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The Reaction of Carbonium Ions in Sulphuric Acid with Acetylene and Substituted Acetylenes

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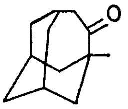
Treatment of adamantan-1-ol in sulphuric acid with acetylene leads to 1-adamantylacetaldehyde or 1-adamantyl methyl ketone as major product (together with 1-methylhomoadamantan-2-one), depending on the experimental conditions (acid concentration and reaction time). The reactions of the adamantyl, diphenylmethyl, and norbornyl cations with acetylene and substituted acetylenes have been examined.

THE known reactions of carbonium ions with carbon monoxide[1] and with nitriles[2] have been extended to include reaction with 1,1-dichloroethylene,[3] and, in the case of the adamantyl cation, also with acetylene.[4]

In attempting to generalise the acetylene reaction we first re-examined the reaction of adamantyl cation with acetylene, since the reaction product appeared to depend on the source of the adamantyl cation, *viz.* adamantan-1-ol–sulphuric acid–acetylene is reported[4] to give the aldehyde (1) together with 1-methylhomoadamantan-2-one (2), whereas from adamantyl bromide–sulphuric acid–acetylene adamantyl methyl ketone (3) has been isolated.[5]

Adamantanol in 98% sulphuric acid reacts with acetylene rapidly to give (90% total yield) 1-adamantylacetaldehyde (1) and the homoketone (2), separable by t.l.c., in a ratio of 9 : 1. The corresponding reaction with adamantyl bromide gave methyl adamantyl ketone (3), together with a small amount of the homoketone (2). The latter reaction, however, was much slower; adamantyl bromide could be detected (g.l.c.) in the reaction mixture after *ca.* 5 h.

$\mathrm{AdCH_2{\cdot}CHO}$
(1)



(2)

AdCOMe
(3)

Ad = adamantyl

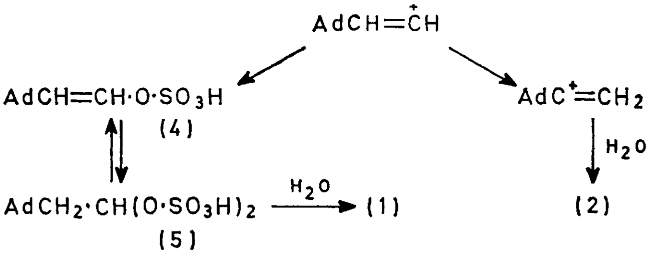
These results show that the simple sequence: $\mathrm{Ad^+ \longrightarrow AdCH{:}CH^+ \longrightarrow AdC{=}CH_2 \longrightarrow}$ (methylenehomoadamantyl)$^+$ is an inadequate reaction scheme, and the effective absence of compound (3) from the adamantanol reaction product suggested that the rearrangement: $\mathrm{AdC^+{=}CH_2 \longrightarrow}$ (methylenehomoadamantyl)$^+$ is fast relative to addition of the nucleophile. We therefore attempted to establish the nature of this nucleophile, and the source of the oxygen in the reaction products, by varying the sulphuric acid strength.

The results in the Table are taken to indicate that the aldehyde (1) originates from reaction of the first formed cation, $\mathrm{AdCH{:}\overset{+}{C}H}$, with sulphuric acid, and is released when the reaction is quenched, whereas methyl homoadamantanone (2) arises from reaction of the rearranged methylenehomoadamantyl cation with water. This leads to the reaction Scheme 1.

Relative % of reaction products * from AdOH + C_2H_2 at varying concentrations of sulphuric acid

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

* The total yield falls with % H_2SO_4. † Separated by t.l.c. or g.l.c.; see Experimental section.



SCHEME 1

The intervention of a sulphate adduct such as (4) or (5) was strongly supported by the results of carrying out the adamantanol–acetylene reaction in methanesulphonic acid as reaction medium, which gave in 70% yield a liquid product, $C_{13}H_{20}SO_3$, showing n.m.r. signals at τ 3·57 (1H, d, *J* 12 Hz), 4·42 (1H, d, *J* 12 Hz), 6·93 (3H, s), and 8·0 and 8·3 (15H), and mass spectral fragmentation consistent with structure (6) (Scheme 2).

