cenylethanol promptly gives the α-carbocation.[10] This result is in agreement with the course of the ionic additions to vinylferrocenes,[15,16] and it seems to substantiate the conclusion by which the similar stability of the α- and β-bridged carbocations examined above is probably due to the ferrocenophane structure, which orients the empty orbital of the carbocation in the proper direction to be stabilized by the ferrocenyl group.

This interaction seems to be specific and is easily perturbed by the substituents in the bridge, as is proved by the observation that by dissolving 7-methyl- and 7-butyl[4]ferrocenophan-7-ol in 50% H_2SO_4 the carbocations derived from 7-methyl- and 7-butyl[4]ferrocenophan-6-ol are obtained.[17]

Another example in the literature of the peculiar interaction of the interannular bridge with the iron is found in the unusual redox potential of [3]ferrocenophane as compared to dialkyl ferrocenes.[18]

Experimental Section

The samples of [4]ferrocenophan-7-ol and -7-one were kindly offered by Professors Hisatome and Yamakawa. [4]Ferrocenophan-6-ol and -6-one were prepared according to literature methods.[19] 9-Methyl[4]ferrocenophan-6-ol and -6-one were prepared by the method of Horspool et al.[20]

The NMR spectra were recorded by a Jeol C-60 HL spectrometer. The electronic spectra and the spectral measurements were made with a Beckmann DB-GT spectrophotometer. The aqueous sulfuric acid solutions were standardized according to the methods described previously.[9,10]

For the assessment of the reversibility of the equilibrium involving [4]ferrocenophane 7-carbocation, 100 mg of the alcohol was dissolved in 3 mL of 30% H_2SO_4; after 15 min, the acid solution was diluted with 10 mL of water, carefully neutralized with aqueous $NaHCO_3$, and extracted with ether; 85 mg of a compound was recovered, mp 160–161 °C ([4]ferrocenophan-7-ol melts at 160–162 °C).[21] [4]Ferrocenophan-7-one was successfully submitted to the same procedure.

The evaluation of the equilibrium constants was carried out according to equations $H_0 = pK_a - \log I$ and $H_R = pK_{R^+} - \log I$, where I is the ionization ratio.[9,10]

Acknowledgments. The authors wish to thank Professor G. Illuminati for helpful discussions.

Registry No. I, 34823-20-6; **II**, 70355-46-3; **III**, 70355-47-4; **IV**, 70355-48-5; **V**, 70355-49-6; **VI**, 70355-50-9; [4]ferrocenophan-7-ol, 34870-41-2; [4]ferrocenophan-6-ol, 55522-48-0; 9-methyl[4]ferrocenophan-6-ol, 70355-45-2; [4]ferrocenophan-7-one, 41583-25-9; [4]ferrocenophan-6-one, 31884-28-3; 9-methyl[4]ferrocenophan-6-one, 12182-14-8.

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Reactions of the Nitrosonium Ion. 11. Fluoride Transfer from Complex Fluoride Anions to Carbenium Ions in the Nitrosative Decomposition of Aliphatic Azides[1]

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Results from nitrosative reactions of aliphatic azides, azido nitriles, and phenoxy azides with nitrosonium salts in chloroform are reported. The presence of the basic nitrile or ether functional group causes a significant increase in the yield of fluoroalkane products, from 5% with 1-azidohexane to 50–81% in reactions with azido nitriles. Elimination reactions and protonic decomposition (Curtius rearrangement), which are major competing processes in the nitrosative decomposition of aliphatic azides, are minimized or not observed in nitrosative reactions with azido nitriles and phenoxy azides. Fluoride transfer is even competitive with intramolecular Friedel–Crafts alkylation from nitrosative reactions of phenoxy azides, but nitrosative decomposition of benzyl 5-azidopentanoate results in the exclusive formation of lactones. Enhancement of fluoride substitution is explained by intimate association of the basic functional group at the surface of the nitrosonium salt causing nitrosative decomposition of the azide to occur in close proximity to the complex fluoride anion.

Although complex fluoride anions such as tetrafluoroborate are generally regarded as very weak nucleophiles, fluoride transfer from complex fluoride anions to an electron-deficient center has achieved both synthetic and mechanistic importance. Decomposition of arenediazonium tetrafluoroborate salts (the Schiemann reaction[2-6]) has long been regarded for its synthetic value as a selective method for the synthesis of aryl fluorides. However, because of the relative instability of the corresponding alkyl diazonium salts and the concomitant formation of water in diazotization processes with primary amines,[7] attempts to extend this useful process to aliphatic

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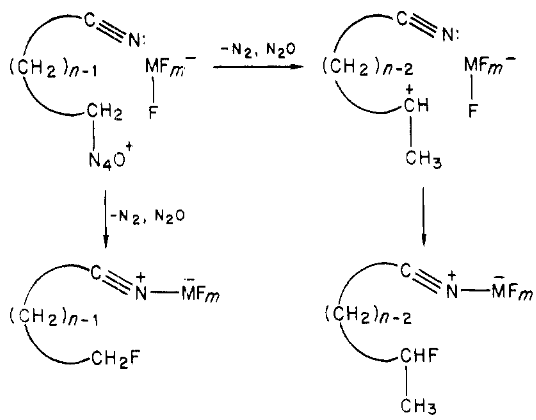
0022-3263/79/1944-2923$01.00/0

Scheme I



systems have generally failed.[8,9] However, alternate approaches to fluoride capture by carbocations through the use of fluoroformates have not been similarly limited for aliphatic systems.[10]

