

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

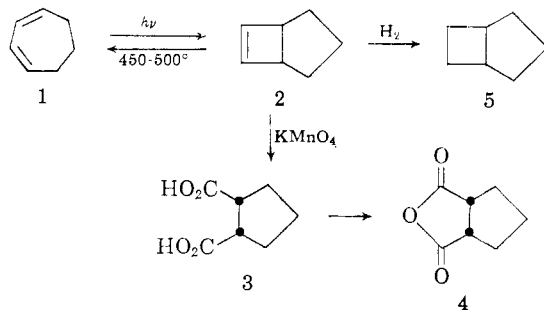
Photochemical Transformations of Conjugated Cycloheptadienes<sup>1</sup>BY O. L. CHAPMAN, D. J. PASTO,<sup>2</sup> G. W. BORDEN AND A. A. GRISWOLD

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A wide variety of conjugated cycloheptadienes undergo light-induced valence tautomerization to bicyclo[3.2.0]heptenes. This photoisomerization coupled with a recently discovered synthesis of conjugated cycloheptadienes provides a powerful synthetic entry to the bicyclo[3.2.0]heptane series. 3,5-Cycloheptadienones do not show the light-induced valence tautomerization characteristic of other conjugated cycloheptadienes, but are cleaved to carbon monoxide and 1,3,5-hexatriene derivatives.

Brief reflection on the possible photochemical transformations of cyclic dienes of various ring sizes suggests that the ring cleavage reactions so prominent in the vitamin D series and simple 1,3-cyclohexadienes should not occur in cyclic dienes containing more than six annular atoms.<sup>3</sup> One possibility which remains for photochemical transformation of cyclic dienes containing seven or more annular atoms is light-induced valence tautomerization. In the case of 1,3-cycloheptadiene such photoisomerization should lead to bicyclo[3.2.0]hept-6-ene. This would provide a novel synthetic entry to the difficultly available bicyclo[3.2.0]heptane system. We considered the possibility of such a photoisomerization particularly intriguing because of our recently discovered route to a wide variety of substituted cycloheptadienes *via* 1,8-addition of Grignard reagents and metal hydrides to troponoid systems.<sup>4</sup>

Irradiation of 1,3-cycloheptadiene (1) with a mercury arc gives a photoisomer<sup>5</sup> (58%) which shows no ultraviolet absorption maxima above 210 m $\mu$ . The photoisomer is formulated as 2 on the basis of the following evidence.



Pyrolysis of 2 at 450–500° gives 1,3-cycloheptadiene (1) quantitatively. Permanganate oxidation of 2 gives *cis*-cyclopentane-1,2-dicarboxylic acid (3). Sublimation of 3 gives the *cis*-anhydride 4 (5.42, 5.63 $\mu$ ). Photoproduct 2 absorbs one mole of hydrogen over platinum giving 5. The nuclear magnetic resonance spectrum of 2 (Fig. 1) is of some interest.

(1) Preliminary communications describing portions of this investigation have been published; O. L. Chapman and D. J. Pasto, *Chemistry & Industry*, 53 (1961); O. L. Chapman and G. W. Borden, *J. Org. Chem.*, **26**, 4185 (1961). Portions of this paper were taken from a thesis submitted to the Graduate Faculty of Iowa State University by D. J. Pasto.

(2) National Institutes of Health Predoctoral Fellow, 1958–1960.

(3) D. H. R. Barton, *Helv. Chim. Acta*, **42**, 2604 (1961).

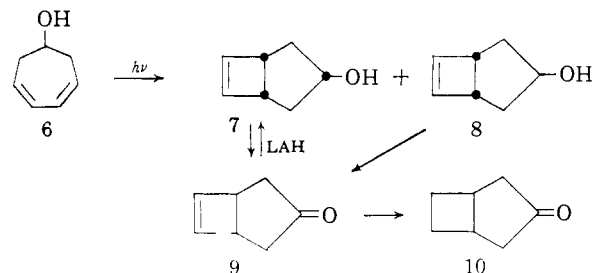
(4) O. L. Chapman and D. J. Pasto, *Chemistry & Industry*, 54 (1961); O. L. Chapman, D. J. Pasto and A. A. Griswold, *J. Am. Chem. Soc.*, **84**, 1213 (1962).

(5) This photoisomer has been reported also by W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961).

The cyclobutene protons appear as a singlet (4.24  $\tau$ ), the bridgehead protons appear as a doublet ( $J = 6$  c.p.s., 6.89  $\tau$ ) and the six methylene protons appear as a complex multiplet (8.58 $\tau$ ). Under very high resolution conditions the cyclobutene protons appear as a closely spaced (0.73 c.p.s.) triplet (Fig. 2). The triplet character of the olefin absorption could be accounted for by assuming  $J_{AB} = J_{AB'} = J_{A'B} = 0.73$  c.p.s.

