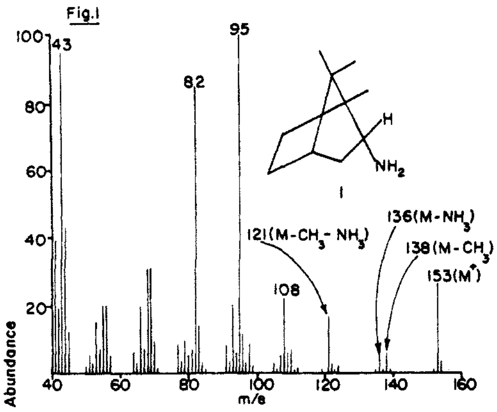


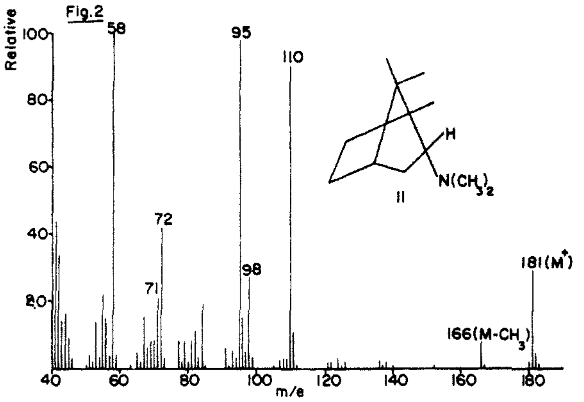


Figure 1.—Mass spectrum of bornylamine (I).

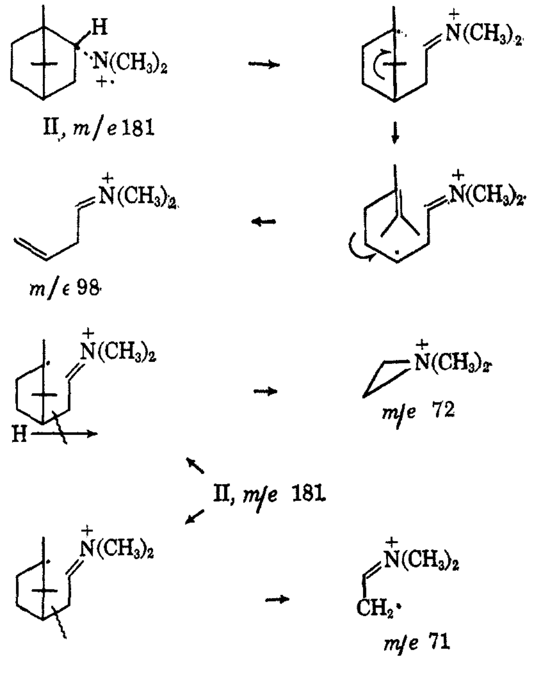
Figure 2.—Mass spectrum of N,N-dimethylbornylamine (II).

explanation may be the greater bulk of the dimethylamino group which interferes with the abstraction of a hydrogen atom.

The remaining peaks of interest in the spectrum (Figure 2) of II are found at *m/e* 71, 72, and 98. These ions have the empirical formulas C_4H_9N, $C_4H_{10}N$, and $C_6H_{12}N$, respectively, and probably arise in the manner shown in Scheme I.

These postulates are fully supported by the deuterium shifts observed in the spectrum of N,N-dimethylaminobornylamine-2,3,3-d_3: *m/e* 98 shifts to *m/e* 101, *m/e* 72 to *m/e* 75, and *m/e* 71 to *m/e* 74.

Scheme I



In conclusion, it is interesting to note that in this bicyclic system the hydrocarbon framework has such a powerful fragmentation-directing ability that it can compete effectively with the otherwise very strong fragmentation-directing dimethylamine function. As a consequence, in contrast to the usual observation[5] that dimethylamino substituents lead to a simplification of a given mass spectrum, a more complicated spectrum ensues in such highly fused systems. These observations further substantiate the earlier[3] conclusion that the *a priori* prediction of the mass spectral fragmentation of bicyclic monoterpenes is fraught with danger.