Unlike nitrosations of primary amines which form water as a byproduct (eq 1), the nitrosation of alkyl azides

$$RNH_2 + NO^+MF_n^- \rightarrow R^+MF_n^- + N_2 + H_2O \quad (1)$$

$$RN_3 + NO^+MF_n^- \rightarrow R^+MF_n^- + N_2 + N_2O \quad (2)$$

produces only nitrogen and nitrous oxide (eq 2).[11] The generation of the nonnucleophilic N_4O ($N_2 + N_2O$) leaving group in nitrosation reactions with azides avoids mechanistic complications from trapping of the resultant carbocation by nucleophiles formed in the evolution of the leaving group. Thus alkyl azides would appear to be effective precursors to reactive carbocations and, from nitrosation reactions that are performed in nonnucleophilic media, to alkyl fluorides (eq 3).

$$R^+MF_n^- \rightarrow RF + MF_{n-1} \quad (3)$$

The generation of carbocations by reactions of alkyl chlorides and alkyl chloroformates with silver salts of complex fluoride anions leads to alkyl fluorides,[9,12] which are similarly formed from alkyl fluoroformates by treatment with boron trifluoride etherate.[10] These results, as well as those from reactions of a variety of similar alcohol derivatives,[3] are described by carbenium ion capture resulting from fluoride donation from the complex fluoride anion (eq 3). The nonnucleophilicity of the leaving group and the reaction medium are implied requirements for these reactions.

We have previously reported that azido nitriles react with nitrosonium tetrafluoroborate to produce fluorosubstituted nitriles in nearly quantitative yield.[13] Remarkably, monofunctional aliphatic azides do not form alkyl fluorides in significant yields when treated with $NO^+BF_4^-$ under the same reaction conditions; alternate reaction pathways that include elimination, alkylation, and oxidation are dominant. This apparent inconsistency has been explained by association of the developing Lewis acid with the basic nitrile group during fluoride transfer from the complex fluoride anion to the carbocation (Scheme I). This paper reports extensions of this novel nitrosative fluoride substitution process and suggests a specific role for basic functional groups in fluoride transfer from complex fluoride anions to carbocations.

Results and Discussion

Azidoalkanes. Although trityl tetrafluoroborate is rapidly formed upon treatment of trityl azide with nitrosonium tetrafluoroborate in anhydrous chloroform,[11] the combination of 1-azidohexane and the insoluble $NO^+BF_4^-$ in chloroform under the same conditions effects a slow evolution of gas and results in a complex mixture of organic products that, following the addition of water to the reaction mixture, consists of 1-fluorohexane (5%), 2-hexene (28%), and hexanal (20%). Hexanal is formed exclusively from the hexylideneiminium ion by water quenching. These results are fully accommodated by the mechanistic sequence that is outlined in Scheme II.

Scheme II

$$CH_3(CH_2)_4CH_2N_3 + NO^+BF_4 \rightarrow CH_3(CH_2)_4CH_2N_4O^+BF_4^- \quad (4)$$

$$CH_3(CH_2)_4CH_2N_4O^+BF_4^- \xrightarrow{-N_2,\ N_2O} CH_3(CH_2)_4CH_2F + BF_3 \quad (5)$$

$$CH_3(CH_2)_4CH_2N_4O^+BF_4^- \xrightarrow{-N_2,\ N_2O} CH_3(CH_2)_2CH{=}CHCH_3 + HBF_4 \quad (6)$$

$$CH_3(CH_2)_4CH_2N_3 + HBF_4 \rightarrow CH_3(CH_2)_4CH_2N_3H^+BF_4^- \xrightarrow{-N_2} CH_3(CH_2)_4CH{=}NH_2^+BF_4^- \quad (7)$$

In contrast to the results of prior investigations in which the production of alkyl fluorides is described as fluoride capture by carbenium ions,[6,9,12] only unrearranged 1-fluorohexane is produced in the reaction of 1-azidohexane with $NO^+BF_4^-$; 2-fluorohexane is not observed within the limits of our detection (<0.5%). 1-Hexene, which is stable under these reaction conditions, is similarly absent.

Acid-promoted rearrangement of 1-azidohexane (Curtius rearrangement) competes favorably with nitrosative decomposition. As has been observed earlier,[14] only hydrogen migration occurs in the acid-promoted Curtius rearrangement of 1-azidohexane (eq 7); the product from alkyl migration is not observed. Surprisingly, oxidative hydrogen abstraction from the α position of 1-azidohexane by the nitrosonium ion[15] does not occur; such a process would have been expected to form hexanenitrile[16] which is not detected.

Except for the production of fluoroalkanes, similar results were observed in the nitrosative decomposition of cyclohexyl and benzyl azides. Treatment of azidocyclohexane with $NO^+BF_4^-$ in anhydrous chloroform at 25 °C produced cyclohexene (35%), cyclohexanone (8%), and ϵ-caprolactam (25%). When the same reaction was performed in the presence of 1 equiv of water, cyclohexene

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Table I. Product Yields from Nitrosative Decomposition of Azido Nitriles in Chloroform at 25 °C[a]

$N\equiv C(CH_2)_nN_3$, n	yield,[b] %				
	$F(CH_2)_nCN$	CH_3CHF-$(CH_2)_{n-2}CN$	CH_3CH_2CHF-$(CH_2)_{n-3}CN$	$H_2C{=}CH$-$(CH_2)_{n-2}CN$	$CH_3CH{=}CH$-$(CH_2)_{n-3}CN$
2[c]	100	<1		<1	
3[d]	36	51	<1	7	6
4	21	75	<2	4	<1
6[e]	25	60	15	<2	<1

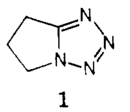
[a] Reactions performed in the absence of added water by addition of the azido nitrile to $NO^+BF_4^-$. [b] Relative product yield (±3% from duplicate runs). Unless specified otherwise, absolute product yields were ≥85%. [c] Starting material was recovered in 50% yield. [d] Trimethylenetetrazole (1) was isolated in 24% yield. [e] Unreacted azide was isolated in 40% yield.