This, however, probably is not true. Abraham and Bernstein<sup>6</sup> have pointed out the dangers in too hurriedly assuming equivalence of coupling constants. In fact it is unreasonable to assume  $J_{AB}$  and  $J_{AB'}$  equal. Examination of other spectra reveals many examples of bicyclo[3.2.0]hept-6-enes in which  $J_{AB} = 0.6-1.0$  c.p.s. and  $J_{AB'} = 0-0.6$  c.p.s.<sup>7</sup> The splitting in the olefinic triplet of 2 gives only  $1/2(J_{AB} + J_{AB'}) = 0.73$  c.p.s. If  $J_{AB} = J_{AB'}$ , the value of  $J_{AB}$  will be 0.73 c.p.s. The olefinic triplet may just as easily be accounted for as part of an  $A_2X_2$  spectrum with  $J_{AB} = 1.0$  c.p.s. and  $J_{AB'} = 0.4$  c.p.s. which is intrinsically more likely. This analysis is closely analogous to the analysis of the nuclear magnetic resonance spectrum of furan.<sup>6</sup> The doublet absorption of the bridgehead protons must arise from coupling of  $H_A$  with  $H_C$  or  $H_D$  (but not both). The dependence of coupling constant on dihedral angle has been studied theoretically, and it is not surprising that  $H_A$  should be coupled strongly to only one of the  $H_C, H_D$  pair.<sup>8</sup>

Irradiation of 3,5-cycloheptadienol (6) gives two photoisomers (7 and 8) in a 3 to 1 ratio. The mixture of photoisomers absorbs one mole of hydrogen over platinum. Separation of the photoisomers by preparative scale vapor phase chromatography gives 7 and 8. The isomeric nature of 7 and 8 is



established by oxidation to the same ketone (9). Hydrogenation of 9 gives 10 which was compared

(6) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216, 905 (1961).

(7) Unpublished observations of O. L. Chapman.

(8) H. Conroy, "Advances in Organic Chemistry," Vol. II, 1960, p. 265, and references therein cited.

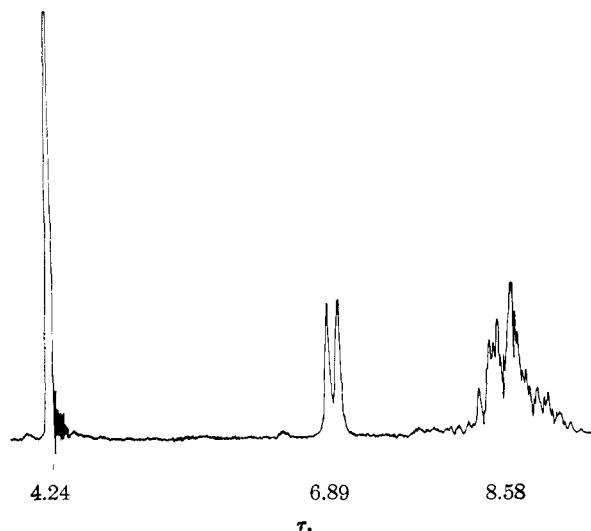
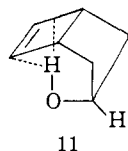


Fig. 1.—Nuclear magnetic resonance spectrum (60 mc.) of bicyclo[3.2.0]hept-6-ene (2). Resonance locations are  $\tau$ -values relative to internal tetramethylsilane.

directly and as the crystalline semicarbazone with an authentic sample of 10 kindly provided by Dr. R. Srinivasan.<sup>9</sup> The stereochemistry of the alcohols 7 and 8 is assigned on the basis of the following evidence. Reduction of ketone 9 with lithium aluminum hydride gives almost exclusively an alcohol identical with the major product of the irradiation. Attack by hydride on 9 should take place predominantly from the least hindered side of the bicyclic structure and should lead to 7. Strong indication that 7 is the endo-alcohol is provided by the vapor phase chromatographic retention times of 7 and 8. Alcohol 7 comes off the column several minutes before 8 under conditions such that 8 and 13 are only partially resolved. This strongly suggests the hydrogen bonded structure 11.<sup>10</sup>



The olefinic protons of 7 appear at lower field (3.73  $\tau$ ) than 2 (4.24  $\tau$ ), 8 (4.05  $\tau$ ), 13 (4.08  $\tau$ ) or even 9 (3.90  $\tau$ ) consistent with an interaction between the cyclobutene double bond and the hydroxyl group which effectively removes electrons from the double bond.

