Photochemical Transformations. XI. Isomerization of 1,3-Cyclooctadiene[1,2]

WILLIAM G. DAUBEN AND ROBERT L. CARGILL

Department of Chemistry, University of California, Berkeley 4, California

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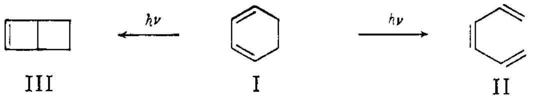
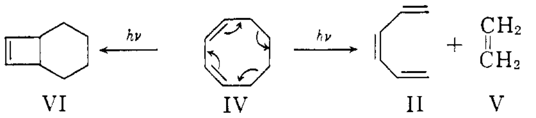
The ultraviolet irradiation of a ring system of $2n$ members containing $n - 1$ conjugated bonds, such as 1,3-cyclohexadiene (I), can yield either an open chain compound possessing n conjugated double bonds, such as 1,3,5-hexatriene (II), or a bicyclic valence tautomer, such as bicyclo-[2.2.0]hexene (III).[3-6] In the ring opening reaction the excited state is deactivated *via* rearrangement of the bonding electrons with concomitant breaking of a saturated carbon-carbon bond. A similar excited state is derivable from other cyclic 1,3-diolefins but such a deactivation step is generally prohibited. However, in the case of 1,3-cyclooctadiene (IV) the excited state could be deactivated by a Grob type[7] of fragmentation reaction to yield 1,3,5-hexatriene (II) and ethylene (V). Also, the excited state could collapse to the valence tautomeric Δ^7-bicyclo-[4.2.0]octene (VI).





It was found that 1,3-cyclooctadiene (IV) upon irradiation in ether solution yielded a single product which was identified as Δ^7-bicyclo[4.2.0]-octene. At no time during the long irradiation was the typical spectrum of 1,3,5-hexatriene detected in the ultraviolet absorption spectrum of the irradiated solution. The photo product upon oxidation with a periodate–permanganate mixture[8] gave *cis*-1,2-cyclohexanedicarboxylic acid. The NMR spectrum of the irradiation product showed a sharp singlet at 4.04 τ, corresponding to two identical vinyl protons on a cyclobutene ring. The bands centered at 7.21 τ and 8.47 τ were complex multiplets and were assigned to the two allylic protons and six-ring protons, respectively. The infrared spectrum of VI was identical with that reported by Evans and Lord[9] for Δ^7-bicyclo-[4.2.0]octene prepared from cyclooctatetraene dibromide.[10]

Experimental[11]

Δ^7-Bicyclo[4.2.0]octene (VI).—A solution of 25 ml· (22.1 g., 0.25 mole) of 1,3-cyclooctadiene[12] [n^{20}D 1.4940, $\lambda_{\max}^{C_2H_5OH}$ 228 mμ (ϵ 5470)] in 2 l. of dry ether was irradiated with a Hanovia high pressure mercury arc lamp, internal probe, type L. The solution was stirred with a magnetic stirrer in an atmosphere of helium and the progress of the irradiation was followed by ultraviolet spectroscopy. After 200 hr., no diene remained and the irradiation was stopped. Most of the ether was removed by distillation through a 1-ft. Vigreux column (bath temperature 40–50°). The yellow residue was distilled through a Nester-Faust, 2-ft. spinning band column, b.p. 131–132°, n^{20}D 1.4720, $\epsilon_{205}^{C_2H_5OH}$ 700, yield 7.97–9.04 g. (36–41%).

Anal. Calcd. for C_8H_{12} (108.18): C, 88.81; H, 11.19. Found: C, 88.58; H, 11.39.

***cis*-1,2-Cyclohexanedicarboxylic Acid.**—To a solution of 2.094 g. (9.78 mmoles) of sodium metaperiodate, 26 mg. (0.16 mmole) of potassium permanganate, and 51 mg. (0.37 mmole) of potassium carbonate in 200 ml. of water was added 112 mg. (1.03 mmoles) of the irradiation product VI. The mixture was stirred at 25° for 25 hr., acidified with 15% sulfuric acid, and extracted continuously for 20 hr. with ether. The ethereal extract was dried, the solvent evaporated, and the residue triturated with petroleum ether to induce crystallization, yield 105 mg. The solid was recrystallized from water and then ether–petroleum ether, m.p. 197.5–198.0°, no depression upon admixture with authentic *cis*-1,2-cyclohexanedicarboxylic acid.

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[1] For Paper X, see W. G. Dauben, David A. Lightner, and William K. Hayes, *J. Org. Chem.*, in press.

[2] This work was supported, in part, by Grant No. A-709, U. S. Public Health Service.

[3] For a general discussion of these types of reactions, see D. H. R. Barton, *Helv. Chim. Acta*, **42**, 2604 (1959).

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[11] All analyses were performed by the Microanalytical Laboratory, Department of Chemistry, University of California. The NMR spectra were measured on a Varian Associates Model A-60 spectrometer.

[12] This material was kindly supplied by Cities Service Research Development Co.

Preparation of 1,3-Difluoro-2,4,6-trinitrobenzene

V. I. SIELE AND MAURICE WARMAN

Explosives Research Section Picatinny Arsenal, Dover, N. J.

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Interest in the fluoro derivatives of symmetrical trinitrobenzene has been growing recently but, to date, the synthesis of mono, di-, or trifluorotrinitrobenzene has not been reported. Recent work in these laboratories has led to the preparation of