Protonation at *sp*-Hybridised Carbon; Generation of Allylic Carbonium Ions from Allenes

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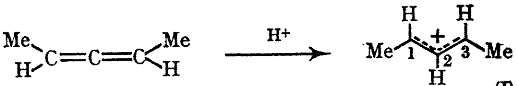
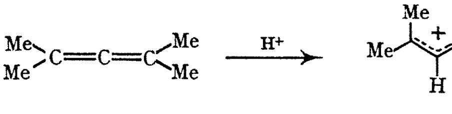
DENO and his co-workers[1] reported the first direct observations of allylic carbonium ions, including cyclopentenyl, cyclohexenyl, and 1,1,3,3-tetramethylallyl cations. In sulphuric acid, acyclic allylic cations, with the exception of 1,1,3,3-tetra-alkyl compounds, form a complex mixture of thermodynamically stable, highly alkylated cyclopentenyl carbonium ions.[2] Olah and Sommer[3] demonstrated that less highly substituted allylic cations were stable in FSO$_3$H–SbF$_5$–SO$_2$ at low temperatures. In this medium, at 30°, pentane-2,4-diol was converted quantitatively into the 1,3-dimethylallyl cation,[3] and allylic cations were also produced by ionization–cleavage of several cyclopropyl halides.[4]


(I)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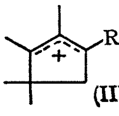
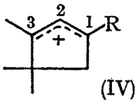

(III)


(IV)

The 1,3-dimethylallyl (I) and 1,1,3,3-tetramethylallyl (II) cations are generated quantitatively by the addition of 1,3-dimethylallene and tetramethylallene, respectively, to FSO$_3$H–SbF$_5$ at −70°. The n.m.r. and u.v. band positions and splittings (Table 1) serve to identify the ions,[3,4] which were unchanged after 1 week at −70°. This is the first example of the direct generation of stable allylic cations by protonation of an allene.†

Direct protonation of the *sp*-hybridised C-2 was confirmed by the quantitative production of deuteriated (I) and (II) in FSO$_3$D–SbF$_5$. The C-2 hydrogen n.m.r. bands of (I) (8·29) and (II) (7·81) were absent, but no further incorporation of deuterium or other rearrangement products were observed. Initial deuteriation at C-1 or C-3 would generate a vinyl carbonium ion, which could undergo either 1,2-methyl or -hydride (deuteride) shift. A 1,2-methyl shift would result in the 1,1,2,3-tetramethylallyl cation from 1,1,3,3-tetramethylallene or the 1,2-dimethylallyl cation from 1,3-dimethylallene. If a 1,2-hydride shift after C-1 protonation had occurred during generation

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† A footnote in reference 4, p. 6083 indicates that similar work is being performed in Professor Olah's laboratory.

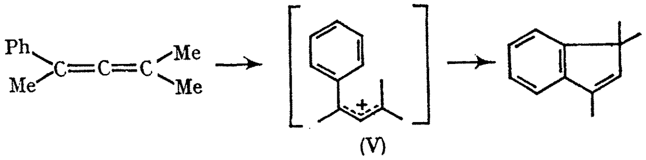
Nuclear magnetic resonance chemical shifts‡ *and ultraviolet spectra of allylic cations at* —70°

Cation	Acid	Methyls C-1, -3	Hydrogen C-1, -3	Hydrogen C-2	U.v. λ_{max} (nm.)
(I)	FSO_3H-SbF_5	3·43d§	9·98m	8·24t¶	299
	FSO_3D-SbF_5	3·43d§	9·98br q**		
(II)	FSO_3H-SbF_5	2·89s		7·81s	305
	FSO_3D-SbF_5	2·89s			

‡ In p.p.m. from Me_4Si (capillary tube) on a Varian HA-100 spectrometer; § *J* 7·3 Hz; ¶ *J* 13·8 Hz; ** *J* 7·3 Hz.

of ion (I), the 8·29 band would have appeared. Since no evidence for these shifts was found, direct protonation at C-2 is invoked. Initial formation of the less stable vinyl carbonium ion is unlikely, since Peterson[5] observed that S_N1 solvolysis of vinyl *p*-bromobenzene sulphonates was at least 5·7 × 10^4 times slower than sp^3-hydridised *p*-bromobenzenesulphonate solvolysis.

Addition of the stated allenes to 96% H_2SO_4 produced a mixture of cations of the types (III) and (IV), which are the expected thermodynamic products of acyclic allyl cations in this medium.[6,7] The ratio of types (III) and (IV) was determined by comparison of the areas of the characteristic[6,7] acid solution n.m.r. bands at 7·8—8·3 [C-2 H in (IV)] and 2·14 p.p.m. [C-2 Me in (III)]. This ratio was 3 : 2 from tetramethylallene and 3 : 7 from 1,3-dimethylallene. Complex mixtures of alkylated cyclopentadienes were formed on pouring the H_2SO_4 solutions into an excess of dilute NaOH.



(V)

2-Methyl-4-phenylpenta-2,3-diene[8] was dissolved into FSO_3H at 10° and then quenched into excess of dilute NaOH to yield 1,3,3-trimethylindene (38%) (n.m.r. and i.r. identical to those reported,[6] b.p. 93—95°/17 mm.[6–9]) and its dimer (47%) (b.p. 200—218°/17 mm.[6]). 1,3,3-Trimethylindene is the known cyclization product of the 1-phenyl-1,3,3-trimethylallyl cation (V) produced on protonation of 2-methyl-4-phenylpenta-1,3-diene.[6–10] Thus, C-2 allene protonation is again implicated.

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