Irradiation of a mixture of 3,5-cycloheptadienol (6) and 2,4-cycloheptadienol (12) prepared by reduction of the 3,5-cycloheptadienone-2,4-cycloheptadienone mixture obtained in the Hofmann degradation of tropinone methiodide<sup>11</sup> gives after separation of the products by preparative scale vapor phase chromatography the alcohols 7 and 8 and an isomeric alcohol formulated as 13 on the basis of its

(9) S. Cremer and R. Srinivasan, *Tetrahedron Letters*, No. 21, 24 (1960).

(10) This is analogous to the case reported by C. H. DePuy and P. R. Story, *ibid.*, No. 6, 20 (1959).

(11) J. Meinwald, S. L. Emerman, N. C. Yang and G. Büchi, *J. Am. Chem. Soc.*, **77**, 4401 (1955).

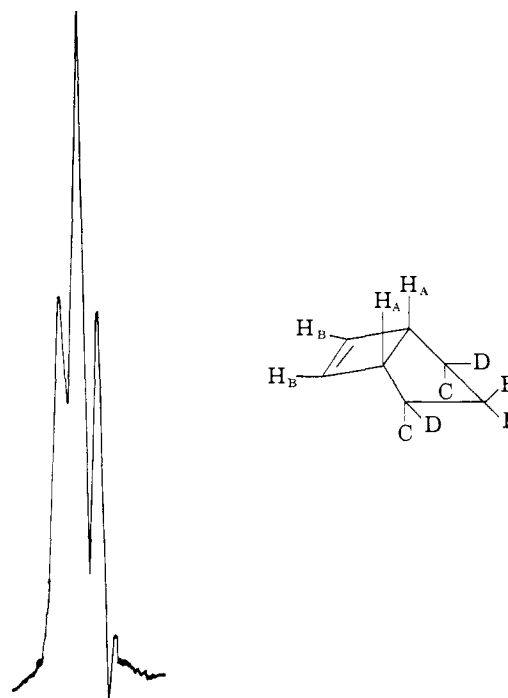
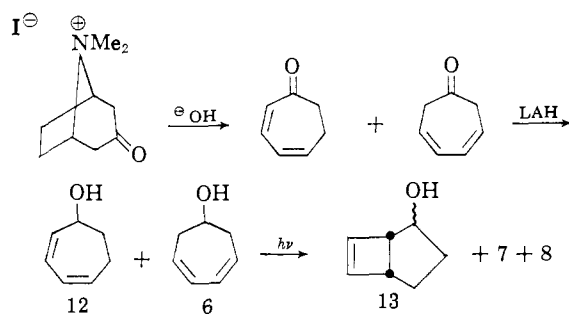
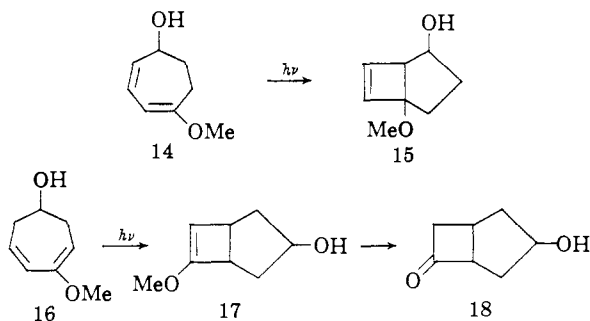


Fig. 2.—High resolution scan of the olefinic proton resonance of bicyclo[3.2.0]hept-6-ene.

nuclear magnetic resonance spectrum. The nuclear magnetic resonance spectrum of 13 shows two olefinic protons at 4.08  $\tau$ , two bridgehead protons as separate peaks at 6.04 and 7.00  $\tau$ , the C-2 proton at 6.70  $\tau$ , four methylene protons as a multiplet at 8.27  $\tau$  and the hydroxyl proton at 7.96  $\tau$ .

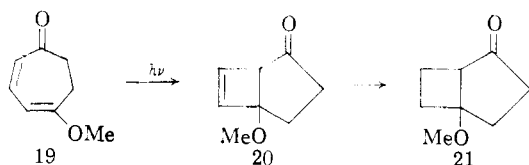


Irradiation of 5-methoxy-2,4-cycloheptadienol (14) gives photoisomer 15 which shows two olefinic protons in the nuclear magnetic resonance spectrum and which is stable to mild acid treatment.<sup>4</sup> Irradiation of 4-methoxy-3,5-cycloheptadienol (16)

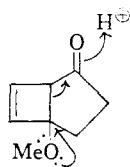


gives a photoisomer (17) which on mild acid treatment is rapidly converted to the cyclobutanone 18.<sup>4</sup> The sequence 16, 17 and 18 illustrates a new and potentially general method for the synthesis of cyclobutanones.