(20%), cyclohexanone (16%), ε-caprolactam (12%), and 2-fluorocyclohexanone (26%) were observed. The formation of cyclohexanone and ε-caprolactam is consistent with the Curtius rearrangement (proton migration and ring expansion),[14] although α-hydrogen abstraction from the reactant azide by the nitrosonium ion[15] could have initiated the production of these products. 2-Fluorocyclohexanone presumably resulted from nitrosyl fluoride addition to cyclohexene.[17] In nitrosation reactions with benzyl azide only benzaldehyde (15%) and Friedel–Crafts alkylation products (50%) were observed.

The results obtained for nitrosation of n-hexyl, cyclohexyl, and benzyl azides describe the relative insignificance of fluoride transfer from the weakly nucleophilic tetrafluoroborate anion to aliphatic carbenium ions (eq 3) or their reactive nitrosyl–azido precursors. Elimination or alkylation reactions are dominant, and the protonic acid produced in these processes is sufficient to promote the Curtius rearrangement of the reactant azides.

Azido Nitriles. In direct contrast to the results obtained with simple azidoalkanes, nitrosation of azido nitriles in chloroform produces fluoro nitriles as the predominant products. Results from nitrosation reactions with a representative series of azido nitriles are presented in Table I. Elimination products are minor contributors to the overall product distribution. Amide products resulting from intermolecular trapping of intermediate carbenium ions are not observed, and products resulting from the Curtius rearrangement are not formed. The observation of rearranged fluoro nitriles as well as olefinic substrates implicates carbenium ion intermediates in these reactions; consistent with this interpretation, attempts to nitrosate azidoacetonitrile with $NO^+BF_4^-$ were not successful even after heating at 50 °C for 2 h.

In addition to the fluoro nitrile and elimination products produced in nitrosation reactions of 4-azidobutanenitrile with $NO^+BF_4^-$, trimethylenetetrazole (1) was also observed



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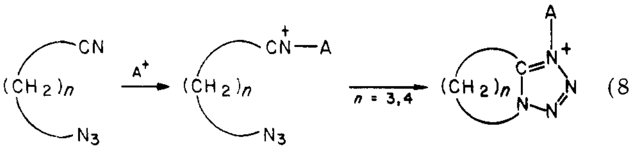
in 28% yield. The formation of tetrazoles by acid-promoted intramolecular cyclization of azido nitriles (eq 8)



(8)

has been well documented,[18] and the formation of 1 in nitrosation reactions of 4-azidobutanenitrile is presumably a consequence of boron trifluoride production. In separate experiments, 4-azidobutanenitrile was shown to form the corresponding tetrazole rapidly in reactions promoted by boron trifluoride and antimony pentafluoride in chloroform.

The striking contrast of the results from nitrosation of azido nitriles and azidoalkanes implicates a mechanistic change through which the nitrile functional group assists fluoride transfer. However, intermolecular nitrilium ion formation cannot account for the observed results since nitrilium ions do not undergo fluoride substitution with tetrafluoroborate.[11,13] Nitrilium ion formation from primary aliphatic azides leads to amide products following quenching with water.[11] For example, treatment of 1-azidohexane with $NO^+BF_4^-$ in chloroform to which 1 equiv of acetonitrile is added produces, in addition to 2-hexene and hexanal after quenching with water, N-(1-hexyl)acetamide and N-(2-hexyl)acetamide in a 1:1.2 molar ratio; neither 1- nor 2-fluorohexane could be detected. Even when only 0.5 molar equiv of acetonitrile is employed for nitrosation of 1-azidohexane, alkyl fluoride products are not formed. Ring-size effects and the absence of cyclic amide products similarly discount the possibility that intramolecular nitrilium ion formation could aid fluoride transfer.

Although previous studies have described the stability of nitrogen heterocycles toward nitrosonium salts,[19] the possibility that tetrazoles could undergo nitrosative decomposition has not been investigated. In a separate experiment, 1 has been found to be stable toward $NO^+BF_4^-$ in chloroform even at 50 °C. This observation, together with our inability to obtain the bicyclic tetrazole (eq 8) when $n = 2$, indicates the improbability of this pathway for alkyl fluoride production.

As described by the data in Table I, treatment of 3-azidopropanenitrile with $NO^+BF_4^-$ in chloroform produced only 3-fluoropropanenitrile; neither 2-fluoropropanenitrile nor acrylonitrile was observed. When the same reaction was performed in the presence of 1 molar equiv of added water, 3-fluoropropanenitrile remained the only reaction product. In contrast, 3-aminopropanenitrile reacted with $NO^+BF_4^-$ under identical conditions to yield 3-fluoropropanenitrile (17%) and 3-hydroxypropanenitrile (38%) as well as the ammonium salt of 3-aminopropanenitrile (45%). These results clearly differentiate nitrosation of azides from nitrosation of amines. The production of 3-hydroxypropanenitrile can be attributed to internal return of the nucleophilic water formed in the diazotization of 3-aminopropanenitrile (eq 1).

