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Synthesis of Fluorides by Metathesis with Sodium Fluoride

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Sodium fluoride suspended in nonaqueous tetramethylene sulfone, acetonitrile, or dimethylformamide has been found to exchange halogen readily with carboxylic acid chlorides, α-chloro ethers, trichloromethanesulfenyl chloride, thiocarbonyl chloride, selenium oxychloride, phosphorus oxychlorides, phosphorus thiochlorides, and phosphonitrilic chlorides. The conversion to fluorides was usually accomplished by heating the reactants at temperatures ranging up to 250° at atmospheric pressure.

Syntheses of aliphatic[1–5] and aromatic[6] fluorides by metathesis of organic halides with metallic fluorides have generally avoided sodium fluoride which has been considered a poor reagent for halogen exchange. However, sodium fluorosilicate has been used in exchange reactions with acyl chlorides and chloroalkanes.[7a] More recently, sodium fluoride has served auspiciously in the synthesis of sulfur tetrafluoride in 90% yield by reaction with sulfur dichloride in acetonitrile at 80°.[7b] This result has led to an exploration of sodium fluoride as a fluorination agent in exchange reactions with chlorine-containing compounds in a nonaqueous polar medium.[6,8,9]

Compounds containing reactive chlorine bonded to carbon, sulfur, or phosphorus have now been converted to the corresponding fluorides by reaction with sodium fluoride in tetramethylene sulfone, acetonitrile, or dimethylformamide.

Synthesis of carbon fluorides. Members of three classes of compounds, namely, acid chlorides, α-chloro ethers, and carbon chlorides bonded to sulfur, were found to exchange readily with sodium fluoride. Thus, oxalyl fluoride, acetyl fluoride, benzoyl fluoride, methyl fluoroformate, cyanuric fluoride, monofluorodimethyl ether, 1,2-difluoro-1,4-dioxane, and trifluoromethanesulfenyl chloride were prepared from the corresponding chlorides. Trifluoromethanesulfenyl chloride was obtained along with bis(trifluoromethyl) disulfide in 47% combined yield in a 3:2 weight ratio by reaction of trichloromethanesulfenyl chloride with sodium fluoride in tetramethylene sulfone at 170–250°. Similar treatment of thiocarbonyl chloride at 85–245° gave bis(trifluoromethyl) disulfide in 37% conversion.

In an interesting modification of the metathesis, fluorocarbonyl cyanide, FCOCN, was obtained in 14% conversion by reaction of phosgene at room temperature with sodium fluoride in hydrogen cyanide which served both as a medium and as a reactant. The chief product was carbonyl fluoride. Fluorocarbonyl cyanide was also prepared directly from carbonyl fluoride and hydrogen cyanide using sodium fluoride as hydrogen fluoride acceptor.

Conditions under which the foregoing reactions were carried out are summarized in Table I.

Synthesis of sulfur and selenium oxyfluorides. Sulfuryl fluoride, sulfuryl chlorofluoride, and thionyl fluoride were prepared from the corresponding chloro compounds in good conversions through reactions with sodium fluoride at atmospheric pressure, and selenium oxyfluoride was obtained from the oxychloride (see Table II). In these syntheses tetramethylene sulfone, acetonitrile, and dimethylformamide were apparently interchangeable as reaction media. The synthesis of the oxyfluorides of sulfur and selenium as reported in the literature[10–14] usually requires reactions under pressure with such reagents as silver (I) fluoride, antimony or arsenic trifluorides, zinc fluoride, hydrogen fluoride, or even elemental fluorine. Sulfuryl fluoride has been prepared in low conversions by the reaction of sodium fluoride with sulfuryl chloride at 400°.[13]

Synthesis of phosphorus fluorides. Sodium fluoride suspended in tetramethylene sulfone has also exchanged fluorine for chlorine bonded to phos-

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(1) A. M. Lovelace, D. A. Rausch, and W. Postelnek, *Aliphatic Fluorine Compounds*, Reinhold Publishing Co., New York, 1958.

