A Synthesis of 4-Protoadamantanone

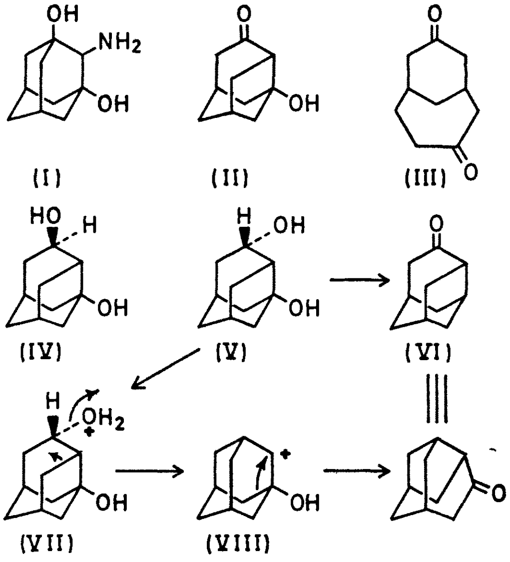
By J. R. ALFORD and M. A. MCKERVEY*
(*Department of Chemistry, The Queen's University, Belfast* BT9 5AG)

Summary 4-Protoadamantanone has been synthesised from 1,3-dihydroxy-2-aminoadamantane in a three-stage sequence involving a protoadamantane–adamantane–protoadamantane rearrangement.

OF all the known C_{10} tricyclic hydrocarbons, adamantane has long been considered the paragon of stability.[1] Nevertheless, the 2-adamantyl cation, as produced in the deamination of 2-aminoadamantane by the phenyltriazine method, undergoes a skeletal rearrangement to the 4-protoadamantyl cation to the extent of *ca.* 7·5%.[2] An analogous rearrangement has been found to occur to a much greater extent in the nitrous acid deamination of 1,3-dihydroxy-2-aminoadamantane (I) and we have used this reaction to develop a synthesis of 4-protoadamantanone.

The hydrochloride of (I) was prepared from 3,7-bicyclo[3,3,1]nonanedione by the method of Stetter and Tacke[3] and treated with sodium nitrite in aqueous acetic acid at 0°. The product, m.p. 240—243°, obtained in 56% yield after purification by chromatography, sublimation, and recrystallisation was characterised as 8-hydroxytricyclo[4,3,1,$0^{3,8}$]decan-4-one (II) on the basis of the analytical data and the following spectral data: the i.r. spectrum (KBr) exhibited strong absorptions at 3400 and 1700 cm^{-1} and the n.m.r. spectrum (100 MHz, CD_3SOCD_3) contained signals at τ 4·85 (1H, s, hydroxy-proton), 7·60—7·70 (3H, m, C-3 and C-5), and 7·70—8·80 (10H, m). The deamination reaction also gave trace amounts of 3,8-bicyclo[4,3,1]decanedione (III) which could be converted into (II) thermally.

In order to complete the synthesis of 4-protoadamantanone (VI) from (II) it was necessary to remove the hydroxy-group at C-8. This was achieved as follows. Lithium aluminium hydride reduction of (II) gave two diols in the ratio *ca.* 3 : 1. Separation was effected by adsorption chromatography over alumina and the major isomer, m.p. 208·5—210°, was assigned configuration (IV) on the basis of its n.m.r. spectrum (CD_3SOCD_3). The >C*H*O– proton on C-4 appeared as a multiplet centred at τ 5·95. The pattern reveals appreciable coupling of this proton to another proton ($J_{4,5}$ 9·5 Hz) and a Dreiding model of (IV) shows a dihedral angle relationship approaching 180° between 4-H and one of the protons on C-5 which is consistent with the large observed coupling constant. The minor isomer (V), m.p. 302—304°, was not amenable to analysis by n.m.r. since the >CHO– proton appeared as a broad, poorly resolved, multiplet centred at τ 6·05.



A Dreiding model of (V) reveals a nearly perfect ***trans***-relationship between the C–O bond and C-2–C-3 bond and it was expected that ionisation at C-4 would initiate a sequence of rearrangements involving first of all migration of the C-2–C-3 bond with restoration of the adamantane skeleton in the form of the 1-hydroxy-2-adamantyl cation (VIII), followed by a second bond shift, regenerating the protoadamantane skeleton as shown in the Scheme, (V) → (VII) → (VIII) → (VI). In the event, brief treatment of (V) with hot 5N-sulphuric acid yielded a saturated ketone (75% yield), m.p. 205—208°, (2,4-dinitrophenylhydrazone, m.p. 193—194·5°), which has been assigned the 4-protoadamantanone structure (IV) on the basis of the analytical and spectral data: mass spectrum *m/e* 150 (M^+, 100%); i.r. (CCl_4): 1723 and 1714 cm.$^{-1}$ (lit.[2] 1729 and 1719 cm^{-1}); n.m.r. ($CDCl_3$): complex multiplets between τ 7·15 and 8·70. Confirmatory evidence was obtained by comparison of the physical and spectral data with those of 4-protoadamantanone prepared by independent methods.[2,4]

We thank Professors M. C. Whiting and P. von R. Schleyer for kindly providing us with the physical and spectral data for 4-protoadamantanone synthesised in their laboratories. J. R. A. acknowledges financial support from the Northern Ireland Ministry of Education.

(*Received, April 8th,* 1970; *Com.* **494.**)

---

[1] For a review see R. C. Fort, jun., and P. von R. Schleyer, *Chem. Rev.*, 1964, **64**, 277.

[2] M. L. Sinnott, H. J. Storesund, and M. C. Whiting, *Chem. Comm.*, 1969, 1000.

[3] H. Stetter and P. Tacke, *Chem. Ber.*, 1963, **96**, 694.

[4] P. von R. Schleyer and D. Lenoir, personal communication.