

solution was refluxed for 6 hr. The solvent was distilled off and the residue was chromatographed on alumina and then fractionated over a 2-ft. spiral column. The central fraction was collected between 92 and 102° (1.25 mm.) (59 g., 36%); v.p.c. analysis on two columns indicated the olefin to be 90% pure. The *trans* configuration of the olefin is supported by a strong infrared band at 965 cm.<sup>-1</sup> and by the method of preparation.<sup>50</sup>

The Simmons-Smith reaction<sup>8</sup> on the olefin was carried out in the same manner as described above for the 1-phenyl-1-butene. The resulting cyclopropane was separated by v.p.c. on a QF-1 column from the unreacted olefin. The conversion of olefin to cyclopropane was 70%. The material isolated from v.p.c.

trappings was compared *via* its infrared and n.m.r. spectra with the 1-butene adduct of *p*-methoxybenzal bromide to which the *anti* configuration had been assigned. The spectra were found to be identical in every respect.

**Acknowledgment.**—The authors are indebted to Mr. J. J. Coyle for synthesizing *trans*-1-phenyl-2-ethylcyclopropane. An equipment grant from the National Science Foundation (NSF GP-827) for upgrading the nuclear magnetic resonance facilities is gratefully acknowledged.

[CONTRIBUTION FROM THE PROCTER & GAMBLE CO., MIAMI VALLEY LABORATORIES, CINCINNATI 39, OHIO]

## The Photochemical Properties of a 2-Methyl-1,4-dien-3-one<sup>1</sup>

BY PAUL J. KROPP

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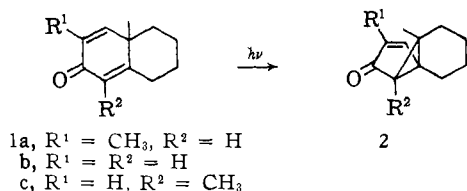
In an effort to learn more about the nature of the effects of alkyl substituents in the photochemical rearrangements of cross-conjugated cyclohexadienones, the photochemical properties of the 2-methyl-1,4-dien-3-one **1a** in both neutral and acidic media were studied. Irradiation of **1a** in dioxane gave the linearly conjugated isomer **5** as the principal product. This unprecedented transformation was resolved into a sequence of at least three distinct photochemical rearrangements involving the cyclopropyl ketones **2a** and **4** as intermediates. In 45% acetic acid the sequence of rearrangements leading to the dienone **5** was again observed, but the principal photoproduct under these conditions was the spiro ketone **17a**. No evidence for the formation of any significant amount of the 5/7-fused ketone **18a** could be detected. This contrasts with 4-methyldienones **1c**, which give predominantly 5/7-fused ketone products **18c**, and with unsubstituted dienones **1b**, which give approximately 1:1 mixtures of the two products **17b** and **18b**. The present results substantiate the view that hydroxy ketone formation is directed by the electronic effects of A-ring alkyl substituents in the cyclopropyl intermediate **16**. Both the dienone **5** and the spiro ketone **10** were obtained in methanol. Two minor products formed in both acidic and neutral media were the phenols **6** and **13**. The former product was shown to arise from the cyclopropyl ketone **4**, which is also the immediate precursor of the dienone **5**. The intermediate **4** showed a marked sensitivity to the nature of the medium, giving a significantly higher ratio of phenol **6** to dienone **5** in acidic media than in neutral media. The formation of **13** is significant in that it does not arise *via* either of the cyclopropyl ketones **2a** or **4**, and thus represents a third reaction pathway for the dienone **1a**, of a type heretofore unrecognized. The role of the 2-methyl substituents in the photochemical properties of **1a** is discussed.

Under the influence of ultraviolet irradiation cross-conjugated cyclohexadienones of type **1** undergo a series of complex, and extremely fascinating, rearrangements.<sup>2</sup> One of the most surprising results from recent studies of these rearrangements has been the discovery that the presence or absence of a methyl substituent at C-4<sup>3</sup> of these dienones has a marked influence on their photochemical behavior.<sup>4,5</sup> In an effort to learn more about the nature of this substituent effect, we have examined the photochemical properties of a 2-methyl-substituted dienone (**1a**) in both neutral

and acidic media. The results of this study, which are described below, reveal several new intriguing photochemical properties and provide additional insight into various mechanistic aspects of these rearrangements.

The required dienone **1a**<sup>6</sup> was prepared in 50% yield from the octalone **3**<sup>7</sup> by oxidation with selenium dioxide.<sup>8</sup> The results from the irradiation of **1a** are summarized in Table I.<sup>10</sup>

**Neutral Media.**—The photochemical properties of several 4-methyl-1,4-dien-3-ones (type **1c**) in dioxane or ethanol have been studied; in each case initial rearrangement to a single photoproduct (type **2c**, commonly known as the "lumiproduct") occurred in yields as high as 70%.<sup>2</sup> On the other hand, the one unsubstituted dienone (type **1b**) to be studied gave in dioxane a complex mixture of ketonic and phenolic products, including the lumiproduct **2b**, with no single product being formed in more than 18% yield.<sup>4a</sup> The irradiation of **1a** in dioxane or methanol resembled that of the 4-methyl derivatives in that a predominate photoproduct



(1) (a) Part IV of the series: Photochemical Rearrangements of Cross-Conjugated Cyclohexadienones; (b) for Part III see P. J. Kropp, *J. Am. Chem. Soc.*, **85**, 3779 (1963); (c) presented in part before the Organic Division, 147th National Meeting of the American Chemical Society, Philadelphia, Penna., April 9, 1964.

(2) For a recent review of the photochemistry of cross-conjugated cyclohexadienones, see O. L. Chapman in "Advances in Photochemistry," Vol. 1, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Eds., John Wiley and Sons, Inc., New York, N. Y., p. 323 ff.

(3) The steroid numbering system is used throughout the Discussion section.

(4) (a) H. Dutler, C. Ganter, H. Ryf, E. C. Utzinger, K. Weinberg, K. Schaffner, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **45**, 2346 (1962);

(b) C. Ganter, E. C. Utzinger, K. Schaffner, D. Arigoni, and O. Jeger, *ibid.*, **45**, 2403 (1962).

(5) P. J. Kropp and W. F. Erman, *J. Am. Chem. Soc.*, **85**, 2456 (1963).

(6) R. Futaki, *J. Org. Chem.*, **23**, 451 (1958), previously obtained **1a** in 36% yield as a pale yellow oil from bromination-dehydrobromination of *cis*-3,9-dimethyl-2-decalone. In the present work **1a** was obtained as a crystalline solid.

(7) J. Cologne, J. Dreux, and J.-P. Kehlstadt, *Bull. soc. chim. France* 1404 (1954).

(8) 2,3-Dichloro-5,6-dicyanobenzoquinone is normally a more convenient reagent for the oxidation of monoenones to cross-conjugated dienones (ref. 9). Quite surprisingly, however, we found that the octalone **3** is totally inert toward this reagent in refluxing benzene.

(9) D. Burn, D. N. Kirk, and V. Petrow, *Proc. Chem. Soc.*, 14 (1960).

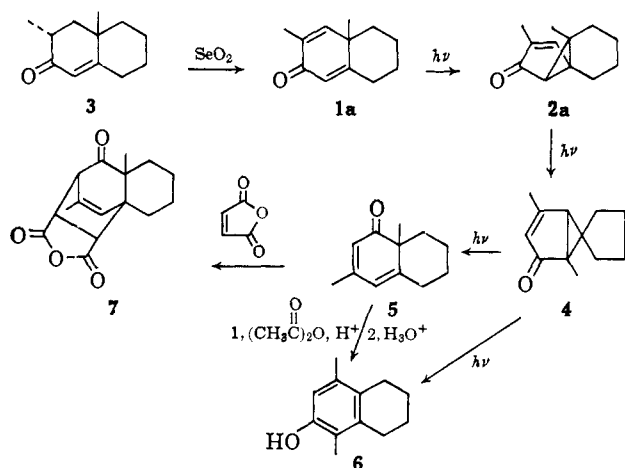
(10) Throughout the course of this work the necessary control runs were conducted to show that all rearrangements classified as being light-induced did not occur under the reaction conditions in the absence of light.

TABLE I  
PHOTOCHEMICAL REARRANGEMENT OF 3,4a-DIMETHYL-5,6,7,8-TETRAHYDRO-2(4aH)NAPHTHALENONE (1a)

Solvent	Lamp	Time, min.	Yields, <sup>a</sup> %						
			Lumiproduct (2a)	Ketone 4	Dienone 5	Spiro ketone 10 or 17a	Phenol 13	Phenol 6	Methyl esters <sup>b</sup>
Methanol	High pressure <sup>c</sup>	30	..	23 <sup>d</sup>	19 <sup>d</sup>	9 (10)	4.5 <sup>e</sup>	2 <sup>e</sup>	3
		70	..	5 <sup>d</sup>	38	10	3 <sup>e</sup>	1 <sup>e</sup>	6
Dioxane	Low pressure <sup>f</sup>	45	40	12 <sup>d</sup>	8 <sup>d</sup>	4 <sup>d</sup>	1	..	Trace
		45	67	7 <sup>d</sup>	2 <sup>d</sup>	..	..	..	..
45% acetic acid	High pressure	300	..	..	50	..	Trace	..	..
		30	Trace	Trace	2	48 (17a)	14 <sup>e</sup>	3 <sup>e</sup>	..
		60 <sup>g</sup>	3	2	4	51	4	..	..
		180 <sup>h</sup>				25	4.5 <sup>e</sup>	2 <sup>e</sup>	..

