7.95 integrated for 0.5 hydrogens and the doublet centered at  $\tau$  8.14 integrated for 6.5 hydrogens. Thus the dienone had methyl groups at C<sub>3</sub> and C<sub>5</sub> which were approximately 90% exchanged.

J. Preparation of 6-Methyl-d<sub>3</sub>-1,3,3,4,5-pentamethylbicyclo[2.2.2]oct-5-ene-2,7-dione (61), and 4,6-Dimethyl-d<sub>3</sub>-1,3,3,5-tetramethylbicyclo-[2.2.2]oct-5-ene-2,7- and 2,8-dione (46 and 47).

The procedures outlined in sections C through E of the experimental part were followed to obtain the labeled isomers 46, 47 and 61.

After separation and purification of the labeled products, their uv and ir spectra were obtained and these proved to be identical with those of the unlabeled compounds except that the ir spectra contained absorptions at 2200 cm<sup>-1</sup> (v  $_{C-D}$ ).

The nmr spectrum of 6-methyl-d<sub>3</sub>-1,3,3,4,5-pentamethylbicyclo[2.2.2]oct-5-ene-2,7-dione  $\pounds$  showed the previously cited signals at  $\tau$  9.10, 8.95, 8.78, 8.87, 8.38 and 8.18; however, the signal at  $\tau$  8.38 integrated for only one proton. No splitting could be observed in the signal at  $\tau$  8.18.

The nmr spectrum (CCl<sub>4</sub>) of 4,6-dimethyl-d<sub>3</sub>-1,3,3,5-tetramethylbicyclo-[2.2.2]oct-5-ene-2,7-dione 46 showed the signals at  $\tau$  9.10, 8.95, 8.87 and 8.18 as in the unlabeled 39. However, the signals at  $\tau$  8.38 and 8.78 were essentially absent and no splitting was observed for the signal at  $\tau$  8.18 (see Figure 10).



FIGURE 10. Nmr spectrum (CC1<sub>4</sub>) of 4,6-dimethyl-d<sub>3</sub>-1,3,3,5,-tetramethylbicyclo[2.2.2]oct-5-ene-2,7-dione (46).



FIGURE 11. Nmr spectrum (CCl<sub>4</sub>) of 4,6-dimethyl-d<sub>3</sub>-1,3,3,5,-tetramethylbicyclo[2.2.2]oct-5-ene-2,8-dione (42).

The nmr spectrum (CC1<sub>4</sub>) of 4,6-dimethyl-d<sub>3</sub>-1,3,3,5-tetramethylbicyclo-[2.2.2]oct-5-ene-2,8-dione 47 showed essentially no peak at  $\tau$  8.85 and the signal at  $\tau$  8.27 integrated for slightly more than three protons. All the other signals (at  $\tau$  9.10, 9.02 and 8.97) were unchanged (see Figure 11).

K. Photolysis of  $\pounds$ : Formation of a Mixture of 2-Methyl-d<sub>3</sub>-1,4,4,5,8pentamethyltricyclo[3.3.0.0<sup>2,8</sup>]octane-3,7-dione ( $\pounds$ 2) and 8-Methyld<sub>3</sub>-1,2,4,4,5-pentamethyltricyclo[3.3.0.0<sup>2,8</sup>]octane-3,7-dione ( $\pounds$ 2).

A solution of 0.1205 g of 60 in 10 ml of acetone was irradiated through Vycor for 3 hours. The solvent was then evaporated and a pure sample of the photoporduct was obtained by vpc collection (5' x 1/4", SE-30, 175°, He flow rate 80 ml/min.).

The nmr spectrum of the photoproduct showed three-proton singlets at  $\tau$  9.15, 8.98, 8.74 and 8.72 and one-proton singlets at  $\tau$  7.87 and 7.80. The only change from 37 was found in the integrated areas of the signals at  $\tau$  8.90 and 8.85. These now integrated for only two protons each.

L. Photolysis of 46: Formation of a Mixture of 2,5-Dimethyl-d<sub>3</sub>-1,4,4,8-tetramethyltricyclo[3.3.0.0<sup>2,8</sup>]octane-3,7-dione (64) and 5,8-Dimethyl-d<sub>3</sub>-1,2,4,4-tetramethyltricyclo[3.3.0.0<sup>2,8</sup>]octane-3,7dione (65).

Irradiation of 0.0864 g of 46 in 8 ml of acetone through a Vycor filter for 3 hours gave a photoproduct which was purified by vpc (5'x 1/4", SE-30, 175°, 80 ml/min. of He). The nmr spectrum (CCl<sub>4</sub>) showed three-proton singlets at  $\tau$  9.15, 8.98 and 8.74 and one-proton singlets at  $\tau$  7.87 and 7.80. The peak at  $\tau$  8.72 present in the unlabeled product 48 was completely missing and the signals at  $\tau$  8.90 and 8.85 integrated for only 1.5 protons each.

M. Dimethylation of the Mixture of 64 and 65: Preparation of 2,5-Dimethyl-d<sub>3</sub>-1,4,4,6,6,8-hexamethyltricyclo[3.3.0.0<sup>2,8</sup>]octane-3,7dione (66) and 5,8-Dimethyl-d<sub>3</sub>-1,2,4,4,6,6-hexamethyltricyclo-[3.3.0.0<sup>2,8</sup>]octane-3,7-dione (67).

0.8 g of the tricyclic labeled dienones 64 and 65 were dimethylated according to the procedure of section G. The product was purified and trapped by vpc (10' x 1/4", SE-30, 195°, 150 ml/min. of He) and an nmr spectrum was taken. The nmr spectrum (CD<sub>3</sub>CN) was identical with that of 53 in all respects except that the signal at  $\tau$  8.69 had disappeared and the peak at  $\tau$  8.82 had been reduced in area to only one methyl group. The spectrum in CCl<sub>4</sub> showed a reduction of the peak at  $\tau$  8.82 to only one methyl group but all the other signals were unchanged.

# N. Large Scale Photolysis of 32.

7 g of 32 was dissolved in 85 ml of acetone and photolyzed in a quartz immersion well through a Vycor filter for 4 hours. The solvent was removed under reduced pressure and 7.2 g of crude product were recovered. This material was sublimed at 1 mm of Hg with a bath temperature of 60° and 6.8 g of pure \$3, mp 84-85° was obtained.

0. Irradiation of 1,3,3,4,5,6-Hexamethylbicyclo[2.2.2]oct-5-ene-2,8-dione
(40).

A solution of 0.085 g of 40 in 8 ml of ether was irradiated using
 a Hanovia-L 450 W lamp through a Corex filter. The photolysis was

monitored by vpc (10' x 1/4", DEGS, 160°, 120 ml/min. of He), which indicated that five photoproducts were formed after two hours. The ratios of these five products changed upon continued irradiation until the starting material and two of the photoproducts had been consumed. The total photolysis time was 38 hours. The retention times were 16.2, 21.8, 24, 28.6 and 34 minutes. The starting material had a retention time of 39 minutes. At the end of the experiment, the compounds with retention times of 21.8 and 24 minutes had disappeared along with the starting material.

2. A solution of 0.5563 g of 40 in 10 ml of acetone was prepared. Aliquots (1 ml) drawn from this standard solution were then diluted to 5 ml with acetone and irradiated under the previous conditions. The same changing product ratio was observed, but all the starting material was consumed in 9 hours. Two photoproducts again built up and disappeared at the same time as 40. The photoproducts had the same retention times (above conditions) as those of the unsensitized reaction. Graphs of the product concentrations are shown in Figure 3.

