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PHOTOCHEMICAL TRANSFORMATIONS—VI[1,2]
ISOMERIZATION OF CYCLOHEPTADIENE AND CYCLOHEPTATRIENE

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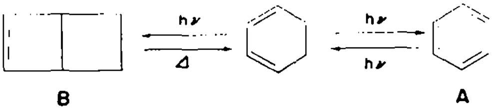
Abstract—Irradiation of 1,3-cycloheptadiene in ether solution gave Δ^6-bicyclo [3.2.0] heptene, the structure of which was established by degradation to *cis*-cyclopentane-1,2-dicarboxylic acid and by dihydrogenation to the known bicyclo [3.2.0] heptane. Irradiation of 1,3,5-cycloheptatriene in ether gave the known $\Delta^{2,6}$-bicyclo [3.2.0] heptadiene. Both photoproducts upon pyrolysis were reconverted to their respective seven membered ring progenitors.

WHEN a conjugated homoannular diene is irradiated in solution with ultraviolet light, it is transformed into valence tautomeric structures, i.e. only carbon–carbon bonds and not carbon–hydrogen bonds are involved in the reaction. Depending on the structure of the starting diene either ring cleavage (product A)[4–7] or intramolecular cyclization[8] (bridging, product B) occurs. In some cases the ring cleavage reaction has been found to be a reversible photochemical reaction[4,5] but such cannot be the case in the bridging reaction since the product formed no longer possesses a chromophoric group capable of being excited (in a preparative sense) by available light sources. Such bridged structures, however, being highly strained can be reconverted to the starting diene by the action of heat. In the six membered ring system both with the dienes[4–7] and the dienones[9] the preferred reaction is the cleavage reaction and, to date, only two cases of a bridging reaction in this series (photoisopyrocalciferol and photopyrocalciferol[8]) have been reported.



In order to evaluate the generality of the intramolecular ring closure reaction, it is desirable to study a system in which the ring cleavage reaction is prohibited. The 1,3-cycloheptadiene ring system is such a structure and, indeed, recently it has been shown that 2,6,6-trimethyl-2,4-cycloheptadiene-1-one (eucarvone) is readlily transformed, photochemically, to its valence tautomeric bicylco[3.2.0]-heptene system.[10]

Irradiation of 1,3-cycloheptadiene (I) in ether solution with a G.E. AH-6 mercury

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[1] For paper V, see W. G. Dauben and J. A. Ross, *J. Amer. Chem. Soc.* **81**, 6521 (1959).

[2] This work supported in part by Grant No. A–709 (C–6)-Bio., U.S. Public Health Service.

[3] Postdoctoral Fellow, U.S. Public Health Service, 1960–1961.

[4] L. Velluz, G. Amiard and B. Goffinet, *Bull. Soc. Chim. Fr*, 882 (1957).

[5] M. P. Rappoldt and E. Havinga, *Rec. Trav. Chim.* **79**, 369 (1960) and earlier papers.

[6] R. L. Autrey, D. H. R. Barton and W. H. Rausch, *Proc. Chem. Soc.* 55 (1959).

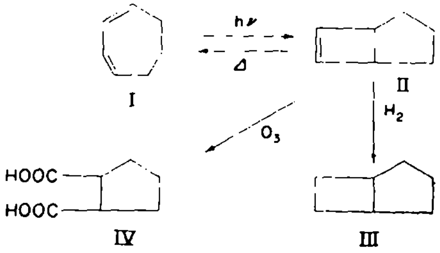
[7] M. P. Rappoldt, *Rec. Trav. Chim.* **79**, 392 (1960).

[8] W. G. Dauben and G. J. Fonken, *J. Amer. Chem. Soc.* **81**, 4060 (1959).

[9] For an excellent summary of such reactions, see D. H. R. Barton, *Helv. Chim. Acta* **42**, 2604 (1959).

