syn-Stereospecificity in an *E*1c*B* Elimination from Sulphonyl-fluoro-ethanes

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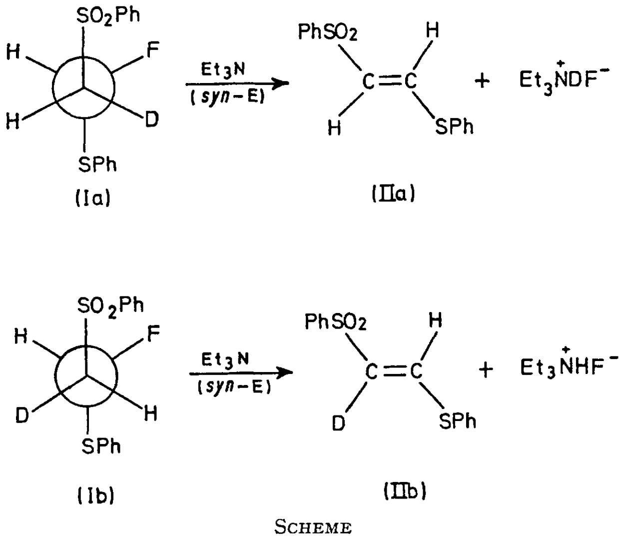
Summary The amine-promoted elimination of HF from sulphonyl-activated fluoroethanes follows a *syn*-stereospecific course which may be associated with an *E*1c*B* mechanism involving ion pairs.

Although the stereochemistry of elimination has been studied widely recently,[1,2] the factors which determine the *syn* or *anti* course of a reaction are still not clear. We report now results on the stereochemical course of an olefin-forming process which shows characteristics of the recently proposed *E*1c*B* mechanism involving ion pairs, *i.e.* $(E1cB)_{\rm ip}$.[3]

The diastereoisomeric ethyl fluorides (Ia) and (Ib) were prepared by the base-catalysed addition of PhSD to *cis*- and *trans*-2-(phenylsulphonyl)vinyl fluorides, a process which was found to follow a highly *syn*-stereospecific course.[4] (Ia) was formed from the *cis*-vinyl-fluoride, and (Ib) from the *trans*-isomer. The configuration of the adducts was unambiguously assigned by n.m.r. spectroscopy.[4] The fluorides (Ia) and (Ib) reacted with triethylamine in benzene yielding quantitatively (IIa) and (IIb) respectively. As shown in the Scheme, complete loss of deuterium was observed from (Ia) whereas the olefin resulting from (Ib) retained all, or nearly all, the original label (i.r. and n.m.r. analysis). Moreover, the isomeric *cis*-olefin was not present in the reacting solutions and control experiments excluded the possibility of the occurence of *cis-trans*-isomerization.

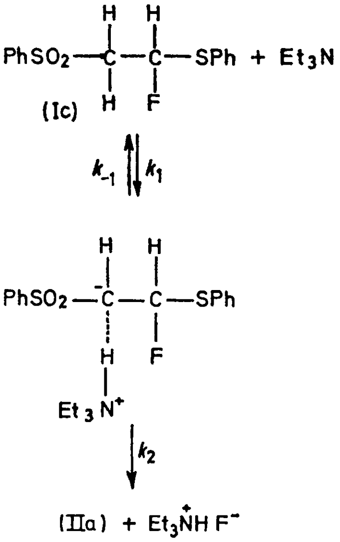
These results are fully consistent with an elimination process of high *syn*-stereospecificity. Such a course is unexpected when eliminations from similar sulphones are considered, in which the *anti*-route appears to be preferred.[2]

A kinetic investigation showed that the *syn*-stereochemistry depends upon, or is associated with, a carbanion mechanism. The following second-order rate coefficients were obtained by measuring olefin formation and/or base disappearance in the reactions of the undeuteriated compound (Ic) with Et_3N in benzene: $10^3k_2/(\rm l\ mol^{-1}\ s^{-1})$ 0·85 at 25°, 1·54 at 35°, 3·50 at 50°; E_a 10·9 kcal mol^{-1}; $\Delta S‡$ $-38{\cdot}2$ cal mol^{-1}deg^{-1}. We have also observed that the geminal deuterium atom causes a secondary isotope effect ($k_{\rm H}/k_{\rm D}$ 1·1 at 50°) in the elimination of HF from (Ib)[5], but an inverse isotope effect ($k_{\rm H}/k_{\rm D}$ 0·8 at 50°) was observed in the elimination of DF from (Ia). Consequently, a mechanism involving C-H bond cleavage during the rate determining step appears very unlikely. However, an anionic centre can easily develop on the atom adjacent to the sulphonyl group, so that a pre-equilibrium *E*1c*B* mechanism is likely for these reactions.[2,3,5,6] The inverse isotope effect measured in the case of (Ia) should arise since



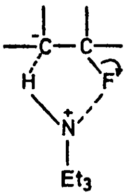
Scheme

the observed rate constant depends upon a product of terms ($k_2 \times k_1/k_{-1}$) in which the isotope effect is unity or tends to cancel out.



Indeed, low or even inverse isotope effects have been measured in H–D exchange reactions involving equilibria similar to those just formulated.[7] Also, it seems reasonable to assume that, since dissociation into ions in benzene is a high energy process, proton abstraction would give an ion pair rather than a discrete carbanion.[3] The lack of rate retardation upon adding $Et_3\overset{+}{N}H\overset{-}{Cl}$ to the reacting solution of (Ic) in C_6H_6–MeCN (85:15 v/v) supports this hypothesis.[3] The intermediacy of alkylammonium carbanides has been suggested both in elimination[3] and H–D exchange reactions,[7,8] and particularly in the latter type of process the nature of the ion pairs has been studied.

The mechanism suggested by the kinetic results is consistent with the observed stereochemistry. In fact, during the collapse of the ion pair to final products attraction between the positive pole and the incipient negative charge of the leaving halogen would favour removal of H–F fragments from the same side.



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