Vinyl Cations in Acid-catalysed Isomerisations of Acetylenes and Allenes

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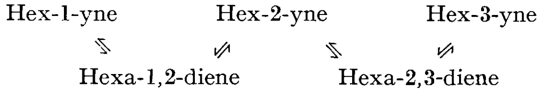
Summary The hexynes and allenic hexadienes have been isomerised in acidic media and the sequence of reactions explained by deprotonation of vinyl cation intermediates to form isomeric acetylenes and allenes.

VINYL cations have been a recent focus of attention.[1] The similarity of these cations to alkyl cations has been noted, particularly with respect to their generation in solvolytic reactions and by electrophilic addition to acetylenes and allenes. One important reaction of alkyl cations is proton loss to form alkenes. The analogous reaction for vinyl cations, proton loss to form alkynes and allenes, has not yet been studied in any detail, being reported only as a side reaction in other investigations.[2] We report here for the first time acid-catalysed acetylene–allene isomerisations; reactions in which protonation of acetylenes and allenes is followed by deprotonation to form isomeric acetylenes and allenes, this being the major reaction undergone.

The five straight chain C_6H_{10} isomers hex-1-, -2-, and -3-yne and hexa-1,2- and -2,3-diene were treated with the acid catalysts "HBF_4", *i.e.* HF/BF_3, "HPF_6" *i.e.* HF/PF_5, and H_2SO_4 in dry sulpholane. The Table shows the approximate times for 20% isomerisation for the catalysts HBF_4, HPF_6, and H_2SO_4. The rates implied by these reaction times roughly reflect the thermodynamic stabilities,[3] with isomers of low thermodynamic stability isomerising rapidly compared to those of high stability. In all the catalytic systems a close study of the initial isomerisation of pure acetylenes and allenes indicated a sequential reaction, as shown in the Scheme.



SCHEME

The isomerisation reaction is best explained by formation of vinyl cations and their deprotonation to acetylenes or allenes:

$$\mathrm{HC\vdots CBu + H^+ \rightleftharpoons H_2C:\overset{+}{C}Bu \rightleftharpoons H_2C:C:CHPr + H^+ \rightleftharpoons}$$
$$\mathrm{Me\overset{+}{C}:CHPr \rightleftharpoons MeC\vdots CPr + H^+}\ etc.$$

Although the main reaction was isomerisation, side reactions were significant and prevented equilibration of the isomers. For example, hexan-2- and -3-one are generated in the H_2SO_4 reaction. This could occur by bisulphate addition to the vinyl cation, followed by hydrolysis during work-up.

TABLE

Approximate times for 20% *isomerisations of the hexynes and hexadienes at* 25°

Catalyst	Isomer				
	Hex-1-yne	Hexa-1,2-diene	Hex-2-yne	Hexa-2,3-diene	Hex-3-yne
0·1 M-HBF_4	30 min	25 s	40 min	35 s	25 min
0·1 M-HPF_6	25 min	<5 s	2 h	6 s	30 min
0·96 M-H_2SO_4	24 h	3 h	>100 h	4 h	40 h
2·07 M-H_2SO_4	—	—	—	20 min	2 h

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