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· 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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TABLE I

REACTION OF AMMONIA-FREE CHLORAMINE WITH 1,1-DIMETHYLHYDRAZINE

Reactants,[a] mmol		Products, mmol		
1,1-Dimethylhydrazine	Chloramine	Ammonium chloride	Triazanium chloride	Tetramethyl-2-tetrazene
30.0 (12.3)	30.0 (0.9)	24.7	4.9	11.2
29.8 (15.2)	30.0 (0.4)	24.9	5.3	8.4
60.2 (44.0)	30.0 (0.0)	23.6	7.4	8.4
30.0 (0.0)	60.2 (12.5)	37.6	11.0	18.8

[a] Figures shown in parentheses indicate mmoles recovered unreacted.

The remainder of the solids was assumed to be ammonium chloride (found 18.2 mmol). The liquid reaction phase was distilled at the lowest temperature possible. The remaining yellow oil was placed on the vacuum line and the remaining ether removed at low pressure. The yellow oil was redissolved in an aliquot portion of dry ether, and its gas chromatogram was taken. Three peaks were observed, in the ratio 86:12:2. The addition of pure tetramethyl-2-tetrazene or pure 1,1-dimethylhydrazine selectively increased the largest or next to largest peaks, respectively; the compound responsible for the smallest peak remained uncharacterized. The experimental results are shown in Table II.

TABLE II

REACTION OF CHLORAMINE–AMMONIA MIXTURES WITH 1,1-DIMETHYLHYDRAZINE (ALL QUANTITIES SHOWN ARE EXPRESSED AS MILLIMOLES)

1,1-Dimethylhydrazine	2,2-Dimethyltriazanium chloride	Ammonium chloride	Tetramethyl-2-tetrazene
33.3	14.0	13.2	1.7
33.3	16.0	16.9	1.2
33.3	16.2	17.0	1.5
33.3	14.7	18.0	1.2

Results and Discussion

It is clear that the ability of chloramine to abstract hydrogen atoms and effect oxidative coupling is demonstrable, not only for relatively acidic hydrogen species[2,3,9] but also may be extended to the generally less acidic class of compounds containing N–H bonds. It is also quite evident that all of the ammonium chloride observed in the reaction of chloramine with 1,1-dimethylhydrazine does not come from decomposition of chloramine on 2,2-dimethyltriazanium chloride or solid ammonium chloride as previously surmised[1] and that the presence of ammonia with chloramine increases the yield of 2,2-dimethyltriazanium chloride and ammonium chloride, while lowering the production of tetramethyl-2-tetrazene.

The mechanism of the attack on 1,1-dimethylhydrazine by chloramine is uncertain, though previous work[1] suggests either an attachment on the $(CH_3)_2N$– moiety to form 2,2-dimethyltriazanium chloride or a direct abstraction of hydrogen atoms[9] to form either $(CH_3)_2NNH$– or[10,11] $(CH_3)_2NN<$ as reactive intermediates

$$(CH_3)_2NNH_2 + NH_2Cl \longrightarrow [(CH_3)_2N(NH_2)_2]Cl \quad (1)$$

$$(CH_3)_2NNH_2 + NH_2Cl \longrightarrow (CH_3)_2NNH{-} + NH_3^+ + Cl^- \quad (2)$$

$$(CH_3)_2NNH_2 + NH_2Cl \longrightarrow (CH_3)_2NN< + NH_4Cl \quad (3)$$

The dimethylazamine fragments in eq 3 could then combine to give tetramethyl-2-tetrazene,[10] or the free radicals formed in eq 2 might combine to yield 1,1,4,4-tetramethyltetrazane, which could be further dehydrogenated[10] by chloramine to give tetramethyl-2-tetrazene. The NH_3^+ species shown in eq 2 may then either react with the radicals formed in (2) to yield the dimethylazamine radical, $(CH_3)_2NN<$, or react with another 1,1-dimethylhydrazine molecule to yield another $(CH_3)_2NNH$– radical. The presence of a high concentration of ammonia with either of the reactive intermediates in eq 2 or 3 could allow them to revert to 1,1-dimethylhydrazine as follows

$$NH_3 + (CH_3)_2NN< \longrightarrow 0.5N_2H_2 + (CH_3)_2NNH_2 \quad (4)$$

$$NH_3 + (CH_3)_2NNH{-} \longrightarrow {-}NH_2 + (CH_3)_2NNH_2 \quad (5)$$

The N_2H_2 formed in eq 4 may then decompose to ammonium azide,[12] nitrogen and hydrazine,[13] or nitrogen and ammonia.[14] Thus, as has been found, the presence of ammonia during the chloramination of 1,1-dimethylhydrazine results in higher yields of 2,2-dimethyltriazanium chloride and lower yields of tetramethyl-2-tetrazene.[15]

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[15] NOTE ADDED IN PROOF.—An alternative explanation may be based on the observation made by us as this paper was in proof that chloramine reacts with tetramethyl-2-tetrazene in the presence of ammonia to give dimethyltriazanium chloride. In the absence of ammonia no dimethyltriazanium chloride is obtained. This reaction is under intensive investigation and will be the subject of an early communication.

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Oxidation of the (3)-1,7-Dicarba-*nido*-dodecahydroundecaborate(−1) Ion. A New Preparation of 1,3-Dicarba-*nido*-nonaborane(13)

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The selective degradation of (3)-1,7-dicarba-*nido*-dodecahydroundecaborate(−1) ion, (3)-1,7-$B_9C_2H_{12}^-$, with chromic acid produced 1,3-dicarba-*nido*-nonaborane(13), 1,3-$B_7C_2H_{13}$, in 76% yield. Previously, 1,3-$B_7C_2H_{13}$ was prepared[1] through the oxidation of 1,8-$B_9C_2H_{11}$. The oxidation of the (3)-1,7-$B_9C_2H_{12}^-$ ion may proceed through a six-electron redox reaction as shown in eq 1. The structures of the (3)-1,7-$B_9C_2H_{12}^-$

$$(3)\text{-}1,7\text{-}B_9C_2H_{12}^- + 6H_2O \longrightarrow B_7C_2H_{13} + 2B(OH)_3 + 5H^+ + 6e^- \quad (1)$$

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