Cyclooctenols.—**3-Cyclooctenol**[16] (b.p. 117° (34 mm.), $n^{22}\mathrm{D}$ 1.4994, phenylurethan[15a] m.p. 101.5–102.5°) and **4-cyclooctenol**[16] (b.p. 115° (34 mm.), $n^{22}\mathrm{D}$ 1.4958, phenylurethan[15a] m.p. 91.8–93°, *p*-nitrobenzoate[15a] m.p. 85–86°) were obtained by lithium aluminum hydride reduction of 1,3-cyclooctadiene monoxide[16] and 1,5-cyclooctadiene monoxide,[29] respectively. Each monoxide was prepared by the addition during 30 min. of an ethyl acetate solution containing 1 equiv. of *m*-chloroperoxybenzoic acid[30] to a solution of diene[31] in ethyl acetate at 25°: 1,3-cyclooctadiene monoxide, b.p. 87–91° (40 mm.), $n^{23.5}\mathrm{D}$ 1.4871; 1,5-cyclooctadiene monoxide, b.p. 97–100° (40 mm.), $n^{23}\mathrm{D}$ 1.4937.

Infrared spectra of **5** and **6** are distinguishable by several absorption bands between 9.5 and 14.5 μ.

Treatment of Cycloalkanediols with Formic Acid.—Under much the same conditions as were used for studies of epoxide solvolyses,[10a,15a] small portions (1–2 g.) of *cis*-cyclooctene glycol and *cis*-cyclodecene glycol were treated separately 'with 90% formic acid (7–20 ml.). After being heated on a steam bath for 3 hr., the solutions were diluted with water and extracted several times with ether. Each organic residue remaining after removal of ether solvent was examined for the presence of ketone: it failed to form a precipitate with 2,4-dinitrophenylhydrazine reagent, and gas chromatograms contained no peaks attributable to ketone (cyclooctanone or cyclodecanone). The residues were separately saponified by refluxing with 30% sodium hydroxide solutions, and the starting glycols, which separated as solids from the alkaline solutions, were purified by vacuum sublimation. *cis*-Cyclooctene glycol, m.p. 76–78°, was recovered in 70% yield, and *cis*-cyclodecene glycol, m.p. 135–136.5°, in 86% yield.

Rearrangement of Cycloalkanediols in Dilute Sulfuric Acid.—A solution of glycol in 1 *M* sulfuric acid (about 50 ml. for 0.01 mole of glycol) was refluxed under a nitrogen atmosphere for 18–24 hr. Usually some oily material separated from the solution during this time. The mixture was extracted several times with ether, and the combined ether solution was dried over magnesium sulfate. After removal of the ether with a rotary evaporator, the crude residue was examined by g.c. and infrared spectroscopy. Identification of g.c. peaks was accomplished by comparison with authentic samples and by spectroscopic[32] and chemical examination of samples obtained by preparative scale g.c. Compositions of product mixtures were computed by comparison of g.c. responses with standard materials, both single compounds and mixtures. Ketone fractions were further identified by preparation of 2,4-dinitrophenylhydrazone derivatives: cyclooctanone 2,4-DNPH,[15a] m.p. 169–170.5°; cyclononanone 2,4-DNPH,[18] m.p. 139–140°; and cyclodecanone 2,4-DNPH,[10b,33] m.p. 161–163.5°. Melting points of these derivatives mixed with authentic samples were undepressed.