3. 0.0546 g of 40 was dissolved in 6 ml of a solution of piperylene (10% by volume) and ether (90% by volume). This mixture was photolyzed for two hours under the same conditions as above. The solvent was removed under reduced pressure and spectra of the non-volatile material were taken after vpc purification (10' x 1/4", DEGS, 165°, 120 ml/min. of He). No products derived from 40 were observed and the spectra were identical to those of the starting material.

P. Identification of the Products from the Irradiation of 1,3,3,4,5,6-Hexamethylbicyclo[2.2.2]oct-5-ene-2,8-dione (42).

1. The compound with a retention time of 16.2 minutes is considered to be <u>1,2,4,6,7,7-hexamethyltricyclo[4.2.0.0<sup>2,4</sup>]octane-5,8-dione</u> (73). The infrared spectrum showed absorptions at 1770 and 1718 cm<sup>-1</sup>. The nmr spectrum (CCl<sub>4</sub>) showed three-proton singlets at  $\tau$  9.08, 8.95, 8.92 and 8.83, a six-proton singlet at  $\tau$  8.78 and a two-proton singlet at  $\tau$  9.33 (see Figure 12). The mass spectrum showed a parent peak at m/e = 220.

2. The compound identified as 1,3,3,4,7,8-hexamethylbicyclo[4.2.0]oct-7-ene-2,5-dione, 69, had a retention time of 21.8 minutes. The mass spectrum showed a parent peak at m/e = 220. The ir spectrum showed carbonyl absorptions at 1705 and 1770 cm<sup>-1</sup>. The nmr spectrum (CCl<sub>4</sub>) had three-proton singlets at  $\tau$  9.22, 8.98, 8.93 and 8.78, three-proton quartets (J = 1 Hz) at  $\tau$  8.45 and 8.42 and a two-proton singlet at  $\tau$  7.33 (see Figure 13).

3. The compound with a retention time of 24 minutes was identified as 1,4,6,6,7,8-hexamethylbicyclo[4.2.0]oct-7-ene-2,5-dione,  $\chi_Q$ . The ir spectrum had absorptions in the carbonyl region at 1700 and 1770 cm<sup>-1</sup> and the nmr spectrum (CCl<sub>4</sub>) consisted of three-proton singlets at  $\tau$  8.86, 8.82, 8.78 and 8.66, a six-proton singlet at  $\tau$  8.32 and two one-proton doublets (J = 16 Hz) centered at  $\tau$  7.46 and 6.61 (see Figure 14). The mass spectrum of  $\chi_Q$  had a parent peak at m/e = 220.

4. The compound with a retention time of 28.6 minutes is assigned the structure 1,2,3,3,4,6-hexamethyltricyclo[ $4.2.0.0^{2,4}$ ]octane-5,8dione, 74. It showed a parent peak at m/e = 220 in the mass spectrum



FIGURE 13. Nmr spectrum (CCl<sub>4</sub>) of 1,3,3,4,7,8-hexamethylbicyclo-[4.2.0]oct-7-ene-2,8-dione (62).





FIGURE 15. Nmr spectrum (CCl<sub>4</sub>) of 1,2,3,3,4,6-hexamethyltricyclo- $[4.2.0.0^2, 4]$ octane-5,8-dione (74).

and absorptions in the ir at 1718 and 1770 cm<sup>-1</sup>. The nmr spectrum (CCl<sub>4</sub>) had three-proton singlets at  $\tau$  9.07 and 8.87, six-proton singlets at  $\tau$  8.94 and 8.82 and two one-proton doublets (J = 17.5 Hz) centered at  $\tau$  7.32 and 7.13 (see Figure 15).

5. For the compound with retention time of 34 minutes the proposed structure is 1,2,4,4,5,8-hexamethyltricyclo[ $3.3.0.0^2,8$ ]octane-2,6dione,  $\chi_1$ . Its ir spectrum had absorptions in the carbonyl region at 1720 and 1738 cm<sup>-1</sup>. The uv spectrum in 95% ethanol showed a maximum at 267 nm ( $\varepsilon$  = 25). The nmr spectrum (CCl<sub>4</sub>) consisted of three-proton singlets at  $\tau$  9.37, 9.09, 8.99 and 8.79, a six-proton singlet at  $\tau$  8.83 and a two-proton singlet at  $\tau$  7.83 (see Figure 16). The mass spectrum of  $\chi_1$  showed a parent peak at m/e = 220.

# Q. Attempted Reduction of 71 with Lithium in Liquid Ammonia.

A solution of 0.1188 g of 7L in 1 ml of anhydrous ether was added to 20 ml of liquid ammonia which contained 0.1 g of dissolved lithium. Dry ice temperature was maintained during the addition and for three hours thereafter. The excess lithium was destroyed by the addition of  $NH_4Cl$ and the ammonia was allowed to evaporate. The remaining ether solution was added to 50 ml of water and then extracted with three 25-ml portions of ether. The extract was dried over  $MgSO_4$  and the solvent was evaporated under reduced pressure. The dark brown oil which remained was analyzed by vpc (5' x 1/4", SE-30, 150°, 80 ml/min. of He). The vpc trace showed 6 components to be present. The two major fractions which could be trapped were analyzed by their nmr spectra. The major one of these was unreacted starting material whereas the other had a poorly defined spectrum with a series of peaks from t 8.6 to 9.4. No identification of this fraction was



FIGURE 16. Nmr spectrum (CCl<sub>4</sub>) of 1,2,4,4,5,8-hexamethyltricyclo-[ $3.3.0.0^{2,8}$ ]octane-3,6-dione (71).

possible; the other fractions were present in only trace amounts and could not be trapped in sufficient ammounts to allow identification.

R. Reduction of Z1: Formation of 1,2,4,4,5,8-Hexamethyltricyclo-

 $[3.3.0.0^{2,8}]$  oct-3-one-6-o1 (94).

1. Approximately 0.005 g of the tricyclic ketone ( $\chi_{L}$  or  $\chi_{Z}$ ) was added in 2 ml of anhydrous ether to a cooled (0-5°) slurry of 0.1 g of lithium aluminum hydride in 15 ml of anhydrous ether. The reaction was allowed to proceed for 15 minutes and the excess reducing agent was destroyed with 0.5 ml of water. The mixture was filtered and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure. The ir spectrum of the non-volatile remainder showed two OH absorptions at 3450 and 3610 cm<sup>-1</sup>. No carbonyl absorptions were present.

2. Approximately 0.010 g of the tricyclic ketone (71 or 72) in 2 ml of anhydrous ether was added to 0.2 g of Li(t-BuO)<sub>3</sub>AlH in 10 ml of anhydrous ether. The reaction mixture was stirred for 30 minutes at room temperature. The excess reducing agent was then destroyed by the addition of 1 ml of water. The solution was filtered, then dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure and a non-volatile oil was isolated. Infrared absorptions at 1720 and 1738 cm<sup>-1</sup> show this to be recovered starting material.

3. The same procedure as in R-2 above was repeated on the recovered material, but the reaction was allowed to proceed for 10 hours. Work-up as in the previous section gave an oil which had absorptions in the ir spectrum at 1620, 1700 and 1720 cm<sup>-1</sup>. No absorptions were found in the OH region. The uv spectrum in 95% ethanol showed maxima at 232 nm ( $\epsilon = 7100$ ) and 205 nm ( $\epsilon = 4900$ ).