(2) K. Wallenfalls and W. Draber, *Chem. Ber.*, **90**, 2819 (1957).

(3) F. Seel and L. Riehl, *Z. anorg. u. allgem. Chem.*, **282**, 293 (1955).

(4) G. Olah and S. Kuhn, *J. Org. Chem.*, **21**, 1319 (1956).

(5) J. H. Fried and W. T. Miller, Jr., *J. Am. Chem. Soc.*, **81**, 2078 (1959).

(6) G. C. Finger and C. W. Kruse, *J. Am. Chem. Soc.*, **78**, 6034 (1956).

(7) (a) J. Dahmlos, *Angew. Chemie*, **71**, 274 (1959). (b) C. W. Tullock, F. S. Fawcett, W. C. Smith, and D. D. Coffmann, *J. Am. Chem. Soc.*, **82**, 539 (1960).

(8) J. E. Leffler and W. B. Bond, *J. Am. Chem. Soc.*, **78**, 335 (1956).

(9) R. L. Burwell, Jr., and C. H. Langford, *J. Am. Chem. Soc.*, **81**, 3799 (1959).

(10) R. N. Haszeldine and A. G. Sharpe, *Fluorine and Its Compounds*, John Wiley and Sons, Inc., New York, 1951.

(11) W. C. Schumb, J. G. Trump, and G. L. Priest, *Ind. Eng. Chem.*, **41**, 1348 (1949).

(12) H. J. Emeleus and J. F. Wood, *J. Chem. Soc.*, 2183 (1948).

(13) M. M. Woyski, *J. Am. Chem. Soc.*, **72**, 919 (1950).

(14) J. H. Simons, *Fluorine Chemistry*, Academic Press, Inc., New York, 1950, Vol. 1, pp. 93–102.

phorus in the tri- and pentavalent phosphorus compounds listed in Table III. Two new compounds, phenylphosphonic difluoride, $C_6H_5POF_2$, and phenylphosphonothioic difluoride, $C_6H_5PSF_2$, were prepared from the corresponding chlorides. The phosphonitrilic fluorides, $(PNF_2)_{3,4}$, previously obtained from the corresponding chlorides and potassium fluosulfinate,[15] have also been prepared by metathesis with sodium fluoride.

Although sodium fluoride has been used in isolated instances to prepare phosphorus fluorides[16–18], arsenic trifluoride, lead difluoride, zinc difluoride, or antimony trifluoride have been employed more commonly in such syntheses.[19–21]

EXPERIMENTAL

With the exception of a few reactions in a sealed vessel under autogenous pressure, the syntheses (Tables I–III) were carried out at atmospheric pressure in Pyrex glass equipment. In most instances the product was distilled from

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(15) F. Seel and J. Langer, *Angew. Chem.*, **68**, 461 (1956).

(16) Hamilton McCombie, B. C. Saunders, and C. L. Wheeler, British Patent **601,210** (1948).

(17) M. Hallman, *J. Chem. Soc.*, 309 (1959).

(18) W. Lange and G. Kruger, *Ber.*, **65**, 1253 (1932).

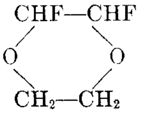
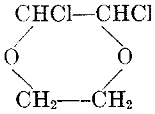
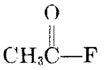
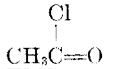
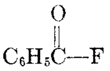
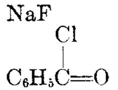
(19) J. H. Simons, *Fluorine Chemistry*, Academic Press, Inc., New York, 1950, Vol. 1, pp. 97–102.

(20) D. M. Yost and H. Russell, Jr., *Systematic Inorganic Chemistry*, Prentice-Hall, Inc., New York, 1944, pp. 234–7.

(21) G. Brauer, *Handbuch Der Preparativen Anorganischen Chemie*, Ferdinand Enke Verlag, Stuttgart, 1954, pp. 154–9.

