2 N NaOH, brine), dried ($MgSO_4$), and concentrated *in vacuo*. The residue, a red oil (7.4 g), was chromatographed on neutral III alumina made up in pentane. Elution by pentane gave 2.11 g which was discarded. Elution by ether gave 2-bis(*tert*-butylthio)methylpyridine (3.05 g, 0.0113 mol, 11%) which was distilled in a short path apparatus: bp 80° (0.1 mm); ir (film) 1588 (s), 1568 (m), 1470 (s), 1432 (s), 1364 (s), 1154 (s), 990 (m), 742 (m), 718 (m) cm^{-1}; uv λ max (MeOH) 271 mμ (ε 4480); nmr ($CDCl_3$) δ 8.42 (broad d, 1, J = 6 Hz), 7.64 (m, 2), 7.10 (q, 1), 5.16 (s, 1), 1.28 (s, 18).

Anal. Calcd for $C_{14}H_{23}NS_2$: C, 62.43; H, 8.61; N, 5.20. Found: C, 62.40; H, 8.95; N, 5.22.

Pyridine (7.9 g, 0.1 *M*) was treated with methyllithium (78 ml of a 1.60 *M* solution, 0.12 mol) and *tert*-butyl disulfide (17.8 g, 0.1 mol) in an analogous manner. The bulk of the products were water soluble, presumably 2-picoline. The material eluted from neutral III alumina by ether (0.91 g, 0.0034 *M*, 3%) was identical (ir, nmr, mass spectrum) with 2-bis(*tert*-butylthio)methylpyridine prepared above. Comparison was also made by tlc (silica gel GF eluted by $CHCl_3$–ethyl acetate 4:1).

Acknowledgment. We wish to acknowledge the support and encouragement of Dr. Max Wilhelm and many helpful discussions with Mr. Louis Dorfman and Professor Peter Yates. We thank Mr. Dorfman's staff for microanalyses and spectra.

Registry No.—**3a,** 53730-69-1; **3b** HCl, 53730-70-4; **3c,** 53730-71-5; **4a,** 53730-72-6; **4b,** 53730-73-7; **4c,** 53730-74-8; **5a,** 53730-75-9; **5b,** 53730-76-0; **5c,** 53778-52-2; **6a,** 53730-77-1; **6c,** 53730-78-2; **7a,** 53730-79-3; **7b,** 53730-80-6; **7c,** 53730-81-7; **7d,** 53730-82-8; **7e** HCl, 53730-83-9; **7f,** 53730-84-0; **8a,** 53730-85-1; **8b,** 53730-86-2; **9,** 53730-87-3; **11,** 53730-88-4; pyridine, 110-86-1; phenylsulfenyl chloride, 931-59-9; phenyl disulfide, 882-33-7; dimethyl disulfide, 624-92-0; *m*-chloroperbenzoic acid, 937-14-4; trifluoroacetic anhydride, 407-25-0; ethyl 2-bromopropionate, 535-11-5; ethyl 4-bromobutyrate, 2969-81-5; butyl disulfide, 629-45-8; ethyl α-bromoisobutyrate, 600-00-0; ethyl bromoacetate, 105-36-2; 2-bis(*tert*-butylthio)methylpyridine, 53730-89-5; 2-picoline, 109-06-8.

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(19) Melting points were obtained in a Thomas-Hoover melting point apparatus and are uncorrected. Nmr spectra were obtained on a Varian A-60 instrument, infrared spectra on a Perkin-Elmer 21 or 521, mass spectra on an A MS902 at 70 eV, and ultraviolet spectra on a Carey 14 instrument.

New Fluorinating Reagents. Dialkylaminosulfur Fluorides[1]

William J. Middleton

Central Research Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898

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Dialkylaminosulfur trifluorides (**2**) and bis(dialkylamino)sulfur difluorides (**5**) are easy to handle fluorinating reagents useful for replacing hydroxyl and carbonyl oxygen with fluorine under very mild conditions. The trifluorides (**2**) were prepared by the reaction of dialkylaminotrimethylsilanes (**1**) with SF_4, and the difluorides (**5**) were prepared by the reaction of **2** with **1**. These fluorides are particularly useful in fluorinating sensitive alcohols and aldehydes. For example, reaction of diethylaminosulfur trifluoride (DAST) with isobutyl alcohol gave isobutyl fluoride as the principal product, reaction of DAST with pivaldehyde at 25° gave $(CH_3)_3CCHF_2$ in 78% yield, and reaction of $Me_2NSF_2NEt_2$ with crotyl alcohol at 25° gave crotyl fluoride in 78% yield.

