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FUNCTIONALISATION REACTIONS OF DIAMANTANE

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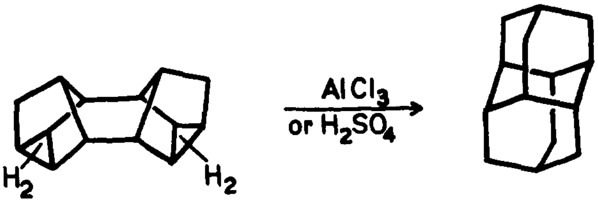
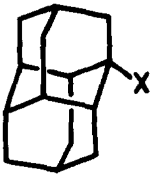
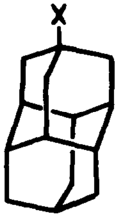
The report[1] of a substantial improvement in the synthesis of diamantane(II), the next higher homologue of the diamondoid hydrocarbon series, and of some functionalisation reactions[2] of this interesting molecule, prompt us to describe our recent experiments with tetrahydro-Binor-S(I)[3], the product of as yet undetermined structure of hydrogenolytic cleavage of both cyclopropane rings of the readily available norbornadiene dimer Binor-S[4].



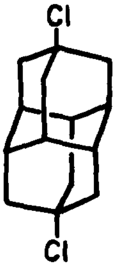
(I) (II)



(IIIa) X=Cl
(IIIb) X=OH



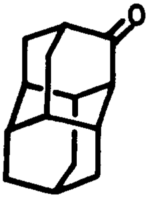
(IVa) X=Cl
(IVb) X=OH



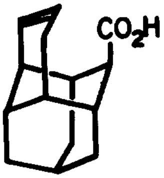
(V)

Aluminium chloride reacts with (I) in boiling dichloromethane, yielding after 12 hr. a product composed of >90% diamantane; the pure compound, m.p. 250°, can be obtained in ca. 70% yield after purification by chromatography over alumina and sublimation. This profound structural change occurs so readily and is so highly selective that in several instances we have even found the isolation and purification of diamantane unnecessary prior to the application of functionalisation procedures developed earlier for adamantane and 1-methyladamantane[5]. For example, treatment of a solution of (I) in dichloromethane containing aluminium chloride after 12 hr. with acetyl chloride at 0° gave a 1:1 mixture of 1-chlorodiamantane (IIIa), m.p. 250.5-252.5°, and 4-chlorodiamantane (IVa) m.p. 75.5-76.5°, in ca. 80% yield. Hydrolysis of the mixture with hydrochloric acid in dimethylformamide gave equal amounts of diamantan-1-ol (IIIb), m.p. 292.5-294.0°, and diamantan-4-ol (IVb), m.p. 206-208°, which were separable by chromatography over alumina. Functionalisation of the 4 position of diamantane in the chlorination reaction is particularly useful since until now 4-substituted derivatives were available only through a roundabout and cumbersome route; the 1:1 product ratio is also the equilibrium ratio at 0° since separate experiments in which (IIIa) and (IVa) were individually treated with aluminium chloride in dichloromethane gave mixtures of approximately equal amounts of the two. Similarly, treatment of either (IIIb) or (IVb) with 98% sulphuric acid for 15 min. at 0° gave mixtures of the two alcohols in the ratio ca. 1:1. The selective introduction of two chlorine substituents was also readily achieved starting with tetrahydro-Binor-S: the rearrangment procedure was conducted as before, paraformaldehyde was then added at 0°[5] and the product isolated in good yield was 4,9-dichlorodiamantane (V), m.p. 308-310°.

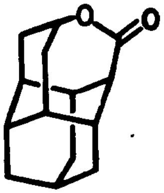
It is generally believed[6] that only strong Lewis acids of the aluminium halide type are capable of catalysing the rearrangement of strained polycyclic hydrocarbons of ten or more carbon atoms into diamondoid structures, but that sulphuric acid, though effective in the interconversion of many substituted adamantanes[7], is catalytically ineffective in such rearrangements. But the remarkable ease of diamantane formation is dramatically illustrated by the reaction of (I) with 96% sulphuric acid at 70°: diamantane sublimes from the reaction flask within 30 min.[8], and at slightly higher temperatures and longer times diamantanone (VI), m.p. 248-249°, is produced in 5% yield; up to 60% yields of (VI) could be realised from pure diamantane in 96% sulphuric acid at 75° for 7 hr.[9].



