Applications of Dialkylaminosulfur Trifluorides for the Syntheses of Acid Fluorides

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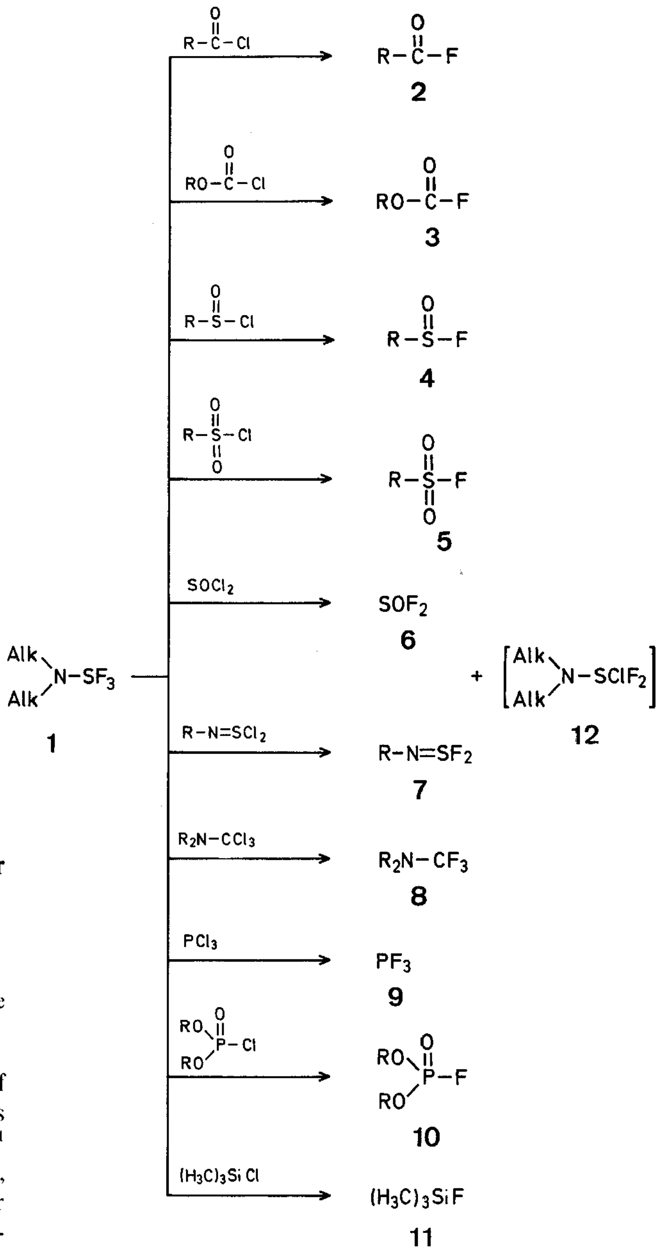
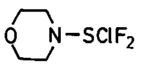
One of the most common methods for the preparation of fluorides of mineral, organic, and elementorganic acids is chlorine/fluorine exchange on the corresponding chloride[1] using hydrogen fluoride, arsenic(III) fluoride, metal fluorides, the 18-Crown-6 complex of potassium fluoride[2], and sulfur tetrafluoride. Although it is one of the most important fluorinating agents, sulfur tetrafluoride is not often used[3], probably because of the inconvenience of using pressure equipment and possible reactions of the formed sulfur chlorides with the initial and final products.

We have recently shown[4] that dialkylaminosulfur trifluorides, like sulfur tetrafluoride, are good fluorine/chlorine exchange agents and can be used for the preparation of fluororganic compounds from aldehydes, ketones, thiono compounds, etc. It has also been shown that dialkylaminosulfur trifluoride can be used to convert alcohols to the corresponding fluorides[5].

We now report that dialkylaminosulfur trifluorides (**1**) can be successfully used to prepare acid fluorides from the corresponding chlorides and to bring about fluorine/chlorine exchange in other suitable compounds (**2–11**; see also Table). The simplicity of the method and the soft reaction conditions are advantageous and allow the fluorine derivatives to be prepared in high yields. The reactions are carried out by mixing the reagents in a solvent or neat.