<sup>a</sup> Yields reported are for a typical run. Substantially the same results were obtained in one or more additional determinations. <sup>b</sup> See footnote 22. <sup>c</sup> Hanovia 200-watt high-pressure mercury vapor lamp. <sup>d</sup> Estimated by gas chromatographic analysis of fractions isolated by column chromatography. <sup>e</sup> Estimated by n.m.r. analysis of fractions isolated by column chromatography. <sup>f</sup> See footnote 15. <sup>g</sup> Dienone 1a recovered in 11% yield. <sup>h</sup> Only the phenolic and spiro ketone fractions were examined.

was formed. However, it was immediately obvious that lumiproduct formation had not been the major result of the irradiation. Instead, the unprecedented transformation of the cross-conjugated dienone 1a to the isomeric, linearly conjugated dienone 5 had occurred.



Both physical and chemical data were employed to establish the structure of the photoproduct as 5. The infrared spectrum showed carbonyl absorption at 6.02  $\mu$  and olefinic absorption at 6.12 and 6.36  $\mu$ , a pattern which is typical of dienone systems. The ultraviolet spectrum (316 m $\mu$ ,  $\epsilon$  4300) revealed that the dienone system was homoannular and linearly conjugated and probably bore two alkyl substituents (the 3-methyl group and C-6).<sup>11,12</sup> This latter point was confirmed by the n.m.r. spectrum, which showed the presence of one vinylic methyl group (7.94  $\tau$ ), one non-vinylic methyl group (8.74  $\tau$ ), and only two vinylic protons (4.12  $\tau$ ).

From these data the approximate structure I could be assigned, with only the exact location of the methyl substituent on ring A in doubt. Of the three possible positional isomers of I, the 4-methyl derivative II could be eliminated, since this compound differs from the photoproduct in the ultraviolet spectrum ( $\lambda_{\max}$  328 vs. 316 m $\mu$ ) and the melting point of its 2,4-dinitrophenylhydrazone derivative (129.5–131° vs. 171.5–172.5°).<sup>12</sup> Of the two remaining isomers, the 3-methyl derivative 5 could be selected on the basis that the photoproduct formed an adduct with maleic an-

hydride (7) in which the methyl substituent had remained at an unsaturated position.<sup>13</sup> Final confirmation of the assignment 5 was obtained by acid-catalyzed dienone-phenol rearrangement of 5 to the expected phenol 6, which was identified by direct comparison with an authentic specimen.<sup>14</sup>



When the irradiation of 1a was monitored gas chromatographically, it was discovered that at least two discrete intermediates intervened between 1a and the dienone 5. In an effort to increase the photostationary concentration of one or more of these intermediates, the effect of replacing the broad mercury spectrum with a monochromatic light source of 2537 Å. was investigated.<sup>15</sup> Under these conditions the dienone 1a gave a new principal photoproduct which proved to be the lumiproduct 2a.<sup>16</sup> This material exhibited the expected absorption at 5.92 (carbonyl) and 6.14  $\mu$  (double bond) and at 234 ( $\epsilon$  5280) and 270 m $\mu$  ( $\epsilon$  1900).<sup>2,4a,5</sup> Moreover, it formed a dihydro derivative (8) which had the typical cyclopropyl ketone carbonyl absorption at 5.84  $\mu$ .<sup>4a,5</sup> The  $\beta$ -vinylic proton of 2a appeared as a quartet at 3.14  $\tau$ , and the  $\alpha$ -methyl substituent was seen as a doublet ( $J_{AB} = 1.5$  c.p.s.) at 8.32  $\tau$ . Oxidative ozonolysis gave a dicarboxylic acid with carbonyl absorption at 5.78 and 5.88  $\mu$ .<sup>17</sup>

(13) A mixture of two adducts was obtained in a ratio of 2:3, which presumably resulted from the two possible orientations of the maleic anhydride moiety on the  $\alpha$ -face of 5. Recrystallization provided a 1:1 mixture which exhibited a three-proton doublet at 8.12  $\tau$  ( $J_{AB} = 1.5$  c.p.s.), indicating that the methyl substituent in question was vinylic in both adducts.

(14) L. F. Fieser and W. C. Lothrop, *J. Am. Chem. Soc.*, **58**, 2050 (1936); K. Paranjpe, N. L. Phalnikar, B. V. Bhide, and K. S. Nargund, *Rasayanam*, **1**, 233 (1943) [*Chem. Abstr.*, **38**, 4267 (1944)]; M. Yanagita and R. Futaki, *J. Org. Chem.*, **21**, 949 (1956); M. Yanagita, S. Inayama, M. Hirakura, and F. Seki, *ibid.*, **23**, 690 (1958).

(15) A Hanau NK 6/20 low-pressure lamp was employed, which emits 95% of its ultraviolet light at 2537 Å.

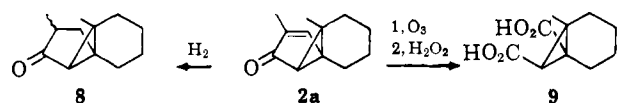
(16) E. Altenburger, H. Wehrli, and K. Schaffner, *Helv. Chim. Acta*, **46**, 2753 (1963), have recently referred to unpublished work by J. Bollini, J. Frei, C. Ganter, D. Kägi, and H. Ryf in which 2-methylandrosta-1,4-dien-3-one-17 $\beta$ -ol was converted to the corresponding lumiproduct using radiation of 2537 Å. Apparently at this particular wave length lumiproducts are sufficiently less labile than the dienones from which they are formed that the concentration of the lumiproduct in the reaction mixture passes through an appreciably large maximum before the subsequent conversion to secondary photoproducts becomes significant. By interruption of the irradiation at the appropriate time, the lumiproduct can be isolated in high yield.

(17) The appearance of two carbonyl bands is not uncommon for dicarboxylic acids in which the carboxylate groups are held in close proximity; see L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 169.

(11) Cf. discussion by W. G. Dauben, P. D. Hance, and W. K. Hayes, *J. Am. Chem. Soc.*, **77**, 4609 (1955).

(12) L. Mandell, D. Caine, and G. E. Kilpatrick, *ibid.*, **83**, 4457 (1961).

This material had the correct molecular weight and analysis for the expected acid **9**, which would be formed from **2a** by the loss of two carbon atoms. By analogy with all of the other known lumiproductions,<sup>2</sup> the structure and stereochemistry **2a** is assigned to the photoproduct.

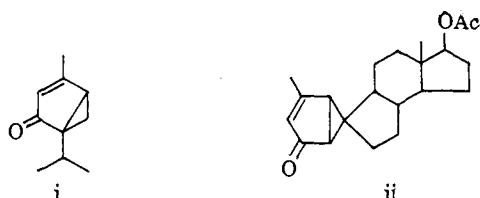


The intermediacy of the lumiproductions **2a** in the transformation of **1a** to **5** was established by irradiation of a pure specimen of **2a** in methanol; **5** was obtained in 62% yield. Moreover, gas chromatographic monitoring of the course of this irradiation revealed that the second intermediate noted above intervened between **2a** and **5**. By interruption of the irradiation of either the dienone **1a** or the lumiproductions **2a** before completion, this second intermediate could be isolated in fair yield. Irradiation of a small specimen of this new material, which was subsequently assigned the structure **4**, gave the linear dienone **5** in 57% yield. None of the lumiproductions **2a** or any other intermediate could be detected during the irradiation of **4**; it therefore appears that **4** is the immediate precursor of **5**.

Insufficient quantities of **4** were available for carrying out the usual degradation experiments; in their absence the structural assignment **4** must be considered somewhat tentative. However, the spectral data in support of this assignment is strongly convincing. Mass spectrometry confirmed that the intermediate had a molecular weight of 176, and was thus isomeric with the dienone **1a**. The infrared spectrum showed carbonyl absorption at 5.92  $\mu$ , which is typical for the bicyclo[3.1.0]hex-3-en-2-one system (as is seen, for example, in all of the known lumiproductions<sup>2,4,5</sup>); the olefinic absorption at 6.22  $\mu$ , however, was much more intense than that of the lumiproductions. The material had ultraviolet absorption at 232 ( $\epsilon$  4200) and 265  $m\mu$  ( $\epsilon$  2250), which is highly reminiscent of that of the lumiproductions<sup>2,4,5</sup> and of other compounds known to have a cyclopentenone chromophore conjugated with a cyclopropane ring.<sup>18</sup> It formed a dihydro derivative with carbonyl absorption at 5.85  $\mu$ , which is characteristic of the bicyclo[3.1.0]hexan-2-one system.<sup>4a,5</sup>

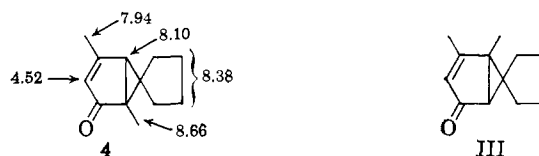
The n.m.r. spectrum was particularly instructive in this case. A correlation of the spectrum with the structure **4** is shown below. The positions of the olefinic proton and the olefinic methyl group indicated that the methyl substituent was  $\beta$ , rather than  $\alpha$ , to the carbonyl group.<sup>19</sup> The appearance of six of the

(18) R. H. Eastman, *J. Am. Chem. Soc.*, **76**, 4115 (1954), reports that umbellulone (i) exhibits maxima in ethanol at 220 and 265  $m\mu$  ( $\epsilon$  5900 and 3290). The closely related ketone ii has absorption at 231 and 268  $m\mu$  ( $\epsilon$  5360 and 4200); see ref. 4a.



(19) A methyl group attached to the  $\beta$ -carbon of a cyclic  $\alpha,\beta$ -unsaturated ketone normally exhibits a doublet around 7.9–8.0  $\tau$  ( $J \sim 1.5$  c.p.s.), and the  $\alpha$ -olefinic proton appears in the region 3.9–4.5  $\tau$ ; see, for example, M. E.

eight methylene protons of ring B as a fairly sharp band at 8.38  $\tau$  (width at half peak height, 5.2 c.p.s.) suggested that the B ring was spirally fused to ring A, thereby making the methylene protons equivalent.<sup>20</sup>



The only question not clearly settled by the spectral data was the position of the methyl substituent on the cyclopropane ring; an unequivocal choice between the structure **4** or the alternative possibility, **III**, could not be made on the basis of these data. However, as will be discussed below, the photochemical properties and the mode of formation of the photoproduct can be readily interpreted in terms of the structure **4**; no such simple accommodation is possible with **III**.

