A Convenient Synthesis of Adamantanone

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ADAMANTANE derivatives substituted at a secondary carbon atom have been difficult to synthesize.[1] We have now found a new and convenient method for the preparation of adamantanone, a useful intermediate in the synthesis of such compounds, in yields of 70—80%. When a 0·8 molar solution of 1-hydroxyadamantane in concentrated sulphuric acid (preferably 96%) is stirred at 75°, adamantanone and adamantane are formed. The adamantane will have disappeared completely after 4—5 hr. The reaction mixture is poured on to ice and extracted with ether. The yield is 84% of crude adamantanone. The product can also be isolated by steam distillation, immediately following the quenching of the reaction, when a 72% yield of pure adamantanone (m.p. 280—282°) can be obtained.

Five different reactions can be distinguished:

(i) Isomerisation of 1-hydroxyadamantane to 2-hydroxyadamantane, which is clearly due to a hydride-transfer reaction. The formation of small amounts (< 1%) of the secondary alcohol was demonstrated by g.l.c. and mass spectrometry.

(ii) Disproportionation reaction of the 2-hydroxyadamantane, which is evidently the intermediate, to adamantane and adamantanone.

(iii) Disproportionation reaction of 1-hydroxyadamantane itself to adamantane and 1,3-dihydroxyadamantane.[2] This diol was proved not to be an intermediate in the formation of adamantanone.

(iv) Oxidation of adamantane to 1-hydroxyadamantane by means of sulphuric acid.

(v) Oxidation of 1-hydroxyadamantane, probably *via* 2-hydroxyadamantane, to adamantanone by means of sulphuric acid. The direct oxidation of an alcohol to a ketone by means of sulphuric acid alone appears to be an exceptional reaction and, in our opinion, has not been reported previously. It may well be restricted to those (secondary) alcohols in which skeletal rearrangements are unlikely.

As might be expected, all these reactions depend on the sulphuric acid concentration. Further details will be published later.

(*Received, March 20th,* 1967; *Com.* 267.)

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[2] H. Stetter and C. Wulff, *Chem. Ber.*, 1960, **93**, 1366.