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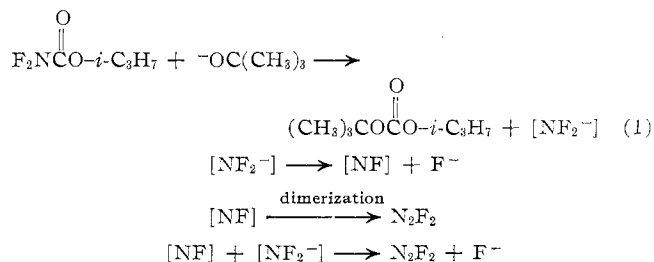
## Preparations of Difluorodiazine and Difluoramine<sup>1</sup>

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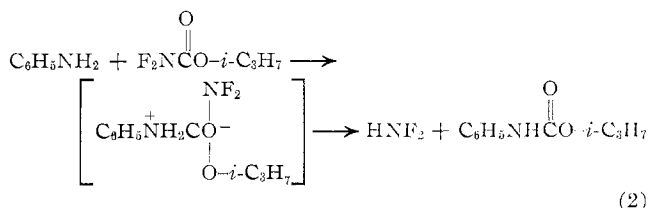
Recently a great deal of work has been carried out concerning reactions and preparations of compounds containing N-F bonds. With an increasing interest in these compounds, the availability of a safe, convenient source of difluoramine (HNF<sub>2</sub>) and difluorodiazine (N<sub>2</sub>F<sub>2</sub>) is very desirable. Isopropyl N,N-difluorocarbamate (F<sub>2</sub>NCO<sub>2</sub>-*i*-C<sub>3</sub>H<sub>7</sub>)<sup>2</sup> is a stable liquid (*d*<sub>25</sub> 1.2, bp 41° (60 mm)) which has been handled under a large variety of conditions in quantities up to 0.1 mole without experiencing any dangers such as explosions or uncontrollable reactions. We have found F<sub>2</sub>NCO<sub>2</sub>-*i*-C<sub>3</sub>H<sub>7</sub> to be a safe, convenient source of both difluorodiazine (N<sub>2</sub>F<sub>2</sub>) and difluoramine (HNF<sub>2</sub>) using nonaqueous conditions.

As pointed out by Johnson,<sup>3</sup> most previous preparations<sup>3-5</sup> of N<sub>2</sub>F<sub>2</sub> require specialized equipment or conditions and are frequently accompanied by low yields. Addition of potassium *t*-butoxide to a chilled solution of F<sub>2</sub>NCO<sub>2</sub>-*i*-C<sub>3</sub>H<sub>7</sub> in dry 1,1,2,2-tetrachloroethane (C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>) gives a quantitative yield of N<sub>2</sub>F<sub>2</sub>. The mass spectral cracking patterns showed that the N<sub>2</sub>F<sub>2</sub> product was obtained as a 3:1 *trans-cis* mixture. In the absence of aqueous conditions, one need not be concerned with side products such as N<sub>2</sub>O, HNF<sub>2</sub>, and N<sub>2</sub>F<sub>4</sub>. The reaction is quite exothermic and the CO<sub>2</sub> produced from decomposition of the dialkyl carbonate is easily removed by KOH (see Experimental Section). Presumably the N<sub>2</sub>F<sub>2</sub> is produced by dimerization of "fluoronitrene" (NF) or by reaction of "fluoronitrene" with the difluoramide anion.<sup>6</sup>



Methods, other than acid hydrolysis of (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>CNF<sub>2</sub>,<sup>7</sup> used to produce difluoramine (HNF<sub>2</sub>)<sup>8-14</sup> re-

quire handling of F<sub>2</sub> or N<sub>2</sub>F<sub>4</sub>. Whereas other procedures generally employ acid hydrolysis, we have observed that a base, aniline, mixed with F<sub>2</sub>NCO<sub>2</sub>-*i*-C<sub>3</sub>H<sub>7</sub> in 1,1,2,2-tetrachloroethane (C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>) produces HNF<sub>2</sub> in a nonaqueous system. When F<sub>2</sub>NCO<sub>2</sub>-*i*-C<sub>3</sub>H<sub>7</sub> is added to a chilled solution of C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> in C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> and the reaction is allowed to reach ambient temperature, a slow steady production of HNF<sub>2</sub> is observed. The reaction goes to completion in 2 hr, giving a 50%