TABLE I

SYNTHESIS OF CARBON FLUORIDES

Products	Reactants	(Moles)	Reaction Conditions	% Conversion of Chloride to Fluoride	Properties
CF_3SSCF_2 CS_2	$CSCl_2$ TMS NaF	(1.03) (2.18) (2.62)	33–89°/1.0 hr. 89–122°/3.0 hr. 122–224°/0.6 hr. 224–245°/0.2 hr.	37	b.p. 31–35°[a]
CF_3SCl CF_3SSCF_3 (3:2 by wt.)	CCl_3SCl TMS NaF	(1.09) (3.16) (4.76)	34–107°/0.5 hr. 107–209°/1.3 hr. 209–240°/2.75 hr.	47	CF_3SCl, b.p. −4° to +2°[b] CF_3SSCF_3, b.p. 27–37°[a,b]
$(CNF)_3$	$(CNCl)_3$ TMS NaF	(0.67) (1.85) (2.50)	43–134°0.2 hr. 134–193°/0.4 hr. 193–248°/0.2 hr.	74	b.p. 72.5–73.5°[c]
FCH_2OCH_3	$ClCH_2OCH_3$ TMS NaF	(1.29) (1.33) (1.90)	33–100°/1.5 hr. 100–145°/1.0 hr. 145–168°/0.7 hr.	47	b.p. 8–11.5°[d]
	 TMS NaF	(0.50) (1.33) (1.50)	32–93°/0.7 hr. 93–143°/1.0 hr. 143–173°/0.75 hr.	42	b.p. 28–30°/21 mm.[e]
FCO_2CH_3	$ClCO_2CH_3$ TMS NaF	(1.00) (1.33) (2.00)	33–81°/0.7 hr. 81–119°/1.4 hr. 119–140°/1.5 hr.	33	b.p. 35–37°[f]
$(COF)_2$ COF_2	$(COCl)_2$ TMS NaF	(0.50) (1.33) (2.00)	59–89°/1.5 hr. 89–122°/2.0 hr.	60	b.p. 0° to 2°[g]
 $CH_3\overset{\overset{O}{\parallel}}{C}-F$	 $CH_3\overset{\overset{Cl}{\vert}}{C}=O$ TMS NaF	(1.02) (1.33) (2.00)	41–60°/1.5 hr. 60–95°/2.4 hr.	48	b.p. 19–20.5°[h]
 $C_6H_5\overset{\overset{O}{\parallel}}{C}-F$	 $C_6H_5\overset{\overset{Cl}{\vert}}{C}=O$ TMS NaF	(1.00) (1.33) (1.50)	29–128°/0.4 hr. 128–188°/0.5 hr. 188–226°/0.6 hr. 226–250°/0.4 hr.	62	b.p. 157–159°[i]

[a] CF_3SSCF_3, b.p. 34°, has been obtained (1) by the fluorination of carbon disulfide with mercuric fluoride [E. L. Muetterties, U. S. Patent **2,729,663** (1954); (2) by the fluorination of carbon disulfide with IF_5 [R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 3223 (1953)]; and (3) by the present method [C. W. Tullock, U. S. Patent **2,884,453** (1959)]; infrared analysis showed the product to contain 70 mole % CF_3SSCF_3 and 25 mole % CS_2. [b] The products were identified by infrared analysis. CF_3SCl, b.p. −1°, has been prepared by the chlorination of CF_3SSCF_3 and of $(CF_3S)_2Hg$ [R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 3219–23 (1953)]. [c] The fluorine NMR spectrum was consistent for $(CNF)_3$. The literature reports a b.p. of 74° [D. W. Grisley, Jr., E. W. Gluesencamp, and S. A. Heininger, *J. Org. Chem.*, **23**, 1802 (1958)]. The product was distilled from the flask as it formed. [d] Fluorine and proton NMR spectra were consistent for FCH_2OCH_3. The literature reports a b.p. of about 19°. The compound was prepared by reacting $ClCH_2OCH_3$ with mercuric fluoride [C. T. Masen and C. C. Allain, *J. Am. Chem. Soc.*, **78**, 1682 (1956)]. [e] The product was separated from the reaction mixture by heating at 163–187°/107 mm. *Anal.* Calcd. for $C_4H_6O_2F_2$: F, 30.60. Found: F, 29.26; Cl, 1.64. This compound was recently synthesized from 2,3-dichloro-*p*-dioxane and mercuric fluoride [C. T. Masen, Southeastern Regional ACS Meeting, Gainsville, Fla., December 1958].