Cyclooctene Glycols.—From both *cis*- and *trans*-cyclooctene glycol, *trans*-2-vinylcyclohexanol (**1**), 1,4- and 1,5-epoxycyclooctanes (**2** and **3**), cyclooctanone (**4**), and 3- and 4-cyclooctenols (**5** and **6**) were obtained as major products. Quantitative analyses of the crude reaction products with periodic acid[34] indicated that the mixture from *trans*-glycol contained 7% and that from *cis*-glycol 4–6% of the starting 1,2-diol. Some material in each mixture remained unaccounted for and may be nonvicinal diols. The actual yields, based on diol consumed (and, in parentheses, the percentage composition of the crude reaction mixtures as indicated by g.c. responses), are summarized here; the products are listed in order of increasing retention time in the gas chromatograph. From *trans*-cyclooctene glycol: an unsaturated hydrocarbon (3%); **1**, 8.4% (10%); a mixture of **2** and **3** (mostly **2** on the basis of infrared spectrum), 34% (40%); **4**, 4.5% (5%); and **5**, 5.5% (6.5%). From *cis*-cyclooctene glycol: an unsaturated hydrocarbon (0.2%); **1**, 4.9% (5.3%); a mixture of **2** and **3** (higher proportion of **3** than above), 18.5% (20.0%); **4**, 7.7% (8.3%); and a mixture of **5** and **6** (mixture designation based on infrared spectrum), 8.6% (9.4%).

cis-**Cyclononene glycol** underwent rearrangement to form cyclononanone in 40% yield; 4–6 minor components, of shorter retention time than cyclononanone and yet unidentified accounted for about 12% of the total g.c. response area. A periodic acid titration[34] indicated that 19% of the starting glycol was present in the product mixture. Column chromatography of a portion of the mixture on Woelm alumina (neutral, Activity II) with petroleum ether and ethyl ether as developing solvents gave first a fraction (12% of the mixture introduced onto the column) whose infrared spectrum suggested a bicyclic ether, and then cyclononanone. (Diols present in the mixture were not eluted by ether solvent; about 65% of the mixture introduced onto the column was recovered.)

cis-**Cyclodecane glycol** rearranged to cyclodecanone in 51% yield; a periodic acid titration[34] indicated that 18% of the starting glycol remained in the product mixture. Analysis by g.c. further indicated that the product mixture contained 3 minor components (3.4% total) and an unidentified component (14%), all of shorter retention times than cyclodecanone. Preparative g.c. successfully separated cyclodecanone from the other components, but they could not be separated from each other. It was possible however to establish that these other components were not carbonyl-containing compounds.

Sulfuric Acid-Catalyzed Rearrangements of 3- and 4-Cyclooctenols.—Separate mixtures of 3- and 4-cyclooctenol and 1 *M* sulfuric acid (about 15 ml. of acid per gram of alcohol) were refluxed under nitrogen for 16–23 hr. Each of the two-phase mixtures was extracted three times with petroleum ether. Each combined organic solution was washed with water, dried over Drierite, concentrated by distillation, and examined with infrared spectroscopy and g.c. (both analytical and preparative) as described before. In addition to several minor components of short retention time, each product mixture contained **1**, **2**, **3**, and **4**. The proportions estimated from gas chromatograms are: from **5**: **1**, 41%; **2** and **3** (mostly **2**), 30%; **4**, 2.5%; and **5**, 22%. From **6**: **1**, 2%; **2** and **3**, 71%; **4**, 22%; and **6**, trace.

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(29) K. Ziegler and H. Wilms, *Ann.*, **567**, 1 (1950).

(30) Commercial sample obtained from FMC Corp. was used as supplied.

(31) We appreciate the gift of samples of 1,5-cyclooctadiene and 1,3-cyclooctadiene from Cities Service Research and Development Co.

(32) We greatly appreciate the helpful cooperation of Professor A. C. Cope, who lent us spectra of *trans*-2-vinylcyclohexanol, 1,4-epoxycyclooctane, and 1,5-epoxycyclooctane from his laboratory for comparison.

(33) V. Prelog, L. Frenkiel, M. Kobelt, and P. Barman, *Helv. Chim. Acta*, **30**, 1741 (1947).

(34) S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p. 39.