Sulfur tetrafluoride is a useful fluorinating agent for replacing oxygen with fluorine in organic compounds.[2] The substitution of one or two of the fluorine atoms in sulfur tetrafluoride with dialkylamino groups would result in aminosulfur fluorides that also may be expected to be fluorinating agents. We have examined the preparation and chemical properties of dialkylaminosulfur trifluorides and bis(dialkylamino)sulfur difluorides with the hope of developing new selective fluorinating reagents.

Preparation. The dialkylaminosulfur trifluorides (**2**) were prepared by an adaptation of a literature procedure,[3] which consists of treating sulfur tetrafluoride with a dialkylaminotrimethylsilane (**1**). Diethylaminosulfur trifluoride[4] (DAST), dimethylaminosulfur trifluoride,[3] and the new pyrrolidinosulfur trifluoride were prepared by this method. When this reaction is conducted in trichlorofluoromethane (bp 25°) at −70°, high yields of a product of very high purity are obtained, since the only appreciable by-product is fluorotrimethylsilane (**3**), an easily separated low-boiling (bp 17°) material. These three trifluorides are stable products that can be distilled and stored in plastic bottles at room temperature.

$$\underset{\mathbf{1}}{R_2NSi(CH_3)_3} + SF_4 \longrightarrow \underset{\mathbf{2}}{R_2NSF_3} + \underset{\mathbf{3}}{FSi(CH_3)_3}$$

Diisopropylaminosulfur trifluoride (**2**, R_2N = diisopropylamino) was also prepared, but it was unstable to distillation and decomposed to isopropyliminosulfur difluoride (**4**) when heated above 60°.

$$\underset{\mathbf{4}}{(CH_3)_2CHN{=}SF_2} \qquad \underset{\mathbf{5}}{R_2N{-}SF_2{-}NR'_2}$$

Bis(dialkylamino)sulfur difluorides (**5**) have not been prepared previously. We prepared them by the reaction of a dialkylaminotrimethylsilane (**1**) with a dialkylaminosulfur trifluoride (**2**) at 25°. The sulfur difluorides were not stable to distillation, but they could be easily purified by removing the volatile solvent (CCl_3F) and by-product (**3**) by evaporation at reduced pressure. The ^{19}F nmr spectra of

Table I
Reactions[a] of Alcohols with Et_2NSF_3

Alcohol	Registry No.	Reaction solvent	Products	Registry No.	Yield, %[b]	Bp, °C (mm)	^{19}F nmr, δ, ppm
1-Octanol	111-87-5	CH_2Cl_2	1-Fluorooctane[c]	463-11-6	90	42–43 (20)	−218.8
2-Methyl-2-butanol	75-85-4	$CH_3O(CH_2CH_2O)_2CH_3$	2-Fluoro-2-methylbutane[d]	661-53-0	88	45–46	−139.2
Isobutyl alcohol	78-83-1	$CH_3O(CH_2CH_2O)_2CH_3$	Isobutyl fluoride[e]	359-00-2	49	20–22	−221.4
			tert-Butyl fluoride[f]	353-61-7	21	10–12	−132.1
Menthol	1490-04-6	CCl_3F	1-Fluoro-2-isopropyl-5-methylcyclohexane[h]	53731-15-0	50	40 (5)	−175.9
Benzyl alcohol	100-51-6	CCl_3F	Benzyl fluoride	462-06-6	75	139	−207.5
Benzyl alcohol[i]		CH_2Cl_2	Benzyl fluoride		100[g]		−207.5
Cyclooctanol	696-71-9	CCl_3F	Cyclooctyl fluoride	53731-16-1	70[g]		−160.5
			Cyclooctene	931-88-4	30[g]		
2-Methyl-3-butyn-2-ol	115-19-5	$CH_3O(CH_2CH_2O)_2CH_3$	2-Fluoro-2-methyl-3-butyne[j]	53731-17-2	75	43–44	−129.3
Ethylene glycol	107-21-1	$CH_3O(CH_2CH_2O)_2CH_3$	1,2-Difluorothane[k]	624-72-6	70	25–27	−225.9
exo-Borneol	124-76-5	CCl_3F	3-Fluoro-2,2-dimethylbicyclo[2.2.1]heptane[l]	53731-18-3	74	Mp 93–94	−134.4
			Camphene		18		
endo-Borneol	507-70-0	CCl_3F	3-Fluoro-2,2-dimethylbicyclo[2.2.1]heptane		72	Mp 93–94	−134.4
			Camphene		17		
3-Buten-2-ol	598-32-3	$CH_3O(CH_2CH_2O)_2CH_3$	3-Fluoro-1-butene[m]	53731-19-4	78[g]	22–24	−171.6
			1-Fluoro-2-butene[n]	53731-20-7	22[g]		−210.0
3-Buten-2-ol		Isooctane	3-Fluoro-1-butene		91[g]		
			1-Fluoro-2-butene		9[g]		
2-Buten-1-ol	6117-91-5	$CH_3O(CH_2CH_2O)_2CH_3$	3-Fluoro-1-butene		72[g]		
			1-Fluoro-2-butene		28[g]		
2-Buten-1-ol		Isooctane	3-Fluoro-1-butene		64[g]		
			1-Fluoro-2-butene		36[g]		
2-Bromoethanol[i]	540-51-2	$CH_3O(CH_2CH_2O)_2CH_3$	1-Bromo-2-fluoroethane	762-49-2	70	72	−213.4
2-Chloroethanol	107-07-3	$CH_3O(CH_2CH_2O)_2CH_3$	1-Chloro-2-fluoroethane[o]	762-50-5	69	50–53	−219.8
Ethyl lactate	97-64-3	CH_2Cl_2	Ethyl 2-fluoropropionate	349-43-9	78	50–51 (50)	−184.6
Ethyl 1-naphthyleneglycolate	53731-14-9	CCl_3F	Ethyl α-fluoronaphthaleneacetate[p]	24021-14-5	60	*q*	−178.4
2-Phenylethanol	60-12-8	CH_2Cl_2[r]	2-Fluoroethylbenzene[s]	458-87-7	60	68–69 (25)	−215.2