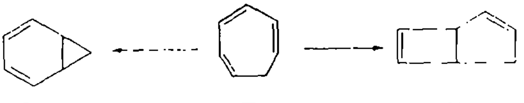
[10] G. Büchi and E. M. Burgess, *J. Amer. Chem. Soc.* **82**, 4333 (1960).

lamp for 40 hours gave a photoisomer (II) in 42 per cent yield. The photoisomer possessed bands in the infrared at 3020, 1560 and 735 cm^{-1}, characteristic of a cyclobutene.[11,12] The ultraviolet spectrum showed only weak end absorption (ε_{205} 940). The nuclear magnetic resonance spectrum possessed three general bands whose integrated intensities were in the ratio of 2:2:6. These spectral features were indicative of valence tautomeric structure II, Δ^6-bicyclo[3.2.0]heptane, for the photoproduct. In the NMR, the low field singlet at 4·20 τ was assigned to the cyclobutene protons, the singlet structure suggesting identity of the vinyl protons. The small coupling with the adjacent ring juncture hydrogens could not be resolved. A doublet centered at 6·89 τ was assigned to the allylic ring juncture protons, the doublet suggesting identity of the protons and their coupling with an adjacent methylene group. Finally, a large broad band centered at 8·58 τ was assigned to the six protons of the remaining saturated methylene groups.



The bicyclic nature of the ring system was established by dihydrogenation of II to the known bicyclo[3.2.0]heptane (III).[13] The presence of the cyclobutene ring was shown by the isolation of *cis*-cyclopentane-1,2-dicarboxylic acid (IV) from the ozonization of the II. Finally, when the photoisomer was pyrolyzed at 400° it was converted back to cycloheptadiene, a thermal rearrangement expected of the valence tautomeric structure II.

The finding of the facile conversion of 1,3-cycloheptadiene to its bicyclic valence tautomer prompted the investigation of the photochemical reaction of 1,3,5-cycloheptatriene (V). It is well established[14,15] that the related tropolones undergo the bridging reaction but the spectral character of this type of compound makes it quite different from the unsubstituted triene. With 1,3,5-cycloheptatriene there are two valence tautomeric structures which can be formed by bridging, one the norcaradiene (VI) and the other the $\Delta^{2,6}$-bicyclo[3.2.0]heptadiene (VII). Previous workers[16]



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[11] R. C. Lord and M. V. Evans, Jr., *J. Amer. Chem. Soc.* **79**, 2401 (1957).

[12] There were also bands of lesser intensity at 1625 and 1670 cm^{-1} which have been assigned as overtones of methylene vibrations.

[13] A. T. Blomquist and J. Kwiatek, *J. Amer. Chem. Soc.* 73, 2098 (1951); E. Vogel, private communication.

[14] E. J. Forbes, *J. Chem. Soc.* 3864 (1955); P. D. Gardner, R. L. Brandon and G. R. Haynes, *J. Amer. Chem. Soc.* 79, 6334 (1957).

[15] O. L. Chapman and D. J. Pasto, *J. Amer. Chem. Soc.* **82**, 3642 (1960).

[16] W. E. Doering and L. H. Knox, *J. Amer. Chem. Soc.* **75**, 247 (1953).

attempted to prepare the norcaradiene by the reaction of diazomethane with benzene but the finding of only 1,3,5-cycloheptatriene led to the conclusion that at ordinary temperatures the norcaradiene is rapidly isomerized to the triene. Such a thermal instability of the diene would prohibit its buildup in a photochemical reaction run at room temperature. On the other hand, the $\Delta^{2,6}$-bicyclo[3.2.0]heptadiene (VII) has been prepared from cyclopentadiene[17] and has been shown to be thermally stable to temperatures up to 200°. Since such a valence tautomer would be stable to ultraviolet light, the photochemically induced bridging reaction could be expected to yield such a material.

Irradiation of 1,3,5-cycloheptatriene (containing a small amount of toluene) in ether solution under the above conditions for a period of 200 hours gave an isomeric photoproduct in 34 per cent yield. In agreement with the expected structure, VII, the photoproduct possessed physical properties which were identical with those reported for VII.[16] The ultraviolet spectrum showed no maximum (ε_{206} 2340) and the infrared spectrum in addition to bands at 3050, 1605 and 1560 cm^{-1}, the last two being characteristic of a cyclopentene and cyclobutene, showed the characteristic three overtone bands at 1625, 1660 and 1690 cm^{-1}.[18] The nuclear resonance spectrum showed three major band series whose integrated areas were in the ratio of 4:2:2. The bands for the two vinyl protons of the cyclobutene ring were centered at 3·67 and 3·92 τ and each band was a doublet with a 3 cps splitting; as in II the coupling with the ring juncture protons was not detected. The cyclopentene proton absorption was centered at 4·36 τ and appeared as a multiplet. The second series of bands were at 6·38 and 6·73 τ, each band representing one proton, and these bands were assigned to the ring juncture protons. The sole methylene group absorbed at 7·67 τ. In addition to these spectral properties which clearly define the structure of the photo-product, the material upon tetrahydrogenation yielded bicyclo[3.2.0]heptane (III) and upon pyrolysis at 400° reconverted to the starting triene.

