from the *trans*-dibenzoylstilbene in the same region as *cis*-dibenzoylstilbene (*ca.* 410 mμ) and also displayed the same time dependence though it initially decreased in intensity, then began the increase in the same manner as the *cis* isomer. When a study on the emission of the product ester was made, the emission again appeared in the same region (*ca.* 420 mμ) and appeared as a very intense band. These results strongly indicate though do not prove that this time dependence occurs from the *cis–trans* isomerization and is enhanced

further by product formation. To minimize these effects, the Stern–Volmer studies were carried out using the narrowest slits possible for the exciting light.

Intermediates in the Photochemical Rearrangements of Bicyclo[3.1.0]hexenones[1,2]

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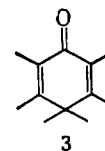
Abstract: Photolysis of hexamethylbicyclo[3.1.0]hexenone (2) in methanol through Pyrex gave the crystalline methoxyenol 4, considered to result from the trapping of a dipolar intermediate (B) by the solvent. The photolysis can be sensitized by benzophenone. Compound 4 loses methanol thermally or in acid, giving the enolic triene 5 which, on further treatment with acid, gives hexamethyl-2,5-cyclohexadienone (3). The latter was synthesized independently by the acid-catalyzed rearrangement of hexamethyl-2,4-cyclohexadienone (1). The course of these photochemical and acid-catalyzed rearrangements was verified using 2 variously labeled in the methyl groups (as CD₃). The photoproduct 4 could be converted by base to its keto form 17, which underwent thermal elimination of methanol to produce the dienone 18. Thermal isomerization of enol 5 gave its keto form 19, isomeric with 18. The implication of these results for the photolysis of bicyclo[3.1.0]hexenones and the tendency to form 1,4- (rather than 1,3-) cyclohexadienes in ground-state reactions are discussed.

I somerization of hexamethyl-2,4-cyclohexadienone (1) on irradiation in ether through Pyrex afforded the bicyclo[3.1.0]hex-3-ene-2-one 2 in excellent yield.[3]
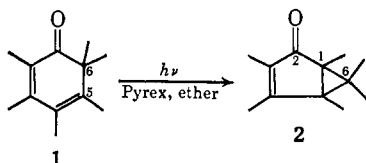
This reaction, which represents a departure from the usual photochemical behavior of 2,4-cyclohexadienones,[4] proceeds *via* a "bond-crossing," rather than alkyl migration mechanism (*i.e.*, carbons 6 and 5 in 1 become respectively carbons 6 and 1 in 2).[3]

In a study of solvent effects on the transformation 1 → 2, it was observed[5] that the reaction proceeded more rapidly in ethanol than in ether; for example, conversions requiring about 5 hr in ether required (all other conditions being the same) only 0.5–1.0 hr in ethanol. However, 2 underwent further photoisomerization in this solvent, and work-up after irradiation for 3 hr led to the isolation of cross-conjugated dienone 3 in excel-

lent yield.[5] Although a few photoisomerizations of bicyclo[3.1.0]hexenones to 2,5-cyclohexadienones are known,[6,7] this result seemed rather strange because the reverse path is much more common,[8] and indeed we have observed (*vide infra*) the photochemical conversion of 3 → 2 in ether.

Accordingly, we undertook a careful study of the photolysis of 2 in methanol (chosen in preference to ethanol, to simplify the nmr spectra). In this paper we show that 3 is *not* a direct photoproduct of 2, but is formed from the photoproduct by thermal and/or acid-catalyzed rearrangements. The photoproduct is shown to have the enolic structure 4, and probably arises from reaction of a dipolar intermediate with a mole of the solvent. The general significance of these results for the various observed photochemical reactions of bicyclo[3.1.0]hexenones is discussed.

Results

Bicyclo[3.1.0]hexenone 2 was irradiated through Pyrex in methanol, the photolysis being monitored by the change in ultraviolet absorption spectrum. In order to prevent the photoproduct from being converted to 3 by acid-catalyzed reactions, all apparatus was washed

(1) Presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

(2) We are grateful to the National Science Foundation (GP 4948) for financial support of this research. We are indebted also to Dr. Peter J. Collins and Professor Shalom Sarel for helpful discussions.

(3) H. Hart, P. M. Collins, and A. J. Waring, *J. Am. Chem. Soc.*, **88**, 1005 (1966).

(4) For a recent review, see G. Quinkert, *Angew. Chem. Intern. Ed. Engl.*, **4**, 211 (1965).

(5) We are indebted to Dr. Richard M. Lange, National Science Foundation Postdoctoral Fellow, 1964–1965, for these initial observations. Dr. Lange was also the first to isolate and characterize the 2,5-dienone 3.

(6) D. H. R. Barton and W. C. Taylor, *J. Chem. Soc.*, 2500 (1958).

(7) D. I. Schuster and A. C. Fabian, *Tetrahedron Letters*, 4093 (1966).

(8) For a review, see O. L. Chapman, *Advan. Photochem.*, 1, 323 (1963).

with 5% sodium hydroxide, and the methanol used as solvent was freshly distilled from sodium methoxide. When these precautions were observed, it was noted that absorptions at 234 and 274 mμ due to **2** disappeared, and the solution became nearly transparent in the ultraviolet [the photoproduct has a λ_{max}^{MeOH} at 202 mμ (ϵ 4300)]. Clearly **3**, which has the expected λ_{max}^{EtOH} at 246 mμ (ϵ 14,800) and which was isolated in excellent yield by a routine work-up of the photolysis solution, could not be a photoproduct, but must be produced during the work-up.

When photolysis was complete, as judged both by ultraviolet and by disappearance of the vpc band due to **2**, the solution was cooled in Dry Ice, or evaporated to dryness, affording a white crystalline photoproduct, which is assigned structure **4**. The product could be stored at −80° without change for extended periods, but decomposed to a yellow viscous oil in the freezer, or on standing overnight at room temperature. Freshly prepared samples had a melting point range of 58–65°, and gave a satisfactory microanalysis.

