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STEREOCHEMICAL ASPECTS OF NUCLEOPHILIC SUBSTITUTION AT UNSATURATED FLUOROCARBON

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While the substitution of various nucleophiles on fluorinated olefins is perhaps the best known reaction in organic fluorine chemistry (1), the stereochemistry of this reaction has been almost completely ignored (2). Furthermore, the likelihood that the intermediate in these reactions is a carbanion (3) would make a stereochemical study an intriguing prospect for carbanion study.

Now that techniques are perfected enabling the separation and isolation of relatively large quantities of close-boiling isomers (preparative gas chromatography) we have initiated a program studying the reaction of potassium alkoxides with cis-and trans-2, 3-dichlorohexafluorobutene-2:

$$\underset{\text{I(cis/trans)}}{CF_3CCl{=}CClCF_3} \xrightarrow[\text{HOR}]{\text{-OR}} \underset{\text{II(cis/trans)}}{CF_3CCl = CORCF_3} \quad \begin{array}{l} \text{a, } R{=}CH_3 \\ \text{b, } R{=}CH_2CH_3 \\ \text{c, } R{=}CH(CH_3)_2 \end{array}$$

With potassium methoxide in methanol solvent at 25°, the cis butene I yields a vinyl ether mixture consisting of 92.8% cis and 7.34% trans IIa, while potassium ethoxide and isopropoxide gave cis/trans distributions of 94.5/5.61 IIb, and 96.5/3.49% IIc, respectively.

On the other hand, trans-butene I produced with methoxide, ethoxide, and isopropoxide cis/trans mixtures of 30.7/69.3, 29.9/70.0, and 28.1/71.9%[†]. These ratios exhibited only a slight temperature dependence; for example, employing ethoxide ion and cis-butene at 0° and 50° gave cis/trans distributions of 97.2/2.89% and 94.9/5.18%, while trans olefin at 50° gave 32.9/67.3%. The relative reactivity of the cis-and trans-butene towards ethoxide ion at 25° was determined by allowing a 48.3/51.7 cis/trans mixture to go 19.9% to completion. The remaining olefin mixture was found to be 54.9/45.2 while the vinyl ether was 47.8/52.2% cis/trans. The ratio of specific rate constants was calculated (4) to be:

$$r = \frac{k_t}{k_c} = 3.82$$

By reasoning in an analogous manner concerning the arguments summarized by S. Patai and Z. Rappoport (5) we conclude that alkoxide substitution on fluorinated olefins is governed by kinetic control. We also believe the results to be most consistent with the concept of a planar carbanion intermediate whose stereochemical fate is determined largely by differences in steric interaction of the various rotamers. Inspection of rotamer models shows that the least favorable configurations would involve trifluoromethyl interactions, a result consistent with expectations.

[†] In all cases a small excess of olefin was employed to detect any olefin isomerization; none occurred. Identity of the isomers was established from their IR and NMR spectra.

1. (a) D. D. Coffman, M. S. Raasch, G. W. Rigby, P. L. Barrick, and W. E. Hanford, *J. Org. Chem.* **14,** 747 (1949). (b) D. Osteroth, *Chemie und Technologie aliphatischer fluororganischer Verbindungen,* p. 67. Ferdinand Enke Verlag, Stuttgart (1964).

2. E. L. Eliel, *Stereochemistry of Carbon Compounds,* p. 368. Mc Graw-Hill Book Co., Inc., New York (1962).

3. See, for example, J. Hine, *Physical Organic Chemistry* 2nd Ed., p. 230. Mc Graw-Hill Book Co., Inc., New York (1962).

4. T. S. Lee in S. L. Friess and A. Weissberger, eds., *Technique of Organic Chemistry* Vol. VIII, p. 103. Interscience Publishers, New York (1953).

5. S. Patai and Z. Rappoport in S. Patai, ed., *The Chemistry of Alkenes,* p. 525. Interscience Publishers, New York (1964)