It was also found that adamantanol with acetylene in [$^2H_2$]sulphuric acid gives a [$^2H_2$]aldehyde, $\mathrm{AdCD_2{\cdot}CHO}$, showing in the n.m.r. no τ 7·92 absorption, the formyl proton signal appearing as a broadened singlet. Thus both CH_2 protons of $\mathrm{AdCH_2{\cdot}CHO}$ appear to be derived from the acid medium. The n.m.r. spectrum of the adamantanol–sulphuric acid–acetylene reaction mixture

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[1] J. Falbe, 'Synthesen mit Kohlenmonoxyd,' Springer Verlag, Berlin, 1967; H. Hoch, *Brennstoff Chem.*, 1955, **36**, 321.

[2] L. I. Krimen and D. J. Coto, *Org. Reactions*, 1969, **17**, 213.

[3] K. Bott and H. Hellmann, *Angew. Chem. Internat. Edn.*, 1966, **5**, 870; K. Bott, *ibid.*, 1967, **6**, 946; K. Bott, *Chem. Ber.*, 1970, **103**, 3650.

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

[5] T. Sasaki, S. Eguchi, and T. Tora, *Chem. Comm.*, 1968, 780.

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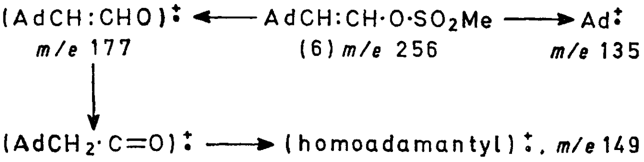
showed signals at τ 5·70 (1H) and 8·60 (2H), the latter being absent in the spectrum of the reaction mixture in [$^2H_2$]sulphuric acid. These results therefore provide some general support for the proposed reaction scheme.



SCHEME 2

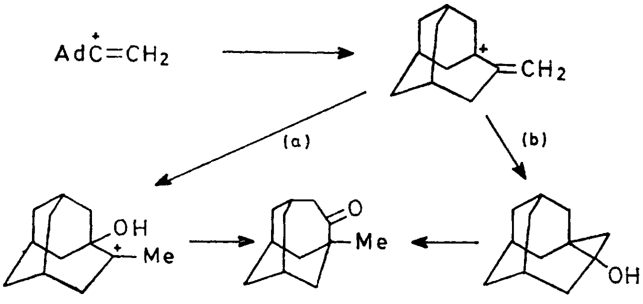
However, adamantanol in sulphuric acid treated successively with acetylene and with carbon monoxide gave adamantane-1-carboxylic acid in high yield; the sequence leading to the sulphate intermediates (4) and (5) is therefore regarded as reversible:

$$\mathrm{AdCH{:}CH{\cdot}O{\cdot}SO_3H} \xrightarrow{H^+} \mathrm{Ad^+ + CH_2{:}CH{\cdot}O{\cdot}SO_3H}.$$

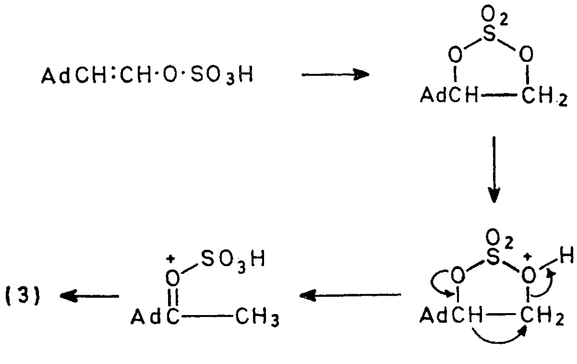
These results led us to examine the use of a less nucleophilic acid catalyst. Adamantanol with acetylene in boron trifluoride–ether complex as solvent gave methylhomoadamantanone as sole product, in support of our general conclusions.

Rearrangement leading to 1-methylhomoadamantan-2-one may be represented[6] as in (a), or (less likely) (b) (Scheme 3), or by a process of fragmentation and re-cyclisation. We have no evidence that this sequence is reversible; a tertiary carbonium ion will be stable relative to an ion $-\overset{+}{C}{=}CH_2$.