The generality of the photoisomerization of conjugated cycloheptadienes is further illustrated by the transformation of 5-methoxy-2,4-cycloheptadienone (19) to the photoisomer 20. The photoisomer 20 regenerates the starting dienone when



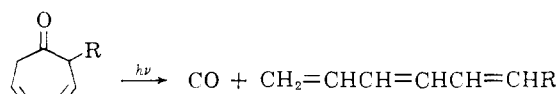
treated with acid or simply on warming (50°) in ethanol.<sup>13,14</sup> Hydrogenation of 20 gives tetrahydrophoto- $\gamma$ -tropolone methyl ether (21) identical to a sample prepared by reduction of photo- $\gamma$ -tropolone methyl ether.<sup>13</sup> The facile ring opening of 20 deserves comment. This is a further manifestation of the importance of satisfactory alignment of the orbitals of the C<sub>1</sub>-C<sub>5</sub> bond with the  $\pi$ -orbitals of the carbonyl group.<sup>13</sup> This is a particularly interesting



example of the push-pull mechanism brought to prominence as the "fragmentation reaction" by Grob.<sup>15</sup> It has not been possible to obtain satisfactory ultraviolet spectra of 20 because of the rapid isomerization to 19 in polar solvents.

The photoisomerizations of 1,3-cycloheptadienes are light-induced valence tautomerizations of the type encountered in the tropolones,<sup>13,16</sup> eucarvone,<sup>12</sup> pyrocalciferol<sup>17</sup> and isopyrocalciferol.<sup>17</sup> The generality of the photoisomerization of 1,3-cycloheptadienes to bicyclo[3.2.0]heptenes coupled with our recently discovered synthesis of 1,3-cycloheptadienes<sup>4</sup> makes this photoisomerization an important synthetic entry to an otherwise difficultly available series of compounds.

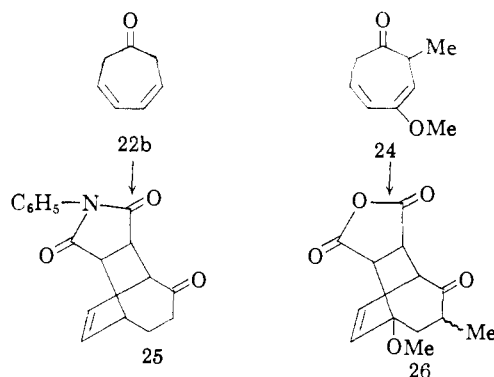
The photochemical behavior of 2-methyl-3,5-cycloheptadienone (22a) presents a surprising contrast to the smooth photoisomerization of the other conjugated cycloheptadienes previously studied. Irradiation of 2-methyl-3,5-cycloheptadienone (22a) in ether gives carbon monoxide (95%) and a mixture of geometric isomers of 1,3,5-heptatriene (23a, 252, 261 and 271 m $\mu$ ) which analyzes for C<sub>7</sub>H<sub>10</sub> and gives *n*-heptane on hydrogenation. In similar fashion irradiation of 3,5-cycloheptadienone



22a, R = Me  
b, R = H

23a, R = Me  
b, R = H

(22b) gives a mixture of isomeric 1,3,5-hexatrienes (23b, 246, 256 and 266 m $\mu$ ).<sup>18</sup> These reactions proceed smoothly in Pyrex vessels suggesting that the reaction is initiated by excitation of the  $n \rightarrow \pi^*$  transition of the carbonyl group.<sup>19</sup> It is surprising that even in quartz vessels (in which the low wave length chromophore is also excited) that the 22 to 23 reaction occurs with no detectable valence tautomerization. The 3,5-cycloheptadienones are remarkable in their physical and chemical properties as well as their photochemical behavior. Both 22a and 22b show anomalously low wave length absorption (214<sup>11</sup> and 217 m $\mu$ ,<sup>4</sup> respectively). In Diels-Alder adduct formation 3,5-cycloheptadienone (22b) and 2-methyl-4-methoxy-3,5-cycloheptadienone (24) isomerize giving 25<sup>11</sup> and 26,<sup>4</sup>



respectively. This isomerization is remarkable in that it suggests that the 2,4-cycloheptadienones react more rapidly than the 3,5-cycloheptadienones in contrast with the usual electronic effects observed in the Diels-Alder reaction. The anomalous properties of the 3,5-cycloheptadienones must be due to the steric problems inherent in this arrangement of trigonal atoms in a seven-membered ring. Examination of Dreiding models reveals that 2,4-cycloheptadienones can assume easily a conformation in which all trigonal atoms are essentially planar (see Fig. 3), but a 3,5-cycloheptadienone in strainless conformations has the diene chromophore badly distorted (see Fig. 4). Estimation by visual projection of the angle between the carbon-carbon double bonds of 22b gives a value of 45°. On this basis it is not surprising that the molecule shows properties more like a non-conjugated than a conjugated diene. This argument also suggests an interesting rationalization of the anomalously low wave length ultraviolet absorption of 3,5-cyclohep-

