Compounds I–VIII were prepared by exchange of the appropriate diamine with dimethylbis(diethylamino)silane or methylphenylbis(diethylamino)silane. N,N′-di-*o*-tolylethylenediamine gave no reaction with dimethylbis(diethylamino)silane at a temperature of 180° and neither could the N,N′-di-*o*-tolyl derivative be obtained by reaction with dimethylbis(dimethylamino)silane. The reluctance of this diamine to react was also observed in the preparation of the spiro compounds[1] and is probably associated with the steric hindrance of the *o*-methyl group or the strain which it imposes on the product ring. N,N′-Di-*p*-nitrophenylethylenediamine also failed to react with dimethylbis(diethylamino)silane at 200°. This can be attributed to the low basicity of the diamine or the high temperature (and consequent possible decomposition of the silylamine) necessary to melt the diamine. The 2,2-diphenyl derivative was prepared by reaction of diphenylbis(dimethylamino)silane with N,N′-dimethylethylenediamine. It is curious that the isomeric compounds IV and IX which differ only by the placement of the phenyl and methyl substituents have such strikingly different physical properties: the N-phenyl compound melts at 124–126°, while the N-methyl isomer is a liquid at room temperature, b.p. 175° (10 mm.), freezing point *ca.* 23°.

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Difluoramine: Preparation of Difluorodiazine and Addition Compounds with Alkali Metal Fluorides

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Difluoramine is amphoteric, as witnessed by its formation of a complex with boron trichloride[1] and the formation of 1:1 complexes with weak bases such as alkyl ethers.[2] We have found that difluoramine also forms complex compounds with the more basic alkali metal fluorides. At higher temperatures, difluoramine is converted smoothly and in excellent yield to difluorodiazine as in eq. 1.[3] With the ready availability of difluoramine from urea,[4] this method constitutes the most convenient laboratory synthesis of difluorodiazine. Of the other methods which have been recently reviewed by Colburn,[5] the most convenient preparation mentioned involved the electrolysis of ammonium bifluoride to form N_2F_2 in 5–10% yields as a by-product in the synthesis of NF_3.

$$2MF + 2HNF_2 \longrightarrow 2MF\cdot HF + N_2F_2 \tag{1}$$

The alkali metal fluorides effective in the dehydrofluorination of difluoramine to difluorodiazine at ambient temperatures are potassium fluoride, rubidium fluoride, and cesium fluoride. Two isomeric forms of N_2F_2 are formed and are the *cis* and *trans* isomers reported previously.[6] No evidence for a third form has been observed.

In connection with our investigation of the conversion of HNF_2 to N_2F_2, evidence was obtained that clearly showed the formation of molecular complexes of alkali metal fluorides and HNF_2. Elucidation of the structure of these complexes by low-temperature infrared techniques has been completed in this laboratory and will be reported separately.[7]

Reproducible dissociation pressures for $KF\cdot HNF_2$ and $RbF\cdot HNF_2$ were measured and, as predicted from the relative basicities of the alkali fluorides, the stability of the complexes formed varied as follows: CsF > RbF > KF > NaF. In fact, no evidence was found for any interaction of difluoramine with NaF, CaF_2, or NiF_2 down to −80°.

A complete study of the CsF–HNF_2 system was not carried out because of the explosive properties of the complex. Condensing difluoramine over CsF and allowing some difluoramine to escape from the system resulted in a dissociation pressure of about 1.5 mm. at −65.8°, a higher pressure than the 0.8 mm. observed with RbF at this temperature. However, removal of about 50% of the complexed difluoramine caused an abrupt drop in the dissociation pressure to less than 0.05 mm. On warming, this complex invariably exploded before it reached 0°.

In addition to the gas–solid reaction shown in (1) it was found that aqueous KF (pH 8.6) effected the smooth dehydrofluorination of HNF_2. A nominally 25% solution of KF in water consumed HNF_2 rapidly with the formation of both isomers of N_2F_2 in approximately 75% yield, as in the equation

$$2F^- + 2HNF_2 \longrightarrow 2HF_2^- + N_2F_2$$

It is interesting to note, however, that experiments carried out with HNF_2 and standard buffer solutions ($Na_2B_4O_7$–K_3PO_4) at pH 8.0 and 9.0, respectively, resulted in only 20% yields.

