Reactions of the 1-Adamantyl-vinyl Cation in Sulphuric Acid

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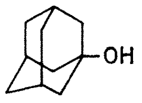
Summary The adamantyl cation with acetylene in sulphuric acid is shown to give an intermediate sulphate which is the precursor of 1-adamantylacetaldehyde or of 1-methylhomoadamantan-2-one, depending on the amount of water present: with carbon monoxide a retrogression is observed giving adamantane-1-carboxylic acid, and in the presence of bromide the acetylene reaction leads to adamantyl methyl ketone.

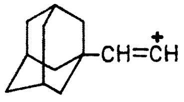
ADAMANTAN-1-OL (I) with acetylene in *ca.* 90% sulphuric acid gives[1] in high yield a product comprising 1-adamantylacetaldehyde (III), and 1-methylhomoadamantan-2-one (V). These products may be separated on silica gel, R_F: (III) 0·63, (V) 0·41 in benzene, or by g.l.c. on polyethylene glycol succinate at 150°, retention: (III) 21·6, (V) 27·2 min, and are characterised by their spectral data: (III) ν_{CO} 1720 cm^{-1}; τ 0·15 (t, 1H, J 3Hz), 7·92 (d, 2H, J 3 Hz): (V) ν_{CO} 1693 cm^{-1}; τ 9·01 (s, 3H), 7·47 (m, 2H).

Formation of (III) and (V) has been rationalised[1] in terms of a vinyl cation intermediate (II) which gives (III), and an isomeric cation (IV) which is rearranged and hydrated to yield (V). Close examination of the reaction shows, however, that this rationalisation is inadequate.

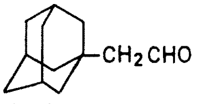
The reaction mixture from adamantan-1-ol (1g) and acetylene in 98% sulphuric acid (25 ml) showed no vinyl proton signals in the n.m.r., but new bands at τ *ca.* 8·6 and 5·7. These signals are not attributable to (I) or (III) in sulphuric acid solution, and the τ 8·6 band was much too strong to be due to the methyl group of (V) which comprises only 10% of the reaction product. Moreover, the τ 8·6 signal was very weak in the spectrum of the reaction mixture formed in D_2SO_4, which when diluted with H_2O gave a product $AdCD_2CHO$ (Ad = adamantyl), *m/e* 180, showing a very weak τ 7·92 band, and the aldehyde proton effectively as a singlet. We therefore inferred that the cation (II) is rapidly trapped by sulphuric acid. This conclusion could be verified. The product of reaction in methanesulphonic acid gave some 70% of a methanesulphonate, *m/e* 256, showing 1H signals at τ 3·57 and 4·42 as doublets, *J* 12 Hz, and a 3H singlet at τ 6·93, *i.e.* corresponding to $AdCH{=}CHOSO_2Me$. We therefore suggest for sulphuric acid solution a sequence: (II) → $AdCH{=}CHOSO_2OH \longrightarrow AdCH_2CH(OSO_2OH)_2$. Certainly the solution contains a very labile intermediate since carbon monoxide passed into the sulphuric acid solution after complete reaction of (I) with acetylene in 98% H_2SO_4 gave in place of (III), adamantane-1-carboxylic acid in 70% yield. Thus the acetylene reaction intermediate may undergo retrogression: $AdCH_2CH(OSO_2OH)_2 \longrightarrow Ad^+ + CH_2{=}CHOSO_2OH + HSO_4^-$; $Ad^+ + CO + H_2O \longrightarrow AdCO_2H$.



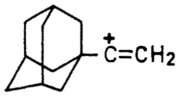
(I)



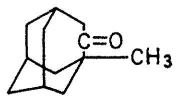
(II)



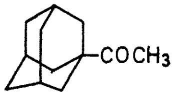
(III)



(IV)



(V)



(VI)

Similarly after complete reaction of (I) with acetylene in 98% H_2SO_4, addition of water in small amount gave (III) in smaller yield and an increased yield of (V). This more aqueous reaction mixture also showed definite signals at τ 8·69 and 7·25 attributable to the CH_3 and CH_2CO protons of (V), the signals being slightly shifted, and broadened, in sulphuric acid solution. Thus (V) arises *via* hydrolysis of an intermediate sulphate, and it was demonstrated by g.c. product analysis that the proportion of (V) increases with the water content of the sulphuric acid (see Table 1).

An intermediate ion (IV) would be expected to lead to formation of some adamantyl methyl ketone and the absence of this product in the reaction indicates that the rearrangement leading to (V) is a synchronous process. However, from 1-bromoadamantane[2] with acetylene in 98% H_2SO_4, adamantyl methyl ketone, *m/e* 178, τ 7·99 (s, 3H), is obtained in 75% yield with only 8% of (III) and (V). The n.m.r. spectrum of the reaction mixture showed a sharp signal at τ 7·25 also seen in the spectrum of (VI) in H_2SO_4, *i.e.* (VI) is formed in the reaction mixture and not subsequently by hydrolysis when water is added. Thus intermediate ions (II) and (IV) give no indication of the kinetic products of reaction which are determined rather by the available nucleophilic addends present; H_2SO_4 gives mainly (III) *via* an intermediate which with water yields (V), and with carbon monoxide undergoes displacement to yield adamantanecarboxylic acid. The mode of formation of (V) from bromoadamantane is not clear, but it is possible that in sulphuric acid Br^- ion acts as a base: $AdCH{=}\overset{+}{C}H \rightarrow AdC{\equiv}CH + HBr$, whence $Ad\overset{+}{C}{=}CH_2 \longrightarrow$ (VI), but other routes may also be envisaged.

TABLE 1

H_2SO_4 w/w %	98	92·5	90	87·6	85·5
(III) %	89·1	71·2	66·0	60·0	57·0
(V) %	10·9	28·8	34·0	40·0	43·0

Using substituted acetylenes, $RC{\equiv}CH$, with adamantanol and 98% sulphuric acid the scope of the reactions has been extended to the preparation of ketones $AdCH_2COR$, characterised as in Table 2. The structures were established by the fragment ion *m/e* 177 = $AdCH_2\overset{+}{C}O$.

TABLE 2

R	$AdCH_2COR$		
Ph	*m/e* 254,105, 77	ν_{CO} 1674 cm^{-1}	$-CH_2-CO$ 7·45 (s)
Pr^n	220, 177, 43,	1710	7·98
$n-C_6H_{13}$	262, 177, 85	1710	7·97

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[1] K. Bott, *Tetrahedron Letters*, 1969, 1747; *Chem. Comm.*, 1969, 1349.

[2] *Cf.* T. Sasaki, S. Eguchi, and T. Torn, *Chem. Comm.*, 1968, 780.