The addition of relatively small amounts of water (1–2 molar equiv) to the nitrosonium salt prior to reaction with

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Table II. **Product Yields from Nitrosative Decomposition of 4-Azidobutanenitrile**[a]

	yield,[b] %				
reactant	$F(CH_2)_3CN$	CH_3CHFCH_2CN	$H_2C{=}CHCH_2CN$	$CH_3CH{=}CHCN$	1
$NO^+BF_4^-$	26	37	5	4	28
$NO^+PF_6^-$	15	61	<1	<1	24
$NO^+SbF_6^-$	4	10	10	8	68
$NO^+BF_4^- + H_2O$	38	61	1	<1	<1
$NO^+PF_6^- + H_2O$	18	72	7	3	<1
$NO^+SbF_6^- + H_2O$	15	37	36	12	<1
$BF_3 + NO^+BF_4^-$	22	16	<1	<1	62
$SbF_5 + NO^+SbF_6^-$	<1	<1	<1	<1	100

[a] Reactions performed in chloroform by addition of the azido nitrile to the nitrosonium salt at 25 °C. [b] Relative product yield. Absolute product yields were ≥85%.

the azido nitrile produces an observable increase in the rate of gas evolution but does not affect product formation: alcohol, nitrite, and ether products were not observed from nitrosation reactions with azido nitriles (n = 2–4, 6). Table II describes the results from reactions of representative nitrosonium salts with 4-azidobutanenitrile in the presence and absence of added water or Lewis acids. The presence of water clearly minimizes tetrazole formation and thus enhances the yield of fluoro nitrile products. Only in nitrosation reactions with $NO^+BF_4^-$ is the ratio of 4- to 3-fluorobutanenitrile markedly affected by the presence of water, possibly because of hydrogen fluoride addition to the alkene products. The role of water in these reactions is primarily aquation of the nitrosonium ion and similar association with Lewis acids formed by fluoride transfer which minimizes tetrazole formation.[20]

If fluoride transfer occurs by the process outlined in Scheme I, saturation of the nitrile functional group with Lewis acid would be expected to inhibit fluoride transfer. To test this hypothesis, we added 4-azidobutanenitrile to $NO^+BF_4^-$ in a chloroform solution that was saturated with boron trifluoride. Although tetrazole formation competes with nitrosative decomposition under these conditions, fluoride substitution products are readily formed (Table II). Indeed, the presence of boron trifluoride provides an increase in the relative yield of the terminal fluoro nitrile.

The results obtained from nitrosative decomposition of azido nitriles can be explained by mechanistic considerations similar to those invoked to describe aryl fluoride production from arenediazonium salts.[4-6] Nitrosation reactions that are performed in nonnucleophilic solvents such as chloroform involve substrate interaction with two phases. Nitrosation presumably occurs at the surface of the solid nitrosonium salt. The basic nitrile functional group of azido nitriles serves to bind the azido nitrile to the surface of the nitrosonium salt and, therefore, in close proximity to the weakly nucleophilic complex fluoride anion. With nitrile association, the nitrosated azido group (RN_4O^+) is restricted to form carbenium ion intermediates at the surface of the nitrosonium salt. In contrast, although nitrosation of azidoalkanes is similarly expected to occur at the surface of the nitrosonium salt, the hydrocarbon end of these compounds is constrained in the solvent phase; carbenium ion formation, which occurs with the loss of nitrogen and nitrous oxide, therefore occurs at a greater distance from the solid surface. At this greater distance elimination or alkylation, rather than substitution, becomes the preferred reaction pathway. This explanation accounts for the absence of 2-fluorohexane in nitrosation reactions of 1-azidohexane and is also consistent with the absence of alcohol products when azido nitriles are nitrosated in the presence of added water.

Association of Lewis acids such as boron trifluoride with the nitrile or azide functional group inhibits further nitrosative decomposition. Indeed the rate of reaction slows significantly after the evolution of approximately 20% of expected gas (eq 2). However, unlike reactions with 3-azidopropanenitrile and 7-azidoheptanenitrile which occur with the stoichiometry predicted by eq 9, nitrosative

$$2N_3(CH_2)_nCN + NO^+BF_4^- \rightarrow F(CH_2)_nCN + N_2 + N_2O + F_3\overset{-}{B}\overset{+}{N}_3(CH_2)_nCN \quad (9)$$

decomposition of 4-azidobutanenitrile and 5-azidopentanenitrile is not terminated with the increase in concentration of the Lewis acid. The observed change in the ratio of primary to secondary fluoro nitrile that is observed when the nitrosation of 4-azidobutanenitrile is performed in the presence and absence of boron trifluoride may reflect a significant change in the rates for hydrogen migration for the associated azido nitriles (eq 10, A = NO, BF_3).

$$A\overset{+}{N}CCH_2CH_2CH_2N_4O^+ \rightarrow A\overset{+}{N}CCH_2\overset{+}{C}HCH_3 + N_2 + N_2O \quad (10)$$

The results presented in Table II for nitrosation of 4-azidobutanenitrile with nitrosonium salts having different complex fluoride anions reflect the relative ease for fluoride transfer. Results obtained with $NO^+PF_6^-$ in the absence of added water describe the highest yield of fluoro nitriles; nitrosation with $NO^+BF_4^-$ produces the highest yield of fluoro nitriles when the reaction is performed in the presence of added water. Thus the ease of fluoride transfer from BF_4^- is similar to that from PF_6^-, and no further differentiation can be made from these results. However, as expected from the relatively high Lewis acidity of antimony pentafluoride,[21] fluoride transfer from SbF_6^- is relatively slow; in nitrosation reactions with $NO^+SbF_6^-$, elimination competes favorably with fluoride substitution.

Attempts to correlate the results obtained for nitrosation of azides or amines with those for halogen abstraction by $Ag^+BF_4^-$ were not successful. 5-Bromopentanenitrile was recovered intact even after heating this compound with silver tetrafluoroborate in chloroform at 70 °C for more than 50 h. Silver halide was not produced in this process nor in an attempted reaction in ether.

Phenoxy Azides. To test the generality of enhanced fluoride transfer with organic azides that possess basic functional groups, we nitrosated a series of phenoxy azides, similar to the azido nitrile series, with $NO^+BF_4^-$. Nitrosation of phenoxy azides was considered to be a sensitive test for this mechanistic interpretation because of the

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[20] By analogy, boron trifluoride etherate does not promote tetrazole formation from azidonitriles.

