opening at high voltage is a further example unless there is prior thermal rearrangement.[12] On the other hand, low-lying excited states in aromatic systems can govern their reactivity.[13] While symmetry and simple MO arguments support our results, more complete calculations of the energetics are desirable.[14] We plan these as well as empirical studies of systems containing only π electrons, to parallel established sigmatropic rearrangements and electrocyclic reactions of solution chemistry.

[12] M. S. Baird and C. B. Reese, *Tetrahedron Lett.*, 2117 (1969).

[13] R. A. W. Johnstone and S. D. Ward, *J. Chem. Soc., C*, 1805, 2540 (1968); but see M. J. Bishop and I. Fleming, *ibid.*, 1712 (1969).

[14] *Cf.* D. T. Clark and R. A. Armstrong, *Theor. Chim. Acta*, **14**, 370 (1969).

[15] Research Fellow of the Alfred P. Sloan Foundation, 1969–1971.

[16] Work supported by the National Science Foundation (GU 2059) and the Advanced Research Projects Agency (Contract SD-100 with UNC Materials Research Center). We acknowledge discussions with Lee G. Pedersen, Ralph C. Dougherty, Don C. DeJongh, and Thomas A. Elwood, and the donation of samples by Milton Honig.

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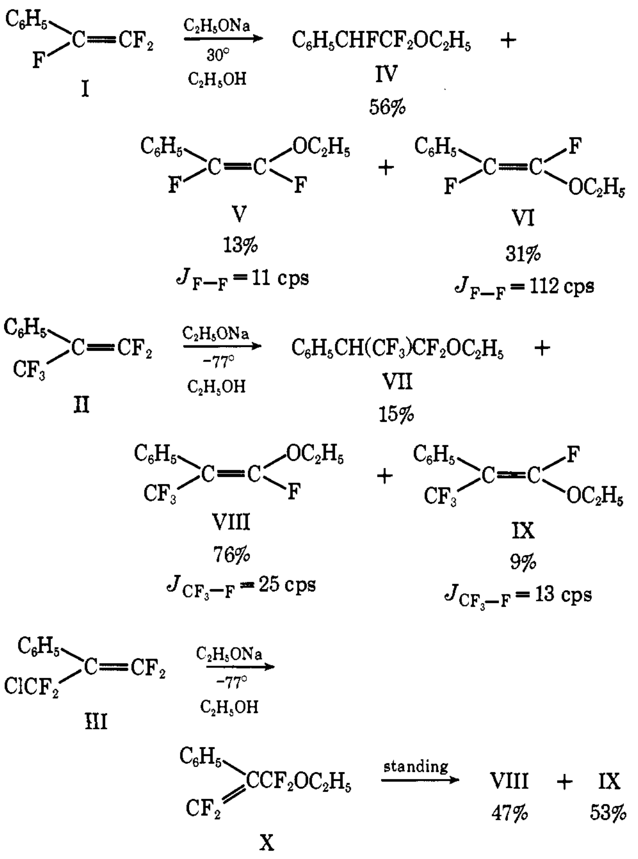
Nucleophilic Reactions of Fluoroolefins. Evidence for a Carbanion Intermediate in Vinyl and Allyl Displacement Reactions

Sir:

The reactions of nucleophiles, N⁻, with fluorinated olefins can lead to three types of products. In the presence of a proton-donating solvent, SH, the addition of NH across the double bond can occur, while in the absence of a readily available proton either vinyl or allyl displacement of halide may take place. However, the preferential displacement of chloride occurs rather than the addition of NH even in good protic solvents such as alcohols. Qualitatively, these reactions have been well documented in the literature.[1] We felt that these fluorinated olefins could therefore provide a good system for a quantitative study of nucleophilicities. First, a detailed mechanistic investigation was initiated and we wish to report some interesting aspects of these studies.