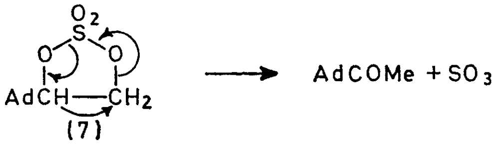
These results make clear that methyl adamantyl ketone, which is the main product of the slow adamantyl bromide–acetylene–sulphuric acid reaction, must arise from slow rearrangement of the intermediate which in the fast reaction of adamantanol leads to adamantyl-acetaldehyde. This conclusion was tested by continuing the adamantanol–acetylene–sulphuric acid reaction for some hours. It was found necessary to maintain the stream of acetylene during this time, otherwise, adamantanol became the sole product. However, sampling and g.l.c. analysis showed progressive formation of adamantyl methyl ketone at the expense of adamantyl-acetaldehyde in the product after quenching, the amount of methylhomoadamantanone remaining constant. This rearrangement may be rationalised as in Scheme 4, or the intermediate (7) may possibly fragment with loss of an SO_3 residue (Scheme 5).



SCHEME 3



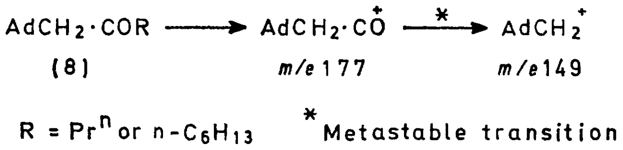
SCHEME 4



SCHEME 5

It thus appears that the first formed cation, $\mathrm{AdCH{:}CH^+}$, is either trapped by sulphuric acid, or yields the homoadamantyl intermediate *via* $\mathrm{Ad\overset{+}{C}{:}CH_2}$ which rearranges too rapidly to be trapped.

The adamantanol–acetylene reaction was extended to the use of substituted acetylenes. Pent-1-yne and oct-1-yne reacted satisfactorily, but phenylacetylene in sulphuric acid is hydrated too rapidly to give a satisfactory yield. The isolated products, $\mathrm{AdCH_2{\cdot}COR}$ (8; R = $\mathrm{Pr^n}$, n-C_6H_{13}, or Ph) could be characterised by their mass spectral breakdown (Scheme 6). The spectral data are also consistent with structure (8):



SCHEME 6

		τ Values	
(8)	$\nu_{max.}$/cm^{-1}	$-CH_2-CO$	$-CO{\cdot}CH_2-$
R = $\mathrm{Pr^n}$	1710	7·98	7·66 (t, *J* 7 Hz)
n-C_6H_{13}	1710	7·97	7·70
Ph	1674	7·45	

Adamantanol with pent-1-yne in [$^2H_2$]sulphuric acid

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[6] M. A. Imhoff, R. H. Summerville, P. von R. Schleyer, A. G. Martinez, M. Hanack, T. E. Deuber, and P. J. Stang, *J. Amer. Chem. Soc.*, 1970, **92**, 3802.

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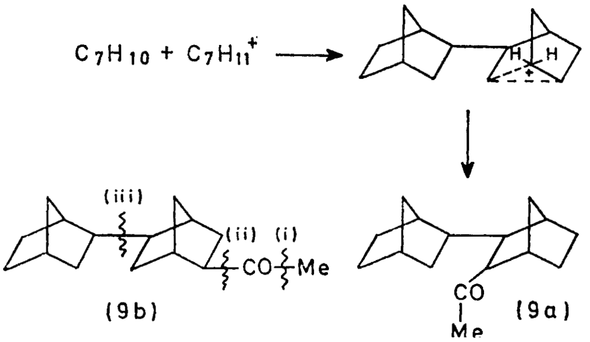
gave $AdCD_2 \cdot COPr$ showing no τ 7·98 n.m.r. signal, and fragmentation: *m/e* 222 ⟶ *m/e* 179 ($AdCD_2 \cdot CO$) ⟶ 151 ($AdCD_2$).

Diphenylmethanol with oct-1-yne in sulphuric acid gave the expected 1,1-diphenylnonan-3-one. However, with acetylene, diphenylmethanol gave, in small yield, β-phenylcinnamaldehyde; the agent responsible for the dehydrogenation step has not been identified, but under the reaction conditions diphenylmethanol yields also *p*-benzylphenyl(diphenyl)methane.[7]

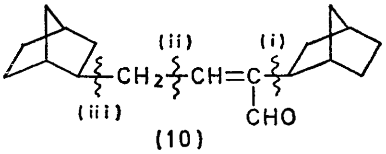
Bicyclo[2,2,1]hept-2-ene with acetylene–sulphuric acid gave a mixed product, separable (t.l.c.) into a ketone, $C_{16}H_{24}O$, *m/e* 232, and an aldehyde, $C_{18}H_{26}O$, *m/e* 258. The ketone, $\nu_{max.}$ 1700 cm^{-1}, gave fragment ions *m/e* 217 ($-CH_3$), 189 ($-COMe$), 137 ($-C_7H_{11}$), and 95 (C_7H_{11}), and n.m.r. signals τ 7·94 (3H, s), 7·58 (1H, m), and 8·60 (20H). These data are most easily accommodated in a structure (9a or b), derived as shown (Scheme 7).