yield of HNF<sub>2</sub>. A 40% yield is obtained after 45 min, and warming the solution increases the rate at which HNF<sub>2</sub> is generated. However, above 35° small amounts of F<sub>2</sub>NCO<sub>2</sub>-*i*-C<sub>3</sub>H<sub>7</sub> come off with the HNF<sub>2</sub>. Higher boiling carbamates could replace the isopropyl compound and would allow one to use higher temperatures and substantially shorten the reaction time. No deaminated product,<sup>15</sup> benzene, is formed under the conditions described.

### Experimental Section

**Preparation of N<sub>2</sub>F<sub>2</sub>.**—A 100-ml three-neck flask with standard taper joints was fitted with a solid addition funnel, a gas inlet tube, and an exit tube. The exit tube was connected to a small KOH train (to remove CO<sub>2</sub>), then to a trap cooled with liquid N<sub>2</sub>, and finally to a water bubbler. The reaction flask was kept in an ice bath and magnetically stirred. Kel-F 90 grease<sup>16</sup> was used for all joints.

A 1.2-ml sample of F<sub>2</sub>NCO<sub>2</sub>-*i*-C<sub>3</sub>H<sub>7</sub> (1.4 g, 0.01 mole) was mixed with 20 ml of dry C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> in the 100-ml three-neck flask. The flask was placed in an ice bath and fitted with a solid addition funnel containing 1.2 g (0.01 mole) of powdered potassium *t*-butoxide (KO-*t*-C<sub>4</sub>H<sub>9</sub>). After 4-5 min of He purging, the trap was placed in a dewar containing liquid N<sub>2</sub>. KO-*t*-C<sub>4</sub>H<sub>9</sub> was added in small amounts to the stirred solution (time of addition, 4-5 min). When addition was complete, the N<sub>2</sub> trap was closed off at one end and a vacuum pump used to remove the helium. Mass spectral analysis (Hitachi Perkin-Elmer RMU-6E) showed the sample to be pure N<sub>2</sub>F<sub>2</sub>. The solution remaining after reaction was inactive toward iodide. From the solution *t*-butylisopropyl carbonate was isolated and identified. Also, 0.57 g of KF (99%) was isolated from the solution. From the amount of KF isolated and the fact that the solution remaining was no longer active toward iodide, it was concluded that the yield of N<sub>2</sub>F<sub>2</sub> was quantitative. For precautions in handling N<sub>2</sub>F<sub>2</sub>, see ref 3.

**Preparation of HNF<sub>2</sub>.**—A 35-ml two-neck flask was fitted with gas inlet and exit tubes. The exit tube was connected to a trap cooled with a methylocyclohexane slush bath (-126°) and then

(1) A portion of a dissertation is to be presented by D. L. K. to the Graduate School of Utah State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Commercially available from Aerojet-General Corp., Azusa, Calif. F<sub>2</sub>NCO<sub>2</sub>-*i*-C<sub>3</sub>H<sub>7</sub> is a lachrymator which slowly hydrolyzes if exposed to air, but can be stored in a desiccator or in solvents for long periods without decomposition.

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(16) Trademark of Minnesota Mining and Manufacturing Co., Minneapolis, Minn.

to a water bubbler. Helium flowed through the system at a slow rate during the course of the reaction.

A 1.5-ml sample of aniline was mixed with 10 ml of  $C_2H_2Cl_4$  in the 35-ml flask and the flask was placed in an ice bath and slowly stirred with a magnetic stirrer. Once the temperature of the solution reached equilibrium with the ice bath, 1.2 ml of  $F_2NCO_2-i-C_3H_7$  (1.4 g, 0.01 mole) was added all at once, and the reaction flask was left in the ice bath for 5 min. The ice bath was then removed and the reaction was allowed to proceed at ambient temperature. Mass spectral analysis at various intervals showed that the off gases consisted of  $HNF_2$  contaminated with about 20%  $CO_2$ . The reported yields of  $HNF_2$  were determined by bubbling the off gases through acidic iodide traps, a method employed by Haszeldine, *et al.*<sup>17</sup> Based on eq 2,  $C_6H_5NHCO_2-i-C_3H_7$  was isolated in 80% yield.