(12) (a) G. Büchi and E. M. Burgess, *J. Am. Chem. Soc.*, **82**, 4333 (1960); J. J. Hurst and G. H. Whitham, *Proc. Chem. Soc.*, 116 (1961).

(13) O. L. Chapman and D. J. Pasto, *J. Am. Chem. Soc.*, **82**, 3642 (1960).

(14) O. L. Chapman and D. J. Pasto, *ibid.*, **81**, 5510 (1959).

(15) C. A. Grob, *Experientia*, **13**, 126 (1957).

(16) W. G. Dauben, K. Koch, O. L. Chapman and S. I. Smith, *J. Am. Chem. Soc.*, **83**, 1768 (1961).

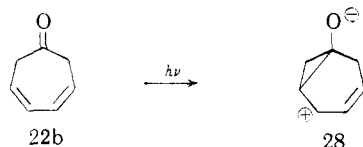
(17) W. G. Dauben and G. J. Fonken, *ibid.*, **81**, 4060 (1959).

(18) J. C. H. Hwa, P. L. De Benneville and H. J. Sims, *ibid.*, **82**, 2537 (1960).

(19) It is possible that intramolecular energy transfer occurs between the excited carbonyl and the diene system. This would be analogous to the intermolecular transfer of energy from the low lying triplet state of benzophenone to acyclic dienes.<sup>20</sup>

(20) G. S. Hammond, P. A. Leermakers and N. J. Turro, *J. Am. Chem. Soc.*, **83**, 2396 (1961).

tadienones. Many  $\beta,\gamma$ -unsaturated ketones show ultraviolet absorption in the 210–220  $m\mu$  region due to  $\pi \rightarrow \pi^*$ -transitions involving the non-conjugated double bond and the carbonyl group.<sup>21</sup> In a 3,5-cycloheptadienone a similar interaction may be occurring (cf. 28). This would give an absorption



maximum in the proper region, and since the transition involves only one double bond it offers a reason for the observation that the diene does not undergo the light-induced valence tautomerization common to other conjugated cycloheptadienes even when irradiated in quartz vessels. Careful examination of the model shown in Fig. 4 shows that the  $\pi$ -orbital of one double bond and the carbonyl  $\pi$ -orbital are well situated for interaction. The remaining double bond is poorly situated for interaction with either the other double bond or the carbonyl. Reduction of the carbonyl group to an alcohol relieves most of the strain inherent in the 3,5-cycloheptadienone, and the diene system becomes normal ( $\lambda_{\max}$  241  $m\mu$ ; and gives a normal Diels–Alder adduct).<sup>4,11</sup>

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### Experimental

**Bicyclo[3.2.0]hept-6-ene.**—1,3-Cycloheptadiene (b.p. 115–118°, 7.0 g., 0.0745 mole) was placed in a 40 × 200 mm. cylindrical quartz tube fitted with an internal cooling condenser and drying tube, and 160 ml. of Mallinckrodt absolute ether (freshly opened can) was pipetted into the reaction vessel. After 54 hours irradiation with a General Electric UA-3 mercury arc lamp, distillation of the ethereal solution through a 10 × 300 mm. silvered, vacuum-jacketed column packed with 3/32" glass helices gave 4.1 g. (58%) of bicyclo[3.2.0]hept-6-ene, b.p. 96.0° at 745 mm., density 0.863 g./ml. at 25°,  $n_D^{25}$  1.4660.

*Anal.* Calcd. for  $C_7H_{10}$ : C, 89.29; H, 10.71. Found: C, 89.47; H, 10.81.

