Evidence for Intimate Ion-pair Formation in the Addition of Acids to Olefins

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Summary Evidence is presented that the addition of acids to α-pinene involves addition of un-ionised acid to give an intimate ion pair, which favours elimination over addition when the counter ion is not strongly nucleophilic.

THE hydration of α-pinene in aqueous 95% acetone, catalysed by 0·06 N-sulphuric acid at 75°, proceeds with rate constant $k_1 = 9 \times 10^{-5}\,s^{-1}$, and yields a mixture of terpene alcohols in which α-terpineol predominates, together with about 25% yield of terpene olefins, in which terpinolene and limonene predominate.[1] The hydration presumably involves protonation of the double bond, followed by capture of the ion formed by water.

In contrast, we have found that when HCl is added to a 10% solution of α-pinene in acetic acid, the main product is bornyl chloride in 40% yield, and this product is also formed in 15% yield when methanol is solvent. Since bornyl chloride is solvolysed in both solvents,[2] the protonation mechanism is untenable, and we suggest the reaction is a further example[3] of addition of un-ionised acid to give an intimate ion pair, which either collapses or ionises. Rearrangement within the ion pair leads to formation of bornyl chloride rather than the unstable pinene hydrochloride.

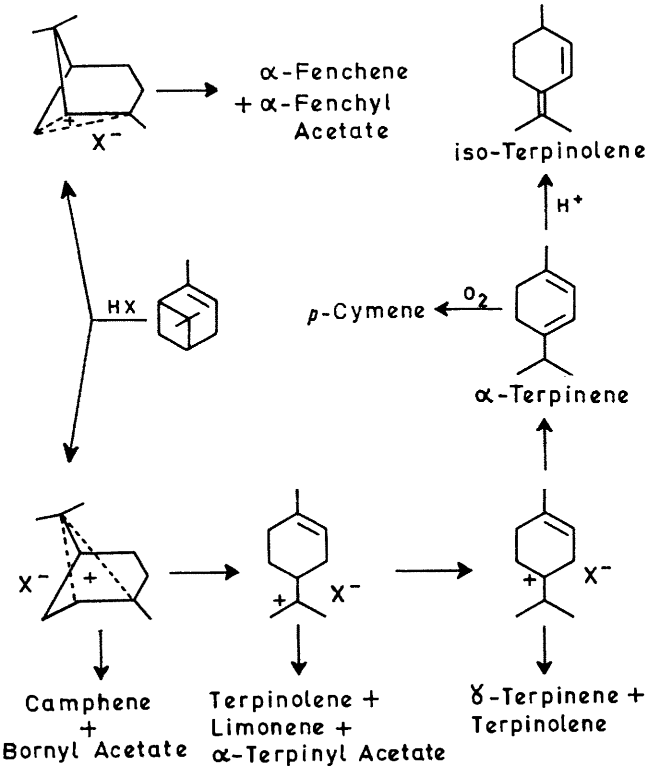
When a catalytic amount (0·2 N) of sulphuric acid is added to a 5% solution of α-pinene in acetic acid, the reaction is very rapid, the α-pinene disappearing within 15 min. at 20°. Under these conditions, there is little addition of acetic acid to α-pinene, the main products being olefins produced by isomerisation of α-pinene. The product composition is given in the Table.

Products of reaction of 0·4 M-*α-pinene with* 0·2 N-*sulphuric acid in acetic acid for* 15 *min. at* 20°

	%
α-Pinene (unreacted)	2
α-Fenchene	Trace
Camphene	13
α-Terpinene	18
Limonene	9
γ-Terpinene	7
p-Cymene	2
Terpinolene	36
Isoterpinolene	1
α-Fenchyl acetate	4
Bornyl acetate	3
α-Terpinyl acetate	4

Analyses by g.l.c. on a 22 ft packed capillary column, 10% Carbowax 20 M on Chromosorb W at 170°. The identities of all but α-fenchene, limonene, and terpinolene were confirmed by i.r. spectra of samples separated on a 30 ft preparative column, using 25% Carbowax 20 M on Chromosorb W at 210°.

All the *p*-menthadienes found are produced from limonene in similar conditions, so may be secondary products; α-terpinene is very readily converted into *p*-cymene on exposure to air. On prolonged reaction, the *p*-menthadienes give α-terpinyl acetate, reported as the main product of this reaction.[4]



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We suggest that this reaction also involves addition of un-ionised acid to α-pinene, giving an intimate ion pair in which the counter ion is not strongly nucleophilic. Collapse of the ion pair is then unlikely, and it must either ionise, giving a "free" ion which can yield acetates, or eliminate, the counter ion withdrawing a proton in a process which is the reverse of formation of the ion pair. Conclusive proof of this process is difficult in the absence of isolable products of ion-pair collapse, but we are investigating slight variations of product composition with counter ion.

Our theory suggests that addition of un-ionised acid to olefins can be detected by a predominance of elimination over addition of solvent in the absence of a nucleophilic counter ion; it is further supported by the observation that the addition of organic acids to α-pinene gives a mixture of the appropriate bornyl ester and limonene, the elimination to substitution ratio depending on the ionisation constant of the acid[5] and hence on the counter ion of an intimate ion pair.

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