This ultraviolet light-induced conversion of cycloheptadiene and cycloheptatriene to the bridged valence tautomeric structures as well as the previously reported[8,10,14,15] results with the pyrocalciferols, tropolones and eucarvone clearly indicate the general occurrence of photochemical intramolecular cyclization or bridging reactions.

EXPERIMENTAL[19]

Δ^6-*Bicyclo*[3.2.0]*heptene* (II). A solution (21·8 g; 0·23 mole) 1,3-cycloheptadiene[20] [b.p. 120–122°, λ_{max}^{EtOH} 246 mμ (ε 7750)] in 2 l. of dry ether was irradiated with a G.E. AH-6 high pressure mercury arc lamp (internal probe). The solution was agitated by a slow stream of nitrogen and the course of the irradiation followed by ultraviolet spectroscopy. After a period of 40 hr (this time varies with the age of the lamp) the characteristic ultraviolet absorption of the diene was absent. The ether was removed by distillation through a 1 meter tantalum spiral column and product distilled through the same column, b.p. 96–98°, n_D^{25} 1·4536, ε_{206}^{EtOH} 940, yield 6·43 g (29·5%). The residual yellow viscous oil was distilled through a short path molecular still and from the distillate an additional 2·9 g (13·3%) of photoproduct was obtained. The Δ^6-bicyclo[3.2.0]heptene was homogeneous to GLC over a 10-ft. asphalt column at 100°; the starting diene is readily separated under these conditions.
(Found: C, 89·39; H, 10·83; Calc. for C_7H_{10} (94·15): C, 89·29; H, 10·71%).

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[17] E. Vogel, *Angew. Chem.* **68**, 189 (1956); M. V. Evans and R. C. Lord, *J. Amer. Chem. Soc.* **82**, 1876 (1960).

[18] The authors are indebted to Professor M. V. Evans, Jr., for kindly supplying the characteristic I.R. bands of VII.

[19] All analyses were performed by the Microanalytical Laboratory, College of Chemistry, University of California.

[20] E. Pesch and S. L. Friess, *J. Amer. Chem. Soc.* **72**, 5756 (1950).

Bicyclo[3.2.0]*heptane* (III). A solution (1·07 g; 11·4 mmoles) Δ^6-bicyclo[3.2.0]heptene in 45 ml 95% ethanol was hydrogenated over 63 mg prereduced platinum oxide at atm press and 25°. After 70 min, 275 ml (11·4 mmoles) hydrogen had been absorbed and no further uptake was observed. The catalyst was filtered and the ethanolic filtrate partitioned between water and ether. The ethereal layer was washed with water, dried and then swirled with 16 g alumina (Woelm, Act. III). The ether was removed by careful distillation through a 1-meter tantalum spiral column and the residue distilled through a short-path molecular still, yield 715 mg (67%). The distillate upon GLC over a 10-ft. asphalt column at 100° showed less than 1% starting material. An analytical sample of bicyclo[3.2.0]heptane was collected from GLC under the above conditions, n_D^{20} 1·4525 (lit.[18] n_D^{20} 1·4532).

(Found: C, 87·19; H, 12·71; Calc. for C_7H_{12} (96·17): C, 87·42; H, 12·58%).