4
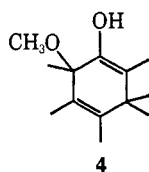
The structure of **4** is based primarily on its analysis, spectra, and chemical conversions. The medium intensity ultraviolet maximum at very low wavelength (202 mμ) eliminates the other mechanistically feasible alternatives **4a**, and **4b**, which should absorb rather intensely at about 278 mμ.[9] The observed ultraviolet spectrum

4a   **4b**
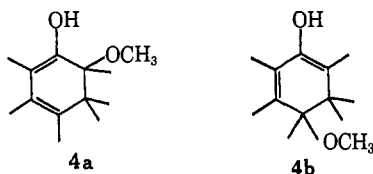
is reasonable for a 1,4-cyclohexadiene.[10] The nmr spectrum (Table I) is consistent with the assigned structure. The hydroxyl proton could be observed when the spectrum was run in carbon tetrachloride. Labeling experiments, to be described below, permit the assignment shown in the table to be made for the three allylic methyls. The three aliphatic methyls cannot be definitively designated, although it seems likely that the one at lowest field is on the carbon bearing the methoxyl. The nmr spectrum, with peaks for three allylic methyl groups, eliminates the cyclopropanone hemiketal structure **4c**.

(9) H. H. Jaffé and Milton Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 200. The observed maximum, although it occurs in a region where the accuracy of the instrument is limited, was reproducible, and at 200 mμ the intensity had fallen considerably below its value at the maximum.

(10) Compare, for example, with 1,2-dimethyl-1,4-cyclohexadiene which has a λ_{max}^{EtOH} at 195 mμ (ϵ 7600); see K. Stich, G. Rotzler, and T. Reichstein, *Helv. Chim. Acta*, **42**, 1480 (1959); also with 3,3,6,6-tetramethyl-1,4-cyclohexadiene, which is reported to have intense end absorption; see W. Reusch, M. Russell, and C. Dzurella, *J. Org. Chem.*, **29**, 2446 (1964).

Table I. Nmr Spectra[a]

| Compd	Chemical shifts (J)[b]	Assignments[c]
2	8.12 (q, 0.9)	C-4 methyl
	8.45 (q, 0.9)	C-3 methyl
	8.78 (s)	C-5 methyl
	8.90 (s)	C-1 methyl
	8.90 (s)	C-6 *exo* methyl
	9.08 (s)	C-6 *endo* methyl
3	8.05 (q, 0.8)	C-3, C-5 methyls
	8.17 (q, 0.8)	C-2, C-6 methyls
	8.79 (s)	C-4 methyls
4[d]	5.75 (s)	Hydroxyl proton
	7.11 (s)	Methoxyl
	8.30 (s)	C-2 methyl
	8.30 (q, 0.9)	C-4 methyl
	8.37 (q, 0.9)	C-5 methyl
	8.70 (s)	C-6 methyl (?)
	8.90 (s)	C-3 methyls (?)
	8.95 (s)	
5	5.05 (s)	Vinyl proton (*cis* to hydroxyl?)
	5.20 (s)	Vinyl proton
	8.18 (s)	C-4, C-5 methyls
	8.23 (s)	C-2 methyl
	8.89 (s)	C-3 methyls
17	7.10 (s)	Methoxyl
	7.28 (q, 7.0)	C-6 proton
	8.27 (s)	C-3 and C-4 methyls
	8.37 (s)	
	8.73 (s)	C-5 methyls (?)
	8.85 (s)	
	9.01 (d, 7.0)	C-6 methyl
	9.22 (s)	C-2 methyl (?)
18	4.74 (s)	Vinyl proton (*trans* to *gem*-dimethyl?)
	4.90 (s)	Vinyl proton
	7.85 (q, 7.0)	C-6 proton
	7.93 (s)	C-3 methyl
	8.20 (s)	C-2 methyl
	8.90 (s)	C-5 methyls
	8.97 (s)	
	9.07 (d, 7.0)	C-6 methyl
19	4.28 (s)	Vinyl proton (*cis* to oxygen?)
	5.00 (s)	Vinyl proton
	8.13 (s)	C-3 and C-4 methyls
	8.89 (s)	C-5 methyls
	9.07 (s)	
	8.96 (d, 7.0)	C-6 methyl[e]

[a] All spectra are in CCl₄ except as noted. [b] Shifts are reported as τ values, with TMS as an internal reference. J's are in cps. All spectra were run at 60 Mc. All areas are consistent with the assignments. [c] A question mark indicates that the assignment is tentative. [d] The spectrum was run in methanol as solvent, except that the chemical shift for the hydroxyl proton is in CCl₄. [e] The C-6 proton responsible for the splitting of this methyl was lost in noise and could not be located with certainty.

The infrared spectrum of **4** showed a hydroxyl stretching frequency at 3555 cm⁻¹, and no carbonyl absorption.

4c
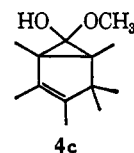
When a CCl₄ solution of **4** was warmed for several minutes, a new band appeared in the nmr spectrum at τ 6.62. This was due to the methyl protons of methanol, as shown by its increase in area when methanol was added to the solution. The formation of methanol was

accompanied by other changes in the nmr spectrum and by the appearance of a new band in the ultraviolet, although no carbonyl band was observed in the infrared. These changes are ascribed to the 1,2 elimination of methanol from **4**, with the formation of the enol **5**.

5   **6**
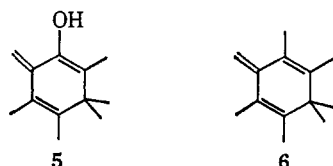
This substance was isolated as a yellow oil with a λ_{max}^{MeOH} of 252 mμ (ϵ 13,400). This compared favorably with the related cross-conjugated triene **6**,[3,11] which has a $\lambda_{max}^{isooctane}$ at 256 mμ (ϵ 21,400). The nmr spectrum (Table I) is consistent with structure **5**. The vinyl proton at τ 5.05 is probably *cis* to the hydroxyl group, since both vinyl protons of **6** are at τ 5.23, close to the other vinyl proton (τ 5.20) in **5**. The three allylic methyls can be assigned as shown in the table, as a result of labeling experiments described below. As expected (and in contrast with **4**) the *gem*-dimethyls appear as a sharp, six-proton singlet at τ 8.89 (*cf.* τ 8.91 for the *gem*-dimethyls of **6**). The infrared spectrum of **5** showed a strong O–H stretch at 3450 cm^{-1} and no carbonyl absorption, confirming the enolic structure.