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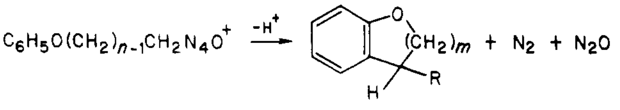
Table III. Product Yields from Nitrosative Decomposition of Phenoxy Azides in Chloroform at 25 °C[a]

$C_6H_5O(CH_2)_nN_3$,	yield,[b] %				
n	C_6H_5O-$(CH_2)_nF$	C_6H_5O-$(CH_2)_{n-2}CHFCH_3$	C_6H_5OH	2[c]	recovered RN_3, %
2	33		53	<1 (**2a**)	70
2 + H_2O	50		46	<1 (**2a**)	74
3	27	13	27	8 (**2b**)	44
3 + H_2O	23	16	35	<3 (**2b**)	57
3 + BF_3	16	<2	<5	5 (**2b**)	57
4	13	32	30	8 (**2c**)	32
4 + H_2O	9	42	26	11 (**2c**)	36

[a] Reactions performed by the addition of the phenoxy azide to $NO^+BF_4^-$. [b] Absolute yield based on reacted azide. Yield of chroman is variable in duplicate runs (±4%). [c] **2a**, $m = 1$, R = H; **2b**, $m = 2$, R = H; **2c**, $m = 2$, R = CH_3.

potential involvement of the nucleophilic phenyl (eq 11, $m < n - 1$, R = H, alkyl) and oxygen (eq 12) functional groups in intramolecular trapping of intermediate carbenium ions. Product yields from these nitrosation reactions are presented in Table III.



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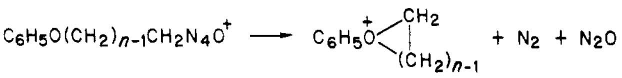


(12)

Reactions of phenoxy azides with $NO^+BF_4^-$ lead to a relatively rapid evolution of gaseous products but terminate at a point that is dependent on the number of methylene groups between the phenoxy and azido functional groups. Subsequent addition of another equivalent of $NO^+BF_4^-$ does not reinitiate nitrosative decomposition. Although reaction termination was also observed in nitrosation reactions of 3-azidopropanenitrile, nitrosation of its next two higher homologues proceeded to completion. The termination of reaction can be explained by association of boron trifluoride, evolved in the fluoride-transfer reaction, with the azido group. This association inhibits or prevents effective nitrosation. Indeed, when 1-azido-3-phenoxypropane is treated with $NO^+BF_4^-$ in a chloroform solution that is saturated with boron trifluoride, less than 18% of the reaction products (<8% yield) result from fluoride transfer. In the absence of added boron trifluoride, phenoxyalkyl fluorides account for 40% of the reaction products (23% yield).

Phenol was produced in nitrosation reactions of phenoxy azides, presumably through hydride abstraction by $NO^+BF_4^-$ at the carbon position α to the ether functional group.[22,23] The addition of water did not inhibit this oxidative process. Olefinic products were not observed, but primary alcohol products were detected in several nitrosation reactions of 1-azido-4-phenoxybutane that were performed in both the presence and the absence of added water (≤5% yield). Chroman (**2**, $m = 2$, R = H) and 4-methylchroman (**2**, $m = 2$, R = CH_3) were also formed in nitrosative reactions of 1-azido-3-phenoxypropane and 1-azido-4-phenoxybutane, respectively. However, fluoride substitution predominated in nitrosative reactions of phenoxy azides.

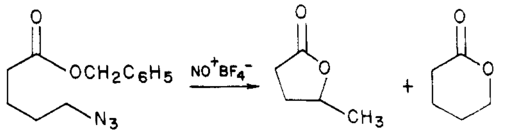
Table IV. Absolute Yields of Fluoroalkanes Produced by Nitrosative Decomposition of Aliphatic Azides

$Z(CH_2)_nN_3$,	yield, % (1°/2°)[a]		
n	Z = H	Z = CN	Z = C_6H_5O
2		50	12
3		59 (0.71)	23 (2.1)
4		81 (0.28)	31 (0.41)
6	5 (>10)	60 (0.33)	

[a] Ratio of primary to secondary (rearranged) fluoroalkane.

The relative effectiveness of fluoride transfer in nitrosative decompositions of aliphatic azides in chloroform can be discerned from the summary of absolute yields for alkyl fluorides in Table IV. When compared to the results for nitrosative decomposition of 1-azidohexane in which elimination and the Curtius rearrangement are the dominant reaction processes, those for nitrosative decomposition of azido nitriles and phenoxy azides show that the presence of the basic functional group significantly alters the product-forming reactions. Elimination is minimized and protonic decomposition of these azides is not observed. Instead, a new set of competing reactions, characteristic of the functionalized azide, is observed. However, the extent of fluoride transfer is markedly enhanced by the presence of this second functional group. This basic functional group is seen to bind the azide onto the surface of the nitrosonium salt. As a result of this association, fluoride substitution is favored over elimination or alkylation by a factor of at least 5 or, relative to the substitution:elimination product ratio for nitrosative decomposition of 1-azidohexane (<0.2), by a factor of at least 30.

The formation of chroman products in nitrosative decomposition reactions of phenoxy azides demonstrates that intramolecular trapping of the intermediate carbenium ions is competitive with intermolecular fluoride transfer. This competition is taken to its full limit in nitrosations of benzyl 5-azidopentanoate. In addition to recovered azide (10%), only lactones **3** and **4** were observed in significant yield (52%, in ratio of 5.4 (**3**):1.0 (**4**)). Loss of the benzyl group resulted in Friedel–Crafts alkylation products (61%), benzoic acid (8%), and benzyl nitrite (11%).



