Although the Cl_2 was not identified, silver chloride was found in the solid.

Reaction with Ag_2O.—In an attempt to produce the compound SF_5NSO[1] about 0.2 g of SF_5NSCl_2 was condensed onto an excess of Ag_2O (about 5 g) and the cylinder was heated to 50° for 24 hr. No SF_5NSO was found, the principal products being equimolar amounts of NSF_3 and SOF_2. Silver chloride was found in the solid.

Discussion

Although no free sulfur or S_2Cl_2 was found among the products of the reaction leading to SF_5NSCl_2, the presence of sulfur in some form in the yellow deposit on the inside of the reaction cylinder suggests that the reaction was

$$SF_5NH_2 + 2SCl_2 \longrightarrow SF_5NSCl_2 + 2HCl + S$$

or perhaps

$$2SF_5NH_2 + 4SCl_2 + Fe \longrightarrow 2SF_5NSCl_2 + 4HCl + \text{"}FeS_2\text{"}$$

The identity of the compound is proved by the combined evidence of the elemental analysis, mass spectral evidence, and particularly the infrared spectrum. The sharp peak at 1240 cm^{-1} may confidently be assigned to the N=S stretch. (The N=S stretch in $SF_5N{=}SF_2$ occurs[1] at 1313 cm^{-1}.) Similarly, the peaks at 913, 862, and 600 cm^{-1} are highly characteristic of the SF_5 group, while the bands at 760 and 714 cm^{-1}, attributed to the SCl_2 group, are very close to those observed by Lustig[3] for the compound CF_3NSCl_2.

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Simple, High-Yield Preparations of Chlorodifluoramine and Difluorodiazine

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Chlorodifluoramine has been prepared by reaction of difluoramine with boron trichloride,[1] phosgene,[2] or hydrogen chloride;[2] by treatment of a mixture of sodium azide and sodium chloride with fluorine;[3] by reaction of chlorine trifluoride with ammonium fluoride;[4] by reaction of chlorine and difluoramine in the presence of potassium fluoride;[5] and by chlorination of $KOCF_2NF_2$.[6]

Difluorodiazine has been prepared by various techniques: the thermal decomposition of fluorine azide,[7] electrolysis of ammonium hydrogen fluoride,[8] reaction of nitrogen trifluoride with mercury vapor in an electric discharge,[9] dehydrofluorination of difluoramine,[10] treatment of a solution of N,N-difluorourea with a concentrated potassium hydroxide solution,[11] reaction of sodium azide and fluorine,[12] decomposition of $N_2F_3Sb_2F_{11}$,[13] and reaction of tetrafluorohydrazine and excess aluminum chloride at 78°.[14]

Although both chlorodifluoramine (NF_2Cl) and difluorodiazine (N_2F_2) have been prepared in a variety of ways, a convenient high-yield synthesis for each compound was not reported. A number of these preparations suffer the disadvantage of low[4,8,9,11,12,14] or erratic[2,3] yields or involve a somewhat circuitous route.[6,13] Explosions have occurred during their preparation.[8,4,7] Difluoramine is used frequently as a source of NF_2 in several of the above preparations;[1,2,5,10] however, this reagent is extremely shock sensitive as a solid and care must be exercised in handling.[5]

We describe herein a convenient method for the preparation of chlorodifluoramine and difluorodiazine in reproducibly good yields by the photolysis of tetrafluorohydrazine and thionyl chloride or bromine, respectively.

Experimental Section

In the following procedures a standard glass vacuum line equipped with a null-point pressure device such as a Booth–Cromer[15] pressure gauge or a spiral gauge was used.

Infrared spectra were recorded with a Beckman IR-5A or Perkin-Elmer 621 spectrophotometer by using a 5-cm gas cell equipped with NaCl or KBr windows. Fluorine-19 nmr spectra were obtained on a Varian HA-100 spectrometer. Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6E mass spectrometer at an ionization potential of 70 eV. The ultraviolet light source was 450-W lamp equipped with a Vycor filter (Hanovia L-679A36, Engelhard Hanovia, Inc., Engelhard, N. J.).

For gas chromatographic separations a 25 ft × 0.25 in. copper column packed with 20% Kel-F-3 polymer oil or FC-43 (3M Co.) on acid-washed Chromosorb P was used at 25 or −63°. In some cases, fractional condensation was used to effect crude separations.