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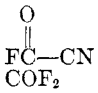
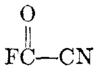
TABLE I (*Continued*)

Products	Reactants	(Moles)	Reaction Conditions	% Conversion of Chloride to Fluoride	Properties
 $FC(=O)-CN$ COF$_2$	COCl$_2$ HCN NaF	(2.00) (2.04) (9.52)	25°/20 hr. in 1-l. reactor at autogenous pressure	14	b.p. −20° to −18°[j]
 $FC(=O)-CN$	COF$_2$ HCN CH$_3$CO$_2$H (3 drops)	(1.00) (1.00)	150°/3 hr. in 1-l. reactor at autogenous pressure; mixture was then transferred to evacuated pressure reactor containing NaF and stored at 25° for 24 hr.	22.5	b.p. −22° to −19°[k]

TMS = tetramethylene sulfone; the compound darkens with partial decomposition above 220°.

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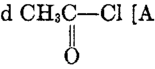
[f] The literature reports a b.p. of 40°. The product was obtained by treating ClCO$_2$CH$_3$ with TlF or potassium fluoride [H. C. Goswami and P. B. Sarkar, *J. Indian Chem. Soc.*, **10**, 537 (1933); G. Olah and S. Huhn, *J. Org. Chem.*, **21**, 1319 (1956)]. In our experiment CH$_3$Cl was obtained in a 20% conversion. [g] The product was characterized by infrared analysis. The literature reports a b.p. of +26° [N. Fukuhara and L. A. Bigelew, *J. Am. Chem. Soc.*, **63**, 788 (1941)]. The amount of COF$_2$ produced was not determined. [h] The product was characterized by infrared analysis. The literature reports a b.p. 21–22°. The product has been obtained from NaF and  $CH_3C(=O)-Cl$ [A. I. Mashentsev, *J. Applied Chem.* (*U.S.S.R.*), **20**, 854–63 (1947)].

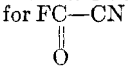
[i] The product was distilled from the mixture as formed. The literature reports a b.p. of 156°. This product has been obtained by heating benzoyl chloride and NaF in the absence of a medium [A. T. Dann, W. Davies, A. N. Hambly, R. E. Paud, and G. Semmens, *J. Chem. Soc.*, **18** (1933)]. [j] The volatile products from three experiments were combined and distilled. The amount of COF$_2$ formed was not determined. C. W. Tullock, U. S. Patent **2,816,131** (1957) describes the preparation of FCOCN. [k] Appreciable reaction probably occurred after the reactants had been stored over sodium fluoride. *Anal.* Calcd. for C$_2$FNO: Mol. Wt. 73. Found: Mol. Wt. 72.4. Mass spectrometric and infrared analyses were satisfactory for  $FC(=O)-CN$; the product was further characterized by reaction with aniline to obtain diphenylurea.