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

Photoisomerization of 1,3,5-Cyclooctatriene[1]

BY O. L. CHAPMAN, G. W. BORDEN,[2] R. W. KING, AND B. WINKLER

RECEIVED JANUARY 13, 1964

Irradiation of 1,3,5-cyclooctatriene in ether gives the expected valence tautomer bicyclo[4.2.0]octa-2,7-diene (II) and a novel valence tautomer tricyclo[5.1.0.0^{4,8}]oct-2-ene (VI). Nuclear magnetic double resonance experiments were prominent in the structure elucidation of VI.

Study of the photochemical transformations of cyclic and acyclic dienes and trienes has led to a variety of interesting compounds and to useful syntheses of bicyclic systems.[3] Our interest in cyclic dienes[4]

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(1) Part XIII of the photochemical transformations series. For Part XII see O. L. Chapman and G. W. Borden, *Proc. Chem. Soc.*, 221 (1963). Portions of this manuscript were abstracted from theses submitted to Iowa State University by G. W. Borden, 1963, and B. Winkler, 1962.

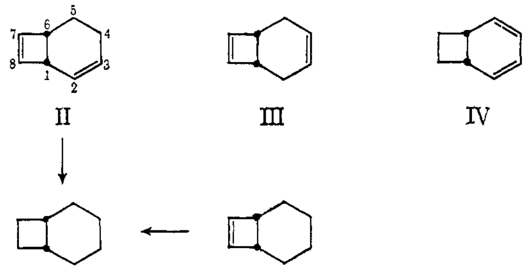
(2) National Institutes of Health Predoctoral Fellow (1962–1963).

(3) For a review see O. L. Chapman in "Advances in Photochemistry," Vol. I, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Ed., John Wiley–Interscience Publishers, Inc., New York, N. Y., 1963.

and an interest in a synthetic approach to functionally substituted bicyclo[4.2.0]octadiene systems prompted a study of the photochemistry of 1,3,5-cyclooctatriene.

Results

Irradiation of 1,3,5-cyclooctatriene (I) in ether solution with a water-cooled mercury arc lamp encased in a quartz immersion well gives a 41% yield of volatile products. The volatile product contains three components (38, 14, 48%). The three components were separated by preparative scale vapor phase chromatography. The major component (48%) was quickly identified as 1,5-cyclooctadiene by direct comparison of infrared and nuclear magnetic resonance spectra with an authentic sample. The starting 1,3,5-cyclooctatriene contained some 1,5-cyclooctadiene (from which it was prepared), but the quantity of 1,3,5-cyclooctatriene isolated in the product suggests that this is also a product of the irradiation.[5] The second component (38%) absorbs two equivalents of hydrogen giving bicyclo[4.2.0]octane identical with a sample obtained by reduction of bicyclo[4.2.0]oct-7-ene from the photoisomerization of 1,3-cyclooctadiene.[6] The second photoproduct thus must be II, III, or IV. The absence of ultraviolet absorption maxima above 220 mμ eliminates structure IV as a possibility. A decision between II and III is possible on the basis of the nuclear magnetic resonance spectrum of the photoisomer. The photoisomer shows one olefinic proton as a doublet at 3.91 τ (J = 2.8 c.p.s.), a multiplet containing three olefinic protons at 4.27 τ, two bridgehead protons as an unsymmetrical multiplet at 6.35 τ, and four methylene protons as a complex multiplet centered at 8.3 τ. The lone olefinic proton at 3.91 τ eliminates from consideration structure III which has a plane of symmetry perpendicular to the planes of the two sets of trigonal atoms and bisecting each double bond. The lowest field proton should be the cyclobutene proton at position 8. The coupling constant (2.8 c.p.s.) for the low field proton is in accord with expectation based on the correlation of *cis*-vinyl proton coupling constants with ring size.[7] Coupling constants of less than 1 c.p.s. for coupling of cyclobutene protons to adjacent saturated protons are normal.[8,9]



