Tetrahedron Letters No.50, pp. 5165-5168, 1968. Pergamon Press. Printed in Great Britain.

ADAMANTANE REARRANGEMENTS. THE BEHAVIOUR OF 2-METHYL-2-ADAMANTANOL IN CONCENTRATED SULPHURIC ACID

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(Received in UK 2 September 1968; accepted for publication 16 September 1968)

In recent years the structure-reactivity relationships of bridgehead ions have received attention and a number of investigations have concentrated on the nature of the 1-adamantyl cation (1). Recently Geluk and Schlatmann (2) described the sulphuric acid catalysed interconversion of 1- and 2-adamantanol via a process involving a 1,2-hydride shift to the tertiary or secondary cation whereas we have been investigating the situation in which the 2-adamantyl cation is also tertiary. We report here a new rearrangement involving the 2-methyl-2-adamantyl cation. 2-Methyl-2-adamantanol (I) (3) was chosen as a source of this ion; the reactions studied and the compounds isolated by ether extraction and adsorption chromatography after dilution with water were as follows:

(a) (I) 0.32 molar in 98% sulphuric acid for 5 minutes at 50°C gave 1-methyladamantane (II) (4) and 2-methyladamantane (III) (3) in the ratio 10:1, three compounds tentatively identified as dimeric ethers (total 38%), 3-methyl-1-adamantanol (IV) (36%) (5), and 4-methyladamantanone (V)* (ca. 3%) m.p. 126-7°; IR(KBr): 1720 cm^{-1}; n.m.r. $(CCl_4)\tau$: sharp singlet at 9.12 (3H, bridgehead CH_3), broad singlet at 7.59 (2H, α to C=O), and a multiplet at 7.8-8.4 (11H, remaining adamantyl protons) .

(b) (I) 0.32 molar in 98% sulphuric acid for 1 minute at 0° gave (III) (16%), starting material (5%), 2-methyl-1-adamantanol (VI)* (22%), m.p. 211-3°, and 4-methyl-1-adamantanol (VII)* (47%), m.p. 163-8°. The structures of these two new alcohols were deduced from the following observations. They were not affected by chromic acid in acetone and their n.m.r. spectra (DMSO) showed sharp singlets for the hydroxy hydrogens, indicating that they were tertiary alcohols; (VI) n.m.r. $(CCl_4)\tau$: a doublet at 9.01 (3H, methyl group) and a multiplet at 7.75-8.75 (15H,

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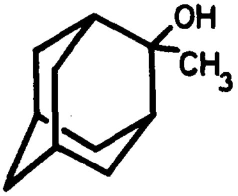
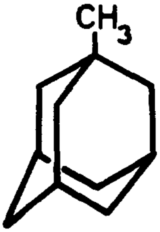
* Satisfactory analytical values were obtained.



(I)



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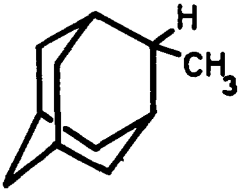

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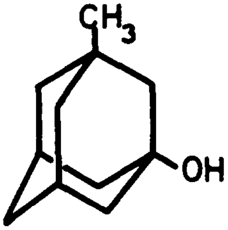

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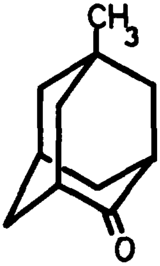

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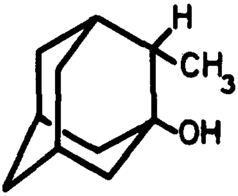

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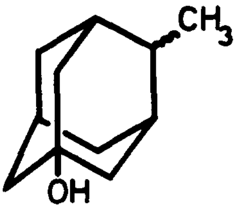
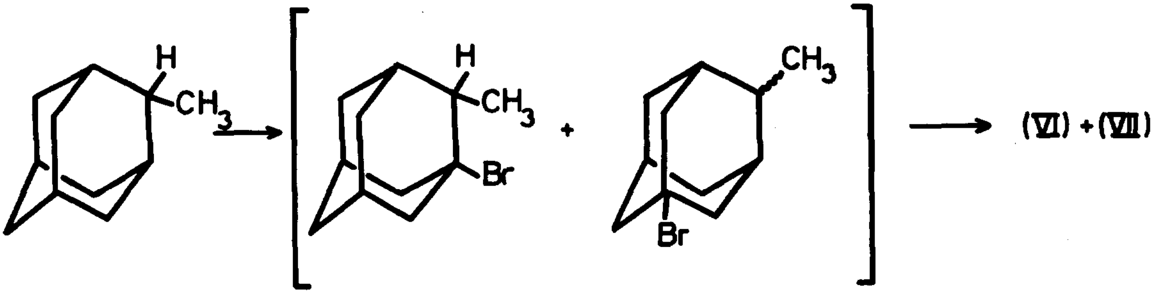