[a] All reactions were carried out between −50 and −78° unless otherwise noted. [b] Yield of isolated products unless otherwise noted. [c] Y. Kobayashi, C. Akashi, and K. Morinaga, *Chem. Pharm. Bull.*, 1784 (1968). [d] K. Wiechart, C. Gruenert, and H. J. Preibisch, *Z. Chem.*, 8, 64 (1968). [e] M. Moissan, *J. Chem. Soc.*, 931 (1888). [f] K. A. Cooper and E. D. Hughes, *J. Chem. Soc.*, 1183 (1937). [g] Product was not isolated in pure state. Yield is based on glc analysis. [h] *Anal.* Calcd for $C_{10}H_{18}F$: F, 12.01. Found: F, 12.12. [i] Me_2NSF_3 used in place of Et_2NSF_3. [j] *Anal.* Calcd for C_5H_7F: C, 73.4; H, 7.2; F, 19.4. Found: C, 73.7; H, 7.3; F, 19.2 [k] A. L. Henne and M. W. Renoll, *J. Amer. Chem. Soc.*, 58, 887 (1936). [l] M. Hanack, *Chem. Ber.*, 94, 1082 (1961). [m] *Anal.* of sample separated by glc. Calcd for C_4H_7F: C, 64.8; H, 9.5; F, 25.6. Found: C, 65.0; H, 9.5; F, 25.5. [n] *Anal.* of sample separated by glc. Calcd for C_4H_7F: C, 64.8; H, 9.5; F, 25.6. Found: C, 65.0; H, 9.5; F, 25.5. [o] W. F. Edgell and L. Parts, *J. Amer. Chem. Soc.*, 77, 4899 (1955). [p] *Anal.* Calcd for $C_{14}H_{13}FO_2$: C, 72.4; H, 5.6; F, 8.2. Found: C, 72.5; H, 5.7; F, 7.9. [q] Viscous oil, $n^{25}D$ 1.5788, purified by chromatography over silica ($CHCl_3$). [r] Reaction temp was 40°. [s] C. H. DePuy and C. A. Bishop, *J. Amer. Chem. Soc.*, 82, 2535 (1960).

the difluorides at −80° and at 30° show a single sharp resonance at 5 to 10 ppm downfield from CCl_3F. This relatively high field absorption and lack of spin–spin coupling indicate that both fluorine atoms are equivalent and are probably in the axial position. These spectra are in contrast to the spectra of the trifluorides (2), which show both equatorial and axial fluorines coupled to each other.[5]

Fluorinations with Aminosulfur Fluorides

Markovskij, Pashinnik, and Kirsanov[6] recently reported that the dialkylaminosulfur trifluorides are useful in replacing carbonyl oxygen of aldehydes and ketones with fluorine. The work that we have done independently fully supports these observations. In addition, we have found that the dialkylaminosulfur trifluorides are perhaps even more useful in replacing the hydroxyl groups of sensitive alcohols with fluorine, and the bis(dialkylamino)sulfur difluorides are also useful reagents for preparing organofluorine compounds.