**Pyrolysis of Bicyclo[3.2.0]hept-6-ene (2).**—Samples (20  $\mu$ l., 17 mg.) of bicyclo[3.2.0]hept-6-ene were dropped through a preheated, vertical pyrolysis column packed with Pyrex helices in a stream of dry nitrogen. The exit end of the pyrolysis column was connected to a vacuum line, and the pyrolysis product was caught in a trap immersed in liquid nitrogen. The product was diluted to 25 ml. with 95% ethanol, and the extinction at 241  $m\mu$  was measured. The yield of 1,3-cycloheptadiene as a function of temperature is

Temp., °C.	$\epsilon$ at 241 $m\mu$	1,3-Cycloheptadiene, %
Below 260	..	0
316	360	6.8
360	4000	75
411	4700	89
468	5200	98
529	5300	100

**Potassium permanganate Oxidation of Bicyclo[3.2.0]hept-6-ene.**—Potassium permanganate (2 g.) was added to a solution of

(21) For recent examples see: E. M. Kosower, W. D. Closson, H. L. Goering and J. C. Gross, *J. Am. Chem. Soc.*, **83**, 2013 (1961); S. Weinstein, L. de Vries and R. Ortoski, *ibid.*, **83**, 2020 (1961); H. Labhart and G. Wagniere, *Helv. Chim. Acta*, **42**, 2219 (1959); and ref. 12a.

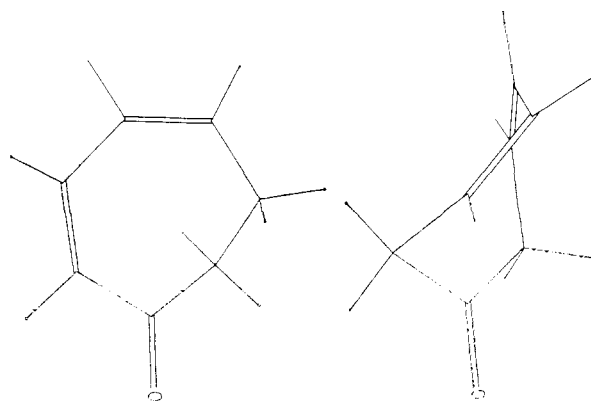


Fig. 3.—2,4-Cycloheptadienone. Fig. 4.—3,5-Cycloheptadienone.

Line tracings of a photograph of Dreiding models taken perpendicular to the plane of the C—C—C group.

bicyclo[3.2.0]hept-6-ene (0.55 g.) in 20 ml. of distilled water and 10 ml. of acetone. The solution was made basic by addition of 1 ml. of 30% sodium hydroxide and then filtered through Celite. The solution was acidified with sulfuric acid and extracted with ether. Removal of the ether after drying over anhydrous magnesium sulfate gave 0.44 g. (47%) of crude *cis*-1,2-cyclopentanedicarboxylic acid. Two recrystallizations from ether gave large, colorless crystals, m.p. 138.0–138.8° (reported<sup>22</sup> for *cis*-1,2-cyclopentanedicarboxylic acid 139–140° and 134–135°).

*Anal.* Calcd. for  $C_7H_{10}O_4$ : C, 53.16; H, 6.32. Found: C, 52.99; H, 6.22.

Sublimation of *cis*-1,2-cyclopentanedicarboxylic acid (100°, 0.1mm.) gave *cis*-1,2-cyclopentanedicarboxylic acid anhydride (5.42, 5.63  $\mu$ ).

**Hydrogenation of Bicyclo[3.2.0]hept-6-ene.**—A solution of bicyclo[3.2.0]hept-6-ene (47 mg.) in 3 ml. of methylene chloride containing pre-reduced platinum oxide (15 mg.) absorbed 0.99 mole of hydrogen. The methylene chloride solution was separated by preparative scale vapor phase chromatography on a 1 meter oxydipropionitrile–Celite (1:4) column. The product was collected in a Dry Ice cooled trap. The product was inert to bromine in carbon tetrachloride.

**Irradiation of 3,5-Cycloheptadienol.**—A solution of 1.7 g. of 3,5-cycloheptadienol in one l. of anhydrous ether was irradiated 4 hours with a quartz jacketed Hanovia immersion lamp (type L). The ether was removed through a Vigreux column, giving 1.5 g. of crude photoproduct.

The crude photoproduct absorbed one equivalent of hydrogen over Adams catalyst in methanol. It was separated on a 3/8 in. by 6-ft. vapor phase chromatography column containing Ucon LB 550-X grease on 80–100 mesh Celite at 148° giving 7 (78%, retention time 11.8 min.) and 8 (22%, retention time 18.1 min.).

*Anal.* Calcd. for  $C_7H_{10}O$ : C, 76.32; H, 9.15. Found (7): C, 76.20; H, 9.25; (8): C, 76.20; H, 9.31.

**Oxidation of *endo*-Bicyclo[3.2.0]hept-6-en-3-ol(7).**—A solution of 8 *N* chromic acid in acetone (prepared according to the procedure of Bowers, Halsall, Jones and Lemin<sup>23</sup>) was slowly added to a solution of *endo*-bicyclo[3.2.0]hept-6-en-3-ol (7, 50 mg.) in 5 ml. of acetone at 0° until the solution maintained a persistent orange color. The solution was diluted with 25 ml. of water and extracted five times with ether (10 ml.). After drying over sodium sulfate, removal of the ether gave bicyclo[3.2.0]hept-6-en-3-one (9, 5.73  $\mu$ ). A sample of the product was purified for analysis by preparative scale vapor phase chromatography.