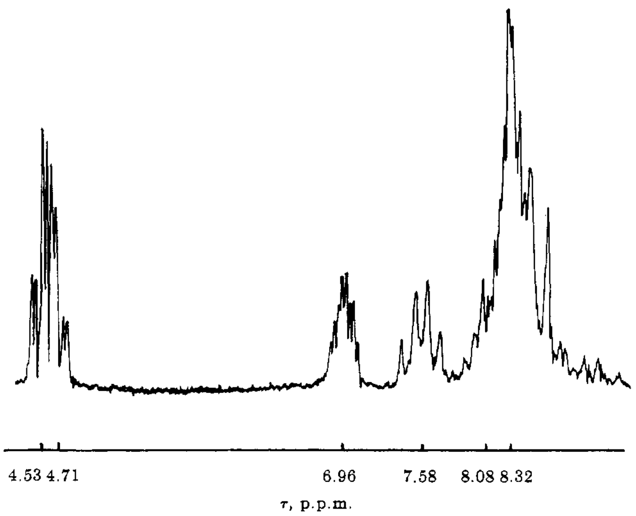
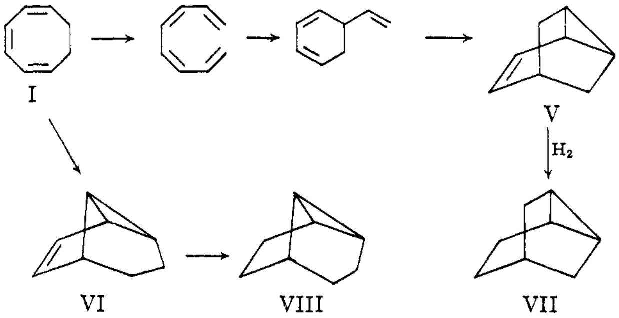


Fig. 1.—Nuclear magnetic resonance (60 Mc.) spectrum of VI in deuteriochloroform. Resonance positions are given as τ-values (p.p.m.) relative to internal tetramethylsilane. The spectrum was run on a degassed sample sealed under vacuum to exclude oxygen.

The third photoproduct (14%) poses a more formidable structure problem. This product is isomeric with 1,3,5-cyclooctatriene (X) and is monomeric (osmometric molecular weight, 111; calcd., 106). Catalytic hydrogenation of this photoisomer requires one equivalent of hydrogen and gives a saturated hydrocarbon. The photoisomer is thus tricyclic. The ultraviolet spectrum (λ_{max} 208 mμ (ϵ 5300)) suggests a vinylcyclopropane chromophore.[10] The nuclear magnetic resonance spectrum of the photoisomer (Fig. 1) shows two nonequivalent olefinic protons (4.53 and 4.71 τ), two unique protons (6.96 and 7.58 τ), and a complex multiplet containing six protons (8.0 to 8.7 τ). Two structures containing vinylcyclopropane units which are consistent with the nuclear magnetic resonance spectrum can be written (V and VI). Both structures can be readily rationalized on the basis of transformations of 1,3,5-cyclooctatriene. Struc-



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(4) O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Am. Chem. Soc.*, **84**, 1220 (1962); O. L. Chapman and D. J. Pasto, *Chem. Ind.* (London), 53 (1961).

(5) The photoreduction of 1,3,5-cyclooctatriene to 1,5-cyclooctadiene is a remarkable reaction in its own right and will be the subject of further study in this laboratory.

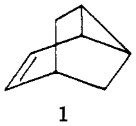
(6) W. G. Dauben and R. L. Cargill, *J. Org. Chem.*, **27**, 1910 (1962); S. F. Chappell, III, and R. F. Clark, *Chem. Ind.* (London), 1198 (1962); R. Srinivasan, *J. Am. Chem. Soc.*, **84**, 4141 (1962). The bicyclo[4.2.0]octane must have *cis*-fused rings since oxidation of the bicyclo[4.2.0]oct-7-ene from which it was prepared gives *cis*-1,2-cyclohexanedicarboxylic acid.