On the basis of the above data the sequence **1a**  $\rightarrow$  **2a**  $\rightarrow$  **4**  $\rightarrow$  **5** seems well established.<sup>21,22</sup> This same sequence was observed in both a hydroxylic (methanol) and a nonhydroxylic solvent (dioxane) and showed no obvious solvent effect. However, irradiation of **1a** in methanol did give, in moderate yield, an additional product which was not observed in irradiations conducted in dioxane. This material was shown to be the methyl ether **10** of the spiro ketone **17a** which, as described below, is the principal photoproduct in aqueous acidic media.

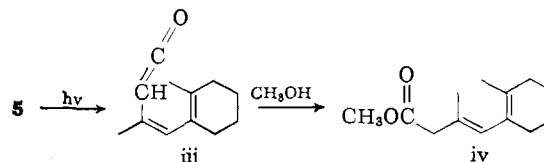
Ketone **10** showed the characteristic cyclopentenone absorptions at 5.86 (carbonyl) and 6.10  $\mu$  (double bond) and 230  $m\mu$  ( $\epsilon$  7000).<sup>2,4b,5</sup> The salient features of the n.m.r. spectrum of **10** are summarized in the cut along with the corresponding structural assignments. The spectrum closely resembled that of the spiro ketone **17a**

Wall, S. Serota, H. E. Kenney, and G. S. Ahernethy, *J. Am. Chem. Soc.*, **85**, 1844 (1963), and W. J. Wechter and G. Slomp, *J. Org. Chem.*, **27**, 2549 (1962). A similar pattern is exhibited also by dienone **5**. By way of contrast, note that the  $\alpha$ -methyl substituents of lumiproductions **2a** and spiro ketone **17a** appear as doublets at 8.32 and 8.22  $\tau$ , respectively, while the  $\beta$ -olefinic protons are seen at 3.14 and 2.76  $\tau$ .

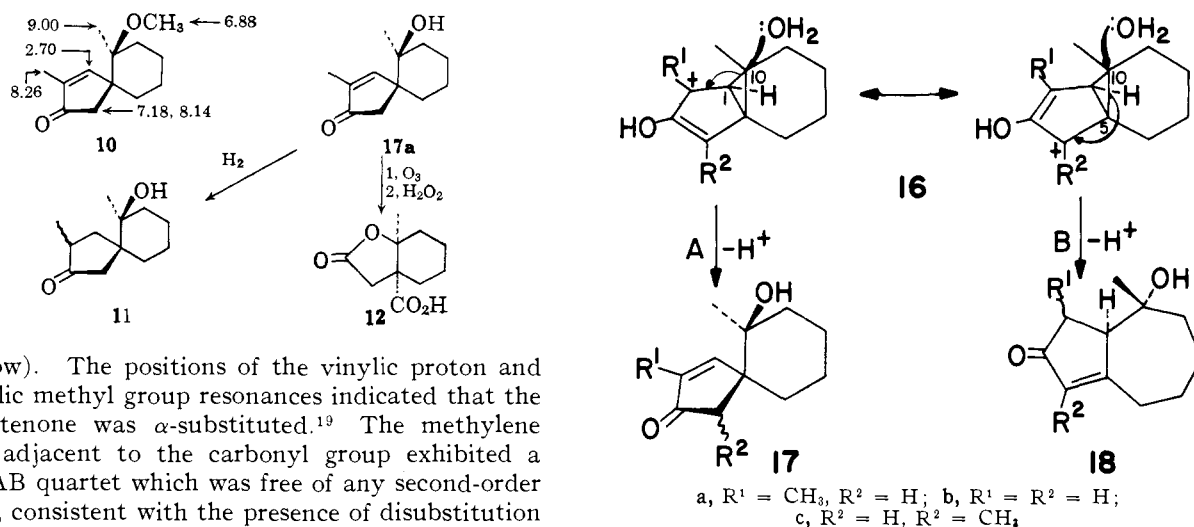
(20) A similar phenomenon was exhibited by the spiro ketones **17a** and **10**, but not by any of the other compounds reported here. The methylene band of **10** was somewhat broader (8.0 c.p.s.).

(21) Two additional intermediates, which had photostationary concentrations of approximately 1 and 2%, were isolated with difficulty from the reaction mixture. It was demonstrated that these intermediates were formed from the lumiproductions **2a** (rather than from dienone **1a**), but insufficient quantities of pure material were available to determine whether they intervened in the formation of **4** or were part of a branch sequence of rearrangements leading to other photoproducts.

(22) The sequence would not be expected to terminate with **5** since it is characteristic of 2,4-cyclohexadienones which are disubstituted at C-6 to undergo photolytic ring fission to a *cis*-diene-ketene such as **iii**; see D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1 (1960). The *cis*-diene-ketene usually undergoes rapid isomerization to a *trans*-diene-ketene which can react with an available nucleophile. Thus, on irradiation in methanol, the dienone **5** should be transformed to the diene-ester **iv**. Although less labile



than the photoproducts **2a** or **4**, the dienone **5** did rearrange on extended irradiation in methanol to a complex mixture of new photoproducts. From this mixture one predominant product was isolated in 43% yield which had absorption at 5.76 (ester carbonyl) and 6.12  $\mu$  (diene) and at 228  $m\mu$  ( $\epsilon$  6400)—consistent with the structural assignment **iv**; see discussion by W. G. Dauben, D. A. Lightner, and W. K. Hayes, *J. Org. Chem.*, **27**, 1897 (1962).



(see below). The positions of the vinylic proton and the vinylic methyl group resonances indicated that the cyclopentenone was  $\alpha$ -substituted.<sup>19</sup> The methylene protons adjacent to the carbonyl group exhibited a typical AB quartet which was free of any second-order splitting, consistent with the presence of disubstitution at the adjacent (spiro) carbon.

Finally, it should be noted that in the irradiations conducted in neutral media a small quantity of a crystalline phenolic product was always obtained. Analysis of this material by n.m.r. revealed that it consisted of an approximately 1:3 mixture of two phenols having aromatic proton absorptions at 3.52 and 3.62  $\tau$ , respectively. Attempts to separate this mixture by column or gas chromatography were fruitless. These data were all identical with that for the phenolic mixture obtained in acidic media (see below), which was clearly shown to consist of the phenols 6 and 13; it can therefore be assumed that the same phenolic products are obtained in neutral media as well.

**Acidic Media.**—The results from the irradiation of the dienone 1a in 45% acetic acid are summarized in Table I.<sup>10</sup> As expected by analogy with unsubstituted (1b)<sup>4b,5</sup> and 4-methyl-substituted dienones (1c),<sup>2</sup> the principal course of rearrangement in this medium was hydroxy ketone formation. Indeed, one hydroxy ketone, which was shown to have the spiro structure 17a, was formed in 48–51% yield. No evidence for the formation of any significant amount of the 5/7-fused ketone 18a could be detected, despite the fact that we have now worked with a number of such compounds and are familiar with their chromatographic behavior.<sup>23</sup>

The spiro ketone 17a had infrared absorption at 5.86 (cyclopentenone carbonyl) and 6.08  $\mu$  (double bond) and ultraviolet absorption at 234  $m\mu$  ( $\epsilon$  9500)—completely analogous with the spiro ketone photoproducts previously reported.<sup>2,4a,5</sup> On treatment with palladium-on-charcoal 17a, absorbed 1 equiv. of hydrogen to give a hydroxy ketone (11) which exhibited the typical cyclopentanone absorption at 5.75  $\mu$ . The  $\beta$ -vinylic proton of 17a appeared in the n.m.r. spectrum as a quartet ( $J_{AB} = 1.5$  c.p.s.) at 2.76  $\tau$ , and the  $\alpha$ -methyl substituent was seen as a doublet ( $J_{AB} = 1.5$  c.p.s.) at 8.22  $\tau$ .<sup>19,20</sup> The methylene protons adjacent to the carbonyl group formed a typical AB pattern of doublets ( $J_{AB} = 18.5$  c.p.s.) at 7.20 and 8.04  $\tau$ . The lack of any additional absorption attributable to an allylic proton and the absence of any additional coupling of any of the protons of the cyclopentenone

ring required that the cyclopentenone ring was disubstituted at the  $\gamma$ -position. In support of the structural assignment 17a, ozonolysis of the photoproduct followed by oxidative cleavage<sup>24</sup> provided a  $\gamma$ -lactone acid which gave analytical data consistent with the expected structure 12 and had absorption at 5.64 and 5.88  $\mu$ . The n.m.r. spectrum exhibited peaks attributable to the methylene protons of the lactone ring (doublets at 6.80 and 7.58  $\tau$ ,  $J = 17$  c.p.s.) and to the methyl group (singlet at 8.60  $\tau$ ).

