Controlling the Outcome of a Carbonium Ion Reaction: the Use of a Trimethylsilyl Group to Dictate the Formation of a Specific Olefin

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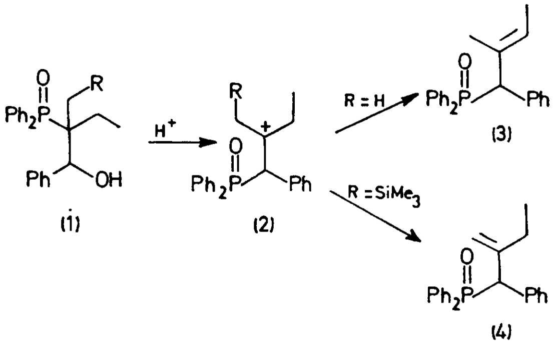
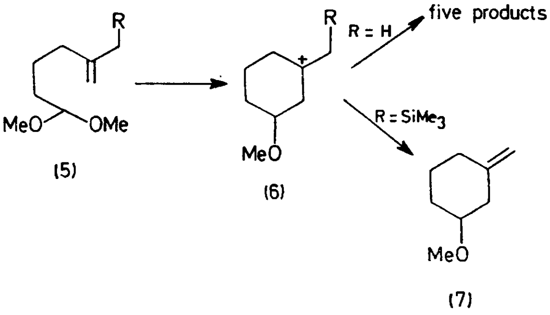
Summary The carbonium ions (**2**, R = $SiMe_3$) and (**6**, R = $SiMe_3$) give only the olefins (**4**) and (**7**), respectively, in contrast to the reactions of the carbonium ions (**2**, R = H) and (**6**, R = H).

A carbonium ion can be a useful intermediate in organic synthesis only when the product to be got from it is easily predictable and when the predictable product is the one that is wanted. In many cases, however, carbonium ions are apt to give either a mixture or an unwanted product. It is not often easy to do much about this, other than to redesign the synthesis. We now show, with two examples, that a carbonium ion can be made to give a single product if a trimethylsilyl group is placed on the appropriate carbon atom in the starting material. The success of this device is a consequence of a useful generalisation: that a silicon–carbon bond is very often more easily broken heterolytically than the corresponding hydrogen–carbon bond.[1]

Our first example removes a limitation in the diene synthesis described in the preceding communication,[2] where it was shown that the carbonium ion (**2**, R = H), derived from the alcohol (**1**, R = H), gives only the more substituted olefin (**3**) and none of the alternative (**4**). We find that if the alcohol (**1**, R = $SiMe_3$) is used instead, the trimethylsilyl group is lost from the carbonium ion (**2**, R = $SiMe_3$), and the olefin (**4**) is produced. What is more, the rearrangement is faster with the trimethylsilyl group than without it.

Our second example follows the work of Johnson *et al.*,[3] who found that the carbonium ion (**6**, R = H), obtained by treating the acetal (**5**, R = H) with methanolic acid, gave all five of the likely products: two diastereoisomeric ethers,





and all three possible olefins. By contrast, we find that the acetal (**5**, R = $SiMe_3$), with $SnCl_4$ in CCl_4,† gives only the olefin (**7**) in which the double bond is formed by loss of the trimethylsilyl group.

Obviously, this solution to a long-standing problem in synthetic design is useful only when the silylated starting materials can easily be made. Nevertheless, we have now shown that one can consider with confidence synthetic designs which hitherto would have foundered on the unpredictable or inflexible behaviour of carbonium ions.

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† With methanolic acid, (**5**, R = $SiMe_3$) underwent protodesilylation without ring closure; Johnson *et. al.* (ref. **3**) did not try the reaction of (**5**, R = H) with $SnCl_4$, but in their work with other acetals the *exo*-methylene product was generally very much the minor one when $SnCl_4$ was used.

[1] C. Eaborn and R. W. Bott, in 'Organometallic Compounds of the Group IV Elements,' Volume 1, 'The Bond to Carbon', Part 1 ed. A. G. MacDiarmid, Dekker, New York, 1968, p. 359.

[2] A. H. Davidson and S. G. Warren, preceding communication.

[3] A. van der Gen, K. Wiedhaup, J. J. Swoboda, H. C. Dunathan, and W. S. Johnson, *J. Amer. Chem. Soc.*, **1973**, **95**, 2656.