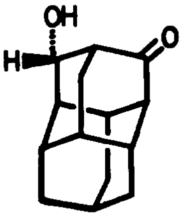
(VI)



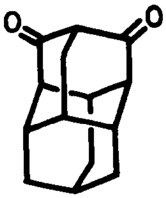
(VII)



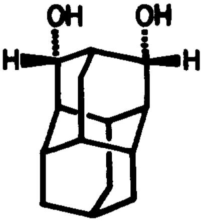
(VIII)



(IX)



(X)



(XI)

Several interesting difuntionalised diamantanes can be prepared from diamantanone via the unsaturated acid (VII). Exposure of (VI) to sodium azide in methanesulphonic acid at 0° followed by 50% aqueous sodium hydroxide gave (VII), m.p. 215-216°, in 16% yield[10,11]. In 96% sulphuric acid at 20° (VII) cyclised to the lactone (VIII), m.p. 275-276°, in 70% yield, whereas in 50% sulphuric acid at 90° for 4 hr. the major product (75%) was 3a-hydroxydiamantan-5-one (IX)[12], m.p. 256-258°. The hydroxyl group was assigned the axial configuration since reduction of (IX) with lithium aluminium hydride gave a diol, m.p. 272-273°, which must be the diaxial isomer (XI) because of the strong intramolecular hydrogen bonding exhibited by its infrared spectrum at high dilution in carbon tetrachloride. Oxidation of (IX) gave diamantane-3,5-dione (X), m.p. 258-260°[13].

Acknowledgement. We thank the Northern Ireland Ministry of Education for postgraduate grants to D. F. and D. E. J.

References and Footnotes

(1) T. M. Gund, V. Z. Williams, Jr., E. Osawa and P. von R. Schleyer, Tetrahedron Letters, 3877 (1970).

(2) T. M. Gund, M. Nomura, V. Z. Williams, Jr., and P. von R. Schleyer, Tetrahedron Letters, 4875 (1970).

(3) The hydrogenolysis was performed in glacial acetic acid at 20° using Adam's catalyst and a hydrogen pressure of 3 atmos.; g.l.p.c. analysis indicated that the product was a single isomer.

(4) G. N. Schrauzer, B. N. Bastian and G. A. Fosselius, J.Amer.Chem.Soc., 4890 (1966); G. N. Schrauzer, R. K. Y. Ho and G. Schlesinger, Tetrahedron Letters, 543 (1970).

(5) M. A. McKervey, D. Grant and H. Hamill, Tetrahedron Letters, 1975 (1970).

(6) Cf. R. C. Fort, Jr., and P. von R. Schleyer, Chem.Rev., 64, 277 (1964).

(7) P. von R. Schleyer, L. K. M. Lam, D. J. Raber, J. L. Fry, M. A. McKervey, J. R. Alford, B. D. Cuddy, V. G. Keizer, H. W. Geluk and J. L. M. A. Schlatmann, J.Amer.Chem.Soc., 92, 5246 (1970).

(8) Treatment of exo-2,3-tetramethylenenorbornane with hot 96% sulphuric acid gives a mixture of 1-methyladamantane, 1-methyladamantan-2-one and 5-methyladamantan-2-one, M. A. McKervey, unpublished observations.

(9) Cf. H. W. Geluk and J. L. M. A. Schlatmann, Tetrahedron, 24, 5361 (1968).

(10) The mechanism of a similar reaction with adamantanone has been discussed by M. A. McKervey, D. Faulkner and H. Hamill, Tetrahedron Letters, 1971 (1970); see also T. Sasaki, E. Eguchi and T. Toru, J.Amer.Chem.Soc., 91, 3390 (1969).

(11) The major product was a lactam (the normal Schmidt reaction product).

(12) The mechanism of a similar reaction with endo-6-bicyclo[3.3.1] non-6-enecarboxylic acid is discussed in ref. 10.

(13) All compounds gave n.m.r., i.r., and mass spectral data in full accord with the proposed structures.