In addition to the spiro ketone 17a, the irradiation of 1a in 45% acetic acid gave a crystalline phenolic product. Although this material gave a single peak on repeated column or gas chromatographic examination, the n.m.r. spectrum clearly revealed that it consisted of a mixture of two phenols, present in the approximate ratio of 1:5. These two phenols showed one-proton multiplets at 3.52 and 3.62  $\tau$ , respectively, in the aromatic region. This provided further insight into the composition of the mixture, as the relatively high frequencies of these peaks indicated that the absorbing protons were either *ortho* or *para* to the hydroxyl group in each case.<sup>25</sup>

There are six possible isomers of the dimethyltetrahydronaphthol structure IV. In only four of these is the single aromatic proton at an *ortho* or *para* position: 6, 13, 14, and 15. Comparison of the aromatic proton region of the n.m.r. spectra of authentic samples<sup>14,26,27</sup> of each of these phenols with that of the product mixture revealed the identity of the major component of the mixture as the isomer 13 (see Table II). This was corroborated by the successful separation of a pure specimen of 13 from the mixture by fractional recrystallization and direct comparison with an authentic sample.<sup>26</sup>

Of the three remaining possibilities for the minor constituent (6, 14, and 15) the isomer 14 could be eliminated since it showed different chromatographic

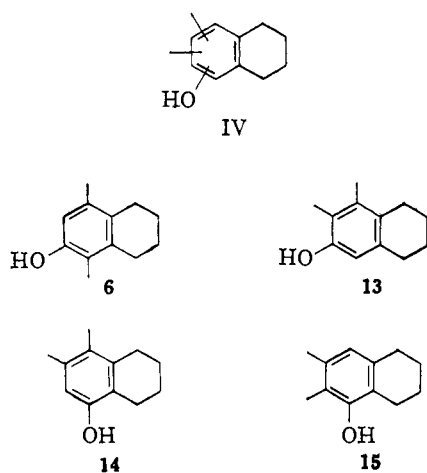
(24) W. S. Johnson, E. R. Rogier, and J. Ackerman, *J. Am. Chem. Soc.*, **78**, 6322 (1956).

(25) Chemical shifts in aromatic molecules tend to reflect the  $\pi$ -electron density on the carbon atom to which the proton is bonded; see, for example, T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963), and references cited therein. We have recently noted that *o*- and *p*-protons of alkyl-substituted phenols generally appear at higher frequencies (3.4–3.6  $\tau$ ) than *m*-protons (3.1–3.2  $\tau$ ); see P. J. Kropp, *J. Am. Chem. Soc.*, **85**, 3280 (1963).

(26) W. Cocker, *J. Chem. Soc.*, 36 (1946).

(27) W. Cocker, B. E. Cross, A. K. Fateen, C. Lipman, E. R. Stuart, W. H. Thompson, and D. R. A. Whyte, *ibid.*, 1781 (1950).

(23) An acetoxy ketone, assumed to be the acetate of 17a, was formed in 2% yield. The spectral data for this material, which were almost identical with that of 17a except for bands characteristic of the acetoxy group, are summarized in the Experimental section.



behavior than the mixture. The isomer 15 did not appear to be a likely candidate either, since the methyl region of its n.m.r. spectrum did not closely resemble that of the mixture. The identity of the remaining isomer, 6, as the minor component was established by

TABLE II  
N.M.R. DATA FOR POSSIBLE PHENOLIC PRODUCTS

Phenol	Chemical shifts, $\tau^a$	
	Aromatic H	-CH <sub>3</sub>
1,4-Dimethyl-2-ol (6)	3.54 <sup>b</sup>	7.88, 7.94
3,4-Dimethyl-2-ol (13)	3.64 <sup>b</sup>	7.86, 7.90
3,4-Dimethyl-1-ol (14)	3.54 <sup>b</sup>	7.82, 7.98
2,3-Dimethyl-1-ol (15) <sup>c</sup>	3.46 <sup>b</sup>	7.78, 7.88
2,4-Dimethyl-1-ol <sup>d</sup>	3.24 <sup>e</sup>	7.86, 7.90
Product mixture	3.52, 3.62 <sup>b,f</sup>	7.86, 7.88 <sup>g</sup>

<sup>a</sup> Determined in 10% deuteriochloroform solution. <sup>b</sup> *ortho* or *para*. <sup>c</sup> Determined in 5% solution. <sup>d</sup> W. Cocker, C. Lipman, and D. R. A. Whyte, *J. Chem. Soc.*, 1519 (1950). <sup>e</sup> *meta*. <sup>f</sup> Relative integrated areas 1:5, respectively. <sup>g</sup> Shoulder at 7.94  $\tau$ .

the finding that irradiation of the lumiprodukt 2a in 45% acetic acid gave 6 (28% yield), along with the dienone 5 (33% yield). Moreover, irradiation of the intermediate cyclopropyl ketone 4 again gave both 5 (47% yield) and 6 (33% yield). Since the dienone 5 could be isolated in low yield from the irradiation of 1a in 45% acetic acid and since the presence of both 2a and 4 in the course of the irradiation could be detected by gas chromatography, there seemed little doubt that the minor component of the phenolic mixture was indeed the isomer 6.

### Discussion

From a synthetic point of view, the photochemical behavior of cross-conjugated cyclohexadienones offers rare versatility. Thus the 2-methyldienone 1a, which itself is easily synthesized in two steps from commercially available materials, can be transformed under the appropriate choice of irradiation conditions to either a spiro ketone (17a), a cyclopropyl ketone (2a), or a linearly conjugated dienone (5)—in a single operation and in good yield (50–70%). None of these materials could be so conveniently prepared by classical methods. Moreover, the formation of the methoxy ketone 10 suggests a whole vista of adducts which could be formed by the attack of carbon or nitrogen nucleophiles, as well as oxygen.

In addition to the possibility of numerous synthetic applications, several other aspects of the photochemical

properties of 1a, which are mechanistically significant, deserve comment. The first of these is the predominant formation of the spiro ketone 17a in aqueous acetic acid. This behavior complements the previously observed pattern that unsubstituted dienones of the type 1b give both spiro (17b) and 5/7-fused hydroxy ketones (18b) in approximately equal yield<sup>5</sup> whereas their 4-methyl analogs give predominantly, if not exclusively, the 5/7-fused ketone product (18c).<sup>2</sup> Thereby, it adds support to our proposal<sup>5</sup> that the Zimmerman-Schuster intermediate 16<sup>25</sup> is a common precursor to both of the hydroxy ketone photoproducts and that the predominant formation of the 5/7-fused ketone product from 4-methyldienones is controlled by an electronic effect of the methyl substituent in the cleavage of 16.<sup>29</sup> It is now seen that transferring the methyl substituent from C-4 to C-2 concomitantly moves the point of cleavage of the cyclopropyl ring of 16 from the 5–10 to the 1–10 bond. The directive influence of the methyl substituent on the mode of cleavage could be attributable either to an inductive effect, which would cause localization of the positive charge of 16 at the substituted position, or to hyperconjugative stabilization by the methyl group of the incipient double bond during the cleavage process. It is perhaps significant that the predominant product in each case is the one in which the methyl substituent is located on the newly formed double bond. In the absence of substitution at either C-2 or C-4 (and of any steric control arising from ring B substituents<sup>1b</sup>), the two modes of cleavage occur with approximately equal facility.<sup>30</sup>

The transformation of the lumiprodukt 2a to the phenol 6 and the dienone 5 is unexceptional in the sense that all of the lumiproduks, both unsubstituted (type 2b) and 4-methyl-substituted (type 2c), which have been studied previously were found to undergo photoconversion to phenols or closely related dienones. However, the intervention of the intermediate 4 in the present case and the sensitivity of its photochemical behavior to the presence of acids indicate that such conversions are not always direct, but are more complex than perhaps was previously appreciated.

The isomerization of 2a to the cyclopropyl ketone 4 can be represented *formally* by the sequence of steps shown in Chart I.<sup>31</sup> We previously noted that the

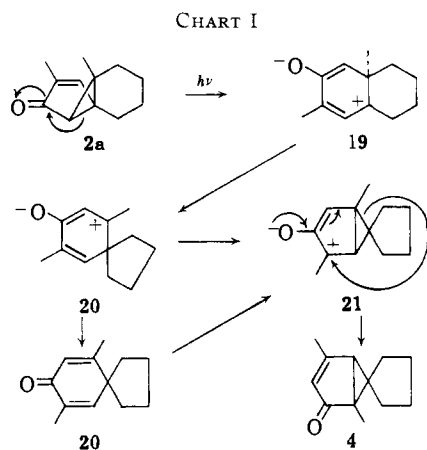
(28) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962), first proposed this intermediate to account for the formation of isophotosantonin lactone from santonin.

(29) It should be emphasized, however, that while the present data provide additional support for the proposal that an intermediate of the type 16 is involved in hydroxy ketone formation, they offer little insight into the precise mode of formation of 16 from the starting dienone.

(30) Originally we suggested that the 4-methyl effect could be explained by either a steric or an electronic effect (ref. 5). However, a subsequent study of steric factors in the photochemical rearrangements of 1,4-dien-3-ones revealed that although steric effects can be important, they do not resemble the effect exerted by 4-methyl substituents (see ref. 1b). The 4-methyl effect was therefore assumed to be principally electronic rather than steric in origin.

(31) There is a rapidly growing consensus that photochemical rearrangements of cyclohexadienones and the cyclopropyl ketones derived from them involve, at least ultimately, dipolar intermediates having negative character localized on the oxygen atom and positive character distributed through the conjugated system of the carbon skeleton (see, for example, ref. 2, 4b, 28, and 32). Although the present results certainly support this contention, they do not answer the important question as to whether this polarization is formed directly in the photoexcitation process or through a sequence of subsequent steps (as proposed in the Zimmerman-Schuster four-step mechanism (ref. 28), for example). Therefore we summarily write such intermediates without making reference to their precise mode of formation.