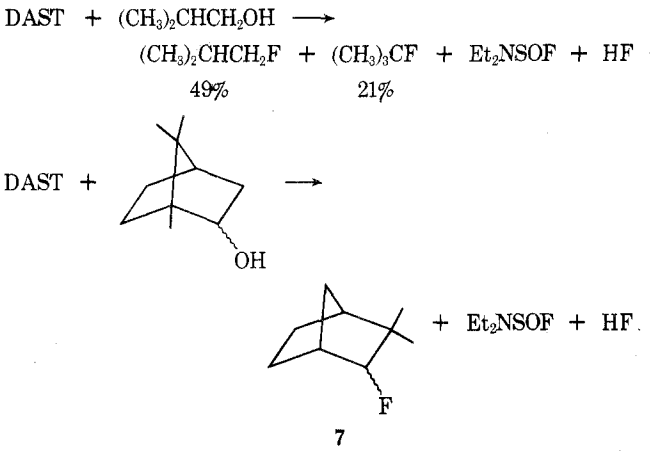
Fluorination of Alcohols

The reaction of DAST and the other dialkylaminosulfur trifluorides with alcohols to replace the hydroxyl group with fluorine appears to be a broadly general reaction with distinct advantages over other reagents used for this purpose, including SF_4,[7] SeF_4 · pyridine,[8] α-fluorinated amines,[7] and HF and HF–amine reagents.[9] Primary, secondary, and tertiary alcohols all react, with high yields of the unrearranged fluoride usually resulting.

These reactions can be conducted under very mild condi-

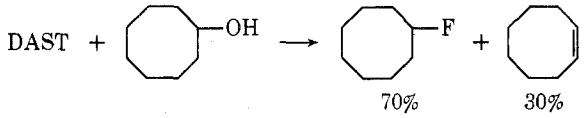
tions so that other groups, including ester groups and other halogens, can also be present. Typically, the alcohol can be added slowly to a solution of DAST in an inert solvent cooled to −50 to −78°. For many alcohols, the reaction occurs rapidly even at this low temperature. Diglyme is a convenient solvent for the preparation of low-boiling fluorides because the product can be distilled out of the reaction mixture and the HF that is formed in the reaction remains behind complexed with the diglyme. For the preparation of higher boiling fluorides, lower boiling solvents such as pentane, methylene chloride, or trichlorofluoromethane are useful. Table I contains a list of the alcohols that have been converted to fluorides.

Two problems can occur when replacing the OH groups of an alcohol with fluorine: carbonium ion type rearrangements and dehydration. The carbonium ion type rearrangements are less likely to occur when DAST is used than when other known fluorinating agents are used. For example, fluorination of isobutyl alcohol with DAST gave more than a 2:1 ratio of isobutyl fluoride (**6**) to *tert*-butyl fluoride, whereas fluorination with SeF_4 · pyridine is reported[8] to give only the rearranged *tert*-butyl fluoride. However, the more easily rearranged *exo*- and *endo*-borneol gave the rearranged fluoride **7**.

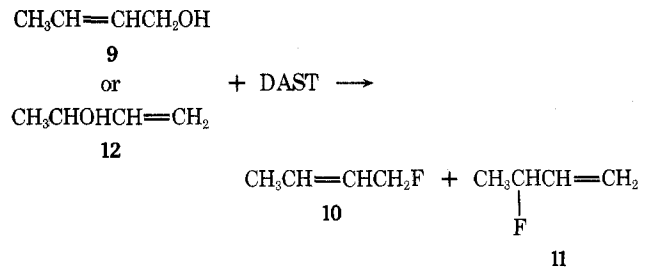


7

Dehydration (elimination) also appears to be less of a problem with DAST than with other fluorinating reagents. For example, cyclooctanol reacts with DAST to give a 70:30 ratio of cyclooctyl fluoride (**8**) to cyclooctene, whereas Et_2NCF_2CHClF reacts to give only cyclooctene.



8



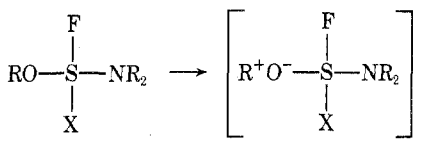
Crotyl alcohol (**9**) is sensitive to both double-bond rearrangement and dehydration. For example, it reacts with SF_4 to give a 90% yield of butadiene, a 9% yield of 3-fluoro-1-butene (**11**), and only a trace of crotyl fluoride (**10**). Reactions of DAST with crotyl alcohol under the same conditions (diglyme solvent) gave virtually no butadiene and a high yield of monofluorides consisting of a 72:28 ratio of **11**–**10**.

