THE CHEMISTRY OF BIS(TRIFLUOROMETHYL)-AMINO COMPOUNDS

H. G. Ang and Y. C. Syn*

Department of Chemistry, University of Singapore, Singapore

I. Introduction

This chapter is intended to bring together the chemistry of compounds which bear the general formula $(CF_3)_2NR$, where R represents an atom or a group. The development of this area of chemistry in recent years has

---

* Mr. Syn provided assistance with the literature.

been stimulated by the discovery of two distinct types of compounds, namely, *N*-chloro- or *N*-bromobis(trifluoromethyl)amine and bis(trifluoromethyl)nitroxyl. The reactivity of the former is facilitated by the ready fission of the halogen–nitrogen bonds under both free radical and ionic conditions. Although bis(trifluoromethyl)nitroxyl is stable at ambient temperatures to both dimerization and decomposition, it is reactive toward a vast number of organic and inorganic compounds. These properties are different from those of a large number of nonfluorinated organic nitroxyls where chemical reactivity does not reside at the oxygen atom. Articles which amply illustrate this fact have appeared in two excellent books: one by Forrester, Hay, and Thomson (*1*) and the other by Rozantsev (*2*), as well as in other reviews (*3*, *4*). Thus, this chapter not only assesses the present status of the chemistry of $(CF_3)_2NR$ compounds, but also serves as a pointer to future developments.

Nitroxide and nitroxyl have been adopted as a group nomenclature for R_2NO free radicals, where R is an organic group. In this Chapter, bis(trifluoromethyl)nitroxyl is the nomenclature adopted for the parent free radical. The term bis(trifluoromethyl)nitroxy is used to describe the presence of $(CF_3)_2NO$ group in any molecular compound; and bis(trifluoromethyl)nitroxide is used either for "salts" of inorganic compounds [e.g., $(CF_3)_2NO^-Na^+$ is named sodium bis(trifluoromethyl)-nitroxide] or whenever this term appears at the end in the naming of any compound {e.g., $[NSON(CF_3)_2]_4$ is named tetrathiazyl tetra-[bis(trifluoromethyl)nitroxide]}. This approach is more in keeping with the IUPAC recommendations (*5*).

II. Mercurials Containing the Hg–N(CF₃)₂ Bond

A. PREPARATIONS

Young and co-workers were the first to synthesize di[bis(trifluoromethyl)amino]mercury in good yield by reacting mercuric fluoride with perfluoro-2-azapropene at an elevated temperature (*6*). Later, Emeléus

$$2CF_3N{=}CF_2 + HgF_2 \rightarrow Hg[N(CF_3)_2]_2$$

and Hurst showed that the mercurial could be conveniently obtained by the fluorination of cyanogen chloride with mercuric fluoride (*7*). (Table I). Although the yield is low, the availability of the starting

TABLE I

PREPARATION OF BIS(TRIFLUOROMETHYL)AMINO-SUBSTITUTED MERCURIALS

Compounds	Reagents	Conditions	Yield (%)	Ref.
$[(CF_3)_2N]_2Hg$	$CNCl + HgF_2$	320°/flow method	25	*7*
	$CF_3N:CF_2 + HgF_2$	100°/15 hr	79	*6*
$[(CF_3)_2NNCF_3]_2Hg$	$(CF_3)_2NN:CF_2 + HgF_2$	140°/6 hr	97	*8*
$(CF_3)_2NHgCH_3$	$(CF_3)_2NBr + (CH_3)_2Hg$	Room temp./rapid	70	*9*
$(CF_3)_2NHgSCF_3$	$(CF_3)_2NCl + (CF_3S)_2Hg$	Room temp./36 hr	50	*9*

material makes this method more convenient for small-scale preparations. The other mercurial, $[(CF_3)_2NNCF_3]_2Hg$, can also be formed in like manner from $(CF_3)_2NN:CCl_2$ (*8*). Mixed mercurials are produced by group exchange reactions as shown below (*9*).

$$(CF_3)_2NX + (CH_3)_2Hg \rightarrow (CF_3)_2NHgCH_3 + CH_3X$$

$$(CF_3)_2NCl + 2(CF_3S)_2Hg \rightarrow (CF_3)_2NHgSCF_3 + CF_3SHgCl + CF_3SSCF_3$$

$$X = Cl, Br$$

$(CF_3)_2NHgCH_3$ is detected in the interaction of a mixture of dimethylmercury with di[bis(trifluoromethyl)amino]mercury by the ^{19}F nuclear magnetic resonance spectrum.

B. PHYSICAL PROPERTIES

Apart from the mercurials, $(CF_3)_2NHgR$ ($R = CH_3, SCF_3$), which are unstable at room temperature, the other symmetrical mercurials are stable if stored in sealed evacuated ampoules. All the mercurials are mononuclear and soluble in fluorocarbon and hydrocarbon solvents. They are extremely sensitive to moisture, hydrolyzing immediately with the formation of yellow mercuric oxide (Table II).