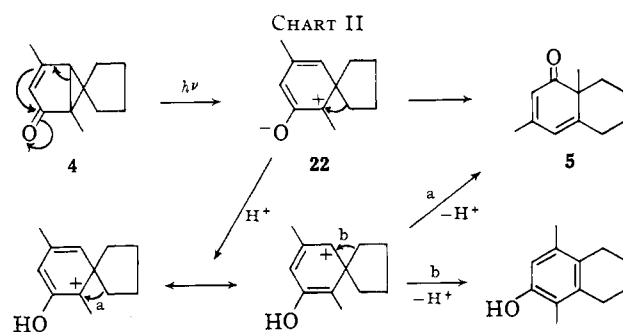
(32) O. L. Chapman and L. F. Englert, *J. Am. Chem. Soc.*, **85**, 3028 (1963);



photochemical behavior of all of the lumiproductions which have been studied thus far can be explained consistently in terms of an initial cleavage of the cyclopropyl bond which is coplanar with the cyclopentenone chromophore (*cf.* 19) followed by subsequent rearrangement through a spiro intermediate (20), provided that the formation of a five-membered B ring is structurally feasible.<sup>1b</sup> The present data do not permit a choice between the alternative possibilities of a direct rearrangement of this spiro intermediate to 4 or of collapse to the dienone 20a followed by a subsequent light-initiated rearrangement of 20a to 4.

A possible pathway for the conversion of 4 to the dienone 5 in neutral media or to a mixture of 5 and the phenol 6 in acidic media is outlined in Chart II. One significant feature here is the marked sensitivity of the photochemical behavior of 4 to the presence of acid. This constitutes a new addition to a steadily growing list of examples of solvent effects in dienone photochemistry. It would appear that in the photoexcited state (22) there is a minimization of charge separation (and hence a localization of positive charge adjacent to the electron-rich oxygen) which causes rearrangement to 5 to be preferred. The difference in behavior in acidic media (*i.e.*, rearrangement to both 5 and 6 with approximately equal facility) is most likely due to protonation of the rearranging species at oxygen.

Finally, special comment should be made concerning the phenol 13, which is the principal phenolic product from irradiation of the dienone 1a in either neutral or acidic media. The formation of 13 is significant in that it does not arise *via* the lumiproductions 2a, and thus represents an alternative photochemical pathway for the dienone 1a. The question arises as to whether the transformation of 1a to 13 is direct or involves one or more isolable intermediates. No intermediate could be detected in the present study. It is perhaps significant that the formation of 13 proceeds in much higher yield in acidic media. It should also be noted that in irradiations conducted in acidic media at 2537 Å, 13 was the only phenolic material to have appeared if the irradiation was terminated at the exact point that all of the starting dienone was consumed. The yield of hydroxy ketone 17a, which is formed from 1a without the intervention of any isolable intermediates, is maximal at this point. On further irradiation no



additional 13 or 17a are formed, but the phenol 6, which arises by way of the intermediates 2a and 4, begins to appear. These data suggest that 13 is formed directly from 1a. However, additional experimentation is obviously needed to settle this very important question.<sup>33</sup>

### Experimental<sup>34</sup>

**3,4a-Dimethyl-5,6,7,8-tetrahydro-2(4aH)naphthalenone (1a).**—The general procedure of Iriarte and Ringold was employed.<sup>35</sup> A solution of 24.75 g. (0.139 mole) of 3 $\alpha$ ,4 $\alpha$  $\beta$ -dimethyl-4,4a,5,6,7,8-hexahydro-2(3H)naphthalenone (3)<sup>7</sup> and 16.0 g. (0.144 mole) of freshly resublimed selenium dioxide in 245 ml. of freshly distilled *t*-butyl alcohol and 6 ml. of glacial acetic acid was heated under reflux in an atmosphere of nitrogen for 65 hr. The resulting mixture was then cooled, diluted with an equal volume of ethyl acetate, and filtered through Celite. The filtrate was concentrated to a small volume under reduced pressure, and the resulting residue was taken up in 500 ml. of water and extracted with 1 l. of ether. The combined ether extracts were then concentrated under reduced pressure. A solution of the residue and 200 ml. of 44% aqueous ammonium sulfide in 400 ml. of ethanol was heated under reflux for 2 hr., then stirred for 2 hr. at room temperature, and, finally, concentrated to a small volume under reduced pressure.<sup>36</sup> The brown residue was extracted with three 250-ml. portions of ether, and the combined ether extracts were washed with 250-ml. portions each of water and saturated sodium chloride solution and then dried over anhydrous sodium sulfate. Distillation through an 18-in. spinning band column gave 12.14 g. (50% yield) of a pale yellow liquid, b.p. 100–101° at 1.2 mm., which crystallized on standing overnight at 0°. Recrystallization twice from petroleum ether gave colorless prisms, m.p. 38–39°,  $\lambda_{\max}$  6.00 and 6.14  $\mu$ ;  $\lambda_{\max}$  242 m $\mu$  ( $\epsilon$  17,000); n.m.r. spectrum: 3.46 (m, 1, CH-4),<sup>37a</sup> 3.92 (m, 1, CH-1), 8.12 (d, 3,  $J_{AB}$  1.5, CH<sub>3</sub>-3),<sup>37b</sup> and 8.78  $\tau$  (s, 3, CH<sub>3</sub>-4a); 2,4-dinitrophenylhydrazone, deep-red platelets, m.p. 169.5–171°; reported<sup>6</sup> for 1a: pale yellow oil, b.p. 105–106° at 6 mm.; 2,4-dinitrophenylhydrazone, m.p. 170°.

**3,8a-Dimethyl-4a,5,6,7,8,8a-hexahydro-1,4a-cyclo-2(1H)-naphthalenone (2a).** A. Preparation.—A solution of 790 mg.

(33) If it is indeed true that phenol 13 arises *via* a 1,2-shift of the angular methyl group of dienone 1a, a striking contrast is seen with the acid-catalyzed dienone-phenol rearrangement of 1a, in which such a shift is unfavored because of steric interaction with the 2-methyl substituent; see P. J. Kropp, *Tetrahedron Letters*, 1671 (1963).

(34) Ultraviolet spectra were determined in absolute ethanol with a Cary Model 14 spectrophotometer, and infrared spectra were obtained in 5% methylene chloride solution with a Perkin-Elmer Infracord spectrophotometer. Unless otherwise stated, gas chromatographic separations were effected at 195° using a 5 ft.  $\times$  0.25 in. column containing 20% GE-silicone fluid 96 over 60/80 mesh firebrick. Melting points were determined on a micro-hotstage and are calibrated and corrected. Nuclear magnetic resonance spectra were obtained in deuteriochloroform solution with a Varian Model A-60 spectrometer, using tetramethylsilane as an internal standard. Molecular weights were determined using a Bendix Model 12-100 time-of-flight mass spectrometer. Microanalyses were performed by Spang Micro-analytical Laboratories, Ann Arbor, Mich.

(35) J. Iriarte and H. J. Ringold, *Tetrahedron*, **3**, 28 (1958).

(36) The use of alcoholic ammonium sulfide to convert selenium-containing products to free 1,4-dien-3-ones in selenium dioxide oxidations of 4-en-3-ones was reported by M. Kocor at the Second International Symposium in the Chemistry of Natural Products, Prague, Aug. 27–Sept. 2, 1962; see *Angew. Chem. Intern. Ed. Engl.*, **1**, 666 (1962).

(37) (a) Indicates multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, and assignment; (b) coupling constants given in c.p.s.

M. Fisch and J. H. Richards, *J. Am. Chem. Soc.*, **85**, 3029 (1963); and H. E. Zimmerman in "Advances in Photochemistry," Vol. 1, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Eds., John Wiley and Sons, Inc., New York, N. Y., p. 183 ff.

of dienone 1a in 100 ml. of dioxane was irradiated for 2 hr. with an Hanau NK 6/20 low-pressure mercury lamp. Vigorous stirring of the reaction mixture was effected by the introduction of a stream of nitrogen through a jet opening in the bottom of the reaction vessel. The reaction mixture was concentrated to a small volume under reduced pressure on a rotary evaporator, and the resulting residue was chromatographed on 24 g. of silica gel. Elution with 4 l. of 1:1 benzene-hexane gave 528 mg. (67% yield) of lumiprodukt 2a as a colorless oil,  $\lambda_{\max}$  5.92 and 6.14  $\mu$ ,  $\lambda_{\max}$  234 ( $\epsilon$  5280) and 270,  $m\mu$  ( $\epsilon$  1900); n.m.r. spectrum: 3.14 (m, 1, CH-4), 8.32 (d, 3,  $J_{AB}$  1.5, CH<sub>3</sub>-3), and 8.88  $\tau$  (s, 3, CH<sub>3</sub>-8a); semicarbazone, colorless prisms, m.p. 183-184.5°, from aqueous ethanol.

*Anal.* Calcd. for C<sub>13</sub>H<sub>14</sub>N<sub>3</sub>O: C, 66.92; H, 8.21; N, 18.01. Found: C, 67.14; H, 8.48; N, 18.32.

Continued elution with 1.5 l. of 3:1 benzene-hexane gave 93 mg. of a colorless oil which was shown by gas chromatography to consist of ketone 4, dienone 5, and starting dienone 1a—present in yields of 7, 2, and 3%, respectively. Pure specimens of each of these were collected and were found to have infrared and n.m.r. spectra identical with authentic samples.

A minor impurity (estimated to be present in a total concentration representing a 2-3% yield) always accompanied lumiprodukt 2a in the 1:1 hexane-benzene eluates. This material was separated into two components by preparative gas chromatography using a 10 ft.  $\times$  0.25 in. column packed with 30% ethylene glycol-succinate polymer on 60/80 mesh Chromosorb W at 175°. One component was obtained as a colorless oil,  $\lambda_{\max}$  6.08, 6.14 (sh), and 6.28  $\mu$ ;  $\lambda_{\max}$  229  $m\mu$  ( $\epsilon$  4100); n.m.r. spectrum: 3.30 (1, m), 4.02 (1, m), and 8.12  $\tau$  (d,  $J_{AB}$  1.5). The second component was isolated as a colorless oil,  $\lambda_{\max}$  5.92 and 6.08  $\mu$ ,  $\lambda_{\max}$  236  $m\mu$  ( $\epsilon$  5600); n.m.r. spectrum: 3.02 (m, 1), 8.34 (d,  $J_{AB}$  1.5), and 8.56  $\tau$  (s, 3). The presence of these materials, in low concentration, could always be detected when pure specimens of either dienone 1a or lumiprodukt 2a were irradiated but not when ketone 4 or dienone 5 were irradiated.