Fluorination of Tetrabromo-2,3-diaza-1,3-butadiene

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The preparation and characterization of tetrafluoro-2,3-diaza-1,3-butadiene ($CF_2{=}N{-}N{=}CF_2$) from the pyrolysis of difluorodiazirine have been reported.[1] We have investigated some of the chemical, physical, and spectral properties of the material obtained from CF_2N_2, and find that they differ from those which have been reported by Schroeder and co-workers[2] from the silver(I) fluoride fluorination of tetrabromo-2,3-diaza-1,3-butadiene (carbonyl bromide azine) or 2,5-dibromo-1,3,4-thiadiazole. In order to obtain further information bearing on this apparent discrepancy, we have examined the fluorination of $CBr_2{=}N{-}N{=}CBr_2$ with both AgF and AgF_2.

Tetrabromo-2,3-diaza-1,3-butadiene was prepared according to Thiele[3] by the acidic stannous chloride reduction of sodium azotetrazole, followed by bromination without isolation of intermediates. This material, after recrystallization from butyl chloride, was used in the fluorination studies.

The reaction of silver(II) fluoride (AgF_2) with tetrabromo-2,3-diaza-1,3-butadiene is rapid. Thus, when a mixture of the two solids is allowed to warm from 0° to room temperature, the reaction is explosive in nature with extremely vigorous gas evolution. The crude volatile product is a mixture of fluorinated azo derivatives, such as $CF_3{-}N{=}N{-}CF_2Br$, $CF_3{-}N{=}N{-}CF_3$, and $CF_3{-}N{=}N{-}CFBr_2$ (in order of decreasing yield). Small quantities of monochloroazo compounds are also isolated owing to the presence of chlorinated impurities (see the Experimental Section). The vigorous nature of this reaction, as well as the mixture of products, implies limited utility as a synthesis technique.

On the other hand, AgF_2 converts tetrabromo-2,3-diaza-1,3-butadiene to hexafluoroazomethane (CF_3—

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(1) R. A. Mitsch, *J. Heterocyclic Chem.*, **1**, 59 (1964).

(2) H. Schroeder, R. Rätz, W. Schnabel, H. Ulrich, E. Kober, and C. Grundmann, *J. Org. Chem.*, **27**, 2589 (1962).

(3) J. Thiele, *Ann.*, **303**, 57, 70 (1898).

$N{=}N{-}CF_3$) in nearly quantitative yields in a flow system (eq 1). Thus, a 92% isolated yield of pure hexafluoroazomethane was obtained by simply volatilizing

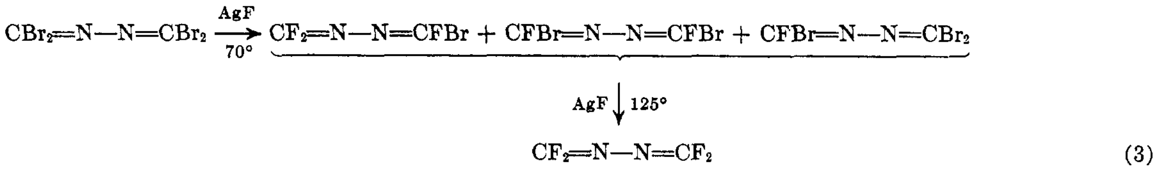
$$CBr_2{=}N{-}N{=}CBr_2 \xrightarrow[100^\circ]{AgF_2} \underset{92\%}{CF_3{-}N{=}N{-}CF_3} + Br_2 \tag{1}$$

$CBr_2{=}N{-}N{=}CBr_2$ over a bed of AgF_2. Bromine and trace quantities of $CF_3{-}N{=}N{-}CF_2Br$ and $CF_3{-}N{=}N{-}CFBr_2$ are the other products. Pure hexafluoroazomethane is obtained by vacuum fractional distillation through −78 and −196° receivers, followed by shaking the contents of the −196° trap with dilute NaOH and drying the gas over phosphorus pentoxide. As such this reaction represents perhaps the most convenient laboratory technique for the preparation of hexafluoroazomethane. It does not require the use of pressure equipment or iodine pentafluoride and avoids the resulting purification difficulties.