4. 0.008 g of the tricyclic ketone (71 or 72) in 2 ml of 95% ethanol was added to a suspension of 0.1 g of NaBH<sub>4</sub> in 15 ml of 95% ethanol. The reaction was allowed to proceed for 12 hours at room temperature. The reaction mixture was treated with dilute HCl to destroy the excess reducing agent and then extracted with ether. The extract was dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The non-volatile material isolated showed absorption in the ir spectrum at 1718 cm<sup>-1</sup> in the carbonyl region and in the 0H region at 3200 cm<sup>-1</sup>. The nmr spectrum (CCl<sub>4</sub>) differed from that of the starting material and had peaks at  $\tau$  9.18, 9.04, 8.95, 8.92, 8.86 and 8.74 (see Figure 17 for the ir spectrum of 94).

S. Irradiation of 4,6-Dimethyl-d<sub>3</sub>-tetramethylbicyclo[2.2.2]oct-5-ene-2,8-dione (47).

Irradiation of 0.0536 g of 47 in 5 ml of acetone using a Hanovia-L 450 W lamp through a Corex filter for 9 hours gave the three photoproducts 71, 73 and 74. Vpc collection (10' x 1/4", DEGS, 160°, 135 ml/min. of He) provided samples of each compound for nmr analysis. The spectrum of 71showed three-proton singlets at  $\tau$  9.37, 9.10 and 8.79 and a three-proton singlet at  $\tau$  8.83 as well as a two-proton singlet at  $\tau$  7.83. This spectrum differed from that of the unlabeled material in that the signal at  $\tau$  8.99 had essentially disappeared while the six-proton singlet at  $\tau$  8.83 now integrated for only three protons.



FIGURE 17. I.R. spectrum (CC14) of 1,2,4,4,5,8-hexamethyltricyclo-[3.3.0.0<sup>2,8</sup>]oct-3-one-6-ol (94).

Compound &4 showed an nmr spectrum in which the signal at  $\tau$  8.95 had disappeared and that at  $\tau$  8.78 had been reduced to one methyl group. All other signals were unchanged. &5 had an nmr spectrum in which the signal at  $\tau$  8.87 had disappeared and that at  $\tau$  8.82 had been reduced by one methyl group. The other signals were the same as in 74.

T. Attempted Reduction of 1,2,4,4,5,6,6,8-Octamethyltricyclo[3.3.0.0<sup>2,8</sup>]octane-3,7-dione (53) with Lithium in Liquid Ammonia.

A solution of 0.5 g of 53 in 80 ml of ether was added over a period of 1 hour to a stirred, dry-ice cooled solution of 0.5 g of lithium in 100 ml of liquid ammonia. Dry-ice temperature was maintained during the addition and four hours thereafter. The excess lithium was destroyed by addition of NH<sub>4</sub>Cl and the ammonia was evaporated by an air stream. The remaining ether solution was added to 20 ml of water and then extracted with three 20-ml portions of ether. The extract was dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The solid material which remained was analyzed by vpc (5' x 1/4", SE-30, 175°, 80 ml/min. of He). Two components were present in the ratio of 95:5. The major component proved to be starting material by retention time and nmr spectrum. Not enough of the minor material could be trapped for identification. When the reduction was attempted without any co-solvent, no further change was observed.

U. Reduction of 48 with Lithium in Liquid Ammonia: 1,2,4,4,5,8-Hexamethylbicyclo[3.3.0]octane-3,7-dione (121).

A solution of 6.1 g of 4% in 50 ml of dry ether was added over a period of 0.5 hour to a stirred, dry-ice cooled solution of 1.5 g of lithium in liquid ammonia. The mixture was stirred with further cooling for 4.5 hours. The excess lithium was destroyed by the addition of NH<sub>4</sub>Cl and the ammonia was evaporated. The remaining ether solution was added to 200 ml of ice water which was then extracted with ether. The extract was dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The slightly yellow oil which remained, crystallized upon cooling. The product was purified by sublimation, affording 5.3 g of a solid, mp 74-76. The yield was 82.7%.

1. N. N.

Anal. Calcd. for C<sub>16</sub>H<sub>26</sub>O<sub>2</sub>: C, 75.63; H, 9.97 Found: C, 75.58; H, 10.12.

The nmr spectrum of the purified product in CCl<sub>4</sub> showed signals at  $\tau$  9.02, 8.97, 8.90 and 8.87 for the methyl substituents and a multiplet centered at  $\tau$  7.90 with major peaks at  $\tau$  7.92 and 7.87 (see Figure 18). The two groups integrated in the ratio of 1:4.4 (1:4.5 is the expected ratio). The mass spectrum showed a parent peak at m/e = 222. The ir spectrum had a band at 1732 cm<sup>-1</sup> as the only major carbonyl absorption.




The uv spectrum in 95% ethanol exhibited a broad band from 350 to 250 nm with the maximum between 275-300 nm ( $\epsilon = 180$ ).

# V. Attempted Methylation of 121.

A solution of 1 g of the bicyclic dione 122 formed in section U was added over a period of 25 minutes to a cooled suspension of 6 g of NaH in 30 ml of ether. A solution of 1 g of methyl iodide in 10 ml of ether was then added over a period of 30 minutes. The reaction was allowed to proceed as in section N above and the same work-up was employed. The solid material isolated proved to be starting material by its nmr spectrum.

A procedure in which refluxing benzene was employed also failed to give any methylated product.

# W. Vapor Phase Irradiation of 121: Attempted Synthesis of 1,2,2,3,4,5-Hexamethylbicyclo[2.2.0]hexane 122.

0.1593 g of 1221 and a drop of clean mercury were placed in a quartz vessel which was then flushed with nitrogen and evacuated to less than  $10^{-2}$  mm of Hg while being cooled in dry-ice. The quartz vessel was then placed in a Rayonet reactor with a bank of lights emitting at 2537Å. Irradiation was carried on for 12 hours at a temperature ranging from 85 to 90°. The material was washed out of the quartz vessel and then analyzed by vpc (5' x 1/4", FFAP, 185°, 100 ml/min. of He) and nmr. The retention time as well as the nmr spectrum matched the starting material No change could be detected when the sample was irradiated for an additional 24 hours.

#### SUMMARY

1. Irradiation of an ether solution of 1,3,3,4,5,6-hexamethylbicyclo-[2.2.2]oct-5-ene-2,7-dione, 39, provided 1,2,4,4,5,8-hexamethyltricyclo-[3.3.0.0<sup>2</sup>,<sup>8</sup>]octane-3,7-dione, 48.

2. Irradiation of 32 with acetone sensitization gave 48 quantitatively.
3. Prolonged irradiation of an ether solution of 1,3,3,4,5,6-hexamethyl-bicyclo[2.2.2]oct-5-ene-2,8-dione, 40, provided 1,2,4,4,5,8-hexamethyl-tricyclo[3.3.0.0<sup>2,8</sup>]octane-3,6-dione, 71, 1,2,4,6,7,7-hexamethyltricyclo-[4.2.0.0<sup>2,4</sup>]octane-5,8-dione, 73, and 1,2,3,3,4,6-hexamethyltricyclo-[4.2.0.0<sup>2,4</sup>]octane-5,8-dione, 74, after complete conversion of 40. With shorter irradiation times, two intermediates were detected. They were 1,3,3,4,7,8-hexamethylbicyclo[4.2.0]oct-7-ene-2,5-dione, 62, and 1,4,6,6,7,8-hexamethylbicyclo[4.2.0]oct-7-ene-2,5-dione, 70, obtained in ratios which depended upon the percentage of conversion of the starting 40. Similar results were obtained with acetone sensitization.

