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THE SYNTHESIS OF TRICYCLO[4.3.1.$0^{3,8}$]DECANE (ISOADAMANTANE) AND SOLVOLYSIS OF ITS C3-CARBINOL

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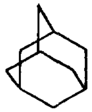
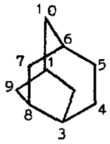
Current interest in the preparation and chemistry of homologs and isomers of adamantane (I) (1) prompts us to report the synthesis of tricyclo[4.3.1.$0^{3,8}$]decane (II) and to describe the solvolysis of one of its carbinols III. We suggest the trivial name "isoadamantane" for this system in view of its structural similarity to I.



I



II

III

The key step in the preparation of this new ring system involved the selective Favorskii-type ring contraction (2) of 3,6-dibromohomoadamantane-10,11-dione (IV) (3) to give the trifunctional isoadamantane V. Reductive removal of the bromo and keto groups afforded the hydrocarbon acid VII, a convenient intermediate for the preparation of other isoadamantanes. Acid VII was converted to the parent hydrocarbon II via the C3-halo derivatives. Solvolysis of the carbinol III, obtained by the reduction of VII, led to the formation of 1-adamantylcarbinol.

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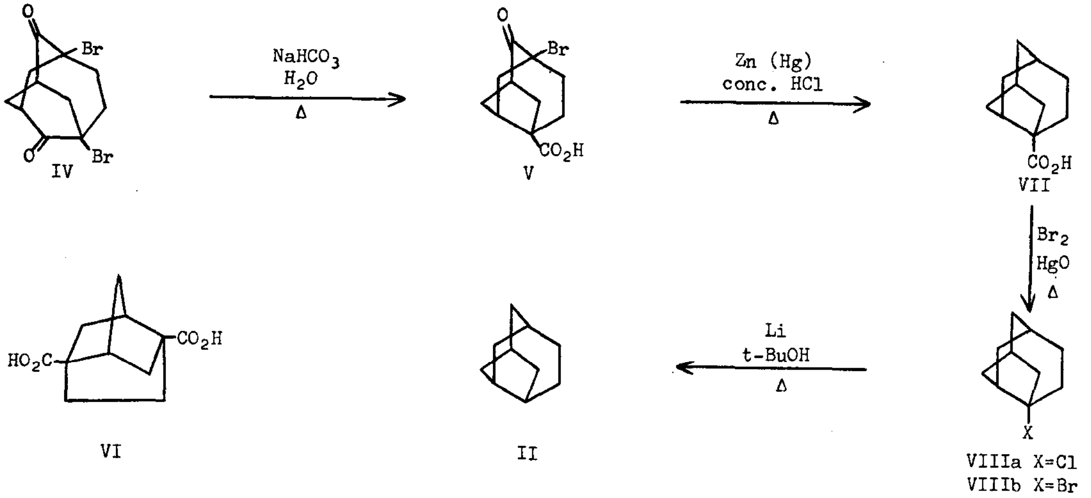
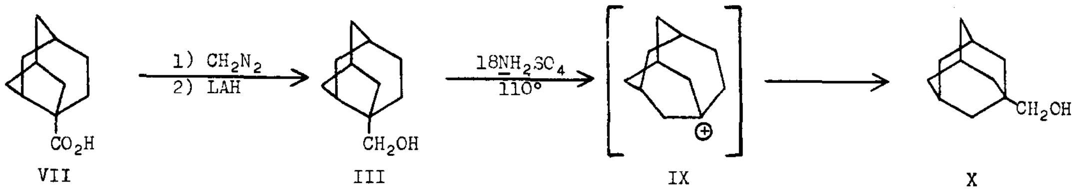


Accordingly, dibromodione IV, on refluxing with sodium bicarbonate in 50% aqueous ethanol for one hour, gave 6-bromotricyclo[4.3.1.$0^{3,8}$]decan-10-one-3-carboxylic acid (V) [yield, 77%; mp 203-205°; C=O stretch 5.80 μ and 5.91 μ] accompanied by small amounts of the doubly contracted product, twist-brendane-3,6-dicarboxylic acid (VI) (3, 4, 5). Removal of the bromine and ketone groups was accomplished by refluxing V with zinc amalgam in concentrated hydrochloric acid, furnishing the isoadamantane carboxylic acid VII [yield, 56%, mp 88-89°; and C=O stretch 5.90 μ] (1b, 6). Transformation of VII to a mixture of the 3-chloro and 3-bromoisoadamantanes, VIIIa and VIIIb respectively, was effected by use of the Cristol modification of the Hunsdiecker reaction, employing mercuric oxide and bromine in refluxing carbon tetrachloride (7). Lithium and t-butyl alcohol in tetrahydrofuran cleanly dehalogenated this mixture to give isoadamantane II [yield, 57%; mp (totally submerged sealed capillary) 215-216°]. The pmr spectrum of II exhibits complex absorptions between δ 1.00-2.50. The hydrocarbon gave a molecular ion peak at m/e 136 (relative abundance, 100) with major peaks at m/e 95 (ra, 56), 94 (ra, 77), 93 (ra, 70), 80 (ra, 66), 79 (ra, 95), 67 (ra, 60), 41 (ra, 51). Isotopic analysis is in accord with the empirical formula.



The ester of acid VII (from diazomethane) was reduced with lithium aluminum hydride in ether to the carbinol III [yield, 37%; mp 157-158°; OH stretch 3.02 μ]. On heating in 18N sulfuric acid at 110° for fifteen minutes, III rearranged to the isomeric 3-adamantylcarbinol (X) in 70% yield (8). This transformation most probably occurs via the homoadamantyl carbonium IX. Under the thermodynamically controlled conditions used, the product obtained is the more stable adamantane carbinol X, rather than the 3-homoadamantanol (9).

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2. Analogous contractions have been used in recent preparations of other strained cage systems. See, for example: P. E. Eaton and T. W. Cole, Jr., J. Am. Chem. Soc., 86, 3157 (1964); G. L. Dunn, V. J. DiPasquo and J. R. E. Hoover, Tetrahedron Letters, 3737 (1966); and R. J. Stedman, L. S. Miller and J. R. E. Hoover, Tetrahedron Letters, 2721 (1966); O. W. Webster and L. H. Sommer, J. Org. Chem., 29, 3103 (1964) and reference 1b.

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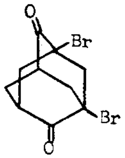
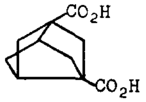
4. It is noteworthy that use of potassium hydroxide as base, a method recently employed for the successful single ring contraction of the analogous 1,4-dibromoadamantane-2,6-dione (i) (1b), in this instance afforded a mixture of the mono and di-Favorskii products, V and VI respectively. This is apparently a reflection of the increased strain of the bisnoradamantane (ii) (the di-Favorskii product of i) relative to the twist-brendane skeletons, resulting in the more facile formation of the latter.



i



ii

5. All new crystalline compounds gave satisfactory elemental analyses and exhibited NMR absorptions (60 mc, $CDCl_3$ solution, TMS internal standard) consistent with their assigned structures. Infrared spectra were taken in Nujol mull. Melting points were taken in sealed capillary tubes (liquid bath). The mass spectrum was carried out by the Morgan-Schaffer Corporation, Montreal.

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8. The product was identified by comparative vapor-phase chromatography, mixed melting points and infrared spectra. Yield determined by VPC.

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