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Evidence against a Carbanion Mechanism for Elimination Reactions of Alkyl Fluorides

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BIMOLECULAR elimination reactions of 2-arylethyl fluorides show a large Hammett ρ-value (+3·1 at 30°),[1] and the Hofmann rule is followed when 2-pentyl and 2-methyl-2-butyl fluorides undergo base-promoted elimination.[2] Since these observations suggest a transition state of considerable carbanion character, we decided to test for the presence of a carbanion intermediate by the isotope-exchange technique.

2-Phenylethyl fluoride was prepared by the method of DePuy and Bishop,[1] and heated at 60° with sodium ethoxide in *O*-deuteroethanol[3] for a time sufficient to give 30% reaction. Unreacted phenylethyl fluoride and product (styrene) were separated from the reaction mixture by gas chromatography using a 15-ft. column of Carbowax 20M at 144°. The reaction of 2-pentyl fluoride with sodium ethoxide in ethanol was carried out in a sealed tube at 120° as before,[2] to about 40% completion. Unreacted 2-pentyl fluoride was separated from the reaction mixture by gas chromatography, using a 20-ft. column of adiponitrile at room temperature.

Mass spectra of 2-phenylethyl and 2-pentyl fluorides were determined both on starting materials and on the samples isolated after partial reaction. The mass spectrum of the isolated styrene was also compared with that of an authentic sample. Values of the pertinent peak-height ratios are recorded in the Table.

The ratios of the parent to the parent-plus-one peaks for the styrene and 2-phenylethyl fluoride both before and after reaction indicate that any deuterium uptake must be well below 0·1%. Nuclear magnetic resonance spectra of both compounds, though less sensitive to the presence of deuterium, similarly showed no significant changes from before to after reaction. The parent peak in the mass spectrum of 2-pentyl fluoride was too weak to be useful. The 71/72 ratio (C_5H_{11}) does change from before to after reaction, but the samples were too small for precise measurements of peak heights, and the difference is probably within experimental error. In any event, the change is in the wrong direction for deuterium incorporation.

TABLE

Mass-spectral data on reactants and products in elimination reactions of alkyl fluorides

Compound	Peaks used	Peak-height ratios Pure sample	 From reaction
$PhCH_2{\cdot}CH_2F$	124/125	11·00 ± 0·02	10·83 ± 0·01
$PhCH{=}CH_2$	104/105	11·16 ± 0·002	11·19 ± 0·02
$C_3H_7{\cdot}CHF{\cdot}Me$	71/72	11·6	13·6

The lack of exchange with deuterated solvent only disproves, of course, a carbanion that returns to reactants at a rate comparable to that at which it gives the final product. In the absence of any positive evidence for the *E*1*cb* mechanism, however, it is reasonable to assume that simple alkyl fluorides undergo normal *E*2 reactions on treatment with base.

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[1] C. H. DePuy and C. A. Bishop, *J. Amer. Chem. Soc.*, 1960, **82**, 2535.

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[3] V. J. Shiner, Jr., and M. L. Smith, *J. Amer. Chem. Soc.*, 1958, **80**, 4025.