(22) S. F. Birch, R. A. Dean, N. J. Hunter and E. V. Whitehead, *J. Org. Chem.*, **20**, 1178 (1955); L. N. Owen and A. C. Peto, *J. Chem. Soc.*, 2383 (1955).

(23) A. Bowers, T. G. Halsall, E. R. H. Jones and A. J. Lemin, *ibid.*, 2548 (1953).

*Anal.* Calcd. for  $C_7H_8O$ : C, 77.75; H, 7.46. Found: C, 77.63; H, 7.58.

Oxidation of *exo*-Bicyclo[3.2.0]hept-6-en-3-ol (8).—Oxidation of *exo*-bicyclo[3.2.0]hept-6-en-3-ol as above gave bicyclo[3.2.0]hept-6-en-3-one (9) identical in infrared absorption with the product obtained in the oxidation of *endo*-bicyclo[3.2.0]hept-6-en-3-ol (7).

Hydrogenation of Bicyclo[3.2.0]hept-6-en-3-one (9).—Bicyclo[3.2.0]hept-6-en-3-one (9, 70 mg.) in 15 ml. of methanol containing Adams catalyst absorbed one equivalent of hydrogen. Careful removal of the solvent gave bicyclo[3.2.0]heptan-3-one (10) identical in infrared absorption to an authentic sample provided by Dr. R. Srinivasan.<sup>9</sup> The semicarbazone of the product melted at 197–199° dec. pure and mixed with authentic bicyclo[3.2.0]heptan-3-one semicarbazone.<sup>9</sup>

Lithium Aluminum Hydride Reduction of Bicyclo[3.2.0]hept-6-en-3-one (9).—A solution of bicyclo[3.2.0]hept-6-en-3-one (9, 5 mg.) in 1 ml. of anhydrous ether was added to a slurry of lithium aluminum hydride (5 mg.) in 0.5 ml. of ether. The excess hydride was decomposed with moist sodium sulfate. Removal of the ether after drying over magnesium sulfate gave the mixed alcohols 7 and 8. Vapor phase chromatographic analysis showed this to be a 9:1 mixture of 7 and 8. The alcohols were identified by adding pure 7 and pure 8 to separate samples of the mixture and observing the enhancement of the v.p.c. peaks due to each component.

Bicyclo[3.2.0]hept-6-en-2-ol.—A mixture of 2,4-cycloheptadienol and 3,5-cycloheptadienol (1.7 g.) obtained by lithium aluminum hydride reduction of the 2,4-cycloheptadienone-3,5-cycloheptadienone mixture obtained in the Hofmann degradation of tropinone methiodide,<sup>11</sup> was dissolved in 100 ml. of anhydrous ether and irradiated in a quartz vessel with a General Electric UA-3 mercury arc lamp for 4 days. The solvent was removed under reduced pressure giving 1.5 g. of crude photoalcohols (7, 8 and 13). This mixture was resolved by vapor phase chromatography on a 6-ft. by 3/8 in. column containing 15% Ucon LB550-X on 80–100 mesh Celite at 148° into three alcohols with retention times 12.8 min. (7), 16.3 min. (13) and 18.1 min. (8). The alcohols 7 and 8 were identified by comparison of infrared absorption and vapor phase chromatographic retention. The remaining alcohol (13) showed nuclear magnetic resonance absorption at 4.08, 6.04, 6.70, 7.00, 7.96 and 8.27  $\tau$ .

*Anal.* Calcd. for  $C_7H_{10}O$ : C, 76.32; H, 9.15. Found: C, 76.18; H, 9.04.

Irradiation of 5-Methoxy-2,4-cycloheptadienone (19).—A solution of 330 mg. (2.39 mM) of 19 in 75 ml. of anhydrous ether in a quartz vessel fitted with a reflux condenser was irradiated with a General Electric UA-3 mercury arc lamp for 70 minutes at a distance of 15 cm. The ether solution was concentrated under reduced pressure, and the yellow residue was molecularly distilled giving 290 mg. (88%) of 20, as a very pale yellow liquid. The ultraviolet absorption spectrum of 20 showed  $\lambda_{max}^{95\% EtOH}$  332 m $\mu$  (1,120) and end absorption.

*Anal.* Calcd. for  $C_8H_{10}O_2$ : C, 69.54; H, 7.30. Found: C, 69.50; H, 7.51.