Reaction of DAST with crotyl alcohol in a less polar solvent (isooctane) gave larger amounts of **10** (36%), but still gave the rearranged **11** as the major product (64%). Fluorination of the isomeric alcohol, 3-buten-2-ol (**12**), gave the same two products, but in different ratios (see Table I). Since both **9** and **12** should form the same carbonium ion, it appears that a free carbonium ion is not involved in the reaction, but from the rearranged products observed in these reactions and in the reactions with borneol, it is clear that these fluorination reactions do have considerable carbonium ion character.

The bis(dialkylamino)sulfur difluorides (**5**) are also useful reagents for replacing hydroxyl groups with fluorine in sensitive alcohols. Although they are less reactive, the difluorides have certain advantages over the trifluorides in that they cause less rearrangement and elimination. For example, diethylaminodimethylaminosulfur difluoride (**5**, R = CH_3; R′ = C_2H_5) reacts with crotyl alcohol (**9**) to give the unrearranged **10** as the principal product, with only smaller amounts of the rearranged **11** formed (ratio 72:21). The difluorides **5** also cause less dehydrations of easily dehydrated alcohols, such as cyclohexanol, as compared to the reaction of the same alcohols with the trifluorides (**2**).

The smaller amounts of rearrangement and dehydration products that are formed in the fluorination of alcohols with the difluorides **5**, as opposed to the trifluorides **2**, can be rationalized by assuming that both reactions go through an unisolated intermediate in which one of the fluorines on sulfur has been replaced by an alkoxide group (**13**). This intermediate could then dissociate to give an ion pair consisting of a carbonium ion and a sulfur oxide anion (**14**). The sulfur oxide ion containing two amino groups (**14**, X = NR_2) would be expected to lose fluoride more readily than the anion containing only one amino group (**14**, X = F), and therefore have a shorter lifetime. Since the ion pair formed in the reaction of the difluoride **5** with an alcohol would have a shorter lifetime than the ion pair formed from **2** and an alcohol, less carbonium ion type reactions would occur.

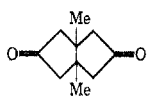
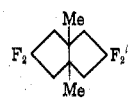
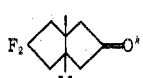
An alternate explanation would be based on leaving group ability instead of fluoride ion transfer. Since the leaving ability of $R_2NSF_2O^-$ should be greater than $(R_2N)_2SFO^-$, the decomposition of intermediate **13** (X = F) to give products should involve more carbonium ion character than decomposition of **13** (X = NR_2), and therefore would be subject to more extensive rearrangement and elimination.



13, X = F, NR_2 **14**, X = F, NR_2

Fluorination of Aldehydes and Ketones. DAST is a convenient reagent for replacing the carbonyl oxygen of aldehydes and ketones with two fluorine atoms (See Table II). This reagent is particularly useful for fluorinating aldehydes and ketones that are sensitive to acidic conditions or contain other functional groups that are unstable in the presence of acid, since no acid other than adventitious HF is formed in the reactions and no additional acidic catalyst is needed. Even aqueous work-ups do not result in the formation of acidic solutions, since the only by-product, diethylaminosulfinyl fluoride (**15**), is hydrolyzed to give sulfur dioxide and diethylamine hydrofluoride.

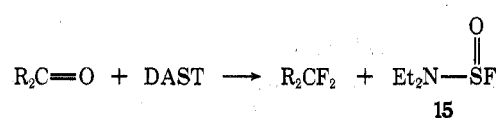
Table II
Reactions of Carbonyl Compounds with DAST

Carbonyl compd	Registry No.	Reaction solvent	Temp, °C	Time	Product	Registry No.	Isolated yield, %	Bp (mp), °C	^{19}F nmr, δ, ppm
Isovaleraldehyde	590-86-3	CCl_3F	25	30 min	1,1-Difluoro-3-methylbutane	53731-22-9	80	59–60	−115.5
Propionaldehyde	123-38-6	CCl_3F	25	30 min	1,1-Difluoropropane	430-61-5	95[a]		−118.2
Pivaldehyde	630-19-3	CCl_3F	25	1 hr	$(CH_3)_3CCHF_2$[b]	53731-23-0	78	47–48	−128.6
Pivaldehyde		Diglyme	25	1 hr	$(CH_3)_3CCHF_2$		24	47–48	−128.6
					$CH_2{=}C(CH_3)CHFCH_3$[c]	53731-24-1	26	51–52	−174.4
					$FC(CH_3)_2CHFCH_3$[d]	53731-25-2	31	65–66	−152.0, −185.5
Benzaldehyde	100-52-7	CH_2Cl_2	25	2 hr	Benzal fluoride[e]	455-31-2	75	57 (35 mm)	−110.9
1-Naphthaldehyde	66-77-3	CH_2Cl_2	25	18 hr	1-(Difluoromethyl)naphthylene[f]	53731-26-3	72	78–79 (0.4 mm)	−111.1
4-Heptanone	123-19-3	CCl_3F	25	7 day	4,4-Difluoroheptane[g]	53731-27-4	68	110–111	−98.6
Acetophenone	98-86-2	Glyme	85	20 hr	1,1-Difluoroethylbenzene[h]	10541-59-0	66	64–65 (40 mm)	−87.7
	53731-21-8	Benzene	78	24 hr		53731-28-5	60[j]	(106–109)	−86.2, −86.6
						53731-29-6	15[j]	(145–150)	−80.9, −81.0

