

S_N2' Reactions of 2,3,3-Trichloro-1,1,3-trifluoropropene

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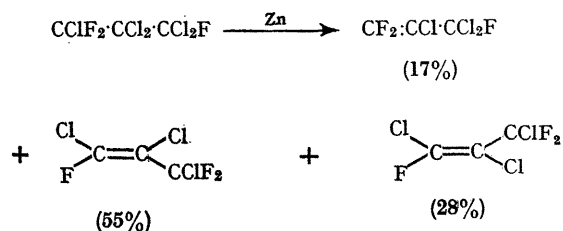
BORDWELL AND SCHEXNAYDER have discussed¹ in detail the mechanistic classification of S_N2' (abnormal allylic substitution) reactions, and have concluded that unambiguous examples of such reactions are rare, and that this mechanistic classification needs to be assigned with increased caution in the future. We report that the reactions of certain fluorinated allylic halides appear to be unambiguous examples of S_N2' reactions, and present the

evidence for this in the case of 2,3,3-trichloro-1,1,3-trifluoropropene.

Miller and his co-workers² have indicated that reactions of a number of fluorinated allylic halides with nucleophiles occurred with rearrangement, and that a direct displacement followed by rearrangement was implausible for such systems. For example the group CCl_2F in saturated chlorofluoroalkanes is not attacked by nucleophiles even

under forcing conditions, whereas in the compounds $\text{CF}_2=\text{CX}\cdot\text{CCl}_2\text{F}$ ($\text{X}=\text{H}$ or F) reaction with such a mild nucleophile as chloride ion is easy, is accompanied by rearrangement, and is presumably initiated at the double bond. The susceptibility of fluorinated olefins to nucleophilic attack is well documented.³ Miller also presented some preliminary evidence⁴ that the reactions of these fluorinated allylic systems were first order in both olefin and nucleophile.

We have studied the kinetics of nucleophilic attack on 2,3,3-trichloro-1,1,3-trifluoropropene, produced by zinc dechlorination of 1,1,2,2,3-pentachloro-1,3,3-trifluoropropane. A typical reaction yielded a product mixture as follows:



The mixture was analysed by ^{19}F n.m.r. and i.r. spectroscopy, and was used directly in the kinetic experiments, since control experiments showed that under the mild conditions used the 1,2,3-trichloro-1,3,3-trifluoropropenes were unaffected by the nucleophiles employed. Reaction kinetics were followed by i.r. spectroscopy at 1732 cm^{-1} ($\text{CF}_2\cdot\text{CCl}\cdot\text{CCl}_2\text{F}$). Reaction with tetraethylammonium

chloride in chloroform solution at 25° converted this olefin quantitatively into $\text{CClF}\cdot\text{CCl}\cdot\text{CClF}_2$. Reaction products were determined by ^{19}F n.m.r. and i.r. spectroscopy. The reaction is pseudounimolecular, since it is an isomerization in which chloride ion acts catalytically. By varying the tetraethylammonium chloride concentration the reaction was found to be first order in both olefin and $\text{Et}_4\text{N}^+\text{Cl}^-$; k_2 (25°) $3.5 \times 10^{-3}\text{ l. mole}^{-1}\text{ sec}^{-1}$. This kinetic result, combined with the observations on rearrangement and the arguments presented by Miller² reinforce the conclusion that this reaction proceeds by an $\text{S}_{\text{N}}2'$ mechanism.

Preliminary studies with other nucleophiles, including trialkyl phosphites,⁵ indicate similar kinetic patterns, and give rearranged products. Tetraethylammonium bromide in chloroform is much less reactive than the chloride ($k_2 = 4 \times 10^{-4}\text{ l. mole}^{-1}\text{ sec}^{-1}$) as was seen earlier with fluorinated systems.^{2,4} This may reflect the relative nucleophilicities of the unsolvated anions,⁶ or may involve the complex question of the extent of ion-pairing, and the relative reactivities of free and paired anions, in the non-polar solvent used. Tetraethylammonium fluoride trihydrate in chloroform is a very ineffective nucleophile in this system. This contrasts strongly with the high reactivity of the monohydrate studied earlier,⁷ and agrees with recent observations on the effect of water in reducing the basicity (and clearly, from the present work, the nucleophilicity) of fluoride ion in non-aqueous solutions.

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