4. Compounds 62 and 72 are formed by a 1,3-acyl migration from 42. The initial build-up in concentration of these products indicates that a photostationary state exists which is then destroyed by further reaction to form 71, 73 and 74.

5. Photoproducts 73 and 74 are secondary photoproducts derived from 69 and 70 by 1,2-acyl migration. 71 may be similarly formed from 69.
6. The photoisomerization of 39 and 40 was shown to occur from the triplet state of the diketones.

### PART II

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THE SYNTHESIS AND LOW TEMPERATURE NMR SPECTRUM OF 1,4-DIETHYL-2,3,5,6,7,8-HEXAMETHYLNAPHTHALENE

#### INTRODUCTION

The characterization of a wide variety of intramolecular processes has advanced rapidly in recent years due chiefly to the capability of nmr spectroscopy to study fast reactions which produce no chemical change<sup>54</sup>. Representative of such processes are valence isomerization, rapid ring inversion, nitrogen inversion and hindered rotation.



The valence isomerization<sup>55</sup> of 1,2-divinylaziridine 123, and the rapid molecular reorientation<sup>56</sup> in the fused bullvalene 125, were conveniently studied by nmr. Kinetic parameters in the cyclohexane 126, where ring inversion interconverts the chair forms, have been determined by studying its nmr spectrum at low temperatures<sup>57</sup>. Similar parameters were determined for the substituted piperidine 127 where nitrogen inversion interconverts the conformations<sup>58</sup>. Nmr spectroscopy has also been of fundamental importance in systems such as the substituted paracyclophane  $128^{59}$  and the tetraarylmethane  $129^{60}$ , to determine the energy of the barrier to rotation.



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In each of these systems one studies processes which effectively exchange the environment of two nuclei. If this exchange is fast on the nmr time scale one simply observes a time averaged equivalence. If the rate of the process is temperature dependent and slow on the nmr time scale, any magnetic non-equivalence (and the resulting spectra) observed will be a function of temperature. The life time of the conformation giving rise to the non-equivalence will determine the line shape of the signals observed and will allow the calculation of various thermodynamic parameters<sup>61</sup>.

The development of a general naphthalene synthesis by Oku, Kakihana and Hart<sup>62</sup> suggested the investigation by nmr spectrosocopy of the <u>peri-</u> interactions in 1,4-diethyl-2,3,5,6,7,8-hexamethylnaphthalene 130.



In the naphthalene molecule, the 1- and 8-positions are said to be <u>peri</u> to each other. Substituents located at these positions are in much closer proximity than similar substituents <u>ortho</u> to each other and their interactions introduce strain into the molecule. This strain can be detected by chemical as well as physical methods. Naphthalenes substituted in the 1- and 8-positions have been studied extensively and are the subject of a comprehensive review<sup>63</sup>. The nmr results cited there indicate that as a general rule an alkyl substituent in the 1-position will deshield a hydrogen or alkyl group in the 8-position.

A search of the literature revealed that until 1966 the 1,8 alkyl substituted naphthalenes which had been prepared contained only methyl groups (see  $131^{64}$  and  $132^{65}$ ) and thus were not suited for nmr studies. In one instance where an isopropyl-methyl interaction was present (133) the low temperature nmr spectrum was not studied<sup>66</sup>.



In 1968 Franck and co-workers<sup>67</sup> reported a method for the preparation of t-butyl substituted naphthalenes. However, a later communication which reports the synthesis of 134 mentions no low temperature nmr studies<sup>68</sup>.



One system in which <u>peri</u> interactions play a part and which has been studied by nmr is the N-alky1-2,3-dihydro-lH-benz(de)isoquinoline  $135^{69}$ . The conformational interchange to the mirror image conformation 136 can occur through ring inversion or nitrogen inversion as the first step, to be followed by nitrogen inversion or ring inversion as the second step. In either case it is the 1,8-interaction which slows down the process. Calculations based on nmr spectra at various temperatures allow the conclusion that the energy of activation for the process is 9.7 kcal/mole at -72°. It can also be concluded from the solvent dependence of the coalescence temperature that nitrogen inversion is the rate controlling step.



In the fully substituted naphthalene 130 the rotation of the C<sub>1</sub> ethyl group should be hindered by the interaction of the methyl of the ethyl group with the methyl group at C<sub>8</sub>. At low temperatures this may

lead to frozen conformations where non-equivalent environments exist for the methyl of the ethyl groups. The synthesis and characterization of 1,4-diethyl-2,3,5,6,7,8-hexamethylnaphthalene 130 and the nature of these conformations will be the topic of Part II of this thesis.

#### **RESULTS AND DISCUSSION**

#### A. Synthesis of 1,4-Diethyl-2,3,5,6,7,8-Hexamethylnaphthalene (130).

The synthetic route shown in Figure 19 is essentially that of Oku, Kakihana and Hart<sup>62</sup> for the synthesis of octamethylnaphthalene. Slight modifications were made in some steps as required by different solubilities or reactivities of the compounds employed.



The nitration of p-diethylbenzene 132 with nitric and glacial acetic acid has been reported<sup>70</sup>. It was found, however, that the reaction proceeded more rapidly and in greater yield when a mixture of nitric acid and sulfuric acid containing some water was used<sup>71</sup>. The substituted nitrobenzene 140 was distilled as a yellow oil at 90° and 0.08 mm of Hg (lit. 137-140° at 12 mm of Hg). As reported in the literature, the product decomposed when the pot temperature exceeded 135°. The ir spectrum of 140 showed absorptions at 1360 and 1540 cm<sup>-1</sup> indicating the presence of the nitro group<sup>72</sup> and at 810, 850 and 1630 cm<sup>-1</sup> characteristic of a phenyl nucleus with two adjacent and one single hydrogen<sup>73</sup>. The yield in this step was 60% of theoretical.





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Conversion of 140 to 2,5-diethylaniline (141) was accomplished by reduction with iron filings in ethanol containing some HCl<sup>74</sup>. Steam distillation of the reaction mixture after it had been made basic by the addition of sodium hydroxide allowed the initial separation of the product. Redistillation after extraction gave pure 141 (90%) as a colorless liquid boiling at 70° and 0.8 mm of Hg. Infrared absorptions at 3400 and 3500 cm<sup>-1</sup> confirm the presence of the amine function.



Initial attempts at the formation of 1,3-diethylisonitrosoacetanilide  $\frac{142}{\sqrt{2}}$ , using the procedure of Organic Syntheses<sup>75</sup> for the phenyl analog, resulted in low conversion and poor yield. It was found that the amount of sodium sulfate to be used was determined by the solubility of the substituted amine hydrochloride employed. The modification used by Newman<sup>76</sup> of making the isonitrosoacetanilide at temperatures below 100° was only employed in part. If the reaction mixture was not heated to boiling yields were still low. Compound 142 obtained in 49.6% yield after recrystallization from 2N sodium hydroxide had a melting point of 122-124°. Its ir spectrum showed absorptions at 1680 cm<sup>-1</sup> for C = N or

C = 0 (amide I band<sup>77</sup>) stretching, at 3380 cm<sup>-1</sup> for N - H stretching and at 3525 cm<sup>-1</sup> for a free OH group.