Treatment of either **4** or **5** with acid gave the crystalline cross-conjugated dienone **3** in essentially quantitative yield. Its structure follows from the elemental analysis and spectra. It had prominent infrared bands at 1653 and 1624 cm^{-1} and the anticipated λ_{max} at 246 mμ.[12] The β-allylic methyls are at lowest field (Table I), and adjacent methyls show homoallylic coupling of about 0.8 cps. Dienone **3**, prepared directly from **1** by treatment with fuming sulfuric acid,[13] was identical with the acid-catalyzed rearrangement product of **4** or **5**.

The over-all sequence established by these experiments is

$$2 \xrightarrow[\text{CH}_3\text{OH}]{h\nu} 4 \xrightarrow[\text{or H}^+]{\text{heat}} 5 \xrightarrow{\text{H}^+} 3$$
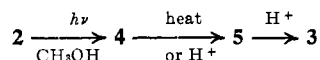
Experimental verification that **4** is not converted directly to **3** by acid, but first forms **5**, was obtained by following the changes in the ultraviolet spectrum when a trace of acid was added to a solution of **4** in methanol. The maximum shifted very rapidly from 202 mμ (**4**) to 252 mμ (**5**), then slowly changed to 246 mμ (**3**) on adding additional acid.

Photolysis of Labeled Bicyclo[3.1.0]hexenones. In order to confirm the structures and reactions which have just been described, and also to assign as many of the nmr positions of the various methyl groups, two labeled hexamethylbicyclo[3.1.0]hex-3-en-2-ones were prepared and photolyzed. Dienone **7**, prepared as previously described,[3] gave ketone **8** on irradiation in ether.[3] The sample of **8** which was carried through the remainder of the sequence was completely labeled at the C-4 methyl, but only about 50% labeled at the C-1

(11) W. von E. Doering, M. Saunders, H. G. Boynton, H. W. Earhart, E. F. Wadley, W. R. Edwards, and G. Laber, *Tetrahedron*, 4, 178 (1958).

(12) A. J. Waring in "Advances in Alicyclic Chemistry," Vol. 1, H. Hart and G. J. Karabatsos, Ed., Academic Press Inc., New York, N. Y., 1966, pp 188–190.

(13) The acid-catalyzed rearrangements of 1 and 2 will be the subject of a separate paper.

7 $\xrightarrow[\text{ether}]{h\nu}$ **8** $\xrightarrow[\text{methanol}]{h\nu}$

9 $\xrightarrow{\Delta}$ **10** $\xrightarrow{\text{H}^+}$

11
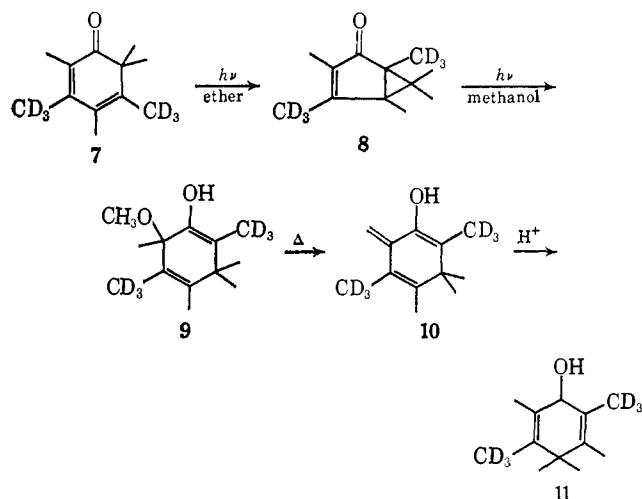
methyl, as judged from its nmr spectrum.[14] Thus the nmr spectrum of **8** was similar to that of **2** (Table I) except that it lacked a band at τ 8.12 (due to the C-4 methyl) and the band at τ 8.45 for the other allylic methyl was a singlet, rather than a quartet. The singlet at τ 8.90 was reduced in area from 6 H to about 4.5 H, consistent with about 50% label at C-1. Irradiation of **8** in methanol gave crystalline **9**, which had an nmr spectrum in methanol similar to **4** (Table I) except that the quartet at τ 8.37 was lacking, and the peak at τ 8.30 was a sharp singlet, area 4.5 H. This permits the assignment of the allylic methyls in **4** as shown in the table, with the highest field allylic methyl at C-5.

Compound **9**, when heated, gave **10**, whose nmr spectrum differed from **5** in that the peak at τ 8.23 was now reduced to a shoulder (at about τ 8.20) on the τ 8.18 peak; the latter was sharp, and the total area was 4.5 H. This permits the assignment of the high-field allylic methyl in **5** to C-2, an assignment which is confirmed by further labeling experiments described below.

Treatment of **9** or **10** with acid gave cross-conjugated dienone **11**. Its nmr spectrum showed only one low-field allylic methyl at τ 8.05, and somewhat over one methyl at τ 8.18; both were singlets rather than quartets (as in **3**), establishing that the labeled methyls must be on "opposite" sides of the ring.

12 $\xrightarrow[\text{ether}]{h\nu}$ **13** $\xrightarrow[\text{methanol}]{h\nu}$

14 $\xrightarrow{\Delta}$ **15** $\xrightarrow{\text{H}^+}$

16
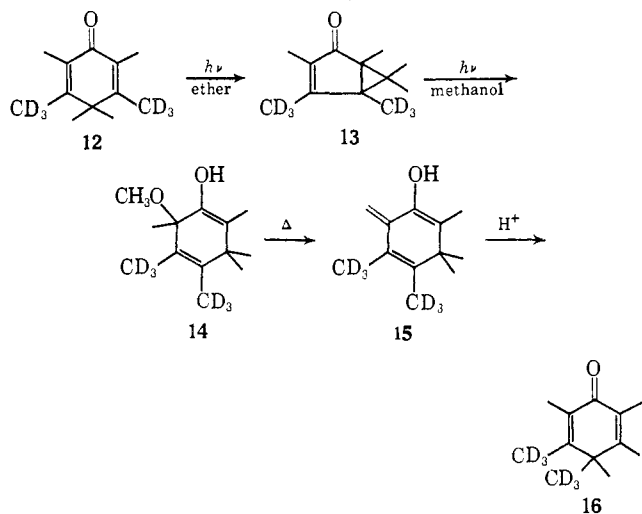
The other sequence of experiments with labeled ketones is shown in the scheme. Cross-conjugated dienone

(14) It is much more difficult to label the C-5 methyl of 7 than the C-3 methyl; see ref 3.