The formation of the incompletely fluorinated azo derivatives, obtained in the batch reaction and in trace quantities in the flow system, suggests that the mechanism of fluorination with AgF_2 involves primary 1,4 addition of fluorine to yield $CFBr_2{-}N{=}N{-}CFBr_2$. Subsequent replacement of bromine atoms by fluorine results in the formation of the observed products. The absence of $CF_2{=}N{-}N{=}CF_2$ as a fluorination product is in agreement with the rationale shown (eq 2).

$$CBr_2{=}N{-}N{=}CBr_2 \xrightarrow{AgF_2} CFBr_2{-}N{=}N{-}CFBr_2 \xrightarrow{AgF} \left\{\begin{array}{l} CF_3{-}N{=}N{-}CF_3 \\ CF_3{-}N{=}N{-}CF_2Br + Br \\ CF_3{-}N{=}N{-}CFBr_2 \end{array}\right. \tag{2}$$

The reaction of silver(I) fluoride (AgF) with tetrabromo-2,3-diaza-1,3-butadiene is less vigorous and could be carried out by heating an intimate mixture of the two reactants under vacuum. The reaction occurs at about 75°, with vigorous gas evolution, and yields $CF_2{=}N{-}N{=}CFBr$ (bp 68°, by vapor pressure extrapolation) as the major product although lesser quantities of $CF_2{=}N{-}N{=}CF_2$ (bp 3°), $CFBr{=}N{-}N{=}CFBr$, $CFBr{=}N{-}N{=}CBr_2$, and unfluorinated starting material are also isolated. Removal of the bromine from $CF_2{=}N{-}N{=}CFBr$ proved somewhat difficult but was achieved by repeated passage of the material through a column of AgF maintained at 125°. In this manner, a 33% over-all yield of chromatographically pure $CF_2{=}N{-}N{=}CF_2$ was obtained (eq 3). This material is spectroscopically identical with that prepared from CF_2N_2.[1]

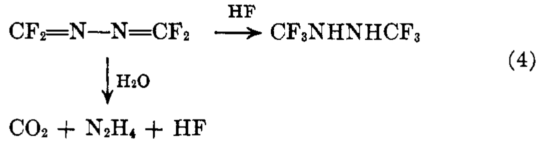


$$\begin{array}{c} CBr_2{=}N{-}N{=}CBr_2 \xrightarrow[70^\circ]{AgF} \underbrace{CF_2{=}N{-}N{=}CFBr + CFBr{=}N{-}N{=}CFBr + CFBr{=}N{-}N{=}CBr_2} \\ \qquad\qquad\qquad {\scriptstyle AgF}\big\downarrow{\scriptstyle 125^\circ} \\ \qquad\qquad\qquad CF_2{=}N{-}N{=}CF_2 \end{array} \tag{3}$$

Thus, the fluorination of $CBr_2{=}N{-}N{=}CBr_2$ with silver(I) fluoride does afford $CF_2{=}N{-}N{=}CF_2$, as reported by Schroeder and co-workers;[2] however, the boiling point of the purified material is 3°[4] (obtained from vapor pressure data) and not 68–73° as reported previously.[2] Although the reported boiling point of the material isolated by Schroeder and co-workers corresponds closely to that of the monobromoazine, $CF_2{=}N{-}N{=}CFBr$ (bp 68°), their elemental analyses appear to discount the presence of bromine. Ginsburg and co-workers[5] report a melting point of 30° for a dimer of $CF_2{=}N{-}N{=}CF_2$ and thus it is possible that the material reported by Schroeder[2] is an oligomer (possibly a dimer) in view of its high boiling point.