A significant improvement in the cyclization of  $\frac{142}{142}$  to 4,7-diethyl isatin,  $\frac{143}{143}$ , was achieved when the reaction was run at 35° or less rather than at 60° as suggested in Organic Syntheses<sup>75</sup> for the formation of isatin itself. After purification by column chromatography over silica gel with methylene chloride as the eluent,  $\frac{143}{143}$ , mp 144-145°, was obtained in 75% yield. The ir spectrum showed absorptions at 825 and 1625 cm<sup>-1</sup> for the phenyl nucleus with two adjacent hydrogens, at 1720 and 1750 cm<sup>-1</sup> for the two carbonyl functions and at 3425 cm<sup>-1</sup> for the N - H stretch. Comparison with absorptions at 850, 1625, 1735, 1760 and 3425 cm<sup>-1</sup> for 5,6-dimethylisatin,  $\frac{148}{148}$ , shows the above to be consistent with the structure.



The oxidation of 143 to 2-amino-3,6-diethylbenzoic acid, 144, was carried out in 2N sodium hydroxide with 15%  $H_2O_2$  at 25°. Higher temperatures resulted in lower yields and large amounts of intractable tar. Compound 144, recrystallized by acidification of a solution in 2N

NaOH, had a melting point of  $110-112^{\circ}$ . Its ir spectrum showed absorptions at 1580, 1600, 1660 (broad), 3380 and 3500 cm<sup>-1</sup>. The Sadtler spectrum<sup>78</sup> of anthranilic acid shows absorptions at 1560, 1580, 1610, 1660, 3500 and 3600 cm<sup>-1</sup>. The absorptions observed for 144 seem consistent with the structure proposed. The yield in this step was 75%.



The method of Stiles<sup>79</sup> was used for the diazotization of 144 to 3,6-diethylbenzenediazonium-2-carboxylate. The presence of a stoichiometric amount of HCl in the reaction mixture allowed the isolation of the more stable 1,3-diethylbenzenediazonium-2-carboxylate hydrochloride 145. A yield of 80% of 145, mp 69° with decomposition, was obtained.



The benzyne addition to 2,3,4,5,6,6-hexamethy1-2,4-cyclohexadienone<sup>26</sup> to give 1,3,3,4,7,8-hexamethy1-5,6-(9,12-diethy1-)benzobicyclo[2.2.2]oct-7-ene-2-one, 146, was carried out according to the method of Oku, et. al.62 The yield of 146, after chromatography on silica gel with petroleum ether as the eluent, was 55.5% of theoretical based on the diazonium carboxylate hydrochloride 145. The ir spectrum contained bands at 820 cm<sup>-1</sup> for the ortho hydrogens on the benzene ring, at 1380  $\rm cm^{-1}$  for the geminal methyl groups and at 1705 cm<sup>-1</sup> for the  $\beta,\gamma$ -unsaturated carbonyl. The nmr spectrum (CC1,) of 146 showed three-proton singlets at  $\tau$  9.34 and 9.04 for the  $C_3$  geminal methyl groups, three-proton triplets (J = 7 Hz) centered at  $\tau$  8.92 and 8.82 for the methyl groups of the ethyl substituents, three-proton signals at  $\tau$  8.3 and 8.24, with some observable coupling, for the allylic methyl groups, three-proton singlets at  $\tau$  8.19 and 8.15 for the bridgehead methyl groups, a four-proton quartet (J = 7 Hz)centered at 7.09 for the methylene hydrogens of the ethyl substituents and a two-proton singlet at  $\tau$  3.25 for the phenyl hydrogens.



Formation of 5,8-diethyl-1,2,3,4-tetramethylnaphthalene  $\frac{147}{47}$ , **Proceeded smoothly in DMSO using dimsyl sodium (prepared according to the method of Corey<sup>80</sup>) as the base to cause elimination of dimethyl ketene.** The product was purified by chromatography on silica gel with **Petroleum ether, CCl<sub>4</sub> and CH<sub>2</sub>Cl<sub>2</sub> as eluents.** The product came off in **the CCl<sub>4</sub> fractions and was obtained in 77.5% yield as a slightly yellow**  oil. The nmr spectrum (CCl<sub>4</sub>) had a six-proton singlet at  $\tau$  7.8 for the C<sub>2</sub> and C<sub>3</sub> methyl groups, a six-proton singlet for the C<sub>1</sub> and C<sub>4</sub> methyl groups at  $\tau$  7.57, a six-proton triplet (J = 7 Hz) at  $\tau$  8.85 and a four-proton quartet (J = 7 Hz) at  $\tau$  7.09 for the ethyl substituents and a two-proton singlet at  $\tau$  3.12 for the aromatic protons. These assignments are in agreement with those for the 1,2,3,4-tetramethylnaphthalene  $\frac{140}{281}^{81}$  and the 1,2,3,4,5,8-hexamethylnaphthalene  $\frac{150}{282}^{82}$ .



Conversion of 147 to 1,4-diethyl-2,3,5,6,7,8-hexamethylnaphthalene 130, was effected by bis-monochloromethylation of 147 followed by reduction of the bis-monochloromethylated product with lithium aluminum hydride. The intermediate product was not isolated. Pure 130, mp 109-111°, obtained in 24% yield in this step, had an nmr spectrum (CCl<sub>4</sub>) which showed a sixproton triplet at  $\tau$  8.85, a twelve-proton singlet at  $\tau$  7.8, a six-proton singlet at  $\tau$  7.57 and a four-proton quartet (J = 7 Hz) at  $\tau$  7.09. These chemical shifts are in good agreement with the values for octamethylnaphthalene  $151^{62}$ . The uv spectrum of 130 (95% ethanol) had maxima at 250 nm ( $\epsilon$  = 50,000) and at 308 nm ( $\epsilon$  = 5750).



B. Low Temperature nmr Spectra of 1,4-Diethyl-2,3,5,6,7,8-Hexamethylnaphthalene (130) and Their Interpretation.

At ambient temperature the nmr spectrum (CC14, see Figure 27) of 130 contains a triplet at  $\tau$  8.85 (J = 7 Hz) and a quartet at  $\tau$  7.09 (J = 7 Hz) for the ethyl substituents. This is to be expected since the ethyl groups rotate freely and the signals observed are the result of a time averaged equivalence of environments for both the methylene and the methyl protons. Figures 20 through 24 show the change in the nmr spectrum (CS<sub>2</sub>) as the temperature was lowered. An initial loss of resolution was observed in both the triplet and the quartet. These signals appeared as broad, coalesced peaks at  $-70^{\circ}$ , at  $\tau$  7.09 for the quartet and at 7 8.97 for the triplet. As the temperature was lowered still further the signals acquired resolution again and at -85° two triplets (J = 7 Hz) became apparent at  $\tau$  8.93 and  $\tau$  8.69 as well as a five line multiplet (J = 7 Hz) at  $\tau$  7.19 (see Figure 23). These positions did not change when the temperature was lowered to -100° although the resolution did improve somewhat. The area ratio of the triplets is hard to assess because of the appreciable overlap of the two signals. However, it seems to lie between 3:2 and 3:1. The five line multiplet may be









FIGURE 21. Nmr spectrum (CS<sub>2</sub>) of 1,30 at -65°.





A share was a second











interpreted as the overlap pattern of two quartets centered at  $\tau$  7.22 and  $\tau$  7.16.



In order to interpret the spectral data it is necessary to obtain some idea of the spatial arrangement of the substituents. Since no accurate data are available for the geometry of this compound, a suitable model must be employed. The best model for which an X-ray structure is known would be octamethylnaphthalene 151. However, the structure of octachloronaphthalene 152 must also be considered since it is especially pertinent to the structure of 151.