**B. Hydrogenation.**—A solution of 124 mg. of lumiprodukt 2a in 10 ml. of absolute ethanol was stirred with 25 mg. of 10% palladium-on-charcoal in an atmosphere of hydrogen. Uptake ceased after 4 min. with 1.05 mole equiv. of hydrogen. Removal of the catalyst by filtration followed by evaporation of the solvent at reduced pressure gave the dihydro adduct 8 as a colorless oil,  $\lambda_{\max}$  5.84  $\mu$ ,  $\lambda_{\max}$  216  $m\mu$  ( $\epsilon$  3700); n.m.r. spectrum: 8.96 (s, CH<sub>3</sub>-8a) and 8.99  $\tau$  (d,  $J_{AB}$  6, CH<sub>3</sub>-3).

**C. Ozonolysis.**—The general procedure of Johnson, Rogier, and Ackerman<sup>24</sup> was employed. Ozone was bubbled for 70 min. through a solution of 150 mg. of lumiprodukt 2a in 36 ml. of ethyl acetate which was cooled with an ice bath. To the solution were then added 10 ml. of acetic acid, 2.5 ml. of water, and 1 ml. of 3% hydrogen peroxide. After being allowed to stand for 20 hr. at room temperature, the resulting mixture was evaporated to dryness at reduced pressure on a rotary evaporator. The last traces of acetic acid were removed by codistillation with two 100-ml. portions of toluene. The resulting residue was taken up in 500 ml. of ether and was extracted thoroughly with a saturated sodium bicarbonate solution. The combined bicarbonate extracts were acidified and extracted three times with 100-ml. portions of ether. The combined ether fractions were dried over 50 ml. of saturated sodium chloride solution and then over anhydrous sodium sulfate. Evaporation of the solvent under reduced pressure gave 104 mg. (62% yield) of *cis*-(6,7-dicarboxy)-1-methylnorcarane (9) as colorless prisms, m.p. 171-174°. Recrystallization twice from acetone-hexane gave colorless prisms, m.p. 189.5-190°,  $\lambda_{\max}^{KBr}$  5.78 and 5.88  $\mu$ <sup>17</sup>;  $\lambda_{inf}$  270 ( $\epsilon$  450) and 223  $m\mu$  ( $\epsilon$  1540).

*Anal.* Calcd. for C<sub>10</sub>H<sub>14</sub>O<sub>4</sub>: C, 60.59; H, 7.12; first neut. equiv., 198. Found: C, 60.49; H, 7.09; first neut. equiv., 199.

**D. Irradiation in Methanol.**—A solution containing 85 mg. of the lumiprodukt 2a and 25 ml. of methanol contained in a quartz flask and stirred magnetically was irradiated in an atmosphere of nitrogen for 295 min. with an Hanovia 100-watt mercury lamp (type 30620) which was placed approximately 3 in. from the flask. Chromatography of the residue obtained on removal of the solvent under reduced pressure on a rotary evaporator gave, on elution with 300 ml. of benzene and 90 ml. of 1:99 ether-benzene, 53 mg. (62% yield) of a colorless oil which had infrared and n.m.r. spectra and retention time on gas chromatography identical with an authentic specimen of the dienone 5.

**E. Irradiation in 45% Acetic Acid.**—A solution of 183 mg. of lumiprodukt 2a in 100 ml. of 45% acetic acid was irradiated for 30 min. with a 200-watt mercury lamp as described below for the dienone 1a. The reaction mixture was neutralized with saturated sodium carbonate solution and was extracted with two 200-ml. portions of ether. The combined extracts were dried over two 200-ml. portions of saturated sodium chloride solution and then anhydrous sodium sulfate. The solution was concentrated to a small volume under reduced pressure on a rotary evaporator, and the resulting residue was chromatographed on 7 g. of silica gel. Elution with 350 ml. of 1:1 benzene-hexane gave 51 mg. (28% yield) of phenol 6 as yellow needles, m.p. 93-102°, n.m.r. spectrum 3.52  $\tau$ . Recrystallization from ether-hexane gave 20 mg. of colorless needles, m.p. 104-106°, m.p. 104-105° on admixture with an authentic sample of 6.<sup>14</sup>

Continued elution with 350 ml. of benzene and 140 ml. of 1:99 ether-benzene gave 60 mg. (33% yield) of a colorless oil which had an infrared spectrum and retention time on gas chromatography identical with a specimen of dienone 5 prepared as described below.

**3,8a-Dimethyl-6,7,8,8a-tetrahydro-1(5H)naphthalenone (5).**  
**A. Preparation.**—A solution containing 201 mg. of dienone 1a in 100 ml. of dioxane was irradiated for 300 min. as described above for the preparation of the lumiprodukt 2a. Chromatography of the crude product on 6 g. of silica gel gave, on elution with 480 ml. of benzene and 240 ml. of 1:99 ether-benzene, 99 mg. (50% yield) of dienone 5 as a colorless oil;  $\lambda_{\max}$  6.02, 6.12, 6.36, and 11.80  $\mu$ ;  $\lambda_{\max}$  316  $m\mu$  ( $\epsilon$  4300); n.m.r. spectrum: 4.12 (2, s, CH-2 and -4), 7.94 (3, d,  $J_{AB}$  0.8, CH<sub>3</sub>-3), and 8.74  $\tau$  (3, s, CH<sub>3</sub>-8a); 2,4-dinitrophenylhydrazone, m.p. 171.5-172.5°.

*Anal.* Calcd. for C<sub>18</sub>H<sub>20</sub>N<sub>4</sub>O<sub>4</sub>: C, 60.66; H, 5.66; N, 15.72. Found: C, 60.63, 60.77; H, 5.39, 5.41; N, 15.61.

**B. Maleic Anhydride Adduct.**—A solution containing 77 mg. (0.437 mmole) of dienone 5 and 330 mg. (3.36 mmoles) of freshly sublimed maleic anhydride in 4 ml. of xylene (which had been distilled from W-5 Raney nickel) was heated under reflux in an atmosphere of nitrogen for 40 hr. The reaction mixture was then concentrated to a small volume under reduced pressure on a rotary evaporator, and the resulting residue was chromatographed on 18 g. of silica gel. Elution with 1.3 l. of 1:99 ether-benzene gave 98 mg. (82% yield) of colorless prisms which showed vinylic proton absorption at 3.96 and 4.20  $\tau$  (relative intensities 3:2, respectively). Recrystallization from ether-hexane gave a 1:1 isomeric mixture of adducts 7 as colorless prism clusters, m.p. 130-131.5°;  $\lambda_{\max}$  5.36, 5.44 (sh), 5.60, and 5.78  $\mu$ ;  $\lambda_{\max}$  299  $m\mu$  ( $\epsilon$  130); n.m.r. spectrum: 3.96, 4.18 (m, 1, relative intensity 1:1, CH-4), 8.12 (d, 3  $J_{AB}$  1.5, CH<sub>3</sub>-3), and 8.86, 8.90  $\tau$  (2s, 3, CH<sub>3</sub>-8a).

*Anal.* Calcd. for C<sub>16</sub>H<sub>18</sub>O<sub>4</sub>: C, 70.05; H, 6.61. Found: C, 70.25; H, 6.59.

**C. Dienone-Phenol Rearrangement.**—The general procedure of Bloom<sup>28</sup> was followed. To a solution of 83 mg. of dienone 5 in 2 ml. of acetic anhydride was added 0.5 ml. of acetic anhydride containing 1 drop of concentrated sulfuric acid. An immediate pink color formed which rapidly developed into a deep blue. After being allowed to stand at room temperature in the dark under an atmosphere of nitrogen for 4 hr., the reaction mixture was poured over crushed ice. After all of the acetic anhydride had been hydrolyzed, the reaction product was isolated by extraction with ether. The resulting brown oil (69 mg.) was heated under reflux in an atmosphere of nitrogen with 4 ml. of ethanol and 0.3 ml. of concentrated hydrochloric acid for 4 hr. The reaction mixture was then concentrated to a small volume under reduced pressure on a rotary evaporator, and the resulting residue was taken up in methylene chloride and dried over anhydrous sodium sulfate. Removal of the solvent gave 100 mg. of a brown solid, which was chromatographed on 3.4 g. of silica gel. Elution with 175 ml. of 1:1 benzene-hexane gave 16 mg. (19% yield) of phenol 6 as colorless prisms, m.p. 85-103°; recrystallization from hexane gave colorless prisms, m.p. 103-105°, with conversion to needles just prior to melting; m.p. 102-106° on admixture with an authentic sample of phenol 6.<sup>14</sup> No other phenolic product could be detected in the reaction mixture.

**D. Irradiation.**—A solution containing 102 mg. of dienone 5 and 125 ml. of methanol was irradiated for 75 min. with the 200-watt lamp as described below for the dienone 1a. The crude product was chromatographed on 4 g. of silica gel. Elution

with 200 ml. of 1:3 benzene-hexane gave 44 mg. (43% yield) of a colorless oil which showed at least seven peaks on gas chromatographic analysis. One peak, at 9.5 min., constituted approximately 85% of the mixture. Isolation of a pure specimen of this material, assumed to have the structure iv, by gas chromatography gave a colorless oil,  $\lambda_{\max}$  5.76 and 6.12  $\mu$ ;  $\lambda_{\max}$  228  $m\mu$  ( $\epsilon$  6400).