3 has two methyls which are easily exchanged with sodium methoxide in CH_3OD. This afforded 12, whose nmr spectrum consisted of two sharp equal singlets at τ 8.18 and 8.78 (compare with 3, Table I). Irradiation of 12 in ether gave 13, whose nmr spectrum differed from that of 2 (Table I) by lacking a band at τ 8.12 (C-4 methyl), with the result that the remaining allylic methyl, τ 8.45, was a singlet. The singlet at τ 8.78 was also absent; this is ascribed to the methyl at C-5.

Photolysis of 13 in methanol gave 14 whose nmr spectrum lacked a band at τ 8.37, and had a sharp three-proton singlet at τ 8.30; otherwise, the spectrum was identical with that of 4. This confirms that the C-2 methyl is at τ 8.30, as assigned above. A methanol solution of 14, on standing overnight in the refrigerator, afforded 15, whose nmr spectrum showed a singlet at τ 8.20 for three protons, and only a slight peak (perhaps 1 H) for the lower field allylic methyls (τ 8.15).[15] Thus the higher field allylic methyl in 5 must be at C-2, as assigned above.

In one photolysis of 13, a trace of acid was present in the methanol, and work-up gave 16 directly. Its nmr spectrum showed three singlets at the same positions as for 3 (Table I), but with relative areas (from low to high field) of 3:6:3. Thus by irradiation of 12 in ether, followed by irradiation in methanol with a trace of acid present, one has in effect interchanged the positions of two of the methyl groups (at C-3 and C-4), giving 16.

The Keto Forms of 4 and 5. The photoproduct 4 and its elimination product 5 are both enolic. In order to provide further chemical support for their structures (other than acid-catalyzed rearrangement to 3), each was converted to its keto form.

A solution of 4 in methanol was treated at 0° for 0.5 hr with 0.2 N sodium methoxide in methanol. Extraction with methylene chloride gave a colorless oil, assigned structure 17, in nearly quantitative yield. It showed a carbonyl frequency of 1716 cm^{-1}, suitable

4 $\xrightarrow[\text{CH}_3\text{OH}]{\text{NaOCH}_3}$

17

18   18a
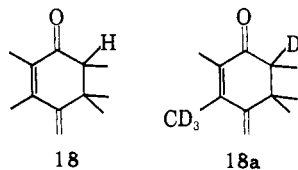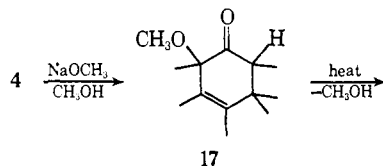
for a saturated, six-membered ring ketone. The nmr spectrum (Table I) is consistent with the structure; significant features are the presence of only two allylic methyls (as contrasted with three in 4) and the expected splitting pattern for the proton and methyl group on C-6. The rather high-field position of the C-6 methyl is also noteworthy; the molecule must assume a conformation which brings this methyl in the shielding region of the adjacent carbonyl group.[16]

(15) These peaks, 0.05 τ unit apart, undoubtedly correspond to the peaks at τ 8.23 and 8.18 reported in the table, the error being due to a displacement of the calibration.

(16) The assignment for the C-2 methyl is tentative, and may possibly be interchanged with one of the peaks assigned to the *gem*-dimethyl at C-5. It is worthwhile pointing out that only one of the two possible stereoisomers of 17 is obtained.

The structure of ketone 17 is reinforced by its thermal, 1,4 elimination of methanol on vpc. The product, a colorless oil with a satisfactory analysis, is assigned structure 18 on spectral grounds. In particular, the infrared spectrum showed a conjugated carbonyl and carbon–carbon double bond (1667, 1600 cm^{-1}) and a terminal methylene group (905 cm^{-1}). Although 17, like 4, showed ultraviolet absorption only at very low wavelengths (203 mμ), 18 had an intense λ_{max} at 280 mμ (ϵ 13,800), reasonable for its structure.[17] The nmr spectrum (Table I) is consistent with the structure. Particular attention is called to the low-field position (τ 7.93) of one of the allylic methyls. This is expected[3] for the β-methyl of an α,β-unsaturated cyclohexenone, but cannot fit structure 19, which would be the 1,2-elimination product of 17.

The structure of 18 was confirmed by the change in its nmr spectrum on treatment with base in deuteriomethanol. In particular, the quartet due to the α proton at C-6 and the band due to the β-allylic methyl at C-3 disappeared, and the doublet ascribed to the C-6 methyl became a singlet (see structure 18a).

Structure 19, the ketonic form of 5, was also prepared, and had quite a different nmr spectrum from 18.

5 $\xrightarrow{\text{vpc}}$

19
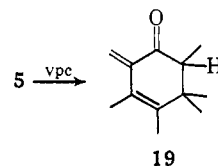
When an ether solution of 5 was injected on the vpc, a product was collected which is assigned structure 19 on the basis of spectroscopic evidence and method of synthesis. The infrared spectrum of 19 showed a carbonyl at 1700 cm^{-1} and a terminal methylene at 920 cm^{-1}.[18] The nmr spectrum of 19 (Table I) is consistent with its structure. In particular, there is no low-field allylic methyl (contrast with 18). Also notable is the large chemical shift difference between the two vinyl protons in 19, as contrasted with the much smaller difference in 18; this is reasonable in view of the environmental differences of the vinyl protons in the two isomers.

Discussion

There seem to be five known photochemical options for bicyclo[3.1.0]hex-3-en-2-ones, depending on their substitution. Four of these, and by far the most common, involve opening of the "central" or C-1–C-5 bond of the three-membered ring.[19] The products may be (a) 2,4-cyclohexadienones (alkyl migration from C-6 to C-1),[7,20] (b) 2,5-cyclohexadienones (alkyl migration

(17) If calculated according to ref 9, p 215, the λ_{max} should be at 290 mμ; however, these rules may give somewhat high values for dienones of this type. Note, for example, entry 4 in Table 10.13 of this reference, which absorbs 11 mμ lower than calculated. The extinction coefficient of 18 is in line with compounds of related structure.