Dialkylaminosulfur chloride difluorides (**12**) formed in the reaction are usually decomposed but morpholinosulfur chloride difluoride (**13**) proved to be rather stable and, in some cases, precipitated as colourless crystals from the reaction mixture. The crystals decompose with elvolution of chlorine on heating.





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Reactions of Dialkylaminosulfur Trifluorides with Chlorine-Containing Substrates General Procedures:

Method A: The dialkylaminosulfur trifluoride (1 mol-equiv per chlorine to be replaced) is added dropwise to the stirred, cooled chlorine derivative (1 mol-equiv). The mixture is stirred 15–20 min at 20° and then at 60° until evolution of gas stops (~30 min). The reaction mixture is then cooled to 20° and fractionated. (Low boiling fluorine derivatives are condensed in a liquid nitrogen cooled trap and purified by repeated fractionation).

Method B: A solution of morpholinosulfur trifluoride (1 mol-equiv per chlorine to be replaced) is added to a cooled, stirred solution of the chlorine derivative (1 mol-equiv) in ether (or benzene, hexane, chlorobenzene). A precipitate of morpholinosulfur chloride

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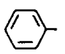
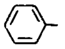
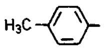
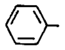
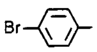
Table. Fluorine Compounds obtained by Reaction of the Corresponding Chlorine Compound with a Dialkylaminosulfur Trifluoride

Product	R	Dialkylaminosulfur Trifluoride Alk	Mol-equiv	Method	Solvent	Yield (%)	M.p. or B.p.	Lit. M.p. or B.p./torr	n_D^{20}	Brutto Formula[a]	Mol. Weight
2	$ClCH_2-$	—[e]	1	A	–	80	74°/755 torr	74–76°/741[6]	1.3780	C_2H_2ClFO	96.5
2	Cl_3C-	—[e]	1	A	–	73	69–70°/755 torr	66–68°[6]	1.4065	C_2Cl_3FO	165.4
2		—[e]	1	C	–	70	48°/12 torr	58°/21[7]	1.4970	C_7H_5FO	24.1
3	C_2H_5	—[e]	1	A	–	51	56–57°/755 torr	57°[8]	1.3370	$C_3H_5FO_2$	92.1
4		morpholino-	1	B	ether	85	35–36°/0.2 torr	60°/2.5[9]	1.5010	C_6H_5FOS	144.1
4		morpholino-	1	B	hexane	91	46°/0.1 torr		1.5000	C_7H_7FOS	158.2
5		—[e]	1	C	–	72	89°/12 torr	207° (n_D^{20} 1.4922)[10]	1.4915	$C_6H_5FO_2S$	160.1
5		—[e]	1	C	–	79	m.p. 64–65°		–	$C_6H_4BrFO_2S$[b]	239.0
7	t-C_4H_9	—[e]	2	A	–	62	80–81°/755 torr		1.3815	$C_4H_9F_2NS$[c]	141.1
8	C_2H_5	morpholino	3	B	Cl-C_6H_5	80	75–76°/755 torr	34–35°/180[11]	–	$C_5H_{10}F_3N$	141.1
10	C_2H_5	—[e]	1	A	–	70	63–64°/12 torr	70–72°/18[12]	–	$C_4H_{10}FO_3P$[d]	156.1

[a] All compounds gave satisfactory fluorine analyses (F ±0.28%).

[b] Calc. C 30.15 H 1.67
found 30.10 1.65

[c] Calc. C 34.04 H 6.37
found 33.96 6.30

[d] Calc. P 19.85
found 19.73

[e] Diethylamino, piperidino, or morpholino.

difluoride (**13**) is formed. The mixture is stirred at 20° for 10 min. The precipitate is filtered off with exclusion of moisture. The filtrate is evaporated and fractionated to give the desired fluoride. The precipitate is pure morpholinosulfur chloride difluoride (**13**); Yield: quantitative; m.p. 66–67° (sealed capillary); white crystals.

$C_4H_8ClF_2NOS$ (191.6)

	C	H	Cl	F	N	S
calc.	25.07	4.20	18.50	19.83	7.31	16.73
found	25.20	4.25	18.00	19.84	7.04	16.98

Method C: The reaction is carried out as described under method A. The mixture is then cooled and poured on to ice in small portions. The organic layer is extracted with ether, the ether extract dried, ether evaporated, and the residue fractionated or recrystallised.

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