[a] Glc yield. [b] *Anal.* Calcd for $C_3H_{10}F_2$: C, 55.5; H, 9.3; F, 35.1. Found: C, 55.7; H, 9.4; F, 35.0. [c] *Anal.* Calcd for C_5H_9F: C, 68.2; H, 10.3; F, 21.6. Found: C, 68.3; H, 10.5; F, 21.8. [d] *Anal.* Found: C, 55.3; H, 9.5; F, 35.4. [e] W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Amer. Chem. Soc.*, **82**, 543 (1960). [f] *Anal.* Calcd for $C_{11}H_8F$: C, 74.1; H, 4.5; F, 21.3. Found: C, 74.2; H, 4.2; F, 21.2. [g] *Anal.* Calcd for $C_7H_{14}F_2$: C, 61.7; H, 10.4; F, 27.9. Found: C, 62.1; H, 10.2; F, 28.1. [h] K. Matsuda, J. A. Sedlak, J. S. Noland, and G. C. Cleckler, *J. Org. Chem.*, **27**, 4015 (1962). [i] *Anal.* Calcd for $C_{10}H_{14}F_4$: C, 57.1; H, 6.7; F, 36.1. Found: C, 57.1; H, 6.8; F, 36.1. [j] Purified by chromatography on Al_2O_3 (pentane–ether). [k] *Anal.* Calcd for $C_{10}H_{14}F_2O$: C, 63.8; H, 7.5; F, 20.2. Found: C, 63.1; Hm 7.3; F, 20.9.

Table III
Effect of Solvent on Product Distribution in the Fluorination of Pivaldehyde with DAST

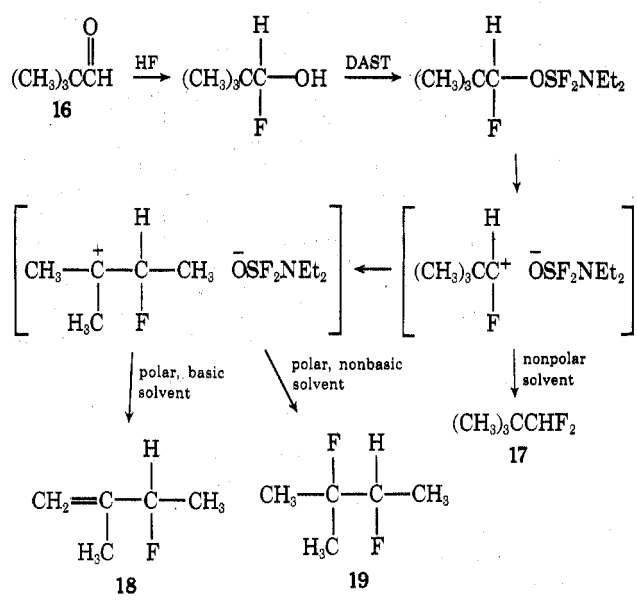
	% of products (glc yields)		
Solvent	$(CH_3)_3CCHF_2$	$CH_2{=}C(CH_3)$-$CHFCH_3$	$FC(CH_3)_2$-$CHFCH_3$
CCl_3F	88	2	10
Pentane	87	3	10
CCl_3H	72	3	25
CH_2Cl_2	72	2	26
Xylene	64	8	28
Tetrahydrofuran	65	20	15
Pivaldehyde	60	10	30
Diglyme	30	32	38



15

Pivaldehyde (16) is an example of an acid-sensitive aldehyde. Previous attempts to prepare the corresponding *gem*-difluoride have resulted in rearrangements or trimerization. However, pivaldehyde can be successfully fluorinated to 17 by the use of DAST in a nonpolar solvent such as pentane or CCl_3F. Carbonium ion type rearrangements will occur, however, if more polar solvents are used (See Table III). Thus, if diglyme (a basic, polar solvent) is used, the rearranged products 18 and 19 are formed, and if chloroform is used (a nonbasic, polar solvent), considerable rearrangement product 19 is formed, but only a small amount of the elimination product 18 is formed. The solvent dependancy of this reaction is consistent with the reaction shown in Scheme I.