(18) For examples of other cisoid α,β-unsaturated ketones with similarly high carbonyl frequencies, see R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960).

(19) The fifth option, which involves breaking the C-5–C-6 bond, is much rarer. See, however, (a) T. Matsuura, *Bull. Chem. Soc. Japan*, 37, 564 (1964); (b) B. Miller and H. Margulies, *Chem. Commun.*, 314 (1965); (c) H. Dutler, C. Ganter, H. Ryf, E. C. Utzinger, K. Weinberg, K. Schaffner, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, 45, 2346 (1962); (d) J. Frei, C. Ganter, D. Kägi, K. Kocsis, M. Miljkovic, A. Siewinski, R. Wenger, K. Schaffner, and O. Jeger, *ibid.*, 49, 1049 (1966).

(20) For examples, see O. L. Chapman and L. F. Englert, *J. Am. Chem. Soc.*, 85, 3028 (1963); M. H. Fisch and J. H. Richards, *ibid.*, 85, 3029 (1963); P. J. Kropp, *ibid.*, 86, 4053 (1964).

from C-6 to C-5),[7,21] (c) phenols (proton loss from C-6,[22] C-6 to C-1 phenyl migration followed by proton loss,[23] or C-6 to C-5 migration followed by proton loss[24]), or (d) isomeric bicyclo[3.1.0]hexenones.[24] In each case, the products can be rationalized in terms of a di-


A
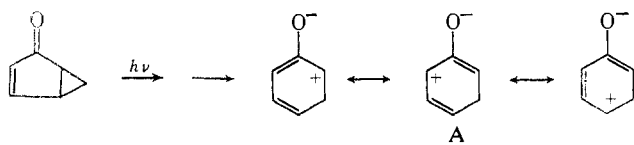
polar intermediate A which undergoes further typical carbonium ion rearrangements.[19d]

In the photolysis of **2**, the corresponding intermediate B[25] would be completely substituted with methyl groups. Of the four alternatives listed above, only 1,2-methyl migrations leading to **1** or **3** are possible (other than the


B
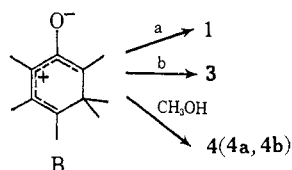
trivial reaction of return to starting material, either directly or with multiple methyl shifts). When the photolysis of **2** is run in methanol, however, the solvent may capture B before methyl migration occurs, leading to **4** (or **4a,b**). This is the interpretation we place on the isolation of **4** as the sole photoproduct of **2** in methanol.

The reason for the exclusive formation of **4**, rather than **4a** or **4b**, despite the fact that the double bonds are conjugated in the two latter structures, may be due to the charge distribution in B. Formation of nonconjugated rather than conjugated product is consistent with our earlier observations in similar systems.[3] For example, alcohol **20** gave only **6**, and not **21**, on dehydra-

21   **20**
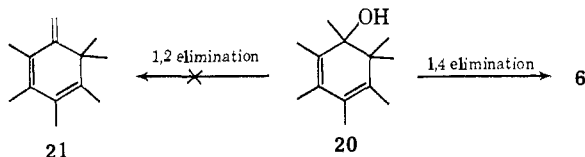
tion. Another example of the preference for formation of 1,4- rather than 1,3-cyclohexadienes is the acid-catalyzed elimination of methanol from **4**. In contrast with **20**, compound **4** underwent 1,2 rather than 1,4

5a
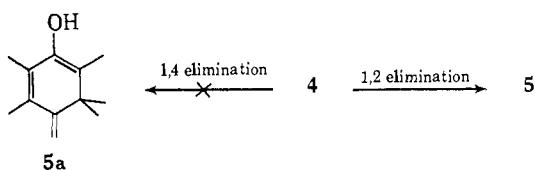
elimination; the product in both cases had nonconjugated double bonds in the six-membered ring (contrast this with the 1,4 elimination of methanol from the keto form of **4**; i.e., **17** → **18**).

(21) For examples, see D. H. R. Barton and W. C. Taylor, *J. Chem. Soc.*, 2500 (1958).

(22) J. W. Wheeler and R. H. Eastman, *J. Am. Chem. Soc.*, **81**, 236 (1959).

(23) H. E. Zimmerman and D. I. Schuster, *ibid.*, **84**, 4527 (1962).

(24) See footnote 20, ref 3.

(25) The observation that the conversion of **2** → **4** can be photosensitized with benzophenone suggests that there are mechanistically important precursors of B. It is also possible that B may be protonated by the solvent, prior to further conversions.

The acid-catalyzed conversion of **5** to **3** may be viewed as still another example. This reaction is considered to proceed *via* ion C, which then might undergo a

C
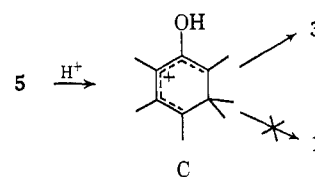
methyl shift in either of two directions, leading to **1** or **3**; once again, the observed product has the 1,4- rather than the 1,3-cyclohexadiene structure. That this is a simple 1,2-methyl shift, and not a process by which methyl groups migrate many times and become scrambled before collapsing to product, is clear from the results with labeled compounds (i.e., **10** → **11** and **15** → **16**).

A brief comment seems in order regarding the formation and stability of the enols **4** and **5**. One might attribute the stability of enol **4** to intramolecular hydrogen bonding with the methoxyl oxygen, but this is not possible for **5**, and examination of models suggests it is also unlikely in **4**. At the moment we have no explanation for the unusual stability of **4** and **5**, particularly since there seem to be no overwhelming factors which destabilize their corresponding keto structures **17** and **19**. In the absence of equilibration experiments, it is not possible to say which form (keto or enol) is the more stable. Formation of **4** may be due to rapid protonation of B on oxygen, by the solvent; i.e., control may be kinetic rather than thermodynamic. However, the acid-catalyzed elimination of methanol from **4** is particularly unusual, since ketonization in this medium should be possible.

Experimental Section

The nmr spectra were obtained with a Varian A-60 spectrometer, using CCl_4 solutions (unless otherwise stated) with tetramethylsilane as an internal reference. Infrared spectra were taken on a Unicam SP200 spectrometer, in CCl_4 solution unless otherwise stated. Varian Aerograph gas chromatographs were used. Melting points are uncorrected. Analyses were performed by Spang Microanalytical Laboratories, Ann Arbor Mich.

