

THE SYNTHESIS OF NORADAMANTANE

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We wish to report the synthesis of the hydrocarbon tricyclo[3.3.1.0<sup>3,7</sup>]nonane (I) and some of its monofunctional derivatives. This hydrocarbon, for which we suggest the trivial name "noradamantane," may be regarded as the next lower homolog of adamantane (II):



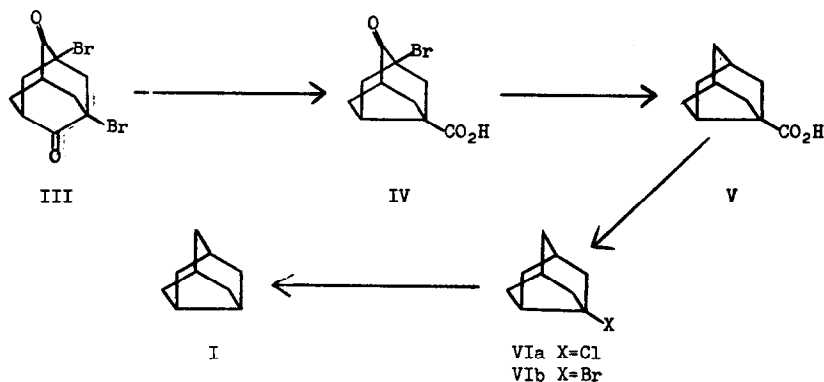
I



II

A few polyfunctional tricyclo[3.3.1.0<sup>3,7</sup>]nonanes have been described by Meerwein, Kiel, Klosgen, and Schloch (1), and by Eakin, Martin, and Parker (2). In both instances, the tricyclic system was formed by direct bridging of the 3 and 7 carbon atoms of appropriate bicyclo[3.3.1]nonanes. In the present case, the noradamantane skeleton was obtained by a Favorskii type ring contraction (3) of 1,5-dibromoadamantane-2,6-dione (III), a compound recently described by Webster and Sommer (4) who doubly contracted it to the tricyclo[3.3.0.0<sup>3,7</sup>]octane system. We were able to carry out the single contraction of III to the corresponding tricyclo[3.3.1.0<sup>3,7</sup>]nonane IV (5). Reductive removal of the remaining keto and bromine functions gave noradamantane carboxylic acid, a convenient intermediate for other monofunctional noradamantanes. The identity of the noradamantane system was supported by ring expansion of the derived carbinol to 1-adamantanol. Elimination of the carboxyl group yielded the parent hydrocarbon.

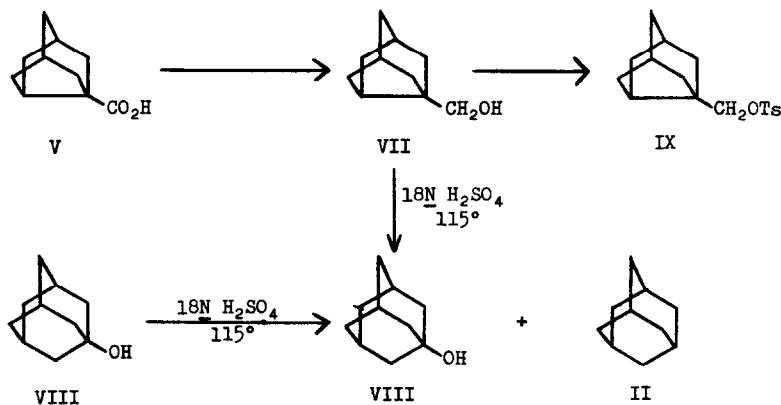
Thus, III, when treated with aqueous ethanolic KOH for two hours at room temperature gave the bromo acid IV [yield, 85%; m.p. 204-205°; C=O stretch, 5.82  $\mu$ , 5.95  $\mu$ ] (6). IV displayed two molecular ion peaks in the mass spectrum, at m/e 258 and m/e 260, consistent with the presence of a single bromine atom.



IV was refluxed with zinc amalgam in concentrated hydrochloric acid for two hours (7) to give the noradamantane carboxylic acid V [yield, 60%; m.p. 106-107°; C=O stretch, 5.92  $\mu$ ]. V, when refluxed with bromine and red mercuric oxide in carbon tetrachloride for one hour (8) gave a mixture of 3-chloro- and 3-bromonoradamantanes, VIa and VIb respectively, in 60% yield. Reductive dehalogenation of this mixture with lithium and t-butyl alcohol in tetrahydrofuran furnished noradamantane (I) [yield, 29%; m.p. 203-204° (totally submerged sealed capillary)]. The NMR spectrum of I had two broad singlets at  $\delta$  2.40 and  $\delta$  2.10 (2H each, methine) and a partially resolved singlet centered at approximately  $\delta$  1.6 (10H, methylene). The hydrocarbon gave a molecular ion peak at  $m/e$  122, with more intense peaks at  $m/e$  81,  $m/e$  79, and  $m/e$  39 and a major peak at  $m/e$  80; the isotopic analysis was in accord with the empirical formula.

Reduction of V with lithium aluminum hydride in refluxing tetrahydrofuran gave alcohol VII [yield, 51%; m.p. 142-144°; OH stretch, 3.05  $\mu$ ]. This, when heated in 18N sulfuric acid at 115° for three hours, gave the expected 1-adamantanol (VIII) accompanied by another major product identified as adamantane (II) (9). To determine whether the adamantane came exclusively from the rearrangement of VII, or from further reaction of 1-adamantanol, the latter was subjected to the same sulfuric acid treatment. Adamantane was indeed formed from 1-adamantanol under these conditions. To date, we have not established the nature of the corresponding oxidation product(s) of this apparent disproportionation reaction.

Tosylate IX [yield, 5% from VII and tosyl chloride in pyridine; m.p. 68-69°;  $\delta$  4.01 (-CH<sub>2</sub>O)] was prepared for solvolytic studies. The results of these studies are reported in an accompanying paper (10).



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#### REFERENCES

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2. M. Eakin, J. Martin and W. Parker, Chem. Commun., 206 (1965).
3. 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).
4. O. W. Webster and L. H. Sommer, J. Org. Chem., **29**, 3103 (1964).
5. Webster and Sommer conjectured that the double contraction proceeded in a stepwise manner and reported, in passing, a crude intermediate, m.p., 197-198°.
6. All new crystalline compounds gave satisfactory elemental analyses and exhibited NMR absorptions (60 mc, CDCl<sub>3</sub> 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 spectra were carried out by the Morgan-Schaffer Corporation, Montreal.
7. A. C. Cope and M. E. Synerholm, J. Am. Chem. Soc., **72**, 5228 (1950).
8. S. J. Cristol and W. C. Firth, Jr., J. Org. Chem., **26**, 280 (1961) and F. W. Baker, H. D. Holtz and L. M. Stock, J. Org. Chem., **28**, 514 (1963).
9. The products were identified by comparative vapor-phase chromatography, mixed melting points and infrared spectra.
10. P. von R. Schleyer and E. Wiskott, Tetrahedron Letters, 2845 (1967).