Scheme I



16 17 18 19

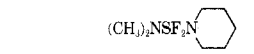
Experimental Section[10]

Dialkylaminosulfur Trifluorides (Table IV). The four trifluorides listed in Table IV were prepared by the reaction of an aminotrimethylsilane with sulfur tetrafluoride in CCl_3F, as illustrated by the preparation of diethylaminosulfur trifluoride (DAST).

A solution of 96 g (0.66 mol) of diethylaminotrimethylsilane in 100 ml of CCl_3F was added dropwise to a solution of 40 ml (measured at −78°, 0.72 mol) of sulfur tetrafluoride in 200 ml of CCl_3F at −65 to −60°. The reaction mixture was warmed to room temperature and then distilled to give 88.9 g (84%) of DAST as a pale yellow liquid.

Bis(dialkylamino)sulfur Difluorides (Table IV). The four

Table IV
Aminosulfur Fluorides

Compd	Registry No.	Bp, °C (mm)	^{19}F nmr, δ, ppm	% yield	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found	Fluorine, % Calcd	Fluorine, % Found	Nitrogen, % Calcd	Nitrogen, % Found	Sulfur, % Calcd	Sulfur, % Found
$(CH_3)_2NSF_3$	3880-03-3	49–49.5 (33)	19.7, 59.2		18.0	18.3	4.6	4.7	42.8	42.6	10.5	10.7	24.1	23.8
$(C_2H_5)_2NSF_3$	38078-09-0	46–47 (10)	31.2, 55.5	84	29.8	30.0	6.3	6.4	35.4	35.1	8.7	8.5	19.9	19.7
	53731-09-2	54–55 (15)		83	30.2	29.9	5.1	5.3	35.8	35.5	8.8	8.8	20.1	20.0
$[(CH_3)_2CH]_2NSF_3$	50713-80-9	*a*		99[b]					30.1	29.9				
$(CH_3)_2NSF_2N(CH_3)_2$	53731-10-5	Mp 64–65.5	6.9	60	30.4	30.5	7.7	7.9	24.0	24.1	17.7	17.6	20.3	19.7
$(CH_3)_2NSF_2N(C_2H_5)_2$	53731-11-6	*a*	10.9	92[b]					20.4	20.4				
$(C_2H_5)_2NSF_2N(C_2H_5)_2$	53731-12-7	*a*	9.7	92[b]					17.7	17.9				
	53731-13-8	Mp 25–26	5.9	99	44.7	44.5	3.2	3.1	20.2	20.0				

[a] Not distilled. [b] Crude yield.

difluorides listed in Table IV were prepared by the reaction of dimethylaminosulfur trifluoride or DAST with an aminotrimethylsilane, as illustrated by the preparation of bis(dimethylamino)sulfur difluoride.

A 29.25-g (0.25 mol) sample of dimethylaminotrimethylsilane was added dropwise to a solution of 33.2 g (0.25 mol) of dimethylaminosulfur trifluoride in 100 ml of CCl_3F cooled to −78°. The reaction mixture was warmed to 25° and then filtered under nitrogen to remove a small amount of suspended solid. The filtrate was evaporated to dryness under reduced pressure to give 23.5 g (60%) of bis(dimethylamino)sulfur difluoride as a white crystalline solid.

***N*-Isopropyliminosulfur Difluoride (4).** Attempted distillation of crude diisopropylaminosulfur trifluoride caused this product to decompose at about 60° (2 mm). The volatile decomposition products were collected in a cooled trap and redistilled to give an 80% yield of 4 as a light yellow liquid: bp 63°; ^{19}F nmr (CCl_3F) δ 72.9 ppm; ^1H nmr (CCl_3F) δ 1.28 ppm (d, J = 6.5 Hz, 6 H) and 4.17 ppm (septet, J = 6.5 Hz, 1H).

Anal. Calcd for $C_3H_7F_2NS$: C, 28.3; H, 5.6; F, 29.9; N, 14.0; S, 25.2. Found: C, 28.4; H, 5.6; F, 29.5; N, 14.0; S, 25.4.

Fluorination of Alcohols (Table I). The alcohols listed in Table I were added to a solution of DAST or dimethylaminosulfur trifluoride in an inert solvent cooled to −50 to −78°. The reaction mixture was then warmed to room temperature or higher. An initial exothermic reaction usually occurred at low temperature. In some cases, a second exothermic reaction was evident during the warm-up period. The lower-boiling product fluorides were distilled out of the reaction mixture at reduced pressure. Reaction mixtures containing higher-boiling fluorides were mixed with water, and the organic layer was separated and dried, and the solvent was distilled off. The product fluorides were purified by distillation, recrystallization, or column chromatography. The following are representative examples.