TABLE II

SYNTHESIS OF SULFUR AND SELENIUM OXYFLUORIDES

Products	Reactants	(Moles)	Reaction Conditions	% Conversion of Chloride to Fluoride	Properties
SOF$_2$	SOCl$_2$ NaF CH$_3$CN	(0.50) (2.00) (2.88)	43–69°/0.4 hr. 69–80°/1.6 hr.	77	b.p. −43° to −36°[a]
SOF$_2$	SOCl$_2$ NaF TMS	(0.50) (2.00) (1.58)	44–70°/0.5 hr. 70–78°/2.0 hr.	52	b.p. −39° to −36°[a]
SO$_2$FCl	SO$_2$Cl$_2$ NaF CH$_3$CN	(0.50) (2.48) (3.24)	80°/3.5 hr.	64	b.p. 3–7°[a]
SO$_2$F$_2$/SO$_2$FCl (1:2 by wt.)	SO$_2$Cl$_2$ NaF DMF	(0.50) (2.00) (1.93)	52–80°/1.1 hr. 80°/1.1 hr.	55	SO$_2$F$_2$, b.p. −49° to −48°[a] SO$_2$ClF, b.p. 3–6°[a]
SO$_2$F$_2$	SO$_2$Cl$_2$ NaF TMS	(1.00) (4.00) (2.50)	60°/1 hr.; 80°/1 hr.; 100°/1 hr.; 125°/1 hr.; 150°/2 hr. 1-l. reactor at autogenous pressure	85	b.p. −49° to −48°[b]
SeOF$_2$	SeOCl$_2$ NaF TMS	(0.64) (1.78) (1.32)	60–100°/0.8 hr. 100–115°/0.5 hr.	28	b.p. 30–32°/6 mm.[c]

TMS = tetramethylene sulfone
DMF = dimethylformamide

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[a] The reported b.p. are: SOF$_2$, −43.8°; SO$_2$FCl, 7.1°; SO$_2$F$_2$, −55.4° (J. H. Simons, *Fluorine Chemistry*, Academic Press, Inc., New York, 1950, Vol. 1, p. 94). These products were identified by infrared analysis. [b] This experiment was carried out by Dr. R. D. Cramer. [c] The product was removed from the reaction mixture by heating at 120–167°/2 mm. for 1.6 hr. The reported b.p. for SeOF$_2$ is 124 ±3° (see J. H. Simons, *Fluorine Chemistry*, Academic Press, Inc., New York, 1950, Vol. 1, p. 95; E. Anysley, R. Peacock, and P. Robinson, *J. Chem. Soc.*, 1231–4 (1952).
Anal. Calcd. for F$_2$OSe: F, 28.57; Se, 59.40. Found: F, 29.57; Se, 58.73.

TABLE III

SYNTHESIS OF PHOSPHORUS FLUORIDES

Products	Reactants	(Moles)	Reaction Conditions	% Conversion of Chloride to Fluoride	Properties
POF_3	$POCl_3$	(0.49)	48–80°/0.4 hr.	43	b.p. −44° to −40°[a]
	NaF	(2.00)	80–96°/2.8 hr.		
	TMS	(1.33)	96–168°/0.5 hr.		
			168–215°/0.5 hr.		
			215–228°/0.2 hr.		
$C_6H_5POF_2$	$C_6H_5POCl_2$	(0.50)		65	b.p. 44°/2.5 mm.[d]
	NaF	(1.50)	75–120°/1.8 hr.		
	TMS	(1.33)			
PSF_3	$PSCl_3$	(0.50)		53	b.p. −52° to −48°[a]
	NaF	(2.00)	37–140°/0.6 hr.		
	TMS	(1.33)	140–170°/2.7 hr.		
$C_6H_5PSF_2$	$C_6H_5PSCl_2$	(0.50)		73	b.p. 47–49°/3 mm.[e]
	NaF	(1.50)	25–89°/0.4 hr.		
	TMS	(1.33)	89–107°/1.8 hr.		
$(PNF_2)_{3,4}$	$(PNCl_2)_{3,4,5,6}$	(4.31)	80°/20 hr.	54	$(PNF_2)_3$, b.p. 51–2°[b]; $n_D^{32} = 1.3183$[c]; m.p. 29–31°
	NaF	(32.14)			$(PNF_2)_4$, b.p. 89–89.5°[b]; $n_D^{32} = 1.3449$; m.p. 30°
	CH_3CN	(34.39)			
PF_3	PCl_3	(0.73)	47–52°/1.0 hr.	18	[g]
	NaF	(2.74)	52–75°/0.6 hr.		
	TMS	(1.85)	75–109°/2.5 hr.		
$ClCH_2POF_2$	$ClCH_2POCl_2$	(0.50)	60–175°/0.6 hr.	76	b.p. 112–113°[f]
	NaF	(2.00)	175–194°/0.9 hr.		
	TMS	(1.33)	194–230°/0.5 hr.		