Photolysis of 1,3,4,5,6,6-Hexamethylbicyclo[3.1.0]hex-3-en-2-one (2) in Methanol. The methanol should be freshly distilled from sodium methoxide, and all glassware should be washed with alkali before use. A solution of 1.81 g of 2[3] in 400 ml of methanol, stirred with a stream of dry nitrogen, was irradiated at 15° with a 200-w Hanovia lamp through a Pyrex filter. The reaction, which was complete in about 250 min, was followed by vpc (disappearance of enone) or by ultraviolet (disappearance of the peaks at 235 and 274 mμ due to 2). Cooling in a Dry Ice bath or evaporation of the solvent *in vacuo* at 20° led to the isolation of **2,3,3,4,5,6-hexamethyl-6-methoxycyclohexa-1,4-dien-1-ol (4)** as white crystals.

Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.03; H, 10.43.

Compound **4** showed a λ_{max}^{MeOH} at 202 mμ (ε 4300). Its nmr spectrum was most easily measured in methanol (see Table I). If one works quickly a similar spectrum is observed in CCl_4 (bands at τ 7.13, 8.33, 8.39, 8.75, 8.92, and 8.96) except for an additional one-proton singlet at τ 5.75 (–OH); at the usual probe temperature (about 35°) this spectrum changes rapidly; see below.

An infrared spectrum of **4** in CCl_4 was obtained by cooling the cells in a desiccator in a freezing chest; the cells were then filled with a solution of 4. and the spectrum was run quickly. Prominent bands appeared at 3555 (O–H), 2980 and 2930 (C–H), 1618 (C=C), 1375, 1345, 1290, 1215, 1105, and 1072 cm^{-1}; there was no carbonyl absorption.

In a separate experiment to determine the isolable yield and stability of **4**. a solution of 0.327 g of 2 in 2 ml of methanol (freshly distilled from sodium methoxide; all glassware alkali washed) in a

Pyrex test tube sealed with a serum cap was irradiated by attaching it to the side of a water-cooled quartz well containing a 450-w Hanovia lamp. Photolysis was complete in 130 min (vpc). The solution was cooled to $-70°$, and the photoproduct was filtered and rinsed with cold ($-70°$) methanol. The yield of white, crystalline **4** was 0.294 g (76%). The crystals could be stored indefinitely at $-70°$, but on standing overnight at room temperature they were transformed to a viscous yellow oil. Starting at room temperature, with a heating rate of 2°/min, **4** has mp 58–65°.

The following experiment was performed to determine whether the photolysis could be sensitized. Starting enone **2** and benzophenone were washed with 5% sodium hydroxide, then water, before use; methanol was freshly distilled from sodium methoxide, and all glassware was washed with alkali. A solution of 0.098 g of **2** in 10 ml of methanol was placed in a 25-ml Pyrex test tube, sealed with a serum cap. In a similar tube was placed a solution of 0.098 g of **2** and 5.02 g of benzophenone in 10 ml of methanol. Both tubes were taped to the side of a water-cooled quartz well containing a 200-w Hanovia mercury vapor lamp. A stream of air was passed over the lamp; this had been observed to decrease the photolysis rate of **2**. The photolysis was followed by injecting 10-μl samples on a gas chromatograph, 5 ft $\times$ 0.25 in. 20% SE-30 column, 180°. Disappearance of starting enone and appearance of photoproduct (or vpc decomposition product thereof) were both followed. After 225 min, photolysis had proceeded to the extent of 13.2 and 53.9%, respectively, in the two tubes.

2,3,3,4,5-Pentamethyl-6-methylenecyclohexa-1,4-dien-1-ol (5). When an nmr tube containing a solution of **4** in CCl₄ was allowed to remain in the probe (about 35°) for 5 min, it was noted that a new band appeared at τ 6.62, owing to methanol. After 10 min this band reached maximum area, and other spectral changes were complete. The product, which is **5**, had an nmr spectrum as shown in Table I. Evaporation afforded a yellow oil with a λ_{max}^{MeOH} at 252 mμ (ϵ 13,400). An infrared spectrum of **5** showed a strong hydroxyl band at 3450 cm⁻¹ and other bands at 2945, 2900, 2840 (C–H), 1620, 1575, 1450, 1375, 1270, 1208, 1108, 1075, 1025, and 864 cm⁻¹.

2,3,4,4,5,6-Hexamethyl-2,5-cyclohexadienone (3).[5] 2,3,4,5,6,6-Hexamethyl-2,4-cyclohexadienone (1), 15.2 g, was added slowly to 70 ml of 20% fuming sulfuric acid at 0°. The resulting brown solution was stirred at room temperature for 10 min, then poured on ice. After dilution to 2 l. with ice water and filtration, the resulting tan solid was dissolved in ether. The ether solution was washed with water and dried over magnesium sulfate. Recrystallization from hexane gave 8.76 g of colorless crystals of **3**, mp 117.5–118.2°.

Anal. Calcd for C₁₂H₁₈O: C, 80.85; H, 10.18. Found: C, 80.91; H, 10.11.

3 had prominent infrared bands at 1653 and 1624 cm⁻¹, and a λ_{max}^{EtOH} at 246 mμ (ϵ 14,800). Its nmr spectrum is reported in Table I.

Acid-Catalyzed Conversion of 4 and 5 to 3. A few crystals of **4** was dissolved in 30 ml of methanol, and two drops of dilute HCl was added. The solution was evaporated *in vacuo* at room temperature, and the nmr spectrum of the residue was identical with that of **3**, except for a small amount of an unknown impurity.

A 10% solution containing a 50:50 mixture of **5** and **3** in methanol was acidified with two drops of dilute HCl. An nmr spectrum run on the resulting solution showed peaks due only to **3**.

To 3 ml of a solution of **4** in methanol in an ultraviolet cell (λ_{max} 202 mμ, A = 0.97) was added 4 μl of 1% HCl in methanol. The solution now had a strong absorbance at 252 mμ (A = 0.88) owing to the formation of **5**. After 10-μl additional HCl, the solution had a λ_{max} at 251 mμ (A = 0.79), and after another 10 μl of HCl, λ_{max} at 247 mμ (A = 0.68), because of complete conversion to **3**.