Ethyl 2-Fluoropropionate. A solution of 1.18 g (0.01 mol) of ethyl lactate in 2 ml of methylene chloride was slowly added to a solution of 1.25 g (0.01 mol) of DAST in 5 ml of methylene chloride cooled to −78°. The reaction mixture was warmed to room temperature and mixed with cold water. The lower layer was separated, washed with water, dried ($MgSO_4$), and distilled to give 0.93 g of ethyl 2-fluoropropionate[10] as a colorless liquid.

1-Bromo-2-fluoroethane. Ethylene bromohydrin, 31.25 g (0.25 mol), was added dropwise to a solution of 33 g (0.25 mol) of dimethylaminosulfur trifluoride in 150 ml of diglyme cooled to −50°. The reaction mixture was warmed to room temperature, and 50 ml of the most volatile portion was distilled out at reduced pressure. The distillate was mixed with water, washed with 5% sodium bicarbonate solution, dried ($MgSO_4$), and redistilled to give 22.2 g of 1-bromo-2-fluoroethane[11] as a colorless liquid.

Fluorination of Crotyl Alcohol with (Diethylamino)(dimethylamino)sulfur Difluoride. A solution of 1.44 g (0.02 mol) of crotyl alcohol (2-buten-1-ol) in 2 ml of diethylene glycol dimethyl ether was slowly added to a stirred solution of 3.7 g (0.02 mol) of (diethylamino)(dimethylamino)sulfur difluoride in 10 ml diethylene glycol dimethyl ether cooled to −78°. The reaction mixture was warmed to 25° and the volatile products were distilled out under reduced pressure to give 1.3 ml of colorless liquid. Redistillation gave 1.06 g (72%) of a mixture containing 79% 1-fluoro-2-butene (crotyl fluoride) and 21% 2-fluoro-3-butene, bp 24–27°.

When the reaction was repeated, using isooctane in the place of diethylene glycol dimethyl ether as the reaction solvent, a 65% yield of fluorobutene was obtained consisting of 87% 1-fluoro-2-butene and 13% 2-fluoro-3-butene.

Fluorination of Alcohols with $(Me_2N)_2SF_2$. A solution of 1.08 g (0.01 mol) of benzyl alcohol in 2 ml of methylene chloride was added slowly to a solution of 0.0066 mol of bis(dimethylamino)sulfur difluoride in 6 ml of methylene chloride cooled to −78°. The reaction mixture was warmed to room temperature and mixed with water. The organic layer was separated, washed with water, and then 5% sodium bicarbonate, and dried ($MgSO_4$). Analysis by glc and ^{19}F nmr showed that benzyl fluoride had been formed in 91% yield. Cyclohexanol was fluorinated in a similar manner to give fluorocyclohexane, ^{19}F nmr (CCl_3F) δ −161.2 ppm (m).

Fluorination of Aldehydes and Ketones with DAST (Table II). The ketones and aldehydes in Table II were fluorinated by stirring them in an inert solvent with DAST at temperatures and for times indicated. The fluorinated products were isolated by pouring the reaction mixture into water, and then separating, drying, and distilling the organic layer. The following example illustrates this procedure.

Fluorination of Isovaleraldehyde. A 1.72-g (0.02 mol) sample of isovaleraldehyde was slowly added to a solution of 2.5 ml (0.02 mol) of DAST in 10 ml of CCl_3F at 25°. The reaction mixture was stirred for 30 min, and then mixed with 25 ml of water. The lower organic layer was separated, washed with water, dried ($MgSO_4$), and distilled to give 1.73 g (80%) of 1,1-difluoro-3-methylbutane as a colorless liquid.

Anal. Calcd for $C_5H_{10}F_2$: C, 55.5; H, 9.3; F, 35.1. Found: C, 55.8; H, 9.6; F, 35.1.

Registry No.—1 (R = Me), 2083-91-2; 1 (R = Et), 996-50-9; 1 [R_2 = $-(CH_2)_4-$], 15097-49-1; 1 (R = Pri), 17425-88-6; 4, 53731-08-1; sulfur tetrafluoride, 7783-60-0.

References and Notes

(1) (a) Portions of this paper were presented at the Second Winter Fluorine Conference, St. Petersburg, Fla., Feb 1974; (b) Contribution No. 2193.
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(10) Melting points and boiling points are uncorrected. ^{19}F nmr spectra were obtained with a Varian A56-60 spectrometer. Peak center positions are reported in parts per million downfield from CCl_3F used as an internal reference. The dialkylaminosilanes used were prepared by the reaction of secondary amines with trimethylchlorosilane.
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