It is interesting to compare the properties of $CF_2{=}N{-}N{=}CF_2$ with those of other simple azines, such as $CH_2{=}N{-}N{=}CH_2$ and $CBr_2{=}N{-}N{=}CBr_2$. Whereas $CH_2{=}N{-}N{=}CH_2$ undergoes rapid polymerization at room temperature,[6] $CF_2{=}N{-}N{=}CF_2$ is recovered unchanged after heating at 200°. Furthermore, tetrafluoro-2,3-diaza-1,3-butadiene is hydrolyzed readily to hydrazine and carbon dioxide, if a gaseous sample of the material is shaken with water. The hydrolytic instability of $CF_2{=}N{-}N{=}CF_2$ is in contrast to the stability of $CBr_2{=}N{-}N{=}CBr_2$ which is isolated by steam distillation.[3]

Heating $CF_2{=}N{-}N{=}CF_2$ is an autoclave at 100° in the presence of excess anhydrous HF produces 1,2-bis(trifluoromethyl)hydrazine (see eq 4 below),



$$\begin{tikzcd} CF_2{=}N{-}N{=}CF_2 \arrow[r, "HF"] \arrow[d, "H_2O"] & CF_3NHNHCF_3 \\ CO_2 + N_2H_4 + HF \end{tikzcd} \tag{4}$$

which was identified by infrared, mass, and F^{19} nmr spectroscopy. It is apparent from molecular weight determinations that $CF_3NHNHCF_3$ (molecular weight, 168) is partially dimerized in the gas phase. Thus, a molecular weight of 262 was obtained from effusion studies whereas the gas density method gave 292. This observation is perhaps not unexpected since Ginsburg and co-workers report the formation of a stable etherate and acetonate with $CF_3NHNHCF_3$.[5]

Experimental Section

The AgF and AgF_2 were obtained from Harshaw Chemical Co., and used without further purification. Mass spectra were measured using a Consolidated 21-103C instrument with an inlet temperature of 30°, ion-chamber temperature 250°, 70 ion v, and 10-μa ion current. Molecular weights were determined by effusion methods using the mass spectrometer, except where otherwise noted. Mass spectra reported consist of the most significant peaks observed together with their

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(4) It should be noted that $CF_2{=}CF{-}CF{=}CF_2$ boils at 7.5°.

(5) V. A. Ginsburg, *et al.*, *Dokl. Akad. Nauk SSSR*, **142**, 354 (1962).

(6) N. P. Neureiter, *J. Am. Chem. Soc.*, **81**, 2910 (1959); U. S. Patent 3,067,252 (1962).

relative abundance in parentheses and probable ion assignment, *i.e.*, *m/e* (relative abundance) ion assignment.

Fluorination with Silver(II) Fluoride.—Silver(II) fluoride (30.0 g, 0.206 mole) and tetrabromo-2,3-diaza-1,3-butadiene (2.0 g, 5.4 mmoles) were placed in a round-bottom flask at 0°, intimately mixed, and connected to a vacuum system through two traps which were maintained at −196°. Upon warming to room temperature, a vigorous reaction occurred and volatile material condensed in the traps.

This material was found to be a mixture of $CF_3—N{=}N—CF_2Br$ (calcd mol wt, 226; found, 228), $CF_3—N{=}N—CF_3$, $CF_3—N{=}N—CFBr_2$, and trace quantities of $CF_3—N{=}N—CF_2Cl$ (calcd mol wt, 182; found, 189) and $CF_3—N{=}N—CFClBr$. The chlorine-containing products arise from the presence of a small amount of partially chlorinated azine in the starting material. The chloroazines are undoubtedly formed during the $SnCl_2$–HCl reduction of sodium azotetrazole immediately prior to bromination. The fluorinated azo compounds were separated by fractional distillation–condensation and vapor phase chromatography and identified by their infrared, mass, and F^{19} nmr spectra.

Vapor Phase Fluorination with Silver(II) Fluoride.—Aluminum boats, containing silver(II) fluoride (30.0 g, 0.206 mole) and tetrabromo-2,3-diaza-1,3-butadiene (2.0 g, 5.4 mmoles), were placed in tandem in a tube which was connected to a vacuum system *via* two −196° traps.