TMS = tetramethylene sulfone; the compound darkens with partial decomposition above 220°.

[a] The reported b.p. for POF_3 is −39.4° and for PSF_3 is −52.3° (J. H. Simons, *Fluorine Chemistry*, Academic Press, Inc., New York, 1950, Vol. 1, p. 100). PSF_3 inflamed on contact with air. The products were further characterized by infrared analysis. [b] The reported b.p. are: $(PNF_2)_3$, 51.8°; $(PNF_2)_4$, 89.7° (F. Seel and J. Langer, *Angew. Chem.*, **68**, 461 (1956). [c] This experiment was carried out by Dr. C. M. Langkammerer. A mixture of phosphonitrilic chlorides was employed; it was obobtained by treating 280 g. ammonium chloride, with 900 g. phosphorus pentachloride in 3000 ml. sym.-tetrachloroethane as reflux with stirring and then removing the solvent by distillation under 0.5–2.0 mm. pressure. The value of 4.31 moles $(PNCl_2)_{3,4,5,6}$ is based on $PNCl_2$ monomer. After reaction with sodium fluoride, the $(PNF_2)_3$, b.p. 50–62°, was distilled directly from the stirred reaction mixture; the $(PNF_2)_4$ codistilled with acetonitrile, b.p. 73–80°. Pure $(PNF_2)_4$ was isolated by washing out the acetonitrile with water, drying, and redistilling.

Anal. Calcd. for $(P_3N_3F_6)$: P, 37.38; Mol. Wt., 236. Found: P, 37.43; Mol. Wt., 236, 255. Mass spectrometric analysis satisfactory for $(PNF_2)_3$.

Anal. Calcd. for $P_4N_4F_8$: N, 16.87. Found: N, 16.69. Mass spectrometric analysis was satisfactory for $(PNF_2)_4$.

[d] The product was removed by heating the reaction mixture to 80–100°/2–3 mm. *Anal.* Calcd. for $C_6H_5F_2PO$: F, 23.42. Found: F, 23.24. [e] The product was removed by heating the reaction mixture to 80–100°/2–3 mm. *Anal.* Calcd. for $C_6H_5F_2PS$: F, 21.35. Found: F, 21.47. [f] The product was removed from the reaction mixture by heating to 80–100°/2–3 mm. for 30–40 min.

Anal. Calcd. for CH_2ClF_2OP: F, 28.25. Found: F, 28.84. [g] Infrared showed the samples to contain 35 mole % PF_3 and 20 mole % HCl.

the reaction mixture as formed and was collected in glass traps cooled in solid carbon dioxide and acetone. When the product was too high boiling to be removed in this way, it was isolated by warming the reaction mixture under reduced pressure. Gaseous products were purified by distillation at low temperature and were identified by boiling point and infrared spectra. Liquids were fractionally distilled through a spinning band column or a 10-inch Vigreux column.

The tetramethylene sulfone, acetonitrile, and dimethylformamide used as reaction medium were purified by distillation. The sodium fluoride employed was dry and finely divided. It was presumed that small particle size was beneficial. Commercial product as supplied by the Mallinckrodt Chemical Works or Baker and Adamson was satisfactory.

The usual procedure was to employ a volume of medium (ml.) numerically equal to the sum of the weights (g.) of sodium fluoride and chloro compound employed. The chloro compound was introduced slowly into the stirred suspension of sodium fluoride at such a rate that the reaction temperature was less than 100°. In many cases the chloro compound could be added in less than 5 min. without an appreciable rise in temperature. Heating was begun only after all the reactants had been added.

WILMINGTON, DEL.