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

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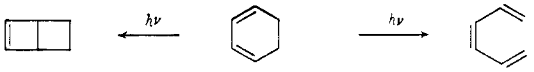
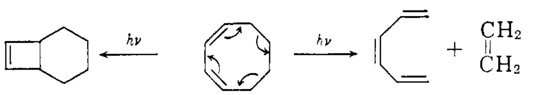
The ultraviolet irradiation of a ring system of $2n$ members containing $n - 1$ conjugated bonds, such as 1,3-cyclohexadiene (I), can yield either an open chain compound possessing n conjugated double bonds, such as 1,3,5-hexatriene (II), or a bicyclic valence tautomer, such as bicyclo-[2.2.0]hexene (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).



III I II



VI IV II V

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, $\lambda^{C_2H_5OH}_{max}$ 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, $\epsilon^{C_2H_5OH}_{205}$ 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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[8] R. U. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33**, 1701 (1955).

[9] M. V. Evans and R. C. Lord, *J. Am. Chem. Soc.*, **83**, 3409 (1961).

[10] E. Vogel, *Angew. Chem.*, **65**, 346 (1953); A. C. Cope and R. W. Gleason, *J. Am. Chem. Soc.*, in press.

[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

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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

1,3-difluoro-2,4,6-trinitrobenzene from *m*-difluorobenzene.

m-Difluorobenzene (I) was nitrated using the procedure described by Zahn and Würz.[1] Pure, 1,3-difluoro-4,6-dinitrobenzene (II) was obtained in 77% yield after recrystallization from boiling carbon tetrachloride.

Difluorotrinitrobenzene (III) was prepared in 28% yield by vigorously nitrating 1 mole of II with an acid mixture consisting of 4.5 moles of potassium nitrate and a quantity of 30% fuming sulfuric acid corresponding to 17.8 moles of free sulfur trioxide. The nitration was conducted for twelve hours at 180°. After pouring the cooled nitrating solution onto crushed ice, a white solid melting at 60° was obtained in 49% yield. A white needle-like solid melting at 147° was collected after carefully recrystallizing the low-melting material from carbon tetrachloride. Evaporation of the solvent gave II.

The molecular weight as determined by the Rast method using triphenylphosphate was found to be 236. Reaction of III with alcoholic ammonia and ethanol gave 1,3-diamino-2,4,6-trinitrobenzene and 1,3-diethoxy-2,4,6-trinitrobenzene, respectively. Nuclear magnetic proton resonance obtained at a frequency of 56.4 Mc. and a field strength of 13,247 gauss revealed that III contained 50% of the protons originally present in II. The elemental analysis was in agreement with the proposed structure.

Experimental[2]

1,3-Difluoro-4,6-dinitrobenzene.—*m*-Difluorobenzene (40 g., (0.195 mole) was added at 0°, with stirring, to an acid mixture containing 85 ml. of 98% nitric acid and 160 ml. of 96% sulfuric acid. The reaction mixture was held at 0° for 0.5 hr. The temperature was then raised slowly to 95° and maintained for 1 hr. The nitration mixture was cooled to −10° and quenched in 1000 g. of crushed ice. The temperature during quenching was not allowed to rise above −10°. The solid which separated was collected by filtration, washed with ice water, and air-dried. Yellow platelets were obtained by recrystallization from 550 ml. of carbon tetrachloride. The yield was 55 g. (77%), m.p. 75–76°, lit. 76°.

1,3-Difluoro-2,4,6-trinitrobenzene.—To a nitrating mixture consisting of 11 g. (0.11 mole) of potassium nitrate and 60 ml. of 30% fuming sulfuric acid was added, with stirring, 5 g. (0.025 mole) of difluorodinitrobenzene. The stirring was continued and the mixture was heated at 180° for 12 hr. The nitration solution was cooled to −10° and then poured slowly, with stirring, onto 120 g. of crushed ice. A cooling bath was used to keep the temperature below −10°. The solid which separated was collected by filtration, washed quickly with three 20-ml. portions of ice water and then dried over sodium hydroxide under approx. 5 mm. This product weighed 3.0 g. (49%) and melted at 60°. Purification was effected by recrystallization from 95 ml. of boiling carbon tetrachloride. The yield of III was 1.71 g. (28%), m.p. 147°. Upon cooling the mother liquor below room temperature, II was obtained.

Anal. Calcd. for $C_6HN_3O_6F_2$: C, 28.93; H, 0.41; N, 16.87; F, 15.26. Found: C, 28.76; H, 0.44; N, 16.86; F, 14.58.

1,3-Diamino-2,4,6-trinitrobenzene.—Anhydrous ammonia was bubbled into a solution of 1 g. (0.005 mole) of III in 20 ml. of absolute methanol for 15 min. at 25°. The mixture was warmed on a *steam bath for 10 min. and then cooled to* room temperature. The yellow solid which separated was collected by filtration and washed with two 10-ml. portions of methanol and finally with 50 ml. of ether. The air-dried solid weighed 0.8 g. (82%), m.p. 288°, lit., 285°.

1,3-Diethoxy-2,4,6-trinitrobenzene.—A solution of 1 g. (0.005 mole) of III in 10 ml. of absolute ethanol was warmed on the steam bath for 10 min. The solution was placed in a refrigerator for 3 hr. During this time a white solid separated. The solid was separated by filtration and recrystallized from ethanol. The yield of diethoxy product was 1.1 g. (91%), m.p. 121°.

Anal. Calcd. for $C_{10}H_{11}N_3O_8$: C, 39.87; H, 3.68; N, 13.95. Found: C, 39.84; H, 3.51; N, 14.23.

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[1] H. Zahn and A. Würz; *Biochem. Z.*, **325**, 182–194 (1954).

[2] All melting points are uncorrected. Microanalyses by Mr. Marcel Blais, Explosives Research Section, Picatinny Arsenal.

Synthesis of Quinolino Steroids

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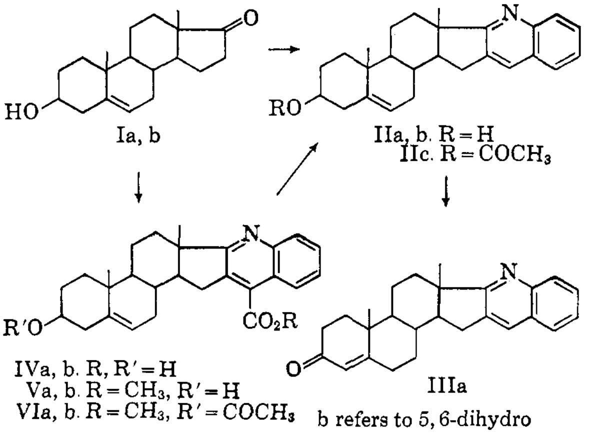
Quinolines fused to a steroid nucleus were first reported[1] in 1924 at a time when the structures of the starting ketocholanic acids were not well established. In 1944 Buu-Hoï and Cagniant[2] reported the preparation of a steroido-quinoline, VIII, and found that its sodium salt possessed hemolitic properties. As part of an effort towards the synthesis of potential carcinogens and antitumor agents, we were interested in studying methods of synthesis of steroido-heterocycles and in applying the Friedlander reaction[3] to the formation of quinolines fused to the D-ring of steroids.



b refers to 5,6-dihydro compounds

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[3] J. Eliasberg and P. Friedlaender, *Ber.*, **25**, 1752 (1892).

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