A two dimensional X-ray structure of 151 by Donaldson and Robertson indicated that the  $\alpha$ -methyl groups are displaced by 28° from the mean plane of the ring. The  $\beta$ -methyl groups were also said to be displaced, but to a smaller extent. Furthermore, the methyls were said to lie alternately above and below the plane. Some distortion of the naphthalene framework was also suspected. These findings seem to be in need of revision in light of the subsequent work on octachloronaphthalene  $152^{83}$ . On the basis of a three-dimensional X-ray analysis, the authors suggested that both the substituents and the nuclear carbon atoms were displaced from coplanarity and that distortion is extensive. The  $\alpha$ - and  $\beta$ -chlorine atoms are displaced out of the plane by 0.54-0.79 and 0.37-0.47 Å respectively, and the out-of-the-plane displacement of each carbon atom is about onethird as much, in the same direction as its halogen substituent. Furthermore, the displacement occured in the same direction for adjacent pairs of atoms and substituents as shown in the following drawing:



c <sub>1</sub> 20	C <sub>6</sub> 14	C1 <sub>1</sub> 60	c1 <sub>5</sub> 79
c <sub>2</sub> 13	C <sub>7</sub> + .14	$C1_240$	c1 <sub>6</sub> 37
c <sub>3</sub> + .11	c <sub>8</sub> + .20	c1 <sub>3</sub> + .40	c1 <sub>7</sub> + .47
C <sub>4</sub> + .22	c <sub>9</sub> 02	C1 <sub>4</sub> + .75	C1 <sub>8</sub> + .54
c <sub>5</sub> 24	c <sub>10</sub> + .01		

The argument for the structural similarity of 151 and 152 is based on the relief of skeletal strain in the suggested arrangement.

"In a propeller-like conformation like the above there is increased substituent interaction energy but less skeletal strain. The authors believe that a double-chair conformation of the nucleus will be energetically favorable only when the bonding is tetrahedral as in cyclohexane; in overcrowded aromatic systems of the type discussed here, a propeller-like conformation is considered more likely<sup>63</sup>." A three-dimensional X-ray structure of 151 has recently been undertaken<sup>84</sup>. Although the analysis is not yet complete, preliminary results indicate that it has a propeller-like geometry analogous to 152. That is, the methyl groups alternate in pairs above and below the mean ring plane.

The nmr spectra of 130 and 151 show several similarities. At ambient temperature the nmr spectrum of 130 shows two types of methyl groups. The  $\alpha$ -methyl groups are found at  $\tau$  7.57 and the  $\beta$ -methyl groups appear at τ 7.80 (see Figure 27). Since the areas are in the ratio 1:2 there is no question as to the assignment. These values are in good agreement with those of octamethylnaphthalene, where the  $\alpha$ -methyl groups appear at  $\tau$  7.59 and the  $\beta$ -methyl groups at  $\tau$  7.75. Nagsampagi<sup>66</sup> has studied the nmr spectra of polymethyl- (and other alkyl-)naphthalenes and has suggested the following generalizations for predicting chemical shifts of methyl groups: (a) an  $\alpha$ -methyl group is deshielded more than a  $\beta$ -methyl group; (b) an alkyl group ortho to a methyl causes a shielding of 4 Hz, whereas a meta alkyl group shields a methyl by only 2 Hz, and a peri alkyl group deshields by 12 Hz; (c) para alkyl groups have no effect, but a 1,4relationship in different rings shields by 3 Hz; (d) standard values for the chemical shifts are 155 Hz for the  $\alpha$  position and 148 Hz for the  $\beta$ position. These generalizations are summarized in the formulas below:



By using these values a chemical shift of  $\tau$  7.37 is predicted for the a-methyl groups of both 130 and 151 (155 + 12 - 4 - 2 - 3 = 158 ÷ 60 = 2.63  $\delta$  =  $\tau$  7.37). For the  $\beta$ -methyl groups the predicted value is  $\tau$  7.75 (148 - 4 - 4 - 2 - 3 = 135 ÷ 60 = 2.25  $\delta$  =  $\tau$  7.75). The prediction agrees rather well for the  $\beta$ -methyl groups but not for the  $\alpha$ -methyl groups. This is, however, not suprising since the strain due to <u>peri</u> interaction would effect the  $\alpha$ -methyl groups most and throw off the predictive values for these groups. As a result of the similarity in chemical shift between the methyl groups of 130 and 151 it will be assumed that the spatial arrangement of the substituents in both peralkylnaphthalenes is essentially the same.

If the structures of both 151 and 130 are similar to the structure of 152, 130 would most likely have a propeller-like conformation in which the adjacent substituents in each  $\alpha$ - or  $\beta$ - pair are displaced in different senses from the mean plane and with the adjacent  $\alpha$ - $\beta$  substituents displaced in the same direction. The largest displacement is to be found for the  $\alpha$  substituents with the adjacent  $\beta$  substituent displaced in the same direction by 1/2 to 2/3 of that distance. A two dimensional representation of the arrangement is attempted below.





Part A of the above representation depicts a view from the  $C_2-C_3$ side of the ring.  $C_9$  and  $C_{10}$  lie essentially in the mean plane, but the other carbon atoms of the naphthalene framework are displaced above and below it, as shown. The spatial relationship of the methyl groups and carbon atoms with respect to the plane of the paper (which runs through  $C_9$  and  $C_{10}$ ) is indicated with solid or dotted lines. Solid lines indicate the groups on the same side as the observer while dotted lines are used for groups on the other side and away from the observer. Part B of the representation shows a view toward the naphthalene ring at  $C_1$  and  $C_8$ . The plane of the paper now bisects the  $C_2-C_3$  and the  $C_6-C_7$  bonds and the same convention as above is used for depicting near and far relationships. The path followed by the methyl group of the freely rotating ethyl substituent is also dotted.

The interpretation of the low temperature nmr spectrum of 130 is based on these representations as good approximations of the spatial arrangement of the substituents in relation to each other and to the ring. At low temperature the methyl group of the ethyl substituent may be frozen on one side of the ring to avoid interaction with the <u>peri</u> and  $\beta$ -methyl groups. Since there are two ethyl substituents, combinations of conformations at C<sub>1</sub> and C<sub>4</sub> will give rise to three distinct geometric possibilities. Numerical estimates for the energies of the methyl-methyl interactions in these different conformations would be meaningless at present and, in the absence of any knowledge of the true structure of 130, the discussion can only be qualitative.

In the first and lowest energy form  $J_3Q_8$ , the methyl group  $E_1$  will avoid interaction with the methyl groups  $M_2$  and  $M_8$ . At the other ethyl substituent the methyl group can avoid interaction with methyl groups  $M_3$  and  $M_5$  by a similar arrangement.



The next lowest energy form, 130b, would have one ethyl group in the same geometric arrangement as in 130a. The other ethyl substituent will be in a new environment by rotation of the methyl group by 180° from its previous position. This brings about a steric interaction with the methyl groups  $M_2$  and  $M_8$  in the case of  $E_1$  or with  $M_3$  and  $M_5$  in the case of  $E_4$ . (Although  $M_2$  and  $M_5$  are displaced in the direction of the ethyl group they

are not as far above the plane as the methylene portion and some repulsion is likely.) The situation for 130b is depicted below.



The highest energy form, 130c, would of course be formed when both ethyl groups have their methyl groups situated so as to interfere sterically with the methyl groups  $M_2$ ,  $M_8$ ,  $M_5$  and  $M_3$ .



