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THE NATURE OF FLUORIDE TRANSFER FROM COMPLEX FLUORIDE ANIONS TO CARBENIUM IONS[1]

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The transfer of fluoride to an electron deficient center from complex fluoride anions, such a tetrafluoroborate, is the basis of numerous methods for forming organic fluorides [3] The Schiemann reaction, for example, achieves aryl fluoride production from aryldiazonium tetrafluoroborate,[4a] hexafluoroantimonate,[4b] or hexafluorophosphate[4c] salts in a process which has been represented as involving fluoride transfer to an aryl cation [4a,5] Curiously, however, a similar generality in fluoride substitution has not been observed in comparable processes that would involve alkyl cations [6,7] We wish to report results that have direct bearing on the mechanism of fluoride transfer from complex fluoride anions to a carbenium ion center

Alkyl azides react with nitrosonium salts to form the corresponding carbenium ion salts, nitrogen and nitrous oxide [8] In contrast to diazotization reactions of amines in which water is produced, alkyl azide-nitrosonium salt reactions yield carbenium ion salts cleanly Thus, the reaction of benzyl azide with $NO^+BF_4^-$ in the nonnucleophilic solvent deuterochloroform[9] would have been expected to yield benzyl tetrafluoroborate and, subsequently, benzyl fluoride and boron trifluoride However, only benzaldehyde (15%) and alkylation products (50%) were observed no benzyl fluoride was formed Similarly, no alkyl fluoride could be detected in reactions of *n*-hexyl azide and cyclohexyl azide with $NO^+BF_4^-$ under the same reaction conditions [10]

Surprisingly, azidonitriles react with $NO^+BF_4^-$ to produce fluoro-substituted nitriles in nearly quantitative yields Results from the reactions of a series of azidonitriles with $NO^+BF_4^-$ in deuterochloroform are given in Table I The nature of the reaction and the extent of rearrangement serve to classify this fluoride transfer process as invloving carbenium ion intermediates However, since fluoride substitution does not occur in similar reactions of $NO^+BF_4^-$ with monofunctional alkyl azides, fluoride transfer cannot be represented simply as an intermolecular reaction of the tetrafluoroborate anion with a carbenium ion The nitrile group is involved in the fluoride transfer process

Table I Product Yields from Reactions of Azidonitriles With $NO^+BF_4^-$ in $CDCl_3$ at 25° [a]

$$N_3(CH_2)_nCN + NO^+BF_4^- \xrightarrow{-N_2,N_2O} F(CH_2)_nCN + CH_3CHF(CH_2)_{n-2}CN + CH_3CH_2CHF(CH_2)_{n-3}CN + BF_3 \qquad (1)$$

n=	1,%[b]	2,%[b]	3,%[b]
2	100		
3[c]	40	60	
4[d]	22	78	
6	30	45	25

[a] The azidonitrile (5 mmol) in 3 ml of $CDCl_3$ was added to $NO^+BF_4^-$ (6 mmol) in 7 ml of $CDCl_3$ Products were identified by spectroscopic and chemical methods [b] Relative product yields Actual yield of *1* + *2* + *3* was generally 90-98% based on GLC and ^1H NMR analyses Variation in relative yields were within ± 2% [c] 8% 3-Butenenitrile was also observed [d] 4% 4-Pentenenitrile was also detected

Two explanations may be advanced to explain the role of the nitrile in these fluoride transfer reactions (1) intermolecular nitrilium ion formation followed by fluoride substitution and (2) intramolecular formation of a relatively unstable nitrilium ion followed by ring opening through fluoride substitution However, nitrilium ions do not undergo fluoride substitution with tetrafluoroborate *N*-Benzylacetonitrilium tetrafluoroborate did not yield benzyl fluoride even after refluxing in acetonitrile for several hours In addition, when either cyclohexyl azide or *n*-hexyl azide was reacted with $NO^+BF_4^-$ in deuterochloroform to which 0 5 equiv of acetonitrile (based on azide) was added, no alkyl fluoride products were observed [11] With respect to intramolecular nitrilium ion formation, ring strain would have been expected to prevent the formation of 3-fluoroalkanenitriles Amide products, resulting from either intermolecular or intramolecular processes yielding nitrilium ions followed by reaction with water, were not observed in those reactions whose results are reported in Table I

