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PHOTOCHEMISTRY OF BICYCLO[3.3.1]NONANES HAVING TWO FUNCTIONAL GROUPS AT 3,7-POSITIONS

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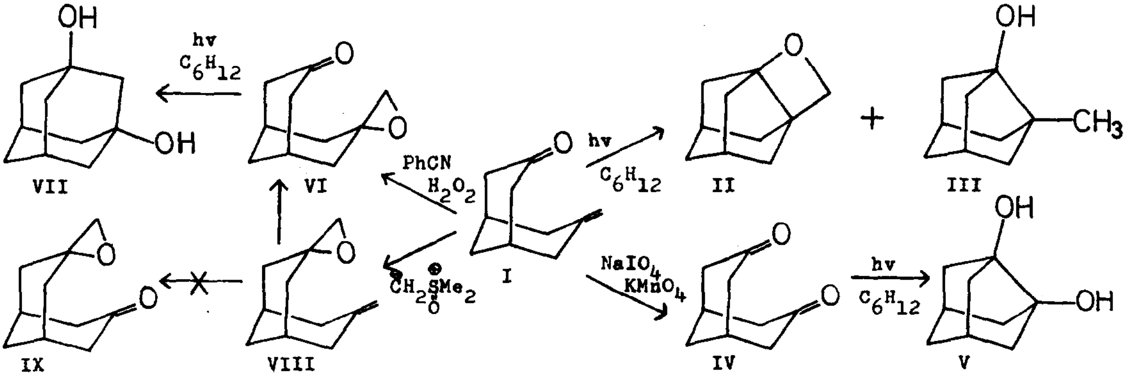
Bicyclo[3.3.1]nonane system prefers twin chair conformation (1) in which functional groups at 3,7-positions are extremely close to each other to induce facile transannular interaction. Ionic cyclization of this type of compounds is well known to form adamantane derivatives (2), but few has been recorded on photochemical reactions (3).

The methylene-carbonyl derivative I is readily accessible by means of alkaline treatment of 1,3-dibromoadamantane (4) and serves as the key substance for this work. Photolysis of I in cyclohexane with 200 W high pressure mercury arc for 48 hr resulted in intramolecular cycloaddition to form oxetane II (33%) and in transannular photoreduction to alcohol III (20%). The oxetane II formed colourless crystals, m.p. 192-194°. IR(KBr): 1284, 1229, 1094, 978, 954, 934 cm^{-1}. NMR(CCl$_4$): δ 4.23 s (2 H, oxetane methylene). MS: m/e 150 (M^+). The alcohol III, m.p. 169-170°, was identical with the authentic sample (5).

Permanganate-periodate oxidation (6) of I afforded diketone IV (7) in a 62% yield. Irradiation of IV in cyclohexane induced pinacolic reduction giving noradamantanediol V, m.p. 297-298°, in a quantitative yield. IR(Nujol): 3300, 1314, 1159, 1037, 982 cm^{-1}.



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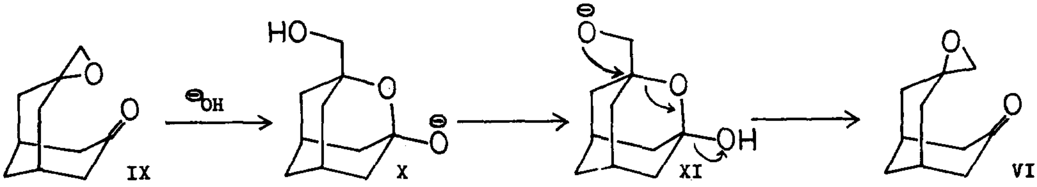
NMR($CDCl_3$): δ 2.24 m (2 H, bridge-head), 2.08 s (2 H, OH), 1.89 s (8 H), 1.43 t (2 H). MS: m/e 154 (M^+).

Epoxidation of I by means of hydrogen peroxide and benzonitrile (8) afforded a single epoxyketone, m.p. 258-260°, in a 34% yield. IR(Nujol): 1700, 915, 867, 833, 804, 759 cm^{-1}. NMR($CDCl_3$): δ 2.48 s (2 H, epoxy ring). MS: m/e 166 (M^+). This epoxyketone was expected to be O-exo VI rather than O-endo IX on the basis of the assumed attack on I in its twin chair conformation. Photolysis of VI in cyclohexane gave 1,3-adamantanediol VII (2a) in a quantitative yield to establish the structure VI. The epoxyketone VI proved to be stable even on heating at 400°.

Preparation of the O-endo epoxyketone IX was attempted as follows. The carbonyl group of I was converted into epoxy group by means of dimethyloxosulphonium methylide to give a single epoxide VIII in ca. 60% yield. IR(Nujol): 910, 879, 868, 825, 791, 762 cm^{-1}. NMR(CCl_4): δ 4.65 s (olefinic), 2.22 s (epoxy). Thermal lability of the epoxide was consistent with the assigned structure and this prohibited its purification. Direct permanganate-periodate oxidation of the crude VIII did not afford the expected O-endo IX. Instead, the O-exo isomer VI was isolated in ca. 30% yield. We may assume possible isomerization of IX into VI proceeding through such intermediates as X and XI.



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