

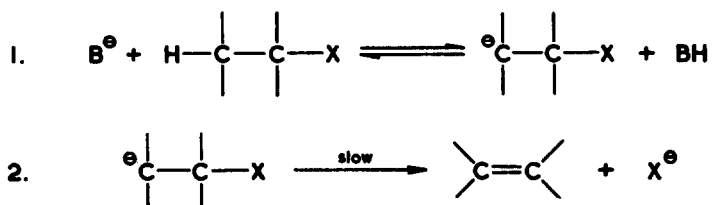
CONCERNING Elcb REACTIONS (1)

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Experimental examples for the Elcb mechanism of elimination, which was first formulated by Ingold (2) and later investigated in particular by Hine (3), have remained scarce. In protic media (4) the mechanism of this two-step elimination involves fast and reversible formation of the conjugate base followed by rate limiting unimolecular loss of the leaving group to yield the olefin:



For some time it seemed generally accepted that such a mechanism is established, if base-catalysed deuterium exchange (step 1) is faster than formation of the olefin (step 2). However, more recently Breslow has challenged the validity of this criterion and argued that deuterium exchange could occur as an irrelevant side reaction which is not connected to the main pathway of a concerted elimination; in other words expulsion of the leaving group would have to occur more readily from an incipient carbanion than from a free carbanion (5). In this discussion I wish to suggest that experimental precedent and theory still favour the earlier views on the Elcb mechanism.

As an example in support of his thesis Breslow cited the elimination from substituted 2-phenylethyl derivatives. For these compounds elimination rates increase as the β -proton is rendered more acidic by electron-attracting substituents, and it was assumed (5a) that in the faster case, nucleophilic push from C_β to C_α was less developed in the transition state. If this assumption were correct, then indeed a limiting situation might arise in which fast base-catalysed deuterium exchange occurred side by side with an E2 reaction. However, using the ratio k_{OTs}/k_{Br} as criterion for C—X bond breaking we have now shown (6) that under otherwise constant conditions more C—H bond breaking (as induced by electron-attracting substituents in the benzene ring) produces an attenuated increase in C—X

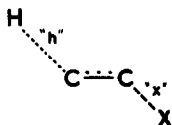


FIG. 1

process "h" - "x", and it can be understood why a transition from the E2 to the nonconcerted Elcb mechanism is virtually forbidden for most olefin-forming elimination (6).

If an Elcb reaction is to occur (3), then the leaving group X^- has to part from an intermediate carbanion in a slow step; microscopic reversibility demands that this particular step also exists in reverse.

bond breaking (process "x", Fig.1) in the transition state. Thus, the Elcb character of an E2 reaction is not simply a function of C—H bond breaking (i.e., process "h"), but has to be described more accurately as

While it is clear that common leaving groups such as halide ions do not add nucleophilically to typical olefins, these anions can add to certain benzyne, (7), carbenes (3), and presumably (8), to certain fluorinated olefins. It is precisely for the formation of some benzyne, carbenes, and certain fluorinated olefins that the E1cb mechanism has been postulated (3,9). The fact that in these cases the "olefin" is a high energy intermediate ensures not only that nucleophilic addition of halide ion to olefin becomes a possible reaction, but also that its reverse, i.e., formation of the olefin from the carbanion is a slow step as demanded for the E1cb reaction.

References

1. For the preceding paper in this series see G.M. Fraser and H.M.R. Hoffmann, Chem. Comm., 1967, 561.
2. C.K. Ingold, Structure and Mechanism in Organic Chemistry, Cornell University Press, New York, 1953, p.422.
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4. E1cb reactions in aprotic media have been discussed by G. Köbrich, Angew.Chem.Internat.Edn., 4, 49 (1965). Under aprotic conditions a fourth elimination mechanism, the E2cb mechanism, may occur; see M. Schlosser, Habilitation Thesis, University of Heidelberg, 1966 and G. Köbrich, Angew.Chem.Internat.Edn., 6, 49 (1967).
5. (a) R. Breslow, Tetrahedron Letters, 399, 1964); (b) idem, Organic Reaction Mechanism, Benjamin, Inc., New York 1965, p.111.
6. G.M. Fraser and H.M.R. Hoffmann, J.Chem.Soc.(B), 265 (1967).
7. G. Wittig, Angew.Chem.Internat.Edn., 4, 737(1965) and references cited therein.
8. F.E. Rogers and J. Hine, 152nd ACS Meeting, New York 1966, Abstracts S 168.
9. L.A. Paquette and L.D. Wise, J.Org.Chem., 30, 228 (1965) have reported an interesting example, in which the "carbanion" is an enolate ion and the leaving group a trimethylammonium group. The nucleophilic addition of an amine to the β -carbon of an α,β - unsaturated ketone is a variant of the Michael addition.