These results indicate that F^- may be particularly effective in the dehydrofluorination reaction, but ex-

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[1] R. C. Petry, *J. Am. Chem. Soc.*, **82**, 2400 (1960).

[2] E. A. Lawton and J. Q. Weber, *ibid.*, **85**, 3595 (1963).

[3] E. A. Lawton and D. Pilipovich, U. S. Patent 3,109,711 (1963).

[4] Difluoramine is released in high yield by adding sulfuric acid drop-by-drop to the fluorinated urea liquids, described by Lawton and Weber,[2] or to difluorourea: E. A. Lawton, E. F. C. Cain, D. F. Sheehan, and M. Warner, *J. Inorg. Nucl. Chem.*, **17**, 188 (1961).

[5] C. B. Colburn, "Nitrogen Fluorides and Their Inorganic Derivatives," chapter in "Advances in Fluorine Chemistry," Vol. 3, Butterworths, Washington, D. C., 1963, p. 103.

[6] C. B. Colburn, F. A. Johnson, A. Kennedy, K. McCallum, L. C. Metzger, and C. O. Parker, *J. Am. Chem. Soc.*, **81**, 6397 (1959).

[7] H. Dubb, C. Greenough, and E. C. Curtis, to be submitted.

tensive work was not done to determine whether there was a peak in yield at some pH near 8.6, so it is premature to postulate whether the F^- or OH^- is most effective in aqueous solution.

Experimental

Preparation of Difluorodiazine. Method I.—In a typical experiment an ampoule containing potassium fluoride (1.25 g., 21.5 mmoles) was evacuated and heated intermittently to about 300° until no more gases were evolved. A measured gas volume of difluoramine (50.5 cc., 2.25 mmoles) was then condensed into the ampoule and the contents were allowed to remain in contact at ambient temperature for 17 hr. The gases were separated quantitatively by fractional condensation in a high vacuum line and identified both by vapor pressure and by infrared spectra. The results of similar experiments are summarized in Table I.

TABLE I

PREPARATION OF N_2F_2

$$MF + HNF_2 \longrightarrow MF\cdot HF + {}^1/_2N_2F_2$$

Metal fluoride	Time, hr.	% HNF_2 reacted	% yield N_2F_2
K	2.5	26.2	100
K	17.0	45.4	100
K	24.0	100.0	100
Rb	16.0	35.0	84
Cs	0.5	27.0	84

Because of the explosive nature of the $CsF-HNF_2$ complex a variation of the above technique was employed to effect the conversion of HNF_2 to N_2F_2 with CsF. Gaseous difluoramine (~0.5 mmole) was introduced into an evacuated ampoule containing CsF at ambient temperature. Even under these conditions, deflagrations often occurred, particularly when larger quantities of difluoramine were used.

Method II.—A reactor was constructed from a 50-cm. length of 12-mm. Pyrex tubing and packed with RbF. The RbF was heated for several hours in a tube furnace at 300–400° with pumping and then the reactor temperature was lowered to the desired level. With pumping maintained, HNF_2 was submitted from a 2-l. bulb to the reactor. The gases were slowly passed through the reactor to a 25-cm. section of 1-mm. capillary tubing and then to two traps maintained at −142 and −196°, respectively. The unreacted difluoramine, if any, was found in the first trap and the difluorodiazine in the second. In a typical run, with the reactor maintained at 120°, 14 cc. of HNF_2 was converted to 6.1 cc. of N_2F_2 with 1.9 cc. of HNF_2 recovered. This corresponds to an 87% conversion with 100% yield.