The tube was pumped for 1 hr to remove moisture. The temperature in the tube was raised to about 100° whereupon the $CBr_2{=}N—N{=}CBr_2$ vapor passed over the AgF_2. The AgF_2 turned red and volatile material condensed in the traps. The volatile product was fractionated through −78 and −196° receivers. The −78° trap contained 1.2 g (7.5 mmoles, 70%) of bromine and trace quantities of partially fluorinated azo compounds. The contents of the −196° trap, after shaking with aqueous NaOH and drying over P_2O_5, yielded pure hexafluoroazomethane (0.83 g, 5.0 mmoles, 92%). Identification was by infrared, F^{19} nmr, and mass spectroscopy.

Fluorination with Silver(I) Fluoride.—An intimate mixture of tetrabromo-2,3-diaza-1,3-butadiene (19.5 g, 0.052 mole) and silver(I) fluoride (125 g, 0.97 mole) was placed in a 500-ml flask. The flask was connected to a vacuum system and evacuated at room temperature for 1 hr to remove moisture. The evacuated reaction mixture was then slowly heated to about 75° at which time vigorous gas evolution occurred. The volatile products of the reaction were collected in two −196° traps. The crude product was predominantly $CF_2{=}N—N{=}CFBr$, with lesser quantities of $CF_2{=}N—N{=}CF_2$, $CF_2{=}N—N{=}CFCl$, and $CFBr{=}N—N{=}CFBr$. Unreacted $CBr_2{=}N—N{=}CBr_2$ and $CFBr{=}N—N{=}CBr_2$, were recovered from the reactor by vacuum distillation.

The products from two such reactions were combined and passed several times through a tower of silver(I) fluoride (200 g), maintained at 125°. After several passes, infrared spectroscopy indicated that bromo azines were still present. Nevertheless, the mixture was fractionated through −30, −111, and −196° receivers and each fraction was separated into its components by vapor phase chromatography. The −111° trap afforded 4.4 g (33%) of pure tetrafluoro-2,3-diaza-1,3-butadiene[1] (calcd mol wt, 128; found, 128) having the following mass spectral pattern: 14 (2.0) N, 26 (2.6) CN, 28 (3.3) N_2, 31 (48.4) CF, 45 (5.5) CNF, 50 (100.0) CF_2, 64 (7.8) CNF_2, 69 (3.3) CF_3, 78 (2.0) CN_2F_2, 109 (9.9) $C_2N_2F_3$, and 128 (50.8) $C_2N_2F_4$.

The following compounds were also separated from the mixture by vapor phase chromatography, using a 2 m × 0.5 in. Kel-F 8126 column and condensing products from the effluent gas at −196° in a trap filled with glass beads, and characterized by spectral means (see Table I for infrared and F^{19} nmr spectra) and elemental analysis.

$CF_2{=}N—N{=}CFBr$ showed the following data.

Anal. Calcd for $C_2N_2F_3Br$: C, 12.7; F, 30.3; Br, 42.7; mol wt, 188. Found: C, 12.3; F, 30.0; Br, 42.3; mol wt, 189.

The boiling point was found to be 68° (isoteniscope).

The mass spectral pattern showed 14 (1.9) N, 26 (3.3) CN, 28 (2.8) N_2, 31 (82.3) CF, 45 (6.4) CNF, 50 (31.6) CF_2, 64 (16.1) CNF_2, 69 (6.6) CF_3, 79 (20.1) Br, 90 (2.9) $C_2N_2F_2$, 109 (100) $C_2N_2F_3$, 110 (14.5) CFBr, 124 (2.7) CNFBr, and 188 (22.6) $C_2N_2F_3Br$.

$CF_2{=}N—N{=}CFCl$ showed the following data.

Anal. Calcd for $C_2N_2F_3Cl$: mol wt, 144. Found: mol wt, 146.

The mass spectral pattern showed 14 (3.2) N, 26 (5.6) CN, 28 (5.9) N_2, 31 (100) CF, 35 (15.6) Cl, 45 (10.3) CNF, 47 (6.3) CCl, 50 (42.0) CF_2, 61 (2.5) CNCl, 64 (14.7) CNF_2, 66 (72.8) CFCl, 69 (7.9) CF_3, 80 (7.7) CNFCl, 90 (4.1) $C_2N_2F_2$, 109 (53.9) $C_2N_2F_3$, 125 (3.5) $C_2N_2F_2Cl$, and 144 (52.8) $C_2N_2F_3Cl$.

