Journal of

The Chemical Society,

Chemical Communications

NUMBER 6/1973 **21 MARCH**

Novel Synthesis of 2-Oxa-adamantane

By NADEZHDA V. AVERINA and NICKOLAY S. ZEFIROV*
(*Department of Chemistry, Moscow University, Moscow, W-234, U.S.S.R.*)

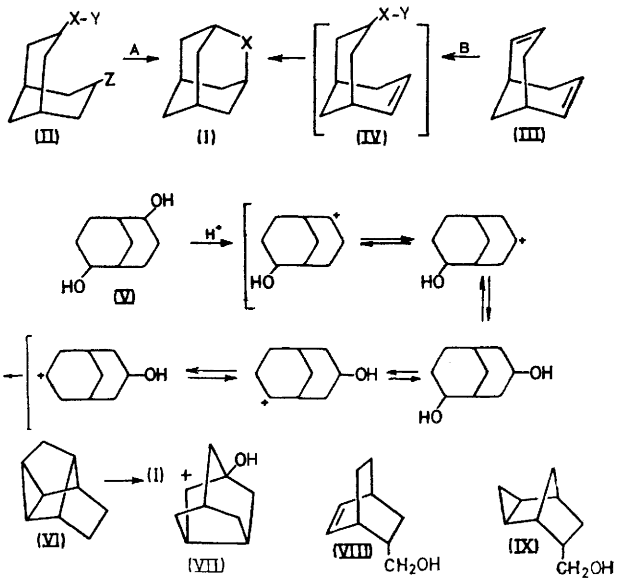
Summary Treatment of bicyclo[3,3,1]nonane-2,6-diol with concentrated sulphuric acid afforded 2-oxa-adamantane in 35—40% yield.

THE considerable interest in adamantane and its derivatives[1] makes the synthesis of simple hetero-analogues important. Existing routes to 2-oxa-adamantane (I; X = O) and its derivatives[2–6] usually involve several steps, and starting materials which are not always readily available. Most routes depend on cyclisation of 3,7-difunctional bicyclo[3,3,1]nonanes[2] (II, route A), or electrophilic addition to bicyclo[3,3,1]nona-2,6-diene (III, route B),[3,5] probably *via* the 3-monofunctional derivatives (IV). Recently a synthesis of (I) from adamantan-2-ol has been described.[6]

Here we report a novel synthesis of 2-oxa-adamantane from bicyclo[3,3,1]nonane-2,6-diol (V) which is readily available from 'Meerwein's ester'.[3,5]

We considered that treatment of the above diol with acid should give the 2-carbonium ion and thence, *via* a 1,2-hydride shift, the 3-carbonium ion (*cf.* refs. 7 and 8) and so the 3-hydroxy-derivative. Various diols, enols, and cyclic ethers, *e.g.* (I), oxatwistane, and oxaprotoadamantane, are possible products of the reaction,[8] but as only compound (I) is stable in strong acid, we expected to obtain (I) preferentially by adjustment of the acidity of the medium. In agreement, we have found that treatment of compound (V) with concentrated sulphuric acid produced 2-oxa-adamantane (I; X = O) in satisfactory yield.

Thus the diol (V) (10 g) was gradually added to stirred 95% sulphuric acid (100 ml) at room temperature. After 2 h the mixture was poured on to ice and extracted with ether. The 2-oxa-adamantane (I; X = O) (3·5—4 g) was purified by chromatography[4] and/or sublimation, and had m.p. 228°. It was identified by its n.m.r. spectrum and comparison (i.r., g.l.c.) with samples[4,5] kindly provided by Professor H. Stetter.



The formation of compound (I) can be rationalised as involving formation of carbonium ions and 1,2-hydride shifts. The reaction requires an optimum concentration of H_2SO_4; an increase (8% oleum) or decrease (75%) of this results in a sharp drop in the yield of (I). Professor P. von R. Schleyer [to whom we are indebted for a gift of $Eu(fod)_3$ and discussions] kindly informed us that treatment of hydrocarbon (VI) with concentrated sulphuric acid yielded (I) (*ca.* 10%) together with alcohol (VII). Formation of the latter represents the other way in which the carbonium species can become stabilised in the acid medium. We have found that the alcohols (VIII) and (IX) do not produce (I), but different isomeric compounds $C_9H_{14}O$.

(*Received*, 18*th December* 1972; *Com.* 2101.)

---

[1] R. C. Fort and P. v. R. Schleyer, *Chem. Rev.*, 1964, **64**, 277; R. S. Bingham and P. v. R. Schleyer, *Fortschr. Chem. Forsch.*, 1971, **18**, 1; H. Stetter, *Angew. Chem.*, 1954, **66**, 217; 1962, **74**, 361.

[2] H. Stetter and J. Meyer, *Angew. Chem.*, 1959, **71**, 430; *Chem. Ber.*, 1959, **92**, 2664; H. Stetter and P. Tacke, *Angew. Chem.*, 1962, **74**, 354; *Chem. Ber.*, 1963, **96**, 694; H. Stetter, P. Tacke, and J. Gärtner, *ibid.*, 1964, **97**, 3480; 1966, **99**, 1435; A. R. Gagneux and R. Meier, *Tetrahedron Letters*, 1969, 1365.

[3] H. Stetter and F. Schwartz, *Chem. Ber.*, 1968, **101**, 2464.

[4] N. S. Zefirov and N. V. Averina, *Zhur. org. Khim.* (*Russ. J. Org. Chem.*), 1969, **5**, 190, 1991.

[5] N. S. Zefirov, V. A. Tartakovsky, and N. V. Averina, *Zhur. org. Khim.* (*Russ. J. Org. Chem.*), 1971, **7**, 504.

[6] R. M. Black, G. B. Gill, and D. Hands, *J.C.S. Chem. Comm.*, 1972, 311.

[7] W. Parker and J. R. Stevenson, *Chem. Comm.*, 1969, 1289.

[8] J. P. Schaefer and L. M. Honig, *J. Org. Chem.*, 1968, **33**, 2655.