tions. These would have occurred *via* nucleophilic displacement by sulfinate oxygen, rather than sulfinate sulfur, on the silver ion–disulfide complex. This observation is consistent with the recent study of Meek and Fowler[5] on alkylation of the ambident *p*-toluenesulfinate anion, where it was shown that alkylation with hard alkylating agents yielded esters while similar reaction with soft alkylating agents resulted in sulfone formation.

Experimental Section

Methyl Methanethiolsulfonate.—To a solution of dimethyl disulfide [0.5 g, 0.0053 mol, bp 108° (1 atm)] in 20 ml of 75% acetone–water was added a solution of silver nitrate (Fisher-ACS, 0.99 g, 0.00585 mol) and sodium methanesulfinate[6,7] (0.542 g, 0.0053 mol) in 20 ml of water. A bright yellow precipitate formed immediately. The mixture was stirred at room temperature for 30 min and the silver methylmercaptide was separated by suction filtration. The filtrate was diluted with water and extracted with several portions of ether. The combined ethereal extracts were dried over sodium sulfate and the ether was evaporated under reduced pressure to yield a colorless oil (0.63 g, 94%) whose ir and nmr spectra were identical with those of authentic methyl methanethiolsulfonate. In addition, the compound exhibited a parent peak in the mass spectrum at *m/e* 126 and was also shown to be pure by gas chromatography on a 6 ft Triton-X305 column at 160°.

Ethyl Methanethiolsulfonate.—To a solution of 2.44 g (0.02 mol) of diethyl disulfide in 75 ml of a 50% aqueous acetone solution was added 75 ml of a 50% aqueous acetone solution containing 4.25 g (0.025 mol) of silver nitrate and 2.53 g (0.025 mol) of sodium methanesulfinate. A white precipitate formed immediately. The mixture was brought to reflux temperature and the precipitate rapidly became bright yellow. Heating at reflux was continued for 4 hr and the product mixture was filtered. The cooled filtrate was extracted several times with ether and the combined ethereal extracts were dried (Na_2SO_4) and evaporated to yield 2.6 g (93%) of a colorless oil whose nmr spectrum in $CDCl_3$ (δ 3.37, s, 3 H; 3.21, q, J = 7.5 Hz, 2 H; 1.45 t, J = 7.5 Hz, 3 H) was consistent with that expected for pure ethyl methanethiolsulfonate. The distilled ester, bp 101° (4 mm), had a refractive index, $n^{25}D$ 1.5005. The mass spectrum showed a parent peak at *m/e* 140 and the ir spectrum exhibited strong absorptions at 1310, 1130, 955, and 750 cm^{-1}. *Anal.* Calcd for $C_3H_8O_2S_2$: C, 25.76; H, 5.75; S, 45.74. Found: C, 25.88; H, 5.72; S, 45.88.

Isopropyl Methanethiolsulfonate.—The procedure used was similar to that described for ethyl methanethiolsulfonate with the modification that the mixture was heated under reflux for 6 hr. From 3.0 g (0.02 mol) of diisopropyl disulfide (K and K) was obtained 2.5 g of product whose nmr in $CDCl_3$ (δ 1.47, d, J = 7 Hz, 6 H; 3.32, s, 3 H; 3.70, h, J = 7 Hz, 1 H) was consistent with that expected for isopropyl methanethiolsulfonate. The ester, distilled at 102° (5 mm), exhibited a refractive index ($n^{25}D$) of 1.4910. The ir spectrum (neat) consisted of strong absorptions at 2980, 2940, 1320, 1130 ,1055, and 750 cm^{-1}, and the mass spectrum exhibited a parent peak at *m/e* 154. *Anal.* Calcd for $C_4H_{10}O_2S_2$: C, 31.14; H, 6.53; S, 41.58. Found: C, 31.23; H, 6.54; S, 41.71.

Registry No.—Methyl methanethiolsulfonate, 2949-92-0; ethyl methanethiolsulfonate, 2043-76-7; isopropyl methanethiolsulfonate, 32846-80-3; silver nitrate, 7761-88-8; sodium methanesulfinate, 20277-69-4.