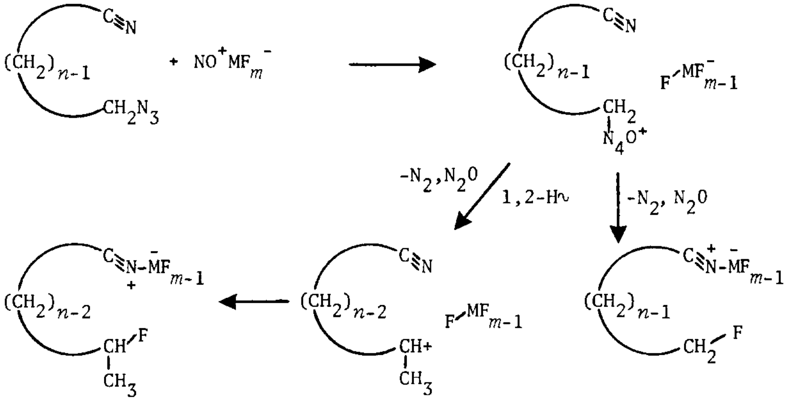
Relatively samll amounts of water (1-2 equiv) added to the nitrosonium salt prior to the azidonitrile produced an observable increase in the rate of gas evolution but did not measurably affect the reaction products No additional products were observed, and the relative yields of fluoride substituted products were essentially constant [12] This observation suggested that aminonitriles might also undergo fluoride substitution in nitrosations with $NO^+BF_4^-$ Treatment of β-aminopropionitrile with $NO^+BF_4^-$ in deuterochloroform under anhydrous conditions did in fact produce β-fluoropropionitrile. However, the yield of the fluoride substitution product was only 34%, a 66% yield of β-hydroxypropionitrile, formed presumably by internal return of water associated with the diazonium group, was also observed.

Variation of the complex fluoride anion of the nitrosonium salt produced a dramatic effect on the rate of reaction with azidonitriles and on the resulting product distribution. Treatment of 4-azidobutanenitrile with $NO^+SbF_6^-$ in deuterochloroform containing 1.0 equiv of water resulted in rapid gas evolution and the product distribution given in eq 2. Under idential reaction conditions

$$N_3CH_2CH_2CH_2CN + NO^+SbF_6^- \xrightarrow[\text{1eq } H_2O]{CDCl_3} \underset{15\%}{\mathit{1}(n{=}3)} + \underset{37\%}{\mathit{2}(n{=}3)} + \underset{36\%}{H_2C{=}CHCH_2CN} + \underset{12\%}{H_3CCH{=}CHCN} \tag{2}$$

4-azidobutanenitrile reacted three-times slower with $NO^+BF_4^-$ to give *1*(*n*=3,32%), *2*(*n*=3,61%), 3-butenenitrile (6%) and 2-butenenitrile (1%). Nitrosonium hexafluorophosphate[13] was only slightly more reactive than $NO^+BF_4^-$ towards 4-azidobutanenitrile yielding *1*(*n*=3,18%), *2*(*n*=3,72%), 3-butenenitrile (7%) and 2-butenenitrile (3%).[14]

These results suggest that fluoride transfer from complex fluoride anions occurs through association of the developing Lewis acid with the basic nitrile group, as described in Scheme I. The reactivities of nitrosonium salts with azidonitriles follow the order of Lewis acidities of the



Scheme I

developing Lewis acids (SbF_5>PF_5>BF_3),[14] and indicate a requirement for association of these developing acids with the nitrile group during nitrosation. Water acts to complex with the developed Lewis acid, decreasing the degree of association of the Lewis acid with unreacted azidonitrile. Intramolecular association with the complex fluoride anion according to Scheme I provides the proper geometry for concurrent fluoride transfer and nitrile-Lewis acid complex formation This geometry, however, would be expected to limit fluoride substitution to carbon positions more than one carbon removed from the nitrile group This, in fact, has been observed, azidoacetonitrile does not form fluoroacetonitrile in reactions with nitrosonium salts

Work is continuing to determine the scope of the fluoride transfer process with other basic functional groups and selected leaving groups

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9 Chloroform-*d* was used to facilitate proton nmr product identifications

10 Cyclohexyl azide gave mainly cyclohexene and cyclohexanone, *n*-hexyl azide did not react appreciably (< 5%) with $NO^+BF_4^-$ under these reaction conditions

11 Cyclohexyl azide gave cyclohexene, cyclohexanone, and *N*-cyclohexylacetamide, *n*-hexyl azide yielded hexene, hexanal, *N*-(2-hexyl)acetamide and *N*-(1-hexyl)acetamide

12 However, in acetonitrile azidonitriles react with $NO^+BF_4^-$ to produce acetamide products to the exclusion of fluoronitriles

13 Nitrosonium salts were purified by recrystalization prior to use

14 The relative merits of aryldiazonium SbF_6^-, BF_4^- and PF_6^- salts in the Schiemann reaction have been discussed [4] The implied reactivities of these salts correspond to those observed here

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