Photolysis of 3,5,6,6-Tetramethyl-1,4-bis(trideuteriomethyl)bicyclo[3.1.0]hex-3-en-2-one (8). Labeled enone **8** was prepared as previously described.[3] Its nmr spectrum showed that label was essentially complete at the C-4 methyl, and 50% complete at the C-1 methyl. The enone was irradiated in methanol as described above for the unlabeled compound. The nmr spectrum of the resulting crystalline photoproduct in methanol was identical with that of unlabeled **4** except that the peak at τ 8.37 was almost absent, and the peak at τ 8.30 was a very sharp singlet, area 4.5 H.

Thermal conversion of this labeled photoproduct (as described above for unlabeled **4**) gave a mixture of **10** and **11**. Disregarding bands due to the latter (see below) gave an nmr spectrum for **10** in methanol which was identical with that of unlabeled material, except that the allylic methyls appeared as a sharp singlet at τ 8.18 with a shoulder at τ 8.20, total area 4.6 H.

Treatment of labeled **9** or **10** with a little dilute HCl led (as described above for unlabeled compounds) to labeled **11** whose nmr

spectrum had bands at τ 8.05, 8.18, and 8.80 with relative areas 2.6:3.4:6.0. The two low-field peaks were singlets.

Photolysis of 2,3,4,4,5,6-Hexamethyl-2,5-cyclohexadienone (3) in Ether. A solution of 2.0 g of **3** in 400 ml of anhydrous ether kept at 15° under a nitrogen atmosphere was irradiated with a 200-w Hanovia lamp through a Vycor filter with magnetic stirring. After 81 min, the photoproduct had reached a maximum concentration as shown by vpc, and the reaction was terminated. Preparative vpc afforded 0.39 g of enone **2**. The photolysis was not allowed to proceed to complete disappearance of the dienone, because the enone photoproduct undergoes further photorearrangement under these conditions.

Preparation of 2,4,4,6-Tetramethyl-3,5-bis(trideuteriomethyl)-2,5-cyclohexadienone (12). To a solution of **3** (7.8 g) in 63 ml of CH₃OD was added a 0.5-cm³ piece of sodium. The resulting solution was refluxed for 70 hr, after which time an nmr spectrum showed that exchange was complete. Most of the methanol was evaporated *in vacuo*, and the remaining solution was poured into 200 ml of methylene chloride. This was extracted with cold (0°) water to remove the remaining methanol, and the solution was dried over anhydrous magnesium sulfate. Evaporation of the solvent afforded 7.6 g (97%) of crystalline **12** which had an nmr spectrum with two equal singlets at τ 8.18 and 8.78.

Photolysis of 2,4,4,6-Tetramethyl-3,5-bis(trideuteriomethyl)-2,5-cyclohexadienone (12) in Ether. The deuterated dienone was photolyzed as described above for the unlabeled dienone. The enone photoproduct **13** had the following nmr spectrum: singlets at τ 8.45, 8.90, and 9.07 with relative areas 3:6:3.

Photolysis of 1,3,6,6-Tetramethyl-4,5-bis(trideuteriomethyl)bicyclo[3.1.0]hex-3-en-2-one (13) in Methanol. Labeled enone **13** was irradiated in methanol as described above for the unlabeled compound. An nmr spectrum of the product in MeOH showed it to be a mixture of **14** and **15**. If peaks due to the hydroxytriene **15** were disregarded, a spectrum owing to labeled **14** resulted which lacked the band at τ 8.37 and showed only a three-proton singlet at τ 8.30; in other respects, the nmr spectrum was identical with that of unlabeled **4**.

The methanol solution of photoproduct was allowed to remain in the refrigerator overnight. It was then evaporated *in vacuo* to 0.5 ml, giving a solution of labeled **15** whose nmr spectrum showed a small singlet (about 1 H) at τ 8.15, and singlets at τ 8.20 (3 H) and 8.90 (6.7 H).

In one photolysis of **13**, a trace of acid must have been present, since the major reaction product was labeled hexamethyl-2,5-cyclohexadienone (**16**). Its nmr spectrum showed singlets at τ 8.05 (3 H), 8.18 (5.2 H), and 8.80 (3.2 H).

2-Methoxy-2,3,4,5,5,6-hexamethylcyclohex-3-en-1-one (17), the Keto Form of 4. A solution of **2** (0.81 g) in 25 ml of methanol was irradiated at 0° in a Pyrex test tube for 74 min with a 450-w Hanovia lamp. After this time white crystals of **4** could be seen suspended in the methanol, and photolysis was complete (vpc). The photolysis solution was poured into 25 ml of 0.2 N sodium methoxide in methanol and stirred for 30 min at 0°. Water (35 ml) was added, the solution was extracted with methylene chloride, and the latter solution was washed with water and dried over anhydrous Na₂SO₄. Evaporation of the solvent *in vacuo* gave **17**, a colorless oil, in nearly quantitative yield. Its infrared spectrum showed bands at 1716 (C=O) and 1115 cm⁻¹ (C–O–CH₃). Its nmr spectrum is reported in Table I. Its ultraviolet spectrum had a λ_{max}^{EtOH} at 203 mμ (ϵ 6000); a small shoulder at 275 mμ (ϵ 1060) may be due to an impurity.

2,3,5,5,6-Pentamethyl-4-methylenecyclohex-2-en-1-one (18). When **17** was injected on a gas chromatograph (5-ft SE-30 column, 200°) one major peak was observed; collection of the product showed that **17** had lost a mole of methanol. The new product, which was a colorless oil, is assigned structure **18**.

Anal. Calcd for C₁₂H₁₈O: C, 80.85; H, 10.18. Found: C, 80.79; H, 10.09.

18 had infrared bands at 1667 (C=O), 1600 (C=O), and 905 cm⁻¹ (terminal CH₂). Its ultraviolet spectrum had a λ_{max}^{EtOH} at 280 mμ (ϵ 13,800). Its nmr spectrum in CCl₄ is reported in Table I.