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Synthesis of *N*-Fluoronitramines[1]

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Little work has been reported on the synthesis and reactions of *N*-halo-*N*-nitro amine derivatives. *N,N'*-Dichloro-*N,N'*-dinitro-1,2-ethylenediamine, isolated by Smart and Wright[2] in 1948, remained the sole example of this class of compounds until the recently reported synthesis of simple *N*-chloro-*N*-nitroalkylamines by the chlorination of aqueous salts of alkylnitramines.[3] The synthesis of *N*-chloro-*N*-nitrocarbamates by this method was reported by Thomas[4] in 1955. *N*-Bromo-*N*-nitro amine derivatives have not been reported. *N*-Chloro-*N*-nitro amines and *N*-chloro-*N*-nitrocarbamates are explosive compounds[2] and decompose rapidly on storage.[4]

We have synthesized *N*-fluoro-*N*-nitrobutylamine, the first *N*-fluoronitramine, by two independent, generally applicable procedures. The compound was obtained in 84% yield in the fluorination of aqueous alkali salts of butylnitramine under reaction conditions similar to those employed in the fluorination of aqueous nitronate salts[5] and carboxylic acid salts (eq 1).[6] The

$$C_4H_9NNO_2^-K^+ + F_2 \longrightarrow C_4H_9NFNO_2 + KF \quad (1)$$

compound was characterized by elemental analysis as well as infrared and nmr spectra. Its fluorine nmr spectrum exhibited a triplet at ϕ −1.10. *N*-Fluoro-*N*-nitrobutylamine was stored at room temperature for several months without apparent decomposition. On the other hand, in one instance a sample of the compound exploded on distillation at 60°. This method of preparation of *N*-fluoro-*N*-nitro amines is of general utility. Graff, *et al.*,[7] used our general procedure[8] to synthesize other *N*-fluoronitramines for thermal stability studies.

N-fluoro-*N*-nitrobutylamine was also synthesized by treating methyl *N*-butyl-N-fluorocarbamate with 100% nitric acid (eq 2). Since *N*-alkyl-*N*-fluorocarbamates

$$C_4H_9NFCOOCH_3 + HNO_3 \longrightarrow C_4H_9NFNO_2 + CO_2 + CH_3ONO_2 \quad (2)$$

are readily available by the fluorination of alkylcarbamates,[9] this route to *N*-fluoro-*N*-nitro amines is also of general synthetic utility.

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The nitrolysis of *N*-butyl-*N*-fluorocarbamate most likely proceeds by the electrophilic displacement of carbomethoxycarbonium ion by nitronium ion (eq 3).

$$C_4H_9NFCOOCH_3 + NO_2^+ \longrightarrow C_4H_9NFNO_2 + [^+COOCH_3] \quad (3)$$

This mechanism is analogous to that proposed for the fluorinalysis of *N*-alkyl-*N*-fluorocarbamates to the corresponding *N,N*-difluoroalkylamines.[9] The nitrolysis of *N,N*-dialkylformamides has also been reported.[10]

Experimental Section

Fluorinations were conducted in a three-necked flask following the previously described technique.[5,6] *Adequate safety shielding* should be used when handling *N*-fluoro-*N*-nitrobutylamine.

Fluorination of Butylnitramine.—Butylnitramine (11.8 g, 0.1 mol) and 0.1 mol of potassium hydroxide in 250 ml of water were fluorinated with 0.1 mol of fluorine over a period of 45 min. A yellow liquid separated. The product was extracted with 70 ml of methylene chloride, and was washed with 75 ml of cold saturated aqueous sodium bicarbonate and 75 ml of water. The methylene chloride solution was dried with sodium sulfate and distilled to give 11.5 g (86% yield) of *N*-fluoro-*N*-nitrobutylamine: bp 40° (25 mm); proton nmr (CCl_4) δ 0.98 (m, CH_3), 1.62 (m, two internal CH_2's), and 6.07 (d, t, J_{HF} = 35, J_{HH} = 11 Hz, $-CH_2$); fluorine nmr ϕ −1.10 (t, J_{HF} = 33.5 Hz); ir 3.39 (m), 3.50 (m), 6.18 (sh), 6.35 (sh), 6.84 (w), 7.01 (w), 7.25 (w), 7.55 (sh), 7.76 (s), 7.93 (sh), 8.14 (w), 8.96 (w), 9.40 (w), 9.61 (w), 10.05 (w), 11.35 (m), and 12.10 μ (m).

Anal. Calcd for $C_4H_9N_2FO_2$: C, 35.3; H, 6.7; N, 20.6; F, 14.0. Found: C, 35.0; H, 6.3; N, 21.2; F, 14.3.