(7) O. L. Chapman, *ibid.*, **85**, 2014 (1963); G. V. Smith and H. Kriloff, *ibid.*, **85**, 2016 (1963); P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2017 (1963).

(8) L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959, p. 86.

(9) O. L. Chapman, unpublished observations.

(10) For comparison (1) shows λ_{max} 206 mμ (ϵ 2.71),[11] (2) shows λ_{max} 215 mμ (1.4),[12] and (3) shows λ_{max} 207 mμ (4.09).[13] For other leading references see W. G. Dauben and G. J. Fonken, *J. Am. Chem. Soc.*, **81**, 4060 (1959), footnote 17, and ref. 11, footnote 26.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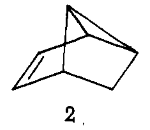
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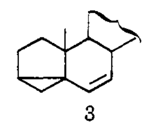
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(11) C. A. Grob and J. Hostynek, *Helv. Chim. Acta*, **46**, 1676 (1963).

(12) P. R. Story, *J. Am. Chem. Soc.*, **83**, 3347 (1961).

(13) R. A. Micheli and T. H. Applewhite, *J. Org. Chem.*, **27**, 345 (1962).

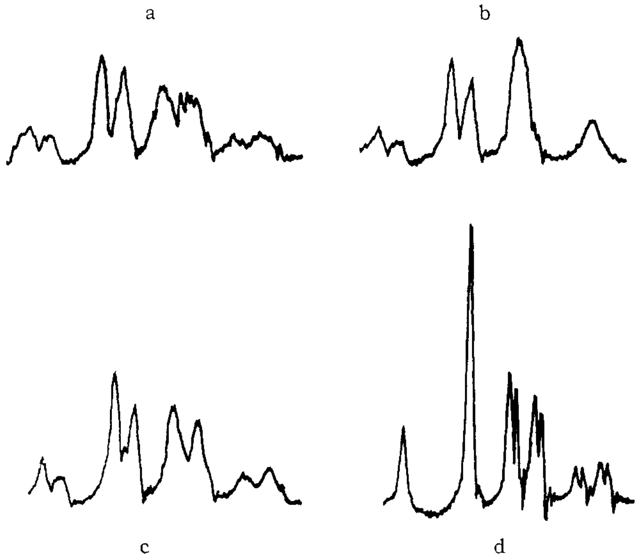


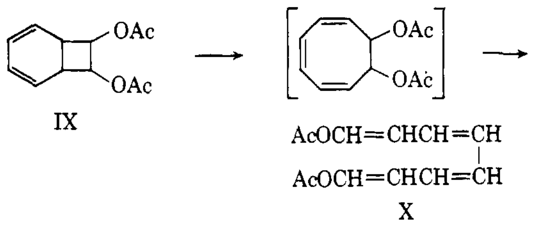
Fig. 2.—(a) Slow scan of olefinic proton resonance with no irradiation. (b) Slow scan of olefinic proton resonance with irradiation at 6.96 τ; difference in scanning and irradiating frequencies, δ = 135 c.p.s. (c) Slow scan of olefinic proton resonance with irradiation at 7.58 τ, δ = 172 c.p.s. (d) Slow scan of olefinic proton resonance with irradiation at 8.08 τ, δ = 214 c.p.s.