Fragmentation (i) ⟶ *m/e* 217, (ii) ⟶ 189, (iii) ⟶ 137

Scheme 7

The second product, $\nu_{max.}$ 1680 and 1690 cm^{-1}, gave fragment ions *m/e* 163 ($-C_7H_{11}$), 134 ($C_{10}H_{14}$), 109 (C_8H_{13}), and 95 (C_7H_{11}), and n.m.r. signals τ 0·0 and 0·80 (together 1H, s), 3·80 (1H, t, *J* 5 Hz), 7·75 (2H), and 7·98 (1H) as broad bands, and 8·60 (20H). These data are rationalised in a structure (10) which could arise as *cis*- and *trans*-isomers, hence showing two formyl proton signals, from aldol-type condensation of norbornylacetaldehyde.



Fragmentation (i) ⟶ *m/e* 163 $\xrightarrow{-H,\ -CO}$ 134, (ii) ⟶ *m/e* 109, (iii) ⟶ *m/e* 95

Scheme 8

EXPERIMENTAL

Adamantanol with Acetylene.—(*a*) Dry acetylene was passed through a solution of adamantan-1-ol (0·5 g) in 98% sulphuric acid (25 ml) at 5—7 °C for 5 min. Quenching in ice and recovery gave 90% of ketonic material separable by g.l.c. on polyethylene glycol succinate at 140 °C, retention times: adamantylacetaldehyde 21·6, 1-methylhomoadamantan-2-one 27·2, and adamantanol 16·3 min, or by t.l.c. on silica gel in benzene, R_F 0·63, 0·41, and 0·10, respectively. Adamantylacetaldehyde was isolated; m.p. 135°, *m/e* 178, $\nu_{max.}$ 1720 cm^{-1}, τ 0·15 (1H, t, *J* 3 Hz), 7·92 (2H, d, *J* 3 Hz), and 7·9 and 8·29 (15H); 2,4-dinitrophenylhydrazone, m.p. 212°. Methylhomoadamantanone was obtained; m.p. 131°, *m/e* 178, $\nu_{max.}$ 1693 cm^{-1}, τ 9·01 (3H, s), 7·47 (2H, d, *J* 5 Hz), and 7·90 and 8·30 (13H).

(*b*) The aldehyde obtained in [$^2H_2$]sulphuric acid was proved to contain 95% [$^2H_2$]-material by mass spectral analysis.

(*c*) The experiments at various acid concentrations (Table) were carried out for 5 min at 7 °C and the products were analysed by g.l.c. and t.l.c.

Adamantanyl Bromide with Acetylene.[5]—Dry acetylene was passed through adamantyl bromide (1 g) in 96% sulphuric acid (40 g) for 5 h at 5°. Adamantyl methyl ketone (80%) was isolated; *m/e* 178, $\nu_{max.}$ 1690 cm^{-1}, τ 7·96 (3H, s), and 7·90 and 8·30 (15H); 2,4-dinitrophenylhydrazone, m.p. 221°.

Adamantanol with Acetylene in Methanesulphonic Acid.—Adamantanol (1 g) in methanesulphonic acid (30 ml) was treated with acetylene for 30 min at 18°. Recovery gave 2-(1-*adamantyl*)*vinyl methanesulphonate* (6) (70%), b.p. 136° at 15 mmHg, R_F 0·7 (silica gel in benzene) (Found: C, 61·15; H, 7·95. $C_{13}H_{20}SO_3$ requires C, 60·9; H, 7·85%).

Adamantanol with Acetylene and Boron Trifluoride–Ether Complex.—Adamantanol (1 g) in boron trifluoride–ether (40 ml) was treated with dry acetylene for 1 h. Recovery (ice–water and ether) gave 1-methylhomoadamantan-2-one (60%), m.p. 131° (from ethanol), together with some adamantanol and adamantane.