Nitration of Methyl *N*-Butyl-*N*-fluorocarbamate.—Methyl *N*-butyl-*N*-fluorocarbamate (4.0 g, 0.027 mol) was added dropwise over a 15-min period to 25 ml of 100% nitric acid at −5°. Carbon dioxide was evolved. The mixture was stirred for 20 min and then poured on 100 g of crushed ice. The product was extracted with two 20-ml portions of methylene chloride, dried over sodium sulfate, and distilled to give 3.1 g (84% yield) of *N*-fluoro-*N*-nitrobutylamine, bp 40° (25 mm).

Registry No.—*N*-Fluoro-*N*-nitrobutylamine, 14233-86-4.

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Amine Hydrochlorides by Reduction in the Presence of Chloroform[1]

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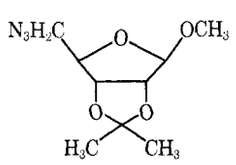
We have developed a new method for the preparation of amine hydrochlorides from azides, nitriles, oximes, and nitro compounds. Catalytic reduction of these compounds in a solvent containing a small amount of chloroform leads directly to the corresponding amine hydrochlorides. In addition to trapping unstable amines as the hydrochloride, an important advantage of the present procedure lies in the fact that it provides a method for the preparation of amine hydrochlorides that contain functional groups which might be unstable to reduction conditions employing acidic media. As can be seen from Table I, reduction in the presence of chloroform affords comparable yields to those afforded by reduction in the presence of hydrochloric acid.

TABLE I
REDUCTION DATA[a]

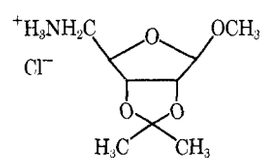
Compd	Proton source	Catalyst	Time, hr	Yield, %
1	$CHCl_3$	Pd/C	1.5	92
n-PrCN	$CHCl_3$	PtO_2	4	96
	HCl	PtO_2	1.75	95
C_6H_5CN	$CHCl_3$	PtO_2	2	98
	HCl	PtO_2	1.5	97
p-$CH_3C_6H_5NO_2$	$CHCl_3$	Pd/C	1.5	89[b]
	HCl	Pd/C	1.5	93[c]
n-$PrNO_2$	$CHCl_3$	PtO_2	18	40[d]
	$CHCl_3$	PtO_2	15	61[e]
	HCl	PtO_2	24	59[f]
n-$C_6H_{13}CH{=}NOH$	$CHCl_3$	PtO_2	1	97
	HCl	PtO_2	2	60

[a] Standard conditions are 3 atm, 2 mmol of starting material, 50 ml of absolute EtOH, 1 ml of $CHCl_3$ or 1 ml of concentrated HCl, 100 mg of 10% Pd/C or 50 mg of PtO_2, except as noted.[g] [b] 83% after sublimation. [c] After sublimation. [d] 0.2 ml of $CHCl_3$. [e] 0.1 ml of $CHCl_3$. [f] 0.2 ml of concentrated HCl. [g] Only 1.0 mmol of 1 was employed.

Methyl 5-azido-5-deoxy-2,3-*O*-isopropylidene-β-D-ribofuranoside (1),[3] which contains the acid-labile isopropylidene and acetal functions, was found to be reduced cleanly in the presence of chloroform to the corresponding amine hydrochloride 2 without affecting



1



2

either of these acid-sensitive groups. By contrast, reduction in the presence of methanolic hydrogen chloride also resulted in removal of the isopropylidene group and anomerization, as judged by nmr. Attempts at reduction of **1** under similar conditions in ether containing hydrogen chloride resulted in recovery of unchanged **1**.

Reduction of aromatic and aliphatic nitriles as well as *p*-nitrotoluene occurred readily in the presence of either chloroform or hydrochloric acid. In the absence of a proton source the reduction of 1-nitropropane produced propylamine, characterized as the hydrochloride, in 95% yield after 1.75 hr. Under the standard conditions with either chloroform or hydrochloric acid, 1-nitropropane was not reduced to any appreciable extent.[4] Upon decreasing the quantity of chloroform and hydrochloric acid, however, reduction was facilitated.

Heptaldoxime was reduced readily in the presence of either chloroform or hydrochloric acid, although the yield in hydrochloric acid was considerably lower. In both cases an additional ether-soluble product was formed.

As a mechanistic test, a blank solution of absolute ethanol, chloroform, and catalyst was hydrogenated for 1 hr. The resulting solution gave a positive silver ni-

(1) Generously supported by a research grant (GM 05829) from the National Institutes of Health.

(2) National Institutes of Health Predoctoral Fellow, 1969–1971.

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