These three arrangements, 130a, 130b and 130c, have the ethyl group in two positions which would give rise to different environments for the methylene as well as the methyl protons. This difference in environment would result in different chemical shifts for the two positions. In the conformation where the methyl groups  $E_1$  and  $E_4$  are so situated as to minimize interactions with peri and ortho methyl groups, these methyls lie

within the shielding region of the ring. In the other conformation  $(E_1 \text{ and } E_4 \text{ turned } 180^\circ \text{ from their previous position})$ , the position of these methyl groups is closer to the plane of the ring, and puts them into a less shielded position. In this manner one can explain the appearance of two methyl triplets and concomittantly, the appearance of two methylene quartets.

Since the triplets are a result of two different spatial arrangements of the methyl groups, the areas of these triplets are indicative of the population of that particular arrangement. Without the true value of the area ratio between the two triplets it is of course not possible to state what combination of the three forms of 130 are present at low temperature. If the area ratio is 3:1 for instance, the simplest combination which would lead to this ratio would be a 1:1 combination of 130a and 130b. This seems a rather likely situation since it is conceivable that the two interactions per ethyl group in the least stable form 130c would preclude its existence.

The combination of 130a:108b:108c in the ratio of 5:2:1 will also result in a three to one area ratio. If the energetics of the least stable form are as stated above, this seems a less likely combination. The third possibility with 130a and 130c in a 3:1 ratio is the least likely combination. This would allow the existence of the least stable 130c without the presence of the more stable 130b at the same time.

Due to the extreme overlap of the two methylene quartets no information can be obtained from these signals.

#### EXPERIMENTAL

# A. Nitration of para-Diethylbenzene 132: Synthesis of 2,5-Diethyl-

## nitrobenzene 140.

25 g of p-diethylbenzene was gradually added to a stirred and cooled solution of 45 ml of concentrated nitric acid, 75 ml of concentrated sulfuric acid and 15 ml of water. The rate of addition was adjusted so as to keep the temperature of the reaction mixture below 10°. The reaction mixture was stirred for 4 hours, then poured into 300 ml of ice-water. The organic material was extracted with 3 x 100 ml of CHCl<sub>3</sub>. The extract was washed with 2 x 100 ml of saturated NaHCO<sub>3</sub> solution and then with 2 x 100 ml of H<sub>2</sub>O. The extract was then dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. Distillation gave the product 140 (bp 90° at 0.8 mm of Hg; lit. bp 137-140° at 12 mm of Hg)<sup>70</sup> in 60% yield. Decomposition occured if the distillation flask was heated above 135°.

The ir spectrum (neat) showed absorptions at 810, 850, 1360, 1540 and 1630 cm<sup>-1</sup>.

B. Reduction of 2,5-Diethylnitrobenzene (140): Formation of 2,5-Diethylaniline (141).<sup>74</sup>

25 g of 140 was dissolved in 250 ml of 95% ethanol containing 10 ml of conc. HCl. The solution was stirred and heated to reflux and 50 g of iron filings was added in three portions. Reflux was continued for 24

hours. The reaction mixture was made basic by the addition of 20 g of NaOH and then steam distilled. The distillate was extracted with 4 x 200 ml of ether. The extract was dried over  $MgSO_4$  and the solvent was then removed under reduced pressure. The remaining oil was distilled and 18.2 g (90%) of 141, bp 70° at 0.8 mm of Hg, was collected. The ir spectrum (neat) showed bands at 825, 880, 1280, 1440, 1620, 3400 and 3500 cm<sup>-1</sup>.

C. Formation of the Isonitrosoacetanilide (142) of 2,5-Diethylaniline

# (141).

9 g of 141 was added with vigorous stirring to 100 ml of  $H_2O$  containing 20 ml of conc. HC1. The resulting hydrochloride salt mixture was further diluted with 200 ml of  $H_2O$  to effect solution and the solution was then added to 185 ml of  $H_2O$  containing 75 g of  $Na_2SO_4$  and 13 g of chloral hydrate. The stirred mixture was then warmed and kept at 50° for 0.5 hours and 17 g of hydroxylamine hydrochloride was then added. The temperature was raised to 65° and kept between 65° and 70° for 1 hour. Finally the mixture was brought to boiling over a period of 20 minutes and as soon as the reaction mixture boiled, it was cooled in an ice bath. The product which had formed as a brown tar mixed with white crystals was dissolved in 2N NaOH and reprecipitated by the addition of dilute HC1. Several fractions of crystals were collected to give a total of 6.6 g (49.67) of 142, with a melting point of 122-124°. The ir spectrum (CC1<sub>4</sub>) had absorptions at 825, 1525, 1620, 1680, 3380 and 3525 cm<sup>-1</sup>.

D. Acid Rearrangement of 142 to 4,7-Diethyl-2,3-indolinedione (4,7-Diethylisatin) 143.


5.35 g of 142 was added, with stirring, to 70 ml of 85%  $H_2SO_4$  at a slow enough rate so as to keep the temperature below 35°. The reaction mixture was stirred for another 2 hours, then poured into 700 ml of icewater. The isatin separated as reddish-brown crystals. Purification of the product 143 was accomplished by column chromatography. A 3 cm diameter column was packed with 100 g of silica gel (60-200 mesh) with  $CH_2Cl_2$  as the solvent. The impure material was introduced as a solution in  $CH_2Cl_2$  and was eluted with the same solvent. The elution could be followed easily because of the crimson color of the product. 4.6 g (92%) of diethylisatin, having a melting point of 144-145°, was collected. Chromatography gave the analytical sample.

Anal. Calcd. for C<sub>12</sub>H<sub>13</sub>NO<sub>2</sub>: C, 70.9; H, 6.4; N, 6.8 Found: C, 70.91; H, 6.41; N, 6.88.

The ir spectrum (CCl<sub>4</sub>) showed absorptions at 825, 1585, 1625, 1720, 1755 and 3425 cm<sup>-1</sup>.

E. The Oxidation of 4,7-Diethylisatin (143): Synthesis of 2-Amino-3,6-diethylbenzoic acid (144).

2.1 g of 143 was dissolved in 80 ml of 107 NaOH on a steam bath. The solution was then cooled to 25°. To this stirred solution was added 10 ml of 157  $H_2O_2$  dropwise over 20 minutes and stirring was continued for two hours. The reaction mixture was acidified with HCl, whereupon the product precipitated. 1.5 g (75%) of 144 were thus obtained, mp 110-112°. The analytical sample was obtained from this recrystallization.

Anal. Calcd. for C<sub>11</sub>H<sub>15</sub>NO<sub>2</sub>: C, 68.37; H, 7.82; N, 7.25

Found: C, 68.28; H, 7.81; N, 7.24.

The ir spectrum (CC1<sub>4</sub>) showed absorptions at 820, 1580, 1610, 1660 broad, 3380 and 3500 cm<sup>-1</sup>.

F. Diazotization of 144: Synthesis of 3,6-Diethylbenzenediazonium-2carboxylate Hydrochloride 145.

2.3 g of 144 was dissolved in 25 ml of absolute ethanol containing 1 ml of concentrated HCl. To this cooled solution (0-10°) 2 ml of isoamyl nitrite was added slowly with vigorous stirring. After 2.5 hours of continuous stirring and cooling, 30 ml of ether was added to precipitate the carboxylate hydrochloride 145. The solution was stirred for another 0.5 hours and then filtered. Further addition of ether and stirring while cooling allowed the separation of two additional crops of crystals. A total of 2.8 g (80.5%) of the salt, mp 69° with decomposition, was collected. No further characterization was attempted.

G. Generation of 3,6-Diethylbenzyne and Addition to 2,3,4,5,6,6-Hexamethyl-2,4-cyclohexadienone: Formation of 1,3,3,4,7,8-Hexamethyl-

5,6-(9,12-diethylbenzo)bicyclo[2.2.2]oct-7-ene-2-one (146).