The nmr spectrum of **18** in CD₃OD consisted of bands at τ 4.66 (1 H, s), 4.88 (1 H, s), 8.06 (1 H, q, J = 7.0 cps), 8.20 (3 H, s), 8.45 (3 H, s), 9.22 (6 H, s), and 9.37 (3 H, d, J = 7.0 cps). Sodium hydroxide (0.0033 g) was added to a solution of **18** (0.075 g) in 0.2 ml of CD₃OD. After the solution had remained at room temperature for 16 hr, its nmr spectrum showed that the quartet at τ 8.06 and the singlet at τ 8.20 were missing, and the peak at τ 9.37 had become a singlet.

3,4,5,5,6-Pentamethyl-2-methylenecyclohex-3-en-1-one (19), the Keto Form of 5. When an ether solution of **5** was injected on a gas

chromatograph (10-ft Apiezon L column, 180°), one major peak (other than solvent) was observed; collection gave a clear oil which is assigned the structure **3,4,5,5,6-pentamethyl-2-methylenecyclohex-** **3-en-1-one (19)**. Its infrared spectrum had prominent bands at 1700 (C=O) and 920 cm⁻¹ (terminal CH₂). Its nmr spectrum is reported in Table I.

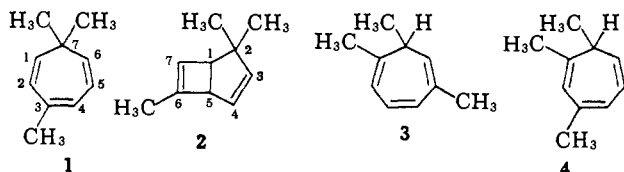# Photolyses of Trienes.   Selective Photoreactions of 3,7,7-Trimethylcycloheptatriene

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Contribution from the Department of Chemistry, University of Arizona, Tucson, Arizona   85721.   Received November 19, 1966

Abstract: Irradiation of a benzene solution of 3,7,7-trimethylcycloheptatriene in a Pyrex tube with a Hanovia high-pressure, mercury arc lamp yields a mixture containing 2,2,6-trimethylbicyclo[3.2.0]hepta-3,6-diene (**2**), 1,5,7-trimethylcycloheptatriene (**3**), 1,3,7-trimethylcycloheptatriene (**4**), and recovered starting material.   Compounds **2** and **3** are primary photoproducts while **4** arises from the further irradiation of **3**.   Under the same conditions, 1-deuterio-3,7,7-trimethylcycloheptatriene gives the corresponding monodeuterated products.   The new trienes arise from highly selective [1,7] sigmatropic methyl and hydrogen migrations, and the bicyclic product arises from a selective electrocyclization reaction.   The origin of these highly selective transformations is discussed.

Recently, there has been considerable interest in the photoisomerization of various cyclic trienes. Cycloheptatriene photoisomerizes to give the valence tautomer bicyclo[3.2.0]hepta-2,6-diene.[1] Thujic acid and its methyl ester upon irradiation yield 1,7-dimethyl-4-carbomethoxycycloheptatriene (or the corresponding acid) resulting from methyl migration, in addition to 2,2-dimethyl-5-carbomethoxybicyclo[3.2.0]hepta-3,6-diene (or the corresponding acid).[2] The formation of the new triene was rationalized on the basis of a highly polarized excited state. ter Borg and Kloosterziel[3] studied the photolysis of 7-deuteriocycloheptatriene and observed a [1,7] sigmatropic hydrogen migration. Similar [1,7] hydrogen shifts have recently been noted in the photolyses of 1,4-bis(cycloheptatrienyl)benzene isomers.[4]

Our interest in these photolysis reactions led us to investigate the photoisomerization of the readily available 3,7,7-trimethylcycloheptatriene (**1**),[5,6] as this compound presents interesting possibilities for the pathway of photoisomerization of olefins containing no readily polarizable functional group. We have found that irradiation of **1** in benzene solution with a 450-w Hanovia high-pressure mercury arc lamp for 3–6 hr results in the formation of 2,2,6-trimethylbicyclo[3.2.0]-hepta-3,6-diene (**2**), 1,5,7-trimethylcycloheptatriene (**3**), and 1,3,7-trimethylcycloheptatriene (**4**).

The assignments of structure to the photoproducts are based on spectroscopic data and quantitative catalytic hydrogenation. Hydrogenation of **2** results in the uptake of 2 moles of hydrogen. The ultraviolet spectrum of **2** shows only end absorption [210 mμ (ε 2640)] indicating that the double bonds are unconjugated. The nuclear magnetic resonance (nmr) spectrum of **2** shows the *gem*-dimethyl group as two nonequivalent singlets at 0.92 and 0.98 ppm. The vinyl methyl group appears at 1.62 ppm. The bridgehead hydrogens at positions 1 and 5 appear as broad bands at 2.70 and 3.39 ppm, respectively. The cyclopentene hydrogen at position 3 appears as a doublet at 5.25 ppm ($J = 6$ cps) further coupled with the bridgehead hydrogen at position 1 ($J = \sim 1$ cps). The remaining cyclopentene hydrogen and the cyclobutene hydrogen appear as a multiplet at 5.52–5.70 ppm.

The ultraviolet spectra of trienes **3** and **4** show medium intensity bands at 267 mμ (ε 3740) and at 266 mμ (ε 3750), respectively, which correspond to those shown by other tropilidenes.[6] Quantitative hydrogenation of a mixture containing 55% **3** and 45% **4** results in the uptake of 3 moles of hydrogen. More definitive evidence for the structures of **3** and **4** comes from the nmr spectra. Previous work[6,7] has indicated a characteristic separation of the 1–6, 2–5, and 3–4 pairs of olefin proton absorptions into upfield, midfield, and downfield regions, respectively. The nmr spectrum of **3** shows a three-proton doublet at 1.06 ppm ($J = 7$ cps). The vinyl methyl groups appear as broadened singlets at 1.69 and 1.78 ppm and obscure the absorption of the proton at position 7 which also appears in this region. The olefinic proton absorptions appear at 4.61 ppm (one-hydrogen doublet, $J = 5.5$ cps), at 5.62 ppm (a broad band corresponding to one hydrogen), and at 6.03–6.18 ppm (two-hydrogen multiplet). The nmr spectrum of **4** shows a three-proton doublet at 1.13 ppm ($J = 7$ cps). The vinyl methyl groups appear

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