ture V could be produced by ring fission followed by two intramolecular Diels–Alder reactions. This sequence has been suggested as the course of the thermal isomerization of I to V.[14] Structure VI is a valence tautomer of I. Although the nuclear magnetic resonance spectrum (Fig. 1) of the photoproduct does not distinguish between V and VI, a series of field-sweep double resonance experiments[15] provided the basis for a rigorous decision in favor of structure VI. Irradiation of the one proton multiplet at 6.96 τ while scanning the higher field olefinic proton simplified it (Fig. 2b) to a doublet retaining only the large coupling (J_{vinyl} = 6 ± 0.5 c.p.s.). The 6.96 τ multiplet thus must be the bridgehead proton adjacent to the higher field olefinic proton. Irradiation of the multiplet at 7.58 τ did not change the lower field olefinic proton but slightly sharpened the higher field olefinic proton (Fig. 2c). This small coupling between the high field olefinic proton and the proton at 7.58 τ (clearly seen in Fig. 2d) must be due to long range coupling. The one proton multiplet at 7.58 τ is thus not a bridgehead proton but is some other unique proton. The second bridgehead proton is located on the low field edge of the six proton multiplet ($\sim$8.08 τ). Irradiation of the multiplet at 8.08 τ collapses the low field olefinic proton quartet to a sharp doublet (Fig. 2d) and substantially sharpens the higher field olefinic proton quartet. The presence of one unique proton in addition to the olefinic and bridgehead protons eliminates structure V from consideration. Structure V cannot account for such a feature in the nuclear magnetic resonance spectrum because it is too symmetrical. The asymmetric structure VI is in good accord with the nuclear magnetic resonance spectrum and with the double resonance data. Furthermore, the vinyl proton coupling constant (J_{vinyl} = 6.0 ± 0.5 c.p.s.) is in accord with expectation for vinyl protons in a five-membered ring but is too small for vinyl protons in a six-membered ring.[7]

Chemical confirmation of the conclusions based on the nuclear magnetic double resonance experiments is provided by comparison of the dihydro derivative of the photoproduct with a sample of VII (provided by Professor N. LeBel[16]) and VIII (provided by Professor W. R. Moore).[17] The dihydro derivative of the photoproduct differs from VII but is identical with VIII.

Discussion

Among the unsaturated eight-membered ring compounds which have been the subjects of recent photochemical investigations are 1,3-cyclooctadiene,[6] 2,4-cyclooctadienol,[18] 2,4-cyclooctadienyl acetate,[18] 1,5-cyclooctadiene,[19] 1,3,5-cyclooctatrien-7-one,[20] cyclooctatetraene epoxide,[20] cyclooctatetraene,[21–24] 1,3,4,6-tetraphenylcyclooctatetraene,[25] and 1,2,3,4-dibenzocyclooctatetraene.[26] Barton has suggested that in photochemical reactions of cyclic olefins ring fission will predominate in rings of n annular atoms containing $(n/2) - 1$ double bonds and valence tautomerization will occur in other systems.[27] Thus a variety of conjugated cyclohexadienes and cyclobutenones undergo photochemical ring fission while cycloheptadienes undergo photochemical valence tautomerization.[3] A case of particular interest is 7,8-diacetoxybicyclo[4.2.0]octa-2,4-diene (IX) which gives 1,8-diacetoxy-1,3,5,7-octatetraene (X) on irradiation.[27] It seems reasonable



to postulate 7,8-diacetoxy-1,3,5-cyclooctatetraene as an intermediate in this transformation,[27] although it is possible that the conversion of IX to X involves a single excitation step.[28] Büchi and Burgess[20] have shown that irradiation of 1,3,5-cyclooctatrien-7-one (XI) in pentane gives the bicyclic photoisomer XII and that irradiation of XI in methanol gives the unsaturated ester XIII *via* the unsaturated ketene XIV.

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[14] W. von E. Doering and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 115 (1963).

[15] For a review of nuclear magnetic double resonance see J. D. Baldeschwieler and E. W. Randall, *Chem. Rev.*, **63**, 81 (1963).

[16] This compound was prepared by reduction of previously reported derivatives: N. LeBel and J. E. Huber, *J. Am. Chem. Soc.*, **85**, 3193 (1963).

[17] This compound was prepared by a previously described technique: W. R. Moore, H. R. Ward, and R. F. Merritt, *ibid.*, **83**, 2019 (1961). See also M. Schwarz, E. R. Nelson, and A. Besold, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 20–22, 1964, p. 34C.

[18] A. C. Cope, S. Moon, C. H. Park, and G. L. Woo, *J. Am. Chem. Soc.*, **84**, 4865 (1962).