Three olefins, α,β,β-trifluorostyrene (I), 2-phenylperfluoropropene (II), and 3-chloro-2-phenylperfluoropropene (III), were chosen to react with sodium ethoxide in absolute ethanol. Addition products were expected from I and II and allylic displacement of chloride was expected from III. The allylic ether, X, was obtained from III. However, I yielded 44% of the vinyl ethers, V + VI, and II gave 85% of the vinyl ethers, VIII + IX. The product ratios of VI/V = 2.5 and VIII/IX = 8.3 indicated that there was some stereoselectivity in the formation of these vinyl ethers. There was no trace of X formed from the reaction of II. The purified allylic ether X rearranged on standing to give an almost 1:1 ratio of VIII:IX.[2] Structural assignments were made on the basis of fluorine-19 nmr spectra and the coupling constants for the various *cis–trans* isomers agreed well with those reported in the literature.[3] Unsaturated ethers arising from the displacement of fluoride are not uncommon products from cyclic fluoroolefins,[4] but are definitely not the expected product from acyclic fluoroolefins.[1] The possibility of VIII and IX arising from the saturated ether VII was ruled out since the dehydrofluorination reaction was at least six orders of magnitude slower than the reaction of ethoxide with II.[5]



There is little argument that addition and vinylic displacement reactions proceed through a carbanion intermediate; however, differences of opinion usually arise in discussing whether or not allylic displacement reactions go through an intermediate carbanion[4] or go through a concerted S_N2′ mechanism[6] similar to those postulated in hydrocarbon systems. One operational check for the presence of an intermediate carbanion would be a kinetic study. Bunnett has made use of the "element effect" as a criterion to differentiate between a one-step S$_N$2-like mechanism and the two-step mechanism involving a metastable intermediate in activated aromatic nucleophilic substitution reactions.[7] If the displacement of two different halogens like fluoride and chloride occurs at a similar rate, then the breaking of the carbon–halogen bond cannot be in-

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[1] An excellent review of this area was made by R. D. Chambers and R. H. Mobbs, *Advan. Fluorine Chem.*, **4**, Chapter 3 (1965).

[2] A similar rearrangement of $CH_3OCF_2CF{=}CF_2$ has been reported by B. L. Dyatkin, L. S. German, and I. L. Knunyants, *Dokl. Akad. Nauk SSSR*, **114**, 320 (1957).

[3] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, New York, N. Y., 1966, Chapter 11.

[4] J. D. Park, J. R. Lacher, and J. R. Dick, *J. Org. Chem.*, **31**, 1116 (1966).

[5] H. F. Koch and A. G. Toczko, unpublished results.

[6] W. T. Miller, J. H. Fried, and H. Goldwhite, *J. Amer. Chem. Soc.*, **82**, 3091 (1960).

[7] J. F. Bunnett, E. W. Garbisch, Jr., and K. M. Pruitt, *ibid.*, **79**, 385 (1957).

Table I. Kinetic Data for Reaction of $C_6H_5C(R){=}CF_2$ with Sodium Ethoxide in Ethanol

Compd	R	$[NaOC_2H_5]$, M	Temp, °C	$k_1 \times 10^3$, sec^{-1}
I	F	0.66	30.0	1.6
II	CF_3	0.34	−77	1.9
III	CF_2Cl	0.30	−77	1.8
XI	CF_2CF_3	0.34	−77	0.67
XII	CF_2Cl (*m*-Cl)	0.34	−77	25

volved in the rate-determining step of the reaction. A two-step mechanism involving a carbanion intermediate would be consistent with these results.

Results of the kinetic runs are summarized in Table I. Since base is not consumed in a 1:1 stoichiometry, rate studies were carried out under pseudo-first-order conditions by starting with at least a tenfold excess of ethoxide. In the low-temperature runs each kinetic point consisted of a separate experiment made by breaking a fragile bulb containing a solution of olefin in ethanol into a temperature-equilibrated solution of ethoxide ion. The reaction was stopped by injecting a slight excess of a dilute precooled solution of sulfuric acid in ethanol. The disappearance of starting olefin was followed using anisole as an unreactive tracer for glpc analysis. Eight points, spanning three half-lives, and an infinity point constituted a run. During the glpc analysis of each point the products were checked. There was no change in the product ratios during the course of each run. Two additional olefins, 2-phenylperfluorobutene-1 (XI) and 3-chloro-2-(*m*-chlorophenyl)perfluoropropene (XII), were also included in the kinetic studies. Four minor products from the reaction of ethoxide with XI have not yet been assigned structures;[8] however, the major product (60%) was $CF_3CF{=}C(C_6H_5)CF_2OC_2H_5$, with the CF_3 and phenyl groups *cis* to each other. This product arose from the displacement of an allylic fluoride. The similarity of the rates of reaction for II, III, and XI strongly suggests that the rate-determining step in all three cases is the initial attack of ethoxide on $CF_2{=}$ to form an intermediate carbanion which then reacts to form the various observed products. Using the rate obtained for XII, an approximate Hammett $\rho = 3$ was calculated. This value is in agreement with reactions proceeding through carbanion intermediates.[9]

