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FRAGMENTATION OF TERTIARY ALKYL CARBONIUM IONS IN SULPHURIC ACID : STERIC EFFECTS.

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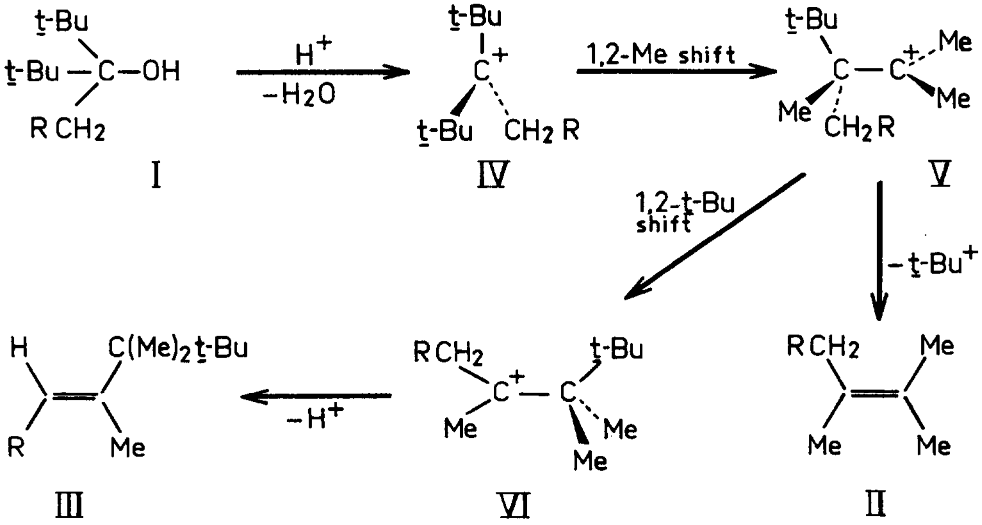
Although tertiary-alkyl carbonium ions are known to fragment (1,2) under certain conditions no systematic study of this reaction has yet appeared. The occurence of fragmentation is known (2) to depend on the ability of the leaving moiety to accomodate the developing positive charge but may also be influenced by other factors such as relief of steric strain, as has been shown by studies on the fragmentation of hydroxyalkyl carbonium ions (3).

We wish now to report that fragmentation occurs very readily when a tertiary alcohol I (R = H, Me, Et, i-Pr, t-Bu) is treated with strong acids.

A rapid exothermic reaction ensues upon addition of conc. sulphuric acid to I. The complex product mixture contains primarily the fragmentated olefin II and the rearranged olefin III (see Schema) in amounts which depend dramatically on the nature of R (see Table), the extent of fragmentation increasing monotonically with the size of R. The stereochemistry of III is probably that shown (4).



TABLE

Products from the reaction of RCH_2(t-Bu)$_2$COH
with conc. Sulphuric acid at 25° (5).

R	% II	% III	% other fragmentation products
H	22	66	2
Me	31	52	14
Et	40	39	15
i-Pr	51	25	16
t-Bu	79	-	17

The results can be rationalised by the following scheme : formation of the carbonium ion is followed by a 1,2-methyl shift to give V, whereupon the t-butyl group either fragments or migrates. It can be appreciated that these two processes are formally very similar and that the critical factor which determines the extent of fragmentation is the degree of steric strain in the intermediate carbonium ion V. While it is possible to conceive of the t-butyl group being lost from the rearranged ion VI, it seems improbable that this ion should fragment rather than V since, except for the case of R = H, this ion is less subject to back strain than V.

Few results on closely comparable systems have been reported. Solvolysis of the p-nitrobenzoate of I (R = t-Bu) gives (6) neither II or III ; alcohol I (R = H) is dehydrated completely in sulphuric acid-dioxane to 1,1-di-t-butylethylene (7).

We would suggest that one of the factors contributing to the differences between these earlier results and those of the present study is the absence of a good base in conc. sulphuric acid. We conclude therefore that it is not sufficient for the fragment formed to be stable : the rate of its formation must be competitive with that of straightforward proton abstraction.

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(5) To the stirred alcohol (0.005 moles) at 25° (bath temperature) was added rapidly conc. sulphuric acid (96% : 0.005 moles). After 10 seconds pentane was introduced. Data are based on glc analysis of the dried (K_2CO_3) pentane solution. Combined glc-mass spectroscopy has enabled us to establish that most of the other fragmentation products are isomeric with II, but complete identification of the minor components has not yet been achieved. All major products were identified by elementary analysis, ir, nmr, and mass spectroscopy.

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