[19] R. Srinivasan, *ibid.*, **85**, 819, 3048 (1963).

[20] G. Büchi and E. M. Burgess, *ibid.*, **84**, 3104 (1962).

[21] H. Yamazaki and S. Shida, *J. Chem. Phys.*, **24**, 1278 (1956).

[22] I. Tanaka and M. Okuda, *ibid.*, **22**, 1780 (1954).

[23] G. J. Fonken, *Chem. Ind.* (London), 1625 (1963).

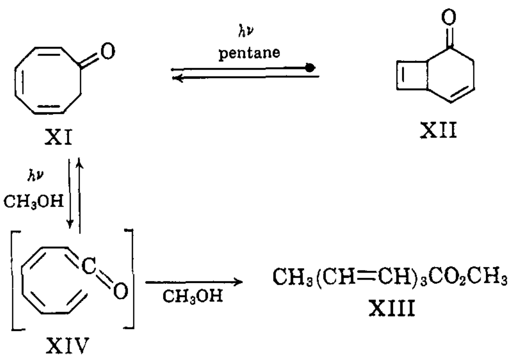
[24] E. Migirdicyan and S. Leach, *Bull. soc. chim. Belges*, **71**, 845 (1962).

[25] R. L. Stern and E. H. White, Abstracts, 141st National Meeting of the American Chemical Society, Washington, D. C., March 26–29, 1962, p. 7-O; *Tetrahedron Letters*, 193 (1964).

[26] E. Vogel, W. Frass, and J. Wolpers, *Angew. Chem Intern. Ed. Engl.*, **2**, 625 (1963).

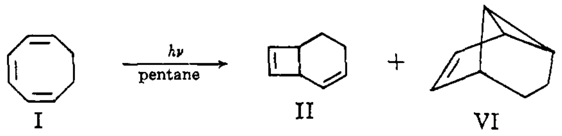
[27] D. H. R. Barton, *Helv. Chim. Acta*, **42**, 2604 (1959).

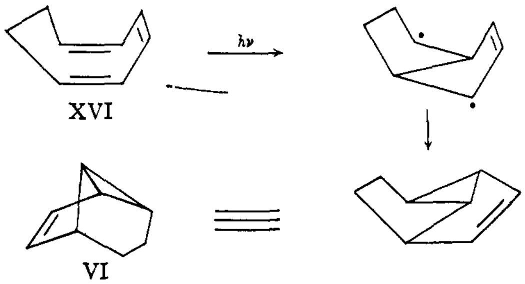
[28] For examples of cleavage of bicyclo[4.2.0]octa-2,4-dienes see R. Anet, *Tetrahedron Letters*, 720 (1961), and H. Hoever, *ibid.*, 225 (1962).



Irradiation of cyclooctatetraene epoxide in pentane or methanol leads only to rapid polymerization even though pyrolysis of the epoxide gives a number of interesting products.[20]

The formation of bicyclo[4.2.0]octa-2,7-diene from 1,3,5-cyclooctatriene is analogous to the formation of XII from XI[20] and the photocyclization of 1,3-cyclooctadienes,[6,18] 1,3-cycloheptadienes,[3] cyclooctatetraenes,[21–24] 1,2,3,4-dibenzocyclooctatetraene,[26] and certain 1,3-cyclohexadienes.[3] The formation of VI is without precedent, although the bridging of the eight-membered ring in the formation of VI is formally analogous to the formation of XV in the photosensitized isomerization of 1,5-cyclooctadiene.[19] The conformation of the excited state necessary for collapse to II and VI differs substantially. The formation of II requires two double bonds to be essentially coplanar at the time of collapse. Such a conformation of 1,3,5-cyclooctatriene is decidedly unstable in the ground state in which a saddle conformation is preferred (XVI).





The saddle conformation XVI is suitable for isomerization to VI.