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(13)

Experimental Section

General Procedures. Proton magnetic resonance spectra were obtained with Varian Models A-60A and FT-80A spectrometers;

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[22] In a separate study selected aliphatic ethers were shown to undergo rapid oxidation by nitrosonium tetrafluoroborate in chloroform. With unsymmetrical ethers such as benzhydryl benzyl ether and benzhydryl methyl ether, these oxidation reactions are relatively unselective when compared to similar processes effected by trityl salts.

[23] Alcohol oxidations by nitrosonium salts have recently been reported: Olah, G. A.; Salem, G.; Staral, J. S.; Ho, T.-L. J. Org. Chem. 1978, 43, 173.

chemical shifts are reported in δ units, using tetramethylsilane as the internal standard. Infrared spectra were obtained on a Perkin-Elmer Model 621 grating spectrophotometer. Analytical gas chromatographic analyses were performed on a Varian Aerograph Model 2720 gas chromatograph with thermal conductivity detectors. Use was made of 5-ft columns of 15% SE-30, 20% Carbowax 20M, and 20% QF-1, all on Chromosorb P. The Finnigan Model 1015 GC/MS spectrometer operated at 70 eV was employed for mass spectral analyses. Nitrosonium salts, obtained from Ozark-Mahoning Co., were recrystallized from acetonitrile and then dried over phosphorus pentoxide in a vacuum desiccator at 20 torr prior to use; silver tetrafluoroborate was similarly dried over phosphorus pentoxide. Chloroform-*d* was employed in nitrosative reactions to facilitate product analyses by NMR spectroscopy. Solvents were rigorously dried and then distilled prior to their use. Azides were prepared from the corresponding alkyl halides by standard procedures.[18,24] Trimethylenetetrazole[18] was prepared from 4-azidobutanenitrile, using antimony pentafluoride in methylene chloride.

Nitrosative Decomposition of Azides. General Procedures. To 5.0 mmol of the nitrosonium salt in 7.0 mL of deuteriochloroform, placed in a three-necked flask fitted with a dropping funnel, reflux condenser, and gas outlet tube, was added dropwise 5.0 mmol of the azide in 3.0 mL of the reaction solvent. The addition to the rapidly stirred solution was at such a rate (15–20 min) as to cause no significant rise in reaction temperature, kept at 25 °C by means of a water bath.

In reactions with aliphatic azides gas evolution did not usually begin until approximately 5 min had elapsed from the time of initial addition. In contrast, immediate gas evolution was observed after the initial addition of azido nitriles and phenoxy azides to the nitrosonium salt. Total gas evolution was measured on the closed system by water displacement from a calibrated gas buret. Total gas evolution reflected the total amount of reacted azide and the different pathways for the production of gaseous products (nitrosative decomposition and Curtius rearrangement). The rate of production of gaseous products slowed markedly after the evolution of 40–60 mL (1–2 mmol of reacted azide); with the exception of nitrosative reactions with 4-azidobutanenitrile and 5-azidopentanenitrile, gas evolution terminated when approximately 50% of the azide had reacted. Gas evolution in the nitrosative reactions of aliphatic azides continued to completion as a result of protonic decomposition. Reactions were usually complete within 2 h.

Product Analyses. Following complete gas evolution an aliquot of the reaction solution was removed for NMR analysis. Subsequently, deuterium oxide (10 equiv) was added to the reaction mixture and a second NMR spectrum was obtained. The acidic solution was then neutralized by the addition of 0.5–1.0 g of sodium bicarbonate, and the resulting mixture was reduced to approximately one-third of its original volume and subjected to NMR and GC analyses.

The hexylideneiminium ion was identified by NMR spectroscopy prior to the addition of water (δ 8.50 (mult, $CH^a_2CH^b{=}N^+H^c_2$, $J_{ab} = 5$ Hz, $J_{bc} = 15$ Hz), 8.03 (d, $CH^b = N^+H^c_2$, $J_{bc} = 15$ Hz), 2.78 (quar, $CH_2CH_2CH{=}$)) and by its facile conversion to hexanal following water addition. 1-Fluorohexane was identified from its characteristic NMR spectrum (δ 4.43 (d of t, $J_{HF} = 47$ Hz, $J_{HH} = 6$ Hz, CH_2CH_2F)). 2-Fluorocyclohexanone was determined by NMR and mass spectral analyses. Other products formed from reactions of aliphatic azides and benzyl 5-azidopentanoate with nitrosonium tetrafluoroborate were identified by NMR and GC analyses through comparisons with authentic samples.

Products formed by nitrosative decomposition of the azido nitriles and phenoxy azides were individually isolated by GC separation.

3-Fluoropropanenitrile: ^{1}H NMR (CCl_4) δ 4.68 (d of t, $J_{HF} = 47$ Hz, $J_{HH} = 6$ Hz, 2 H), 2.80 (d of t, $J_{HF} = 23$ Hz, $J_{HH} = 6$ Hz, 2 H).

4-Fluorobutanenitrile: ^{1}H NMR ($CDCl_3$) δ 4.60 (d of t, $J_{HF} = 47$ Hz, $J_{HH} = 6$ Hz, 2 H), 2.53 (d of t, $J_{HF} = 1.5$ Hz, $J_{HH} = 6$ Hz, 2 H), 2.10 (d of quin, $J_{HF} = 26$ Hz, $J_{HH} = 6$ Hz, 2 H); IR ($CDCl_3$) 2245 (C≡N) cm^{-1}; mass spectrum *m/e* (relative intensity) 86 (4, M − 1), 73 (2), 59 (7), 47 (56), 41 (100).

