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DOUBLE 1,2-METHYL SHIFT IN THE REARRANGEMENT OF A VINYL CATION TO AN ALLYL CATION

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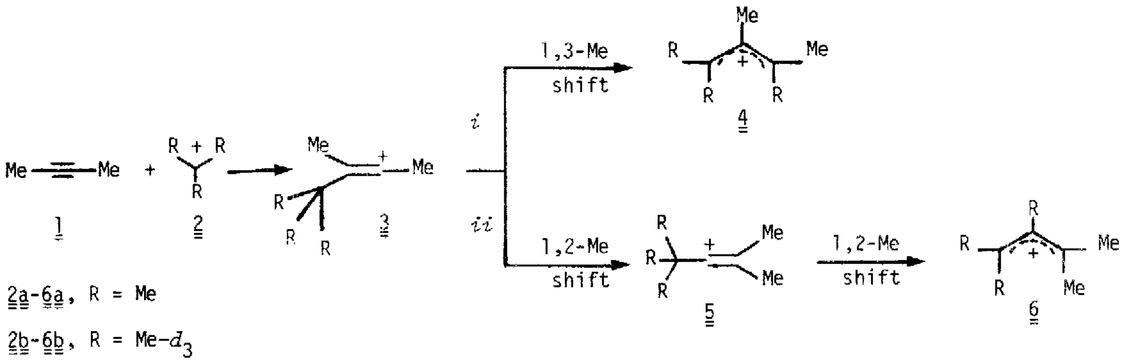
IN recent papers[1] we have established the intermediacy of vinyl cations in the Lewis acid catalyzed addition of alkyl halides to acetylenes. We have also shown[2] that thiirenium ions, *i.e.* sulphur-bridged vinyl cations, may be generated and observed at low temperature in sulphur dioxide by transfer of the electrophilic species RS^+ from a suitable precursor to acetylenes. Following an analogous procedure we have studied the addition of *t*-butyl cation 2a to 2-butyne 1 in order to detect by nmr spectroscopy the 2-*t*-butyl-1,2-dimethyl vinyl cation 3a.[3] However, cation 3a escaped direct observation,[4] and the exclusive formation of pentamethylallyl cation 4a was ascertained. We report here a mechanistic study of this interesting rearrangement.

The reaction was carried out by addition of a slight excess of 2-butyne 1 to a solution of *t*-butyl chloride and antimony pentafluoride in almost equimolecular amounts[5,6] in sulphur dioxide at -78°. The ^1H nmr spectrum of the reaction mixture showed signals at δ (internal TMS) 3.11, 2.96 and 2.33 in the ratio of 2:2:1 respectively, which are in good agreement with the reported values[7] for pentamethylallyl cation 4a. No signal reasonably attributable to the first formed vinyl cation 3a was detected, even at the lowest experimentally accessible temperature (-75°).



2a-6a, R = Me

2b-6b, R = Me-d_3

Two pathways may be proposed for the rearrangement (see Scheme): a 1,3-methyl shift leading directly to the final product (path *i*), or a double 1,2-methyl shift *via* the α-*t*-butyl substituted vinyl cation **5a** (path *ii*). In order to solve this ambiguity we have traced the methyl migration by using *t*-butyl chloride-d_9 [8] to generate the *t*-butyl cation **2b** in the same conditions as above. The ^{1}H nmr spectrum of the reaction mixture showed two signals of the same intensity at δ 3.11 and 2.96, indicating the formation of allyl cation **6b** according to path *ii*. No signal corresponding to the methyl group in the 2-position was detected.

Both types of 1,2-methyl shifts, the one *across* the double bond[9,10] (leading in our case to vinyl cation **5**) and the other *to* the double bond[9,11] (leading to allyl cation **6**) have been observed separately. Our experiment provides the first evidence that they may also occur in sequence and, furthermore, indicates that two subsequent 1,2-methyl shifts instead of a single 1,3-methyl shift, what is a common feature in trivalent carbonium ion chemistry,[12] are also preferred by vinyl cations.

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