Irreversible *E*1*cb* Mechanism in the *syn* Eliminations from 1,2-Dihalogenoacenaphthenes Promoted by Potassium t-Butoxide in t-Butyl Alcohol

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Summary The lack of a significant leaving group effect and the preferential departure of the 'poorer' leaving group suggest an irreversible *E*1*cb* mechanism for the title reactions.

SINCE the realisation that in base-promoted β-eliminations stepwise mechanisms could be at least as frequent as concerted ones,[1] studies aimed at defining the range of applicability of these mechanisms are certainly of interest. We report here results which strongly suggest that the *syn* eliminations from the *trans*-1,2-dihalogenoacenaphthenes (**1**)—(**4**),† promoted by Bu^{t}OK in Bu^{t}OH, take place by a stepwise mechanism involving the irreversible formation of a carbanion intermediate, an $(E1cb)_I$ mechanism.‡ Another interesting conclusion is that the operation of this mechanism causes the preferential loss of the 'poorer' leaving group from (**1**) and (**3**). The preference is small with (**1**) (it gives 51·5 and 48·5% of 1-bromo- and 1-chloro-acenaphthylene, respectively), but very large with (**3**), 1-chloroacenaphthylene being obtained as the sole product.§ When the eliminations from (**3**) and (**4**) were carried out in Bu^{t}OD no incorporation of deuterium was detected in the unchanged material.

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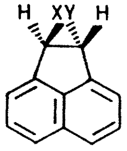
† All the substrates had n.m.r. spectra and elemental analyses in agreement with the given structure and, where available, with the literature data.

‡ The elimination reaction of (**2**) with OH$^-$ in EtOH has already been investigated (ref. 2); in this pioneering work an *E*1*cb* mechanism was considered likely, but no experimental support for this suggestion was given.

§ The products were analysed by g.l.c. In the eliminations from (**3**) no peak attributable to 1-fluoroacenaphthylene was detected in the gas chromatogram.



(1) X = Br, Y = Cl
(2) X = Y = Cl
(3) X = Cl, Y = F
(4) X = Y = F

The kinetics were investigated spectrophotometrically (at 332 nm) by following the build-up of the acenaphthylene formed An excess of the base was used in each case and clean first-order kinetics were observed The second-order rate constants, k_2, are reported in the Table In the case of (**1**), where both HCl and HBr are eliminated, k_2 values for each elimination process have been calculated

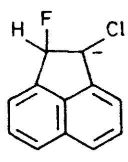
TABLE Kinetic data for the eliminations from *trans*-1 X 2 Y-acenaphthenes promoted by potassium t-butoxide in t butyl alcohol at 30 °C [a]

X	Y	HX eliminated	k_2/l mol^{-1} s^{-1}
Br	Cl	HBr	1 15
		HCl	1 22
Cl	Cl	HCl	0 92[b]
Cl	F	HF	3 88
F	F	HF	2 18 × 10^{-4} [b]

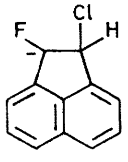
[a] The concentration of Bu^{t}OK was between 0 01 and 0 02 M
[b] Corrected for the statistical factor

It is noted that (**1**) (loss of HBr), (**2**) (loss of HCl), and (**3**) (loss of HF) react at a very similar rate, even though different leaving groups are involved More significantly, (**3**) is more reactive than (**2**), in spite of the fact that the carbon–fluorine bond is much stronger than the carbon–chlorine bond Clearly, the breaking of the carbon–halogen bond cannot have significantly affected the slow step of these eliminations, thus strongly suggesting an $(E1cb)_I$ mechanism It is remarkable that such a mechanism is preferred to the $E2$ mechanism even when a leaving group as good as bromine is involved, this may be due to the *syn* stereochemistry of these reactions

The surprising loss of only fluorine (the 'poorer' leaving group) in the elimination from (**3**) is a consequence of the operation of the $(E1cb)_I$ mechanism Accordingly, out of the two possible carbanions which can be obtained from (**3**), (**5**) should be much more stable than (**6**), since it is well known that an α-chlorine substituent is far more effective than an α-fluorine substituent in promoting carbanion formation[3] and also that the reverse situation holds, though to a much smaller extent, when the two halogens are at the β-positions ¶ Thus, if (**5**) is the sole carbanion formed from (**3**), the exclusive loss of HF from this substrate is easily accounted for **



(5)



(6)

In agreement with the expected effects of α- and β-halogens on the carbanion stability are the easier loss of chlorine with respect to bromine from (**1**) and the observations that (**3**) reacts faster than both (**4**) and (**2**) and that (**1**) is more reactive than (**2**) in the HCl forming process

Finally it is interesting that the difference in reactivity between (**3**) and (**4**) (*ca* 10^4) is quite similar to that observed (3·2 × 10^3) between 9-chloro- and 9-fluoro-fluorene in the sodium methoxide catalysed isotope exchange reaction[4] The latter observation suggests that the difluoro-derivative (**4**) also reacts by an $(E1cb)_I$ mechanism

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¶ The σ^* values for $-CH_2F$ and $-CH_2Cl$ groups are 1 10 and 1 05, respectively

** Recently, preferential loss of fluorine has been also found in the *syn* eliminations from *trans* 1 chloro 2-fluoro-cyclohexane and -cyclopentane promoted by complex base (J G Lee and R A Bartsch, *J Am Chem Soc* , 1979, **101**, 228) This finding has been rationalized by invoking a cyclic transition state where the interaction between the metal cation of the ion paired base and the leaving group makes fluorine a better leaving group than chlorine We can exclude that such an interaction plays a major role in our reactions Accordingly, we have observed exclusive loss of fluorine from (**3**) in solvent-base systems also (Me_2SO–Me_4NOH and EtOH–EtONa) where ion pairing is of little importance Moreover when the reactions of (**1**) and (**3**) were studied in Bu^{t}OH–Bu^{t}OK, in the presence of 18 crown-6 ether, a Cl/F leaving group effect of 0 43 was observed which is not significantly different from that (0 24) found in the absence of the crown ether

[1] F G Bordwell, *Acc Chem Res* , 1972, **5**, 374
[2] S J Cristol, F R Stermitz, and P S Ramey, *J Am Chem Soc* , 1956, **78**, 4939
[3] J Hine 'Structural Effects on Equilibria in Organic Chemistry,' Wiley-Interscience, New York, 1974, p 181, J Hine, R Wiesboeck, and R G Ghirardelli, *J Am Chem Soc* , 1961, **83**, 1219 This conclusion appears to be valid when planar or near planar carbanions are involved (ref 4), which should be the case with our substrates
[4] A Streitwieser and F Mares, *J Am Chem Soc* , 1968, **90**, 2444