It is interesting that ring fission does not play a role in the photochemical transformations of 1,3,5-cyclooctatriene but does assume a prominent role in the thermal isomerization.[14,29]

Experimental

Nuclear magnetic resonance spectra were obtained with a Varian Associates HR-60 instrument operating at 14,100 gauss. Spin decoupling was done with a modified version of the method of Johnson,[30] using irradiating and scanning radiofrequency fields of approximately 1.5 and 0.06 mgauss, respectively,

Irradiation of 1,3,5-Cyclooctatriene.—A solution of 1,3,5-cyclooctatriene[31] (25 g.) in absolute ether (2 l.) was irradiated for 220 hr. with a 550-watt mercury arc lamp (Hanovia Type A) encased in a quartz immersion well. The ether solution was carefully concentrated to 50 ml. using a rotary evaporator. The products were separated by vapor phase chromatography using a $^3/_8$ in. × 12 ft. copper column filled with 5% Ucon LB550-X on 60-80 mesh Chromosorb P. The total yield of volatile material was 41%. The volatile product consisted of II, 38%, retention time 10 min.; VI, 14%, retention time 11.9 min.; and 1,5-cyclooctadiene, 48%, identified by comparison with an authentic sample. Compound VI shows an ultraviolet maximum at 208 mμ (5300) and infrared maxima (in CCl_4) at 328 (s), 3.42 (m), 3.51 (s), 6.91 (m), 6.94 (m), 7.42 (s), 7.59 (w), 7.74 (w), 9.10 (w), 9.43 (w), 9.57 (w), 10.10 (m), 10.43 (m), 10.55 (m), 11.02 (m), 11.10 (m), and 11.48 (w)μ.

Anal. Calcd. for $C_8H_{10}O$: C, 90.51; H, 9.49; mol. wt., 106. Found for II: C, 90.39; H, 9.75. Found for VI: C, 90.50; H, 9.56; mol. wt., 111 (osmometric determination).

Reduction of Bicyclo[4.2.0]octa-2,7-diene (II).—A solution of bicyclo[4.2.0]octa-2,7-diene (II, 271 mg.) in 3 ml. of carbon tetrachloride containing suspended 10% palladium-on-charcoal (50 mg.) absorbed 1.96 equiv. of hydrogen. After removal of the catalyst by filtration the product was found to be identical in infrared and nuclear magnetic resonance absorption with bicyclo[4.2.0]octane prepared by catalytic reduction of bicyclo[4.2.0]oct-7-ene as previously described.[6]

Tricyclo[5.1.0.0^{4,8}]octane (VIII).—A solution of tricyclo[5.1.0.0^{4,8}]oct-2-ene (211 mg.) in carbon tetrachloride (3 ml.) containing 10% palladium-on-charcoal (50 mg.) adsorbed 0.99 equiv. of hydrogen. The product was identified as tricyclo[5.1.0.0^{4,8}]octane by comparison of infrared and nuclear magnetic resonance spectra with an authentic sample provided by Professor W. R. Moore.[11]

Acknowledgment.—This research was supported by the National Science Foundation (G-15832). Ultraviolet spectra were recorded with an instrument made available by a National Science Foundation grant (G-14916). The authors are indebted to Professor W. R. Moore and Professor N. LeBel for samples and to Dr. P. R. Story for spectra of tricyclo[4.1.0.0^{3,7}]hept-4-ene.

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(29) For examples of facile cleavage of 1,3,5-cyclooctatrienes see A. C. Cope and D. J. Marshall, *J. Am. Chem. Soc.*, **75**, 3208 (1953), and T. S. Cantrell and H. Schechter, *ibid.*, **85**, 3300 (1963).

(30) L. F. Johnson, "Proton–Proton Spin Decoupling Using the Varian V-3521 Integrator," Varian Associates, Palo Alto, Calif., 1962.

(31) A. C Cope, C. L. Stevens, and F. A. Hochstein, *J. Am. Chem. Soc.*, **72**, 2510 (1950).