**Irradiation of 3,4a-Dimethyl-5,6,7,8-tetrahydro-2(4aH)-naphthalenone (1a).** A. In Methanol.—A solution of 504 mg. of the dienone 1a in 125 ml. of methanol was irradiated for 70 min. at 25° using an Hanovia 200-watt high-pressure mercury lamp and the apparatus previously described.<sup>5</sup> The resulting solution was concentrated to dryness on a rotary evaporator under reduced pressure, and the residue was chromatographed on 17 g. of silica gel. Elution with 850 ml. of 1:3 benzene-hexane gave 37 mg. (6% yield) of an oily mixture of diene esters, which was shown by gas chromatography to consist principally of the isomer assumed to have the structure iv. Continued elution with 1 l. of 3:1 hexane-benzene gave 20 mg. (4% yield) of a mixture of 1,4-dimethyl- and 3,4-dimethyl-5,6,7,8-tetrahydro-2-naphthol (6<sup>14</sup> and 13<sup>26</sup>), colorless prisms, m.p. 95–115° with conversion to long needles from 71°; n.m.r. spectrum: 3.52 and 3.62  $\tau$  (relative intensities 1.0:2.85).

Elution with 500 ml. of 3:1 benzene-hexane gave 49 mg. of a complex mixture in which the ketone 4 was estimated to be present in 5% yield from gas chromatographic analysis. Continued elution with 2.2 l. of 1:3 hexane-benzene gave 189 mg. (38% yield) of a colorless oil shown to be the dienone 5 by comparison of the infrared spectrum and gas chromatographic retention time with that of the sample prepared as described above.

Elution with 340 ml. of benzene and 850 ml. of 1:99 ether-benzene gave 62 mg. (10% yield) of 3,8a-dimethyl-4a,5,6,7,8,8a-hexahydro-8a $\beta$ -methoxy-1(8a $\rightarrow$ 4a $\beta$ )-abeo-2(1H)naphthalenone (10) as a colorless oil,  $\lambda_{\max}$  5.86 and 6.10  $\mu$ ,  $\lambda_{\max}$  230  $m\mu$  ( $\epsilon$  7000); n.m.r. spectrum: 2.70 (1, q,  $J_{AB}$  1.6, CH-4), 6.88 (3, s, -OCH<sub>3</sub>), 7.18 and 8.14 (2, 2d,  $J_{AB}$  19, CH<sub>2</sub>-1), 8.26 (3, d,  $J_{AB}$  1.6, CH<sub>3</sub>-3), and 9.00  $\tau$  (3, s, CH<sub>3</sub>-8a $\alpha$ ); semicarbazone, colorless blades, m.p. 164–165°.

*Anal.* Calcd. for C<sub>14</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>: C, 63.37; H, 8.74; N, 15.84. Found: C, 63.03; H, 8.70; N, 15.81.

In a subsequent experiment the above irradiation was repeated exactly except that the reaction was interrupted after 30 min. Chromatography of the crude product gave, on elution with 2.5 l. of 1:3 hexane-benzene, 208 mg. of an oily mixture of the lumiprotect 2a, the cyclopropyl ketone 4, and the linear dienone 5. Gas chromatographic analysis revealed that these components were present in the yields indicated in Table I. The spiro ketone 10 was isolated in 9% yield by elution with 600 ml. of 1:99 ether-benzene.

**B. In Methanol at 2537 Å.**—A solution containing 242 mg. of dienone 1a in 100 ml. of methanol was irradiated for 45 min. at 2537 Å. as described above for the preparation of lumiprotect 2a. The solvent was removed from the reaction mixture under reduced pressure on a rotary evaporator, and the resulting residue was chromatographed on 7.5 g. of silica gel. Elution with 0.5 l. each of 1:1 hexane-benzene and benzene gave 96 mg. (40% yield) of the lumiprotect 2a. Continued elution with 0.5 l. of 1:99 ether-benzene gave 56 mg. of a colorless oil, which was shown by gas chromatographic analysis to consist of a mixture of spiro[cyclopentane-1,6'-(1',4'-dimethylbicyclo[3.1.0]hex-3'-en-2'-one)](4), the dienone 5, and the spiro ketone 10—present in yields of 12, 8, and 4%, respectively.

Separation of a pure specimen of the ketone 4 by gas chromatography from several similar experiments and further purification by short-path distillation of 120° (0.2 mm.) gave a colorless oil,  $\lambda_{\max}$  5.92, 6.22, and 11.72  $\mu$ ;  $\lambda_{\max}$  232 ( $\epsilon$  4200), 265 ( $\epsilon$  2250), and 320  $m\mu$  ( $\epsilon$  400); n.m.r. spectrum: 4.52 (1, m, CH-3'), 7.94 (3, d,  $J_{AB}$  1.5, CH<sub>2</sub>-4'), 8.10 (1, s, CH-5'), 8.38 (8, brs, CH<sub>2</sub>-2,3,4,5), and 8.66 (3, s, CH<sub>3</sub>-1'); mol. wt., 176.

*Anal.* Calcd. for C<sub>12</sub>H<sub>16</sub>O: C, 81.77; H, 9.15. Found: C, 81.55; H, 9.29.

**C. In 45% Acetic Acid.**—A solution of 547 mg. of dienone 1a in 125 ml. of 45% acetic acid was irradiated for 0.5 hr. at 20° using a 200-watt mercury lamp as described above. The resulting solution was diluted with an equal volume of toluene and concentrated to a small volume on a rotary evaporator under reduced pressure. The last traces of acetic acid were removed by codistillation with toluene two additional times. The resulting residue was chromatographed on 16 g. of silica gel. Elution with 1 l. of 1:1 hexane-benzene gave 88 mg. of a mixture

of 1,4-(6)<sup>14</sup> and 3,4-dimethyl-5,6,7,8-tetrahydro-2-naphthol (13),<sup>26</sup> m.p. 106–116°. The n.m.r. spectrum showed aromatic proton absorptions at 3.52 and 3.62  $\tau$ ; integration indicated that the isomers were present in yields of 3 and 14%, respectively. Recrystallization of the mixture from ether-hexane gave a pure specimen of 13 as long colorless needles, m.p. 115.5–116.5°,  $\lambda_{\max}$  283 ( $\epsilon$  2400) and 287  $m\mu$  ( $\epsilon$  2440); n.m.r. spectrum: 3.64  $\tau$  (s, 1, CH-1); m.p. 115–117° on admixture with an authentic sample of 13.<sup>26</sup>

Further elution with 900 ml. of 1:50 and 500 ml. of 1:20 ether-benzene gave 113 mg. of a complex mixture of unidentified products. Continued elution with 1.8 l. of 1:20 ether-benzene gave 275 mg. (48% yield) of 3,8a-dimethyl-4a,5,6,7,8,8a-hexahydro-8a $\beta$ -hydroxy-1(8a $\rightarrow$ 4a $\beta$ )-abeo-2(1H)naphthalenone (17a) as a colorless oil,  $\lambda_{\max}$  2.76, 5.86, and 6.08  $\mu$ , and  $\lambda_{\max}$  234  $m\mu$  ( $\epsilon$  9500); n.m.r. spectrum: 2.76 (1, q,  $J_{AB}$  1.5, CH-4), 7.20 and 8.04 (2, 2d,  $J_{AB}$  18.5, CH<sub>2</sub>-1), 8.22 (d,  $J_{AB}$  1.5, CH<sub>3</sub>-3), and 8.80  $\tau$  (3, s, CH<sub>3</sub>-8a $\alpha$ ); semicarbazone, fine colorless needles, m.p. 201–203°.

*Anal.* Calcd. for C<sub>13</sub>H<sub>21</sub>O<sub>2</sub>N<sub>3</sub>: C, 62.12; H, 8.42. Found: C, 62.28; H, 8.40.

**D. In 45% Acetic Acid at 2537 Å.**—A solution containing 386 mg. of dienone 1a in 100 ml. of 45% acetic acid was irradiated for 1 hr. at 2537 Å. as described above for the preparation of the lumiprotect 2a. The reaction mixture was then concentrated under reduced pressure, and the last traces of acetic acid were removed by codistillation with toluene. The results from chromatography of the residue on 13 g. of silica gel in the manner described immediately above are summarized in Table I. The phenolic fraction in this case consisted of pale yellow prisms, m.p. 102–110°, which showed only one aromatic proton peak (3.58  $\tau$  at 5%). Recrystallization from hexane gave colorless needles, m.p. 115–118°; m.p. 115–117° on admixture with an authentic specimen of 13.<sup>26</sup>

Elution with 500 ml. of 1:20 ether-benzene gave 21 mg. of a colorless oil from which 8 mg. of a crystalline acetoxy ketone, assumed to be the acetate of 17a, was isolated by gas chromatography. Recrystallization from petroleum ether gave colorless prisms, m.p. 70–71°;  $\lambda_{\max}$  5.78, 5.86, and 6.08  $\mu$ ;  $\lambda_{\max}$  229  $m\mu$  ( $\epsilon$  9700); n.m.r. spectrum: 2.80 (1, q,  $J_{AB}$  1.5, CH-4), 7.22 and 8.00 (2, 2d,  $J_{AB}$  18.5, CH<sub>2</sub>-1), 8.06 (3, s, OCOCH<sub>3</sub>), 8.22 (3, d,  $J_{AB}$  1.5, CH<sub>3</sub>-3), and 8.54  $\tau$  (3, s, CH<sub>3</sub>-8a $\alpha$ ); mol. wt., 236.