Some generalizations about subsequent reactions can be made by using the model of a discrete carbanion intermediate. Clearly, the loss of a β chloride is the fastest process;[10] however, loss of fluoride is competitive with the rate of protonating the carbanion intermediate. Ritchie has reported that rates of reaction of methanol with carbanions become diffusion controlled only when the ΔpK is greater than 18.[11] We estimate the pK_a's $C_6H_5CHFCF_3 \cong 30$ and $C_6H_5CH(CF_3)_2 \cong 25$. The ΔpK values with respect to methanol would be about 15 and 10, which fall within the limit of 18.[12] The different ratios of adduct to displacement products for I and II can be attributed to the differences in the rates of protonation of the two carbanions which in turn are attributed to the different ΔpK values. An alternate explanation involves the possible difference in geometry of the two carbanions. The carbanion arising from I could be in a pyrimidal configuration due to the α fluorine while that generated from II could be planar to allow conjugation with the phenyl ring. This type of argument has been used by Streitwieser to explain the relatively slow deuterium and tritium exchange reaction for benzal fluoride relative to toluene.[13] We are continuing to carry out experiments which will attempt to find out which of the above reasons best fits these systems.

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[8] From their proximity in glpc analysis, it is assumed that one represents the addition product, two are the corresponding vinyl ethers, and the fourth is the other allylic ether.

[9] A. Streitwieser, Jr., and H. F. Koch, *J. Amer. Chem. Soc.*, **86**, 404 (1964).

[10] This is consistent with acyclic olefins having terminal =CFCl groups as well as allylic chloride and is also true in the cyclic systems (see ref 4).

[11] C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, **90**, 3415 (1968).

[12] We are indebted to Professor Streitwieser for sending us a copy of David Holtz's Thesis (University of California, Berkeley, Calif., 1968) which allowed us to estimate the pK_a values.

[13] A. Streitwieser, Jr., and F. Mares, *J. Amer. Chem. Soc.*, **90**, 2445 (1968).

[14] (a) Based in part on a Senior Honors Thesis by A. J. Kielbania, Jr., Ithaca College, Ithaca, N. Y., 1969; (b) supported by an NSF-URP, GY 4287 grant during the summer of 1968.

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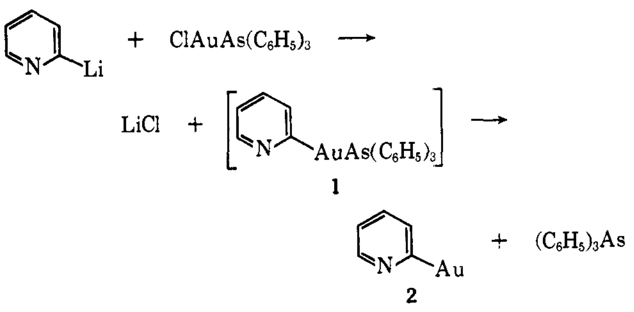
Organogold Chemistry. III.[1] 2-Pyridylgold(I)

Sir:

This communication reports the preparation of 2-pyridylgold(I) (**2**), the simplest member of a new class of organogold compounds. The compound is prepared by addition of solid chloro(triphenylarsine)gold(I) to a THF (or ether) solution of 2-pyridyllithium at −40°. As the solution warms, the arsine complex dissolves (*ca.* −25°), followed by precipitation of the product (*ca.* −5°) in 90–100% yield. The reaction presumably proceeds through compound **1** as an intermediate, followed by displacement of triphenylarsine by the unshared electron pair on nitrogen. Triphenylarsine can be isolated from the solvent in yields of 75–95%.



2-Pyridylgold(I) is insoluble in most common organic solvents, but can be recrystallized from high-boiling

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[1] Paper II: L. G. Vaughan and W. A. Sheppard, *J. Organometal. Chem.*, in press; Paper I: L. G. Vaughan and W. A. Sheppard, *J. Amer. Chem. Soc.*, **91**, 6151 (1969).