TABLE I

F^{19} NMR AND INFRARED SPECTRA

Formula	Group	F^{19} nmr, ϕ^{*a}	Infrared, μ
$CF_2{=}N—N{=}CF_2$	$CF_2{=}N$	74.0^b 52.1	5.75
$CF_2{=}N—N{=}CFBr$	$CF_2{=}N$	72.7^c 49.1^d	5.70
	$CFBr{=}N$	25.1^e	5.99
$CF_2{=}N—N{=}CFCl$	$CF_2{=}N$	72.8^f 49.7^g	5.72
	$CFCl{=}N$	36.9^h	5.97
$CFBr{=}N—N{=}CBr_2$	$CFBr{=}N$	24.4	6.14
	$CBr_2{=}N$		6.37
$CBr_2{=}N—N{=}CBr_2$	$CBr_2{=}N$		6.37
$CF_3—N{=}N—CF_3$	CF_3	79.7^i	
$CF_3—N{=}N—CF_2Br$	CF_3	74.5	
	CF_2Br	49.1	
$CF_3—N{=}N—CF_2Cl$	CF_3	74.7	
	CF_2Cl	54.5	
$CF_3—N{=}N—CFBrCl$	CF_3	73.8	
	CFBrCl	44.6	
$CF_3NHNHCF_3$	CF_3	67.6^j	

[a] F^{19} nmr spectra were obtained on a Varian V-4300-2 instrument at 40.0 Mc, utilizing an internal standard of $CFCl_3$ for the determination of chemical shifts. See O. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959). Infrared spectra were run on a Perkin-Elmer Model 21 double-beam instrument. [b] AB-type pattern analysis, J_{AB} = 65 cps. [c] Double (J = 74.4 cps) doublet (J = 33.5 cps). [d] Doublet (J = 74.4 cps). [e] Doublet (J = 33.5 cps). [f] Double (J = 73.0 cps) doublet (J = 32.7 cps). [g] Doublet (J = 73.0 cps). [h] Doublet (J = 32.7 cps). [i] W. J. Chambers, C. W. Tullock, and D. D. Coffman, *J. Am. Chem. Soc.*, **84**, 2337 (1962). [j] Doublet (J = 6.6 cps).

1,2-Bis(trifluoromethyl)hydrazine.—A mixture of tetrafluoro-2,3-diaza-1,3-butadiene and excess anhydrous HF was heated at 100° overnight in a stainless steel autoclave. The crude product mixture was separated by vapor phase chromatography on a 2 m × 0.5 in. Kel-F tetramer column operating at 25°. 1,2-Bis(trifluoromethyl)hydrazine (relative retention time 520, $CFCl_3$ standard) was identified by infrared, F^{19} nmr, and mass spectroscopy (mol wt 262 by effusion, 292 by gas density; $C_2N_2H_2F_6$ requires 168); mass spectral pattern showed 19 (2.3) F, 20 (12.4) HF, 27 (3.7) CNH, 28 (3.2) N_2, 29 (40.4) N_2H, 30 (7.2) N_2H_2, 31 (26.8) CF, 32 (3.0) CHF, 43 (6.7) C_2F?, 45 (9.8) CNF, 46 (17.7) CNHF, 47 (6.1) CNH_2F, 50 (29.6) CF_2, 51 (6.4) CHF_2, 64 (6.2) CNF_2, 65 (10.5) $CNHF_2$, 66 (2.1) CNH_2F_2, 69 (100) CF_3, 79 (3.2) CN_2HF_2, 97 (4.4) CN_2F_3, 99 (23.6) $CN_2H_2F_3$, 109 (31.1) $C_2N_2F_3$, 128 (15.8) $C_2N_2F_4$, 129 (55.4) $C_2N_2HF_4$, 148 (13.2) $C_2N_2HF_5$, 149 (3.8) $C_2N_2H_2F_5$, and 168 (20.0) $C_2N_2H_2F_6$.

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