Conversion of 5-Methoxybicyclo[3.2.0]hept-6-en-2-one to 5-Methoxy-2,4-cycloheptadienone.—(A) A  $2.26 \times 10^{-4}$  M solution of 5-methoxybicyclo[3.2.0]hept-6-en-2-one (20) in ethanol after 30 min. at 60° showed an ultraviolet spectrum identical to that of 5-methoxy-2,4-cycloheptadienone (19). The extinction at 328 m $\mu$  showed that transformation was quantitative.

(B) A solution of 5-methoxybicyclo[3.2.0]hept-6-en-2-one (20) in 0.1 N sulfuric acid after 1 min. at room temperature showed the same ultraviolet absorption maxima as 5-methoxy-2,4-cycloheptadienone (19) in 0.1 N sulfuric acid. Both solutions slowly developed the 235 m $\mu$  absorption characteristic of 2-cyclohepten-1,5-dione (the acid hydrolysis product of 19).<sup>4</sup>

5-Methoxybicyclo[3.2.0]heptan-2-one (21).—A solution of 0.1016 g. of 5-methoxybicyclo[3.2.0]hept-6-en-2-one (20) in 25 ml. of methanol absorbed 0.98 equivalent of hydrogen using Adams catalyst. The catalyst was removed by filtration, and the methanol was removed under reduced pressure. Molecular distillation of the residue gave a colorless, sweet-smelling liquid. The infrared absorption spectrum of 21 was identical to that of authentic tetrahydrophoto- $\gamma$ -tropolone methyl ether.<sup>13</sup>

Irradiation of 2-Methyl-3,5-cycloheptadienone.—A solution of 2-methyl-3,5-cycloheptadienone (0.73 g.) in 100 ml. of ether in a quartz vessel equipped with an internal cooling coil and an outlet for gas collection was irradiated with a General Electric UA-3 mercury arc lamp for 6.5 hr. Carbon monoxide (95% of theory) was collected and identified by infrared comparison. The ethereal solution was concentrated by careful distillation, and the product was separated by preparative scale vapor phase chromatography. The product thus obtained showed  $\lambda_{max}^{EtOH}$  252 (26,800), 261 (36,400), 271 m $\mu$  (28,900) and infrared maxima at 3.23, 3.32, 3.43, 3.51, 5.56, 6.11, 6.16, 6.91, 6.98, 7.29, 10.42, 10.67 and 11.19  $\mu$ .

A portion of the product absorbed 3.07 equivalents of hydrogen over palladium-on-carbon in pentane. The product was identified as *n*-heptane by comparison of vapor phase chromatographic retention and infrared absorption with an authentic sample.

Irradiation of 3,5-Cycloheptadienone.—A solution of 3,5-cycloheptadienone (2.73 g.) in 50 ml. of anhydrous ether was irradiated (General Electric UA-3 mercury arc lamp) in a quartz vessel fitted with an internal cooling coil and a gas collection apparatus. After 27 hours no more gas was evolved, and the irradiation was stopped. The gas which had been collected was identified as carbon monoxide by comparison of infrared spectra. The ether and low boiling product were separated from starting material by distillation. The product was separated from the ether by preparative vapor phase chromatography on a 6-ft. by 3/8 in. column containing 15% Ucon LB 550-X on 80–100 mesh Celite at 71°. The product showed ultraviolet absorption at 246, 256 and 266 m $\mu$  and infrared maxima at 3.22, 3.31, 4.30, 5.52, 6.15, 6.90, 7.00, 9.95, 10.15, 10.67 and 11.10  $\mu$  in good agreement with the values reported for a mixture of *cis*- and *trans*-1,3,5-hexatrienes.<sup>13</sup>

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY, NEW HAVEN, CONN.]

## The Structure of Two Minor Products of the Pyrolysis of Thujone

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The hypothesis of Eastman<sup>1</sup> that the extrusion of methylene is needed to explain the formation of two  $C_9$ -ketones in the pyrolysis of thujone is no longer required, since the ketones are in fact  $C_{10}$  and have the structures 2,5-dimethyl-5-isopropylcyclopent-2-enone (I) and 2,4-dimethyl-4-isopropylcyclopent-2-enone (II).

Having for some years been interested in various aspects of carbenes, including their preparation and addition to olefins, we noted with more than casual

(1) R. H. Eastman and A. V. Winn, *J. Am. Chem. Soc.*, **82**, 5908 (1960).

concern the recently published assertion that thujone decomposes thermally to give, along with carvotanacetone, two  $C_9$ -ketones by the loss of methylene.<sup>1</sup> We contemplated confirming the intermediacy of methylene by trapping experiments, but