Tetrafluorohydrazine (Air Products Co.) and reagent grade bromine were used without further purification. Thionyl chloride was purified by a trap-to-trap distillation.

Caution! Care should be exercised in handling tetrafluorohydrazine, chlorodifluoramine, and difluorodiazine since nitrogen–halogen compounds are known to exhibit explosive properties. Any apparatus used should be clean and free of organic materials.

Preparation of NF_2Cl.—$SOCl_2$ (0.714 g, 0.006 mol) and N_2F_4 (0.104 g, 0.001 mol) were condensed into a 850-ml Pyrex vessel equipped with a water-cooled quartz probe. After the mixture had warmed to room temperature, it was photolyzed through a Vycor filter for about 1 hr and then passed through a series of

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traps at −130, −184 (−160° if liquid oxygen is not available), and −195° under dynamic vacuum. A small amount of nitrogen (identified by mass spectroscopy) formed in the reaction was expelled. The first trap contained $SOCl_2$, SO_2, SOFCl, SO_2FCl, and some SOF_2; NF_3 was found in the last trap. The photolysis vessel contained elemental sulfur. Chlorodifluoramine contaminated with SiF_4, Cl_2, SOF_2, and any N_2F_4 was held at −184°. This mixture was bubbled through a 2 *N* NaOH solution and again passed through traps at −130 and −195°. Chlorodifluoramine and a small amount of N_2F_4 (~4%) were found in the latter trap. For most purposes further purification was not required. However, NF_2Cl may be separated from N_2F_4 by gas chromatography using the Kel-F-3 column. The yield was 65–70% based on N_2F_4 consumed.

With a 5-l. vessel using 5.95 g (0.05 mol) of $SOCl_2$ and 0.832 g (0.008 mol) of N_2F_4 and photolyzing for 90 min, a 50% yield of NF_2Cl resulted. A significant amount of N_2F_2 (70% *trans*) was observed (roughly 12% relative to the amount of NF_2Cl produced).

Since chlorodifluoramine is known to decompose to N_2F_4 and Cl_2 in the presence of ultraviolet radiation after roughly 1 hr,[16] it was important to complete the photolysis in a minimum amount of time. During the initial run it was advantageous to monitor the reaction to determine the optimum reaction time (either all of the N_2F_4 is consumed or the $NF_2Cl:N_2F_4$ ratio begins to decrease as determined by using gas chromatographic separation on successive aliquots).

The product was identified by its infrared spectrum,[1] molecular weight (calcd, 87.5; found, 88.0), and ^{19}F nmr. The latter is a broad triplet ($J_{N-F} \approx 122$ cps) centered at ϕ −141.5 (Figure 1) (previously reported as a single broad band centered at −217.2 ppm relative to CF_3COOH[17]).[18]

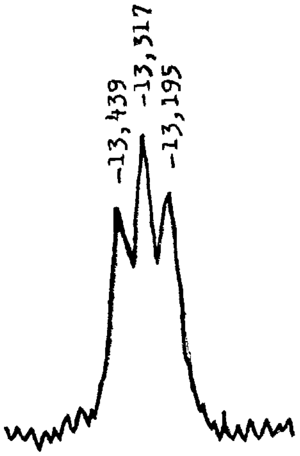

Figure 1.—The ^{19}F spectrum (cps) of NF_2Cl in CCl_3F (at 94.1 Mc).

Preparation of N_2F_2.—Br_2 (0.638 g, 0.004 mol) and N_2F_4 (0.208 g, 0.002 mol) were photolyzed in the 850-ml vessel for 90 min through a Vycor filter. A trap-to-trap separation was performed on the reaction products using traps at −140 and −195°. Small amounts of nitrogen produced in the reaction were expelled. A volatile white solid, probably $(NO)_2SiF_6$, was found in the photolysis vessel, and N_2O_4 and Br_2 were held at −140°. Difluorodiazine (trapped at −195° with SiF_4 and NF_3) was purified using the FC-43 column at −63°. This column, as well as ^{19}F nmr, was also useful for determining the *trans*:*cis* ratio. A typical yield was 70% N_2F_2 (53% *trans*). The same percentage resulted after 90 min of photolysis using a 5-l. bulb with 2.39 g (0.015 mol) of Br_2 and 0.936 g (0.009 mol) of N_2F_4.