Ozonolysis of Δ^6-*bicyclo*[3.2.0]*heptene* (II). Ozone was passed through a solution (500 mg. 5·3 mmoles) II in 100 ml methylene chloride cooled in a Dry Ice-isopropanol bath at the rate of 0·41 mmole/min for 21 min. The resulting solution had the characteristic blue color of a methylene chloride solution of ozone. The solvent was removed under reduced press and the residual oily ozonide was allowed to react with 30% hydrogen peroxide in alkaline solution on a steam-bath for 2 hr. The solution was acidified and evaporated to dryness. The residue was digested with chloroform, the chloroform solution decolorized and the solvent evaporated. The remaining oil was crystallized from ether-petroleum ether (30–60°), yield 91 mg (11%), and after two additional recrystallizations from the same solvents gave pure *cis*-cyclopentane-1,2-dicarboxylic acid (IV), m.p. 137–139°. A mixed m.p. with an authentic sample, prepared from the *trans*-diacid,[21] is 137–139°, and the infrared spectra (KBr pellet) of the two samples of diacid were identical.

Pyrolysis of Δ^6-*bicyclo*[3.2.0]*heptene* (II). The pyrolysis apparatus consisted of a 7-mm (I.D.) Pyrex tube packed to a height of 16 cm with Pyrex helices and heated to 400–420°. A slow stream of nitrogen was constantly passed through the apparatus and the material to be pyrolyzed was slowly injected into the column from a syringe. The bicycloheptene, II (250 mg, 2·6 mmoles), was injected and the pyrolysate collected in a trap cooled in a Dry Ice–isopropanol bath, yield 157 mg (63%). The pyrolysate was homogeneous to GLC over a 10 ft. asphalt column at 100° and had an infrared spectrum which was superimposable on that of 1,3-cycloheptadiene.

$\Delta^{2,6}$-*Bicyclo*[3.2.0]*heptadiene* (VII). A solution (26·0 g; 0·28 mole) freshly distilled 1,3,5-cycloheptatriene[22,23] in 2 l. dry ether was irradiated as above for 200 hr at which time more than 90% of the triene spectrum had disappeared. The ether was removed through a 1-meter tantalum spiral column and the product distilled through the same column, yield 8·80 g (34%), b.p. 97–98° (lit[17,24] b.p. 96·0–97·5°), ϵ_{204}^{EtOH} 2340. By GLC on a DEGS column at 40°, the distillate was found to contain 95–97% of $\Delta^{2,6}$-bicyclo[3.2.0]heptadiene and 3–5% of toluene and unchanged starting material. A non-volatile residue of 11·5 g was recovered and presumably is polymeric material.

The photoproduct was purified by GLC using a ¼ inch diameter DEGS column at 40° and the material collected was dried over lithium aluminum hydride, n_D^{25} 1·4721 (lit[24] n_D^{20}1·4751.

(Found: C, 91·25; H, 8·94; Calc. for C_7H_8 (92·13): C, 91·25; H, 8·75%).

Hydrogenation of $\Delta^{2,6}$-*bicyclo*[3.2.0]*heptadiene* (VII). A solution (603 mg; 6·6 mmoles) bicycloheptadiene (VII) in 15 ml 95% ethanol was hydrogenated over 38 mg prereduced platinum oxide at atm press and 25°. After 100 min 328 ml (13·5 mmoles) hydrogen had been absorbed. The product was processed as before and collected from GLC (DEGS ¼ inch column at 40°) and the infrared spectrum of the material was superimposable on that of bicyclo[3.2.0]heptane. Co-injection of hydrogenated materials from the bicycloheptene and bicycloheptadiene on a DEGS column gave a single band.

Pyrolysis of $\Delta^{2,6}$-*bicyclo*[3.2.0]*heptadiene* (VII). The bicycloheptadiene VII (86 mg; 0·91 mmole) was pyrolyzed as described above. The product (32 mg, 37%) was homogeneous to GLC on a DEGS column at 40° and its infrared spectrum (CS_2) was identical with that of 1,3,5-cycloheptatriene (collected from GLC and free of toluene).

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[21] L. N. Owen and A. G. Peto, *J. Chem. Soc.* 2383 (1955).

[22] Kindly supplied by the Shell Development Corporation, Emeryville, California.

[23] The 1,3,5-cycloheptatriene was distilled through a Vigreux column, b.p. 114–116° (lit b.p. 117°, W. G. Woods, *J. Org. Chem.* **23**, 110 (1958)), and the distillate contained a few per cent of toluene.

[24] E. Vogel, private communication.