**Explosive Nature of Difluoramine.**—Difluoramine has been known to explode violently when condensed with liquid nitrogen.<sup>14</sup> On rare occasions  $HNF_2$  has been known to explode when condensed with a methylcyclohexane slush bath ( $-126^\circ$ ) as well.<sup>18</sup> Although no explosions occurred during the course of this study, small quantities and adequate protective precautions are advised.

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## Germyl Chemistry. V. Hexamethylphosphoramide as a Solvent for the Preparation and Reaction of Alkali Metal Derivatives of Silane and Germane<sup>1a</sup>

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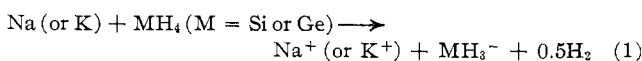
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Previous workers have prepared alkali metal derivatives of  $SiH_4$  and  $GeH_4$  in a variety of solvents. Liquid ammonia has been used in the preparation of  $NaGeH_3$  and  $KGeH_3$ ,<sup>2-4</sup> ethylamine in the preparation of  $Li-GeH_3$ ,<sup>4</sup> and both liquid ammonia and 1,2-dimethoxyethane in the preparation of  $KSiH_3$ .<sup>5-7</sup> Each of these solvents, however, suffers from various disadvantages which have prevented the realization of the full potential of these derivatives as intermediates in the synthesis of silyl and germyl compounds. Ammonolysis reactions make the use of liquid ammonia unreliable, while the volatility of the solvent necessitates the use of special apparatus. In addition, the low temperatures which are required often tend to slow down reactions. Ethers are not sufficiently active solvents for

alkali metals, and long reaction times are always necessary. Little work has been reported on the use of amines as solvents, but it seems that, even here, solvolysis reactions often complicate the preparations.<sup>4</sup>

We have investigated the use of the aprotic solvent hexamethylphosphoramide,  $[(CH_3)_2N]_3PO$  (HMPA), for the preparation and reaction of sodium and potassium derivatives of  $SiH_4$  and  $GeH_4$ . This solvent is involatile and moderately inert chemically. It is reported to dissolve alkali metals to concentrations of 1 *M*, giving blue solutions which are stable over a period of a few hours at or below room temperature.<sup>8</sup> It also appears to dissolve certain alkali halides (notably  $LiCl$ ) to give conducting solutions.<sup>9</sup>

We find that both  $SiH_4$  and  $GeH_4$  react rapidly with solutions of sodium or potassium in HMPA to give a permanent gas (presumed to be hydrogen) and a pale yellow solution. The amount of  $SiH_4$  or  $GeH_4$  taken up corresponds to the reaction



Potassium was used for most of the reactions, since it dissolved more rapidly than did sodium. When  $SiH_4$  was used, the final solution had a deeper yellow color than when  $GeH_4$  was used. In no case was evidence obtained for reaction of  $SiH_4$  or  $GeH_4$  with 2 equiv of alkali metal, as is observed in the reaction of sodium with  $GeH_4$  in liquid ammonia.<sup>2</sup>

The over-all yield of alkali metal derivative could not be determined directly. The solvent is effectively involatile at room temperature, and the salts remain soluble even on addition of 10 parts of xylene to 1 part of solution. The solutions were therefore treated with alkyl halides to give alkyl derivatives of  $SiH_4$  and  $GeH_4$ .



Alkyl halides used were  $CH_3I$ ,  $C_2H_5Br$ , and  $CH_3O-CH_2Cl$ . For the chloride and bromide derivatives, a white precipitate formed, presumably the sodium or potassium halide. For the iodide, no precipitate was formed when potassium was used. This implies that  $KI$ , at the concentrations employed, is soluble in HMPA. The alkylsilanes and -germanes were isolated by distillation from the reaction vessel and low-temperature vacuum fractionation. The purity and over-all yield of the products were determined by gas chromatography. Identification was made by gas chromatographic retention times and infrared data.<sup>10-14</sup> The usual impurities observed were the excess of alkyl halide added, together with  $SiH_4$  or  $GeH_4$  as appropri-

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