The two isomers of N_2F_2 were identified by their molecular weight (calcd, 66.0, found, 65.9) and infrared and ^{19}F nmr spectra.[18]

Results and Discussion

Both chlorodifluoramine and difluorodiazine can be prepared in about 70% yields by ultraviolet irradiation of N_2F_4 and thionyl chloride or bromine. Under the experimental conditions used, if the time of photolysis is greater than approximately 1 hr, the yield of NF_2Cl decreases which is in agreement with an earlier study of the rate of photochemical decomposition of NF_2Cl.[16] While ^{19}F nmr chemical shift measurements agree reasonably well with literature data for NF_2Cl,[1] we have now been able to observe the broadened triplet of peaks (of roughly equal areas) expected to arise from nitrogen–fluorine coupling ($J \approx 122$ cps). Nitrogen–fluorine coupling constants on similar compounds are in this range; *e.g.*, for N_2F_4, $J = 117$ cps; for NF_3, $J = 155$ cps.[19]

Bumgardner and Lustig[20] have suggested (1) as the initial step in the photolysis of N_2F_4. Appropriate combinations of $F\cdot$ with $\cdot NF_2$ and NF dimerization lead to NF_3 and N_2F_2.[21] However, we observed relatively little or no NF_3 and N_2F_2 in the preparation of NF_2Cl. Under our experimental conditions NF_2Cl forms readily (eq 3 or 4) with little or no decomposition (as evidenced by the absence of Cl_2) which may explain our higher yield. Petry showed that irradiating N_2F_4 and Cl_2 at 25° was not a practical route to NF_2Cl since chlorine radicals catalyze the photochemical decomposition of NF_2Cl. Therefore, $SOCl_2$ is either a poorer source of chlorine radicals than Cl_2, *i.e.*, reaction 2 is inefficient, and chlorine atoms are consumed by $\cdot NF_2$ immediately or the reaction may occur mainly *via* $\cdot NF_2$ radical attack on $SOCl_2^*$. In the former case, a large excess of $\cdot NF_2$ radicals would be present and should lead to the production of significant amounts of N_2F_2 and NF_3 which is not observed. The latter seems more attractive since when the thermochemical reaction of a mixture of N_2F_4 and $SOCl_2$ was attempted at 100° and at 175°, no NF_2Cl was obtained. This suggests that an excited $SOCl_2$ species, in addition to $\cdot NF_2$, is necessary for reaction to occur. However, the thermal stability of NF_2Cl is open to question. Chlorine is not formed in the reaction until at least 95% of the N_2F_4 is consumed. The appearance of chlorine may be due to photochemical decomposition of NF_2Cl or lack of $\cdot NF_2$ radicals available to interact with $SOCl_2^*$ *via* reaction 4.

$$N_2F_4 \xrightarrow{h\nu} \cdot NF_2^* \longrightarrow NF + \cdot F \qquad (1)$$

$$SOCl_2 \xrightarrow{h\nu} SOCl_2^* \longrightarrow \cdot Cl + \cdot SOCl \qquad (2)$$

$$\cdot NF_2 + \cdot Cl \longrightarrow NF_2Cl \qquad (3)$$

$$SOCl_2^* + \cdot NF_2 \longrightarrow \cdot SOCl + NF_2Cl \qquad (4)$$

The reaction between $SOBr_2$ and N_2F_4 was initially investigated but when it was found that bromine gave identical NF-containing compounds, work with $SOBr_2$

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was discontinued. Since we were not able to detect the unstable NF_2Br in this reaction, stabilization of the $\cdot NF_2$ moiety is precluded by this route. Therefore, the most likely reaction of $\cdot NF_2$ is its dissociation into NF and $F\cdot$ which would result in the production of significant amounts of N_2F_2 (eq 5) and NF_3 (eq 6). It

$$2NF \longrightarrow N_2F_2 \qquad (5)$$

$$\cdot F + \cdot NF_2 \longrightarrow NF_3 \qquad (6)$$

seems reasonable that $\cdot NF_2$ and $\cdot Br$ would compete for the fluorine radical which would also result in the formation of bromine fluorides. This is supported by the observed decrease in the yield of NF_3 when the initial $Br_2:N_2F_4$ ratio is increased. Bromine monofluoride, which is a likely intermediate, would readily disproportionate to BrF_3 and bromine. The former readily attacks glass to give Br_2, O_2, and SiF_4. As a result, no bromine is consumed in the over-all reaction and the vessel is badly etched.