Difluoramine–Alkali Fluoride Addition Compounds.—Alkali fluorides (0.2–2 g.) were placed in a Pyrex ampoule which had large indentations on the bottom to provide a maximum surface exposed to the salt. The salts were heated *in vacuo* as in the preparation of difluorodiazine, after which gaseous difluoramine (20–40 cc.) was condensed therein. At least 45 min. was allowed for temperature equilibration at each temperature. A mercury manometer, with the mercury protected by Fluorolube, was used for the pressure measurements. Pressures were read with a cathetometer and all points were reproduced on other samples.

Potassium Fluoride–Difluoramine.—The dissociation pressures of $KF\cdot HNF_2$ measured as a function of temperature are (given as t (°C.), P (mm.)): −81.8, 1.2; −71.4, 4.6; −58.8, 7.9; and −46.6, 20.2. This temperature dependence is correlated by the equation $\log K_p = -1467/T + 7.784$, which corresponds to $\Delta H = 6.7$ kcal./mole for $KF\cdot HNF_2(s) = KF(s) + HNF_2(g)$.

Rubidium Fluoride–Difluoramine.—The dissociation pressures of $RbF\cdot HNF_2$ measured as a function of temperature are (t (°C.), P (mm.)): −81.6, 0.0; −72.0, 0.0; −65.0, 0.8; −57.8, 1.9; −45.8, 6.5; and −31.6, 23.5. This temperature dependence is correlated by the equation $\log K_p = -2166/T + 10.338$, which corresponds to $\Delta H = 9.9$ kcal./mole for $RbF\cdot HNF_2(s) = RbF(s) + HNF_2(g)$.

Cesium Fluoride–Difluoramine.—In a typical experiment, HNF_2 (19.7 cc., 0.88 mmole) was condensed over a sample of dried CsF (1.1233 g., 7.47 mmoles) contained in a Pyrex ampoule similar to that used in the above experiments. The equilibrium dissociation pressure at −64.2° was 1.5 mm. and bleeding off small portions of the vapor resulted in no decrease in pressure until 9.2 cc. of gas was removed when the pressure dropped to essentially zero. Even pumping did not remove additional difluoramine. In all three experiments run, the ampoule was allowed to warm up and the contents exploded before reaching room temperature.

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Donor–Acceptor Function in Organofluorophosphoranes

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Phosphorus pentafluoride forms moderately stable complexes with a variety of organic donor molecules[1,2] but appears inactive toward strong acceptors. We have further assayed the acceptor and donor functions in phosphorus(V) fluorides by examining the interaction of alkyl and aryl derivatives of PF_5 with representative donor and acceptor molecules.

Acceptor Behavior.—Phenyl tetrafluorophosphorane possesses sufficient acceptor strength to yield isolable complexes with strong donors such as dimethylformamide and pyridine. These complexes in solution display a simple doublet F^{19} spectrum in which the splitting arises from FP spin–spin coupling.[3] The doublet sharpens with decreasing temperatures and shifts slightly to higher fields, but no significant change in the doublet separation occurs. Apparently the complexes are dissociated to some extent in solution

$$C_6H_5PF_4\cdot\text{donor} \rightleftharpoons C_6H_5PF_4 + \text{donor}$$

and the rate constants are sufficiently large that the n.m.r. spectra represent an averaged FP environment. Estimated lifetimes for fluorine atoms in the complex are of the order of 10^{-4} sec. For solutions of $C_6H_5PF_4$ in donor solvents of lower base strength like acetonitrile or highly hindered donor solvents like triethylamine, the F^{19} spectrum is the same as for pure $C_6H_5PF_4$; no change occurs in the FP coupling constant. Thus there is no significant complex formation in these solvents.

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[1] S. Johnson, Ph.D. Thesis, Purdue University, 1953.

[2] E. L. Muetterties, T. A. Bither, M. W. Farlow, and D. D. Coffman, *J. Inorg. Nucl. Chem.*, **16**, 62 (1962).

[3] The J_{PF} values fall in the range 840–880 c.p.s. These compare with 900–1000 c.p.s. for RPF_4 species and ~740 c.p.s. for $F_5P\cdot$base complexes.