(VII)

hydroxyl and remaining adamantyl protons). (VII) n.m.r. (CCl_4)τ: two doublets at 8.97 and 8.99 (3H, methyl group) and a multiplet at 7.75-8.75 (15H, hydroxyl and remaining adamantyl protons). The two methyl doublets (ratio ca. 1:1) in the spectrum of (VII) indicated the presence of both cis- and trans-isomers and glpc analysis (20 m. 5% Apiezon L) of the trifluoroacetates gave the isomer ratio as 1:1. Furthermore, adsorption chromatography of (VII) on alumina gave one of the isomers (VIIa)*, m.p. 184-6°, of > 98% isomeric purity. Additional support for structures (VI) and (VII) was obtained from the synthetic sequence below.



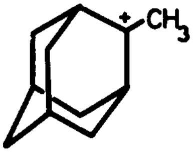
2-Methyladamantane was treated with boiling bromine for 4 hr. and the resulting bromide mixture was hydrolysed (without purification) in aqueous potassium carbonate. Adsorption chromatography then gave (VI) and (VII) in 42 and 22% yields, respectively, after purification by crystallisation and sublimation. The isomer ratio of (VII), obtained in this way, was also 1:1.

(c) (I) or (IV) in 98% sulphuric acid for 5 hr. at 65° gave (V) in ca. 10% yield.

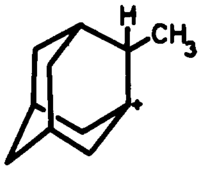
(d) (VI) or (VII) in 98% sulphuric acid for 1 minute at 25° gave a 1:2 mixture of the two, together with small amounts of (II), (III), and (IV). With longer reaction times, the concentrations of (VI) and (VII) decreased and (IV) and (II) were the major products after 40 minutes.

(e) (VIIa) in 98% sulphuric acid for 1 minute at 0° gave (VII)(isomer ratio 1:1) and (VI).

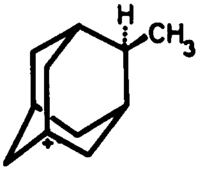
Whatever the precise mechanism, a clear sequence of events emerges from these experiments. The 2-methyl-2-adamantyl cation (VIII) is presumably the first intermediate; in spite of its planar tertiary structure, it isomerises rapidly to an equilibrium mixture of all the other tertiary cations [(+)- and (-)-(IX), and the cis-trans-pair (X) and (XI)] derived from 2-methyladamantane. A 1,2-methyl shift on cation (IX) could give a secondary adamantyl cation which would be expected to isomerise rapidly to the bridgehead ion (XII) via a 1,2-hydride shift.



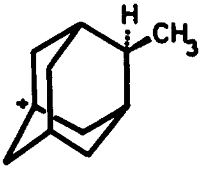
(VIII)



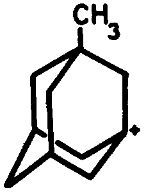
(IX)



(X)



(XI)



(XII)

It may be that reversible isomerisations to secondary adamantyl cations via 1,2-hydride shifts are the mechanistic links between the ions (IX), (X), and (XI). The isolation of small amounts of 4-methyladamantanone supports this view since it can result from oxidation of the corresponding secondary alcohol. It is also in accord with the observation that 1-adamantanol is oxidised to adamantanone by concentrated sulphuric acid (2). The formation of 1- and 2-methyladamantane may result from a disproportionation reaction; this possibility is being investigated.

Acknowledgement: We thank the Northern Ireland Ministry of Education for Postgraduate Grants to J.R.A. and E.J.F.R.

REFERENCES

1. R. C. Fort, Jr., and P. von R. Schleyer, Advances in Alicyclic Chemistry (Edited by H. Hart and G. J. Karabatsos) Vol. I, p.283. Academic Press. New York, London (1966).
2. H. W. Geluk and J.L.M.A. Schlatmann, Tetrahedron, 24, 5361 (1968).
3. P. von R. Schleyer and R. D. Nicholas, J. Am. Chem. Soc., 83, 182 (1961).
4. H. Stetter, M. Schwarz, and A. Hirschhorn, Ber., 92, 1629 (1959).
5. R. C. Fort, Jr., and P. von R. Schleyer, J. Org. Chem., 30, 789 (1965).