Based on the two syntheses described here and on the earlier work of Petry,[16] the reactions of N_2F_4 with chloro molecules which are poor sources of radicals should lead to relatively high yields of NF_2Cl, while systems that produce either high concentrations of radicals or form unstable NF_2-containing products will give rise to large amounts of difluorodiazine.

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The Reaction of Chloramine with 1,1-Dimethylhydrazine. Formation of Tetramethyl-2-tetrazene

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Recent investigations in these laboratories have been concerned with the reaction of 1,1-dimethylhydrazine with chloramine[1] and also with the reactions of chloramine and dimethylchloramine with primary and secondary phosphines[2] and arsines.[3] The present communication involves a further study of the reaction of chloramine with 1,1-dimethylhydrazine, a more extensive elucidation of the products, and possible intermediates in product formation. Specifically, tetramethyl-2-tetrazene, $(CH_3)_2NN{=}NN(CH_3)_2$, has been shown to be a product of the reaction.

Experimental Section

The Reaction of 1,1-Dimethylhydrazine with Ammonia-Free Chloramine.—Chloramine, prepared by the gas-phase reaction of ammonia and chlorine,[4] was collected in cooled dry diethyl ether. Ammonia was allowed to evaporate as the volume of ether was reduced to give a concentrated (*ca.* 0.4 *M*) solution of chloramine. Final traces of ammonia were removed[5] by passing the solution through anhydrous copper(II) sulfate just prior to the performance of an experiment. The chloramine content of the solution was determined before each experiment by withdrawal of an aliquot portion, its addition to an acidified potassium iodide solution, and subsequent titration of the released iodine using standard thiosulfate solution. A typical experiment consisted in adding 61 ml of 0.495 *M* chloramine (30.0 mmol) solution dropwise to 1.80 g of 1,1-dimethylhydrazine (30.0 mmol) in 25 ml of dry diethyl ether. External cooling by means of an ice bath was maintained with stirring over a 4-hr reaction period. The solid which formed during the course of the addition was removed, pumped dry in a vacuum desiccator, and weighed. It was subsequently added to an acidified potassium iodide solution and the resulting iodine was titrated with standard thiosulfate solution,[6] the reaction being $3H^+ + 2I^- + (CH_3)_2N(NH_2)_2^+ \rightarrow H_2NN(CH_3)_2H^+ + NH_4^+ + I_2$. From this titration, the number of moles of 2,2-dimethyltriazanium chloride, $(CH_3)_2N(NH_2)_2Cl$, was calculated (found 4.9 mmol). The difference between total sample weight and the weight of triazanium chloride was assumed to be ammonium chloride (found 24.7 mmol). In some experiments, a small portion of the solids was withdrawn and its infrared spectrum was taken; the spectrum thus obtained agreed well with that of a sample of pure ammonium chloride, since ammonium chloride was in fivefold excess over triazanium chloride. An additional experiment was performed as described above, but the triazanium chloride was isolated[1] and characterized by its melting point (137–138°) and infrared spectrum.

At this point we turned to an investigation of materials remaining in the reactant solvent, which is normally discarded,[1] in an attempt to isolate any liquid products and recover unreacted 1,1-dimethylhydrazine. The reaction liquid was distilled at atmospheric pressure, half of the yellow, oily residue obtained was dissolved in carbon tetrachloride, and its nmr spectrum was determined. The other half was used to determine its infrared spectrum. Identification of the oil as tetramethyl-2-tetrazene was accomplished by comparison of its nmr and ir spectra with those of known samples[7,8] and by the observation that the single observed nmr peak was increased by the addition of pure tetramethyl-2-tetrazene synthesized in a standard manner[7] (τ 7.31 in CCl_4, TMS internal standard). Evidence of the presence of a small amount of unreacted 1,1-dimethylhydrazine was found in some of the nmr spectra (11.2 mmol of tetramethyl-2-tetrazene was found). The results of all experiments are summarized in Table I.

The Reaction of 1,1-Dimethylhydrazine with Effluent Gases from Chloramine Generator.—A typical reaction involved bubbling the ammonia–chloramine effluent from a chloramine generator[4] through a solution of 33 mmol of 1,1-dimethylhydrazine in dry ether; the amount of chloramine so added was *ca.* 100 mmol. The reaction vessel was allowed to stand for 24 hr, and the liquid and solid products were then separated. The solid was dried in a vacuum desiccator, weighed, and added to an acidic potassium iodide solution. The liberated iodine was titrated with standard thiosulfate solution (found 14.0 mmol).

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