1-*Adamantylmethyl Phenyl Ketone*.—Phenylacetylene (3 g) in carbon tetrachloride (10 ml) was added during 15 min to adamantanol (1 g) in 98% sulphuric acid (30 ml) at 5°. Recovery gave a good deal of acetophenone, removed by distillation, together with 1-adamantylmethyl phenyl ketone (7%), b.p. 182—184° at 15 mmHg, isolated by t.l.c. (R_F 0·50) on silica gel in benzene; 2,4-dinitrophenylhydrazone, m.p. 141—142°, $\lambda_{max.}$ 384 nm (ε 27,000).

1-(*Adamantyl*)*pentan*-2-*one* was obtained in 40% yield as a liquid, b.p. 168—170° at 15 mmHg, R_F 0·58 on silica gel in hexane, from adamantanol (2 g) with pent-1-yne (3 g) and sulphuric acid (Found: C, 81·6; H, 11·2. $C_{15}H_{24}O$ requires C, 81·75; H, 11·0%); 2,4-dinitrophenyl hydrazone, m.p. 163—164°.

1-(1-*Adamantyl*)*octan*-2-*one* was obtained similarly (43%), b.p. 205—207° at 15 mmHg, R_F 0·60 on silica gel in hexane (Found: C, 81·8; H, 11·9. $C_{18}H_{30}O$ requires C, 82·4; H, 11·5%); 2,4-dinitrophenylhydrazone, m.p. 198°.

β-*Phenylcinnamaldehyde*.—Diphenylmethanol (2 g) in carbon tetrachloride (15 ml) was added to 96% sulphuric acid (30 ml) during 15 min in a stream of acetylene. The product on silica gel in benzene–hexane (1 : 1) gave a substance of R_F 0·2, shown to be β-phenylcinnamaldehyde (12%), m.p. 44°, *m/e* 208, τ 0·38 (1H, d, *J* 8 Hz) and 3·33 (1H, d, *J* 8 Hz).

1,1-*Diphenylnonan*-3-*one*.—Diphenylmethanol (3 g) with oct-1-yne (3 g) in carbon tetrachloride (20 ml) and 96% sulphuric acid gave 1,1-*diphenylnonan*-3-*one* (23%), b.p.

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[7] E. Bergmann, *Chem. Ber.*, 1930, **63**, 1717, 1737.

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260° at 15 mmHg, R_F 0·1 (silica gel in hexane), *m/e* 294, 209 ($Ph_2CH{\cdot}CH_2{\cdot}CO$), and 167 ($Ph_2CH$), τ 2·90 (10H), 5·46 (1H, t, *J* 5 Hz), 7·07 (2H, d, *J* 5 Hz), 7·90 (2H, t, *J* 5 Hz), 8·87, and 9·18 (Found: C, 85·55; H, 9·0. $C_{21}H_{26}O$ requires C, 85·65; H, 8·9%).

A by-product from these experiments with diphenylmethanol was a hydrocarbon, R_F 0·41 (silica gel in benzene), *m/e* 334 ($C_{26}H_{22}$), 257 ($-C_6H_5$), 178 ($C_{14}H_{10}$), 165 (fluorenyl), and 91, regarded as *p*-benzylphenyl(diphenyl)methane,[7] τ 2·72 (19H), 6·06 (2H), and 4·54 (1H).

Bicyclo[2,2,1]*hept*-2-*ene with Acetylene*.—Bicyclo[2,2,1]-hept-2-ene (3 g) in carbon tetrachloride (25 ml) was added to 90% sulphuric acid (30 g) at 5° and acetylene was passed with stirring during 1 h. The product, isolated in ether after adding ice–water, was chromatographed on silica gel with hexane and benzene as eluants to give material which was separated by t.l.c. to give a ketone regarded as 2-(norborn-2-yl)-3-(or 5-)acetylnorbornane, R_F [silica gel in benzene–hexane (1 : 1)] (Found: C, 82·9; H, 10·6. Calc. for $C_{16}H_{24}O$: C, 82·7; H, 10·4%), and an aldehyde, R_F 0·67 [silica gel in benzene–hexane (1 : 1)]; 2,4-dinitrophenylhydrazone, m.p. 208—210°, which, however, was not analysed satisfactorily.

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