3-Fluorobutanenitrile: ^{1}H NMR ($CDCl_3$) δ 4.94 (d of sextets, $J_{HF} = 49$ Hz, $J_{HH} = 6$ Hz, 1 H), 2.70 (d of d, $J_{HF} = 19$ Hz, $J_{HH} = 6$ Hz, 2 H), 1.52 (d of d, $J_{HF} = 24$ Hz, $J_{HH} = 6$ Hz, 3 H); IR ($CDCl_3$) 2235 (C≡N) cm^{-1}; mass spectrum *m/e* (relative intensity) 86 (1, M − 1), 72 (5), 59 (3), 47 (100), 41 (46).

5-Fluoropentanenitrile: ^{1}H NMR (CCl_4) δ 4.50 (d of t, $J_{HF} = 47$ Hz, $J_{HH} = 6$ Hz, 2 H), 2.40 (t, $J_{HH} = 6$ Hz, 2 H), 2.2–1.5 (m, 4 H); IR (CCl_4) 2250 (C≡N) cm^{-1}; mass spectrum *m/e* (relative intensity) 100 (1, M − 1), 61 (14), 59 (10), 55 (18), 54 (43), 41 (100).

4-Fluoropentanenitrile: ^{1}H NMR (CCl_4) δ 4.77 (d of sextets, $J_{HF} = 48$ Hz, $J_{HH} = 6$ Hz, 1 H), 2.48 (d of t, $J_{HF} = 1.5$ Hz, $J_{HH} = 6$ Hz, 2 H), 1.97 (complex d of quar, $J_{HF} = 21$ Hz, $J_{HH} = 6$ Hz, 2 H), 1.38 (d of d, $J_{HF} = 23$ Hz, $J_{HH} = 6$ Hz, 3 H); IR (CCl_4) 2240 (C≡N) cm^{-1}; mass spectrum *m/e* (relative intensity) 100 (1, M − 1), 86 (5), 66 (5), 61 (10), 59 (16), 55 (100), 54 (52), 47 (61), 41 (40).

7-Fluoroheptanenitrile: ^{1}H NMR ($CDCl_3$) δ 4.51 (d of t, $J_{HF} = 49$ Hz, $J_{HH} = 6$ Hz, 2 H), 2.37 (t, $J_{HH} = 6$ Hz, 2 H), 2.2–1.3 (m, 8 H); IR (CCl_4) 2260 (C≡N) cm^{-1}.

6-Fluoroheptanenitrile: ^{1}H NMR ($CDCl_3$) δ 4.60 (d of sextets, $J_{HF} = 49$ Hz, $J_{HH} = 6$ Hz, 1 H), 2.32 (t, $J_{HH} = 6$ Hz, 2 H), 2.15–1.25 (m, 6 H), 1.27 (d of d, $J_{HF} = 24$ Hz, $J_{HH} = 6$ Hz, 3 H); IR (CCl_4) 2262 (C≡N) cm^{-1}.

5-Fluoroheptanenitrile: ^{1}H NMR ($CDCl_3$) δ 4.48 (d of quin, $J_{HF} = 49$ Hz, $J_{HH} = 6$ Hz, 1 H), 2.42 (d of t, $J_{HF} = 1.2$ Hz, $J_{HH} = 6$ Hz), 2.4–1.2 (m, 6 H), 0.98 (d of t, $J_{HF} = 0.8$ Hz, $J_{HH} = 6$ Hz, 3 H); IR (CCl_4) 2263 (C≡N) cm^{-1}.

2-Fluoro-1-phenoxyethane: ^{1}H NMR ($CDCl_3$) δ 7.60–6.75 (m, 5 H), 4.86 (dist d of t, $J_{HF} = 43$ Hz, $J_{HH} = 4$ Hz, 2 H), 4.23 (dist d of t, $J_{HF} = 23$ Hz, $J_{HH} = 4$ Hz).

3-Fluoro-1-phenoxypropane: ^{1}H NMR ($CDCl_3$) δ 7.5–6.8 (m, 5 H), 4.67 (d of t, $J_{HF} = 47$ Hz, $J_{HH} = 6$ Hz, 2 H), 4.11 (t, $J_{HH} = 6$ Hz, 2 H), 2.14 (d of quin, $J_{HF} = 25$ Hz, $J_{HH} = 6$ Hz, 2 H).

2-Fluoro-1-phenoxypropane: ^{1}H NMR ($CDCl_3$) δ 7.5–6.8 (m, 5 H), 4.96 (d of m, $J_{HF} = 49$ Hz, 1 H), 4.05 (d of d, $J_{HF} = 21$ Hz, $J_{HH} = 5$ Hz, 2 H), 1.46 (d of d, $J_{HF} = 23$ Hz, $J_{HH} = 6$ Hz, 3 H).

4-Fluoro-1-phenoxybutane: ^{1}H NMR ($CDCl_3$) δ 7.6–6.7 (m, 5 H), 4.50 (d of t, $J_{HF} = 48$ Hz, $J_{HH} = 6$ Hz, 2 H), 4.02 (t, $J_{HH} = 6$ Hz, 2 H), 2.3–1.5 (m, 4 H).

3-Fluoro-1-phenoxybutane: ^{1}H NMR ($CDCl_3$) δ 7.6–6.7 (m, 5 H), 4.87 (d of quin, $J_{HF} = 49$ Hz, $J_{HH} = 6$ Hz, 1 H), 4.10 (d of t, $J_{HF} = 1.2$ Hz, $J_{HH} = 6$ Hz, 2 H), 2.08 (complex d of quar, $J_{HF} = 21$ Hz, $J_{HH} = 6$ Hz, 2 H), 1.40 (d of d, $J_{HF} = 24$ Hz, $J_{HH} = 6$ Hz, 3 H).