2.8 g of 145 was stirred in 40 ml of 1,2-dichloroethane and to it was added 2.5 g of 2,3,4,5,6,6-hexamethy1-2,4-cyclohexadienone and 5 ml of propylene oxide. The reaction proceeded at foom temperature for 15 minutes with vigorous evolution of gas. The mixture was then refluxed for 1.5 hours. The reaction mixture was poured into 100 ml of water and extracted with 3 x 50 ml of ether. The extract was dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure. A vpc trace (5' x 1/4" SE-30 column at 170°, 100 ml/min of He) showed the residue to contain two fractions. Pure 146 was obtained by column chromatography on silica gel (1 x 34 cm, 60-200 mesh) with petroleum ether as the eluent. 2 g of 146 were thus eluted before the second component, which proved to be the starting cyclohexadienone, came off the column as well. Further purification and trapping by vpc (above conditions) gave the analytical sample.

Anal. Calcd. for C<sub>22</sub>H<sub>30</sub>O: C, 85.11; H, 9.47

Found: C, 84.97; H, 9.63.

The ir spectrum (CCl<sub>4</sub>) of 146 contained absorptions at 830, 1030, 1070, 1380, 1460 and 1705 cm<sup>-1</sup>. The nmr spectrum (CCl<sub>4</sub>) showed a twoproton singlet at  $\tau$  3.25, a four-proton quartet (J = 7 Hz) at  $\tau$  7.19, three-proton singlets at  $\tau$  8.15, 8.19, 9.34 and 9.04, three-proton quartets (J = 1 Hz) at  $\tau$  8.3 and 8.24 and three-proton triplets (J = 7 Hz) at  $\tau$  8.82 and 8.92 (see Figure 25).

## H. Reaction of 146 with Sodium Methylsulfinylcarbanion: Preparation of 5,8-Diethyl-1,2,3,4-tetramethylnaphthalene (147).

Sodium methylsulfinylcarbanion (dimsyl sodium) was prepared according to the method of Corey and Chaykovsky <sup>77</sup> from 0.5 g of NaH and 15 ml of DMSO. 1 g of 146 dissolved in 10 ml of ether was added to this solution and the reaction was allowed to proceed at 50° for two hours. The reaction mixture was poured into 300 ml of ice water and the organic material was extracted with 2 x 100 ml of ether. The extract was washed with large amounts of water to remove as much DMSO as possible. The extract was then dried over MgSO<sub>4</sub> and the solvent was then removed under reduced pressure. The product was separated from the crude reaction mixture by column chromatography on silica gel (1 x 30 cm, 60 -200 mesh)





using 100 ml of petroleum ether, 100 ml of  $CCl_4$  and 100 ml of  $CH_2Cl_2$  as eluents. 0.6 g of 147 (77.5%) was eluted with petroleum ether and  $CCl_4$ and unreacted starting material came off the column with  $CH_2Cl_2$ . The analytical sample was obtained by vpc purification and trapping (5' x 1/4" SE-30 column at 200°, He flow of 120 ml/min.).

Anal. Calcd. for C<sub>18</sub>H<sub>24</sub>: C, 89.94; H, 10.06

The nmr spectrum (CCl<sub>4</sub>) of 147 showed a two-proton singlet a  $\tau$  3.12, a four-proton quartet (J = 7 Hz) at  $\tau$  7.09, two six-proton singlets at  $\tau$  7.57 and 7.8 and a six-proton triplet (J = 7 Hz) centered at  $\tau$  8.85 (see Figure 26).

I. Bis-monochloromethylation of 5,8-Diethyl-1,2,3,4-tetramethylnaphthalene (147): Preparation of 1,4-Diethyl-2,3-bis-monochloromethyl-5,6,7,8-tetramethylnaphthalene.

Dry HCl gas was bubbled through a mixture of 2 g of paraformaldehyde and 10 ml of glacial acetic acid until the mixture became homogeneous. A solution of 0.6 g of  $\frac{147}{47}$  in 5 ml of glacial acetic acid was added. The solution was stirred at room temperature for 5 hours, then poured into 50 ml of ice water. The organic material was extracted with 3 x 50 ml of ether and the extract was then dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure. The dark-brown oil which remained was used in the next step without further purification.





J. Reduction of 1,4-Diethyl-2,3-monochloromethyl-5,6,7,8-tetramethylnaphthalene: Preparation of 1,4-Diethyl-2,3,5,6,7,8-hexamethylnaphthalene (130).

The crude product obtained in Section I above was dissolved in 2 ml of anhydrous ether and added over a period of 10 minutes to a stirred and cooled suspension of 0.8 g of lithium aluminum hydride in 15 ml of ether. The reaction mixture was then stirred at room temperature for 12 hours. Addition of 3 ml of water to destroy the excess reducing agent gave a filterable slurry of alumina. The solution was filtered and then dried over MgSO4. The ether was removed under reduced pressure and a brown oil was obtained. The product mixture was chromatographed on silica gel (1 x 25 cm, 60 - 200 mesh) with 80 ml of petroleum ether, 80 ml of CCl<sub>4</sub> and 80 ml of CH<sub>2</sub>Cl<sub>2</sub> as eluents. The first CCl<sub>4</sub> fraction gave 0.135 g of 130, mp 92.5-102°, after recrystallization from methanol. The second and third CCl<sub>4</sub> fractions, analyzed by nmr, showed aromatic protons and were thus contaminated with starting material or heptasubstituted naphthalene. These fractions were also recrystallized from methanol and the crystalline material was combined with the previous fraction. Sublimation at water aspirator pressure and a bath temperature of 90° gave 0.165 g of 130, mp 109-111°. The yield for the last two steps is 24% based on the starting material  $\frac{14}{14}$ . The analytical sample was obtained by sublimation.

Anal. Calcd. for C<sub>20</sub>H<sub>28</sub>: C, 89.49; H, 10.51 Found: C, 89.29; H, 10.44. The nmr spectrum (Figure 27) 130 showed a six-proton triplet (J = 7 Hz) at  $\tau$  8.85, a twelve-proton singlet at  $\tau$  7.80, a six-proton singlet at  $\tau$  7.57 and a four-proton quartet (J = 7 Hz) at  $\tau$  7.09. The uv spectrum (95% ethanol) showed maxima at 250 nm ( $\varepsilon$  = 50,000) and at 308 nm ( $\varepsilon$  = 5750).

The low temperature nmr spectra were obtained by dissolving 0.060 mg of 130 in .6 ml of CS<sub>2</sub>. The spectrum lost resolution as the temperature was lowered. At -70° both the triplet and quartet had coalesced. The quartet signal appeared at  $\tau$  7.40 and that for the triplet at  $\tau$  8.97. At -85° two triplets (J = 7 Hz) could be observed at  $\tau$  8.93 and 8.69 as well as a five line multiplet centered at  $\tau$  7.19 (J = 7 Hz).



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## SUMMARY

1. The nmr spectrum of 1,4-diethyl-2,3,5,6,7,8-hexamethylnaphthalene, 130, at ambient temperature indicates that the <u>peri</u> interactions in the compound are not sufficient to cause hindered rotation at that temperature.

2. The low temperature nmr spectrum of 130 shows a coalescence temperature of  $-70^{\circ}$  and indicates that the rotation of the ethyl groups can be sufficiently hindered to give rise to two signals for these substituents at  $-85^{\circ}$ .

3. According to nmr data the spatial arrangement of the methyl groups in 130 is similar to that of octamethylnaphthalene.

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