**Reactions of 3,8a-Dimethyl-4a,5,6,7,8,8a-hexahydro-8a $\beta$ -hydroxy-1(8a $\rightarrow$ 4a $\beta$ )-abeo-2(1H)naphthalenone (17a).** A. Hydrogenation.—A solution of 95 mg. of spiro ketone 17a in 10 ml. of absolute ethanol was stirred with 50 mg. of 10% palladium-on-charcoal in an atmosphere of hydrogen at atmospheric pressure. Hydrogen uptake ceased after 7 min., at which time 0.98 mole equiv. of hydrogen had been consumed. The catalyst was removed by filtration, and the solvent was evaporated under reduced pressure on a rotary evaporator to give 96 mg. of the dihydro derivative 8 as a colorless oil,  $\lambda_{\max}$  2.75 and 5.75  $\mu$ ; semicarbazone, colorless compact prisms, m.p. 196–197°.

*Anal.* Calcd. for C<sub>13</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub>: C, 61.63; H, 9.15; N, 16.59. Found: C, 61.29; H, 9.19; N, 16.88.

**B. Ozonolysis.**—The general procedure of Johnson, Rogier, and Ackerman<sup>24</sup> was followed. Ozone was bubbled for 90 min. through a solution of 143 mg. of spiro ketone 17a in 36 ml. of ethyl acetate which was cooled with an ice bath. To the solution were then added 10 ml. of acetic acid, 2.5 ml. of water, and 1 ml. of 30% hydrogen peroxide. After being allowed to stand for 24 hr. at room temperature, the resulting mixture was evaporated to dryness under reduced pressure. The last traces of acetic acid were removed by codistillation with 100 ml. of toluene. The resulting residue was taken up in 500 ml. of ether and was extracted thoroughly with saturated sodium bicarbonate solution. The bicarbonate extracts were acidified and extracted three times with 100-ml. portions of ether. The combined ether extracts were dried over 100 ml. of saturated sodium chloride solution and then over anhydrous sodium sulfate. Evaporation of the solvent under reduced pressure gave 103 mg. of a colorless oil which was chromatographed on 3 g. of silica gel. Elution with 200 ml. of 1:10 ether-benzene gave 44 mg. (30% yield) of 1 $\alpha$ -carboxy-2 $\beta$ -hydroxy-2-methylcyclohexanecetic acid  $\gamma$ -lactone (12) as colorless prisms, m.p. 158–163°. Recrystallization from ether-hexane gave colorless prisms, m.p. 160–162°,  $\lambda_{\max}$  5.64 and 5.88  $\mu$ ; n.m.r. spectrum: 6.80 and 7.58 (2d,  $J_{AB}$  17, CH<sub>2</sub>-lactone) and 8.60  $\tau$  (s, CH<sub>3</sub>-2 $\alpha$ ).

*Anal.* Calcd. for C<sub>10</sub>H<sub>14</sub>O<sub>4</sub>: C, 60.59; H, 7.12. Found: C, 60.78; H, 7.27.



**Irradiation of the Cyclopropyl Ketone 4. A. In Methanol.**—A solution of 30 mg. of ketone 4 and 10 ml. of methanol was irradiated for 120 min. with a 100-watt mercury lamp as described above for lumiprodukt 2a. The reaction mixture was concentrated under reduced pressure on a rotary evaporator, and the residue was chromatographed on 1.5 g. of silica gel. Elution with 200 ml. of benzene gave 17 mg. (57% yield) of a colorless oil which had an infrared spectrum and gas chromatographic retention time identical with the pure specimen of dienone 5 described above.

**B. In 50% Acetic Acid.**—A solution of 58 mg. of ketone 4 in 10 ml. of 50% acetic acid was irradiated as described above for 2 hr. The reaction mixture was then concentrated under reduced pressure, and the last traces of acetic acid were removed by codistillation with toluene. The resulting amber oil (60 mg.) was chromatographed on 3 g. of silica gel. Elution with 120 ml. of 1:1 hexane-benzene gave 19 mg. (33% yield) of phenol

6, n.m.r. spectrum 3.52  $\tau$ , long colorless needles, m.p. 103–105° after recrystallization from hexane, m.p. 103–107° on admixture with an authentic sample of 6.<sup>14</sup>

Continued elution with 60 ml. of 1:1 hexane-benzene and 80 ml. of 1:3 hexane-benzene gave 4 mg. which was discarded. Further elution with 260 ml. of benzene gave 27 mg. (47% yield) of dienone 5 as a colorless oil which was identical with an authentic specimen in the infrared spectrum and gas chromatographic retention time.

**Hydrogenation of the Cyclopropyl Ketone 4.**—A solution of 22 mg. of cyclopropyl ketone 4 in 10 ml. of absolute ethanol was stirred with 10 mg. of 10% palladium-on-charcoal in an atmosphere of hydrogen. Uptake ceased after 10 min. with 1.0 mole equiv. Removal of the catalyst by filtration followed by evaporation of the solvent at reduced pressure gave the dihydro derivative as a colorless oil,  $\lambda_{\max}$  5.85  $\mu$ ,  $\lambda_{\max}$  217 m $\mu$  ( $\epsilon$  4300).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE STATE UNIVERSITY, DETROIT 2, MICH.]

## Conformational Analysis. XXXVIII. The Conformations of Cyclohexanone Rings<sup>1,2</sup>

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A generalized approximate method for the conformational analysis of the flexible form of cyclohexanone is presented, and the method is applied to a few examples, including 2- and 4-methylated-3-keto steroids. The exact conformational arrangements of these compounds and for the D ring in 17,17-dimethyl-17a-keto-D-homosteroids are predicted. Rotatory dispersion measurements and dipole moments are consistent with all of the predictions.

Increasingly detailed studies on the conformations of cyclohexanone rings have brought to light a number of examples of molecules in which such a ring exists primarily in a form other than that of an ordinary chair. It has also become apparent that these nonchair forms are not all alike, and evidence has been accumulated which shows that a number of distinctly different arrangements in fact exist.<sup>3,4</sup>

Some years ago we began a study of nonchair forms in cyclohexanone rings.<sup>5</sup> Since the subject has now become of rather general interest, and because recent papers on the subject have always been limited in discussion to special cases, it seemed to us that it would now be appropriate to state in expanded form our earlier comments,<sup>5</sup> and to carry out the conformational analysis of the general case of the flexible form of cyclohexanone itself, and then to apply these results to some specific examples of more complicated molecules to show the generality of the method.

Sachse<sup>6</sup> recognized the flexibility of the boat form of cyclohexane as early as 1890, but this flexibility was lost sight of by most chemists until Hazebroek and Oosterhoff called attention to it in 1951.<sup>7</sup> Because of

the relatively high energy of the flexible form compared to that of the chair (5–6 kcal.), the former is met with only rarely in molecules which are in principle able to adopt the latter.<sup>3,8</sup> For a cyclohexanone, however, the situation is rather different. Because in certain arrangements of the flexible form of cyclohexanone there is only one eclipsed ethane unit, the energy of this form is thought to be less than 3 kcal./mole above that of the boat.<sup>5</sup> This energy difference is sufficiently small that it may be outweighed by the effects of substituents, and the result is that boat forms are, in fact, quite common among cyclohexanone derivatives.<sup>3</sup>

The flexibility of the boat form is conveniently described in terms of a pseudorotational parameter,  $\theta$ .<sup>9</sup> For cyclohexanone we can picture a series of conformations through which the molecule passes as  $\theta$  goes from 0 to 360° (Fig. 1). Starting with the ketone at the prow of the boat ( $\theta = 0^\circ$ ), pseudorotation leads to six classical boat forms as each carbon becomes the prow in turn. Between these regular boats are the stretched<sup>7</sup> (also called twist<sup>10</sup>) forms. The various forms are illustrated by the cycle shown in Fig. 1. As the rotation proceeds from 180 to 360°, the mirror images of the structures shown result. The approach taken here is that the energy for the cyclohexanone ring as a function of  $\theta$  can be calculated, and will be approximately the same in any substituted cyclo-

(1) Paper XXXVII: C. Djerassi, R. A. Schneider, H. Vorbrueggen, and N. L. Allinger, *J. Org. Chem.*, **28**, 1632 (1963).

(2) This work was supported by grant A-5836 from the Public Health Service, National Institutes of Health.

(3) The first example of the proof of the existence of a nonchair form in a molecule which was free to adopt either a boat or a chair conformation was reported by D. H. R. Barton, D. A. Lewis, and J. F. McGhie (*J. Chem. Soc.*, 2907 (1957)). Subsequent examples are numerous and are summarized in review articles: (a) J. Levisalles, *Bull. soc. chim. France*, 551 (1960); (b) M. Balasubramanian, *Chem. Rev.*, **62**, 591 (1962). For a discussion of the different types of boats possible and the experimental demonstration of the existence of a form which is in between the chair and the boat, see ref. 4.

(4) N. L. Allinger and M. A. DaRoogé, *J. Am. Chem. Soc.*, **84**, 4561 (1962).

(5) N. L. Allinger, *ibid.*, **81**, 5727 (1959).

(6) H. Sachse, *Ber.*, **23**, 1363 (1890); *Z. physik. Chem.*, **10**, 203 (1892).

(7) P. Hazebroek and L. J. Oosterhoff, *Discussions Faraday Soc.*, **10**, 87 (1951).

(8) M. Svoboda, M. Tichy, J. Fajkos, and J. Sicher, *Tetrahedron Letters*, 717 (1962).

(9) From Fig. 1 it is qualitatively clear how the geometry depends on  $\theta$ . A mathematical definition of  $\theta$  is complicated. Such a definition is given for the more symmetrical cyclohexane in ref. 7. A similar definition could be formulated for cyclohexanone using any assumed values for bond angles and bond lengths. For present purposes the asymmetry in the carbon system can be neglected, and  $\theta$  here is then equivalent to  $\theta + \pi/2$  in ref. 7. We have chosen to offset the origin because by so doing, a convenient correspondence between  $\theta$  and the sign of the Cotton effect results.

(10) W. S. Johnson, V. J. Bauer, J. L. Margrave, M. A. Frisch, L. H. Dreger, and W. N. Hubbard, *J. Am. Chem. Soc.*, **83**, 606 (1961).