4-Methylchroman: ^{1}H NMR ($CDCl_3$) δ 7.4–6.7 (m, 4 H), 4.17 (t, $J = 5$ Hz, 2 H), 2.94 (sextet, $J = 7$ Hz, 1 H), 2.2–1.6 (m, 2 H), 1.33 (d, $J = 7$ Hz, 3 H).

Chroman was identified by spectral comparisons with an authentic sample.

Product yields were determined by integration of the individual and characteristic NMR absorption signals of each compound through reference to an internal standard. Further yield analysis was performed by gas chromatography. The average of product yields from at least two nitrosation reactions was employed.

Acknowledgments. We gratefully acknowledge the financial support of the National Science Foundation for this work and for matching funds to purchase the Varian FT-80A spectrometer. We thank Mary A. Zaleta for her preliminary results with aliphatic azides and azido nitriles.

Registry No. 1, 5817-87-8; **2b**, 493-08-3; **2c**, 16982-89-1; **3**, 108-29-2; **4**, 542-28-9; 1-azidohexane, 6926-45-0; azidocyclohexane, 19573-22-9; benzyl azide, 622-79-7; 1-fluorohexane, 373-14-8; 2-hexene, 592-43-8; hexanal, 66-25-1; cyclohexene, 110-83-8; cyclohexanone, 108-94-1; ε-caprolactam, 105-60-2; 2-fluorocyclohexanone, 694-82-6; benzaldehyde, 100-52-7; benzyl 5-azidopentanoate, 70659-88-0; hexylideneiminium, 70659-89-1; 3-azidopropanenitrile, 23648-56-8; 4-azidobutanenitrile, 21994-40-1; 5-azidopentanenitrile, 21994-41-2; 7-azidoheptanenitrile, 58793-92-3; 1-azido-2-phenoxyethane, 70659-90-4; 1-azido-3-phenoxypropane, 70659-91-5; 1-azido-4-phenoxybutane, 70659-92-6; 3-fluoropropanenitrile, 504-62-1; 4-fluorobutanenitrile, 407-83-0; 3-fluorobutanenitrile, 58793-93-4; 5-fluoropentanenitrile, 353-13-9; 4-fluoropentanenitrile, 58793-94-5; 7-fluoroheptanenitrile, 334-44-1; 6-fluoroheptanenitrile, 58793-95-6; 5-fluoroheptanenitrile,

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58793-96-7; 2-fluoro-1-phenoxyethane, 405-97-0; 3-fluoro-1-phenoxypropane, 70659-93-7; 2-fluoro-1-phenoxypropane, 70659-94-8; 4-fluoro-1-phenoxybutane, 70659-95-9; 3-fluoro-1-phenoxybutane, 70659-96-0; 3-butenenitrile, 109-75-1; 4-pentenenitrile, 592-51-8; 2-butenenitrile, 4786-20-3; nitrosonium tetrafluoroborate, 14635-75-7; nitrosonium hexafluorophosphate, 16921-91-8; nitrosonium hexafluoroantimonate, 16941-06-3; BF_3, 7637-07-2; SbF_5, 7783-70-2; phenol, 108-95-2.

Steric Course of Halocyclopropyl Acetate Opening Reactions

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A number of acetoxydifluoro-, -dichloro-, -fluorochloro-, and monofluorocyclopropanes have been treated with base. The various products obtained seem to indicate that the course of the ring opening follows several pathways, resulting from the steric and electronic factors which are operative.

An efficient scheme for the expansion of cyclic ketones to the homologous compounds results from the addition of dichloro-[2-6] and dibromocarbene[6,7] to the enol ether or enol acetate derived from the parent ketone, followed by ring opening. In a previous study,[8] we have investigated the addition of difluorocarbene to various enol acetates, as well as the nature of the products obtained after base or acid treatment of the resulting acetoxydifluorocyclopropanes. This reaction sequence was shown to be a convenient homologation method, which can lead either to α-difluoro ketones or α-fluoro enones depending on the nature of the starting material. In addition, in all cases studied thus far the bond which is cleaved is the central bond of the cyclopropane ring, i.e., the bond opposite to the difluoromethylene group.

The mechanism of ring-opening reactions of cyclopropyl derivatives to carbonium ions is well documented, and the transformation of a cyclopropyl cation to an allylic cation has been treated as an electrocyclic ring opening. This reaction has been predicted[9,10] and found[11] to be stereospecific and disrotatory.

However, some observations made with difluorocyclopropyl acetates, yielding α-difluoro ketones,[8] suggested that their ring opening could follow a different pathway, without involving a carbonium ion intermediate, in contrast to simple dihalocyclopropanes. This is illustrated by the fact that no solvolysis was observed with the halocyclopropyl acetates **2b** and **2g**, **2h**, when treated with silver nitrate in pyridine solution in the presence of water, conditions known to open dihalocyclopropanes.[12] Thus, it appears that the presence of the acetoxy function on the three-membered ring is a determining factor, since the carbon–fluorine bonds present in both cases should not be dramatically different in nature and strength.[13,14]

It has been reported that base treatment of the 2α,3α-difluorocarbene adduct **2a**, easily obtained from the steroidal enol acetate **1a**, provided exclusively the *A*-homodifluoro ketone **3a**, while the opening reaction under acidic conditions afforded the corresponding 17-acetate **3b**.

In contrast, addition of difluorocarbene[15] to the ring D cyclopentanone enol acetate **4** gave the *D*-homo α-fluoro enone **6a** as the main product, resulting from in situ ring opening of the strained pentacyclic intermediate **5a**, followed by elimination of fluoride. The adduct **5a** could be isolated in low yield and base treatment gave only one

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