TABLE II

PHYSICAL DATA FOR BIS(TRIFLUOROMETHYL)AMINO-SUBSTITUTED MERCURIALS

Compounds	B.p. (°C)	M.p. (°C)	Ref.
$[(CF_3)_2N]_2Hg$	127	17.5	*6, 7*
$[(CF_3)_2NNCF_3]_2Hg$	—	29.5	*8*
$(CF_3)_2NHgCH_3$	Unstable	At room temp.	*9*
$(CF_3)_2NHgSCF_3$	Unstable	At room temp.	*9*

C. CHEMICAL PROPERTIES

1. *Introduction*

The N–Hg bonds in all the mercurials are susceptible to ready cleavage in the presence of halogens, sulfur, or suitable halides. Advantage is taken of this property either to furnish the *N*-halogenoamines, which are important precursors, or to prepare a number of derivatives containing the amino groups. The products from these reactions are given in Table III.

2. *Reactions with Acid Halides*

Although a few amides of the general formula $RCON(CF_3)_2$ have been obtained by electrochemical fluorination, the metathetical method involving the use of hydrocarbon as well as fluorocarbon acid halides gives improved yields and can be controlled to allow wide variation in the nature of R. The methyl derivative is not readily attacked by water, showing that compounds bearing both fluorinated and fluorine-containing groups on nitrogen tend to be hydrolytically stable as long as the nitrogen is tertiary and fluorine cannot be split off as HF from adjacent atoms (*10*).

With other halides of Group IIIB, IVB, or VB elements, di[bis(trifluoromethyl)amino]mercury undergoes reactions to give perfluoro-2-azapropene and the fluorinated derivatives:

$$2MX_n + nHg[N(CF_3)_2]_2 \rightarrow 2nCF_3N{=}CF_2 + nHgX_2 + 2MF_n$$

The production of perfluoro-2-azapropene seems to be a common feature in a large number of such reactions and certainly reflects the ease of intramolecular fluorination by the bis(trifluoromethyl)amino group.

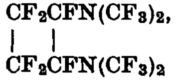
3. *Reactions with Sulfur Compounds*

The main products obtained from the interaction of di[bis(trifluoromethyl)amino]mercury with sulfur and substituted sulfenyl chlorides are shown in Table III. Both SO_2Cl_2 and CCl_3SCl fail to give derivatives containing the $(CF_3)_2N$ group (*11*). Instead, perfluoro-2-azapropene is formed in quantitative yield, indicating that the desired compounds could have undergone intramolecular fluorination.

With sulfur, two distinct types of reactions are observed. The first involves the thermal dissociation of the mercurial to HgF_2, $CF_3N{=}CF_2$, and $(CF_3)_2NCF{=}NCF_3$, while the other reaction affords HgS, $[(CF_3)_2N]_2S$,

TABLE III

Reactivity of Bis(trifluoromethyl)amino-Substituted Mercurials

Compound	Reagent	Conditions	Products (% yield)	Ref.
$[(CF_3)_2N]_2Hg$	Cl_2	Room temp.	$(CF_3)_2NCl$ (98)	*6, 9*
	Br_2	Room temp.	$(CF_3)_2NBr$ (96)	—
	I_2	Room temp./21 days	$(CF_3)_2NI$ (67)	*9*
	S_8	—	$CF_3N{:}CF_2$, $(CF_3)_2NCF{=}NCF_3$, $[(CF_3)_2N]_2S$, $[(CF_3)_2N]_2S_2$, $(CF_3)_2NSCl$ (50)	*12*
	SCl_2	—	$[(CF_3)_2N]_2S$, $(CF_3)_2NCl$, $CF_3N{:}CF_2$	*13*
	CF_3SCl	80°/4 days	$(CF_3)_2NSCF_3$	*11*
	CH_3SCl	Room temp./rapid	$(CF_3)_2NSCH_3$ (96)	—
	CCl_3SCl	80°/16 hr	$CF_3N{:}CF_2$ (95)	—
	SO_2Cl_2	—	$CF_3N{:}CF_2$ (95)	—
	CF_3COCl	—	$(CF_3)_2NCOCF_3$ (90)	*10*
	CH_3COCl	—	$(CF_3)_2NCOCH_3$ (62)	*10*
	$PhCOCl$	—	$(CF_3)_2NCOPh$ (95)	*10*
$[(CF_3)_2N]_2Hg$	Prolonged irradiation	—	$(CF_3)_2NN(CF_3)_2$ (53), $CF_3N{:}CF_2$ (15), $(CF_3)_2NF$ (13), $(CF_3)_2NN(CF_3)CF_2{\cdot}N(CF_3)_2$ (15)	*14*
	cyclo-C_4F_6	$h\nu$/31 days	$(CF_3)_2NN(CF_3)_2$ (47), $CF_3N{:}CF_2$ (13), $(CF_3)_2NF$ (6),  (25)	*14*
	170°/48 hr	—	$(CF_3)_2N{\cdot}CF{:}NCF_3$	*12*
$(CF_3)_2NHgCH_3$	NOCl	Room temp.	$(CF_3)_2NNO$ (62), CH_3HgCl	*9*
	Br_2	20°/rapid	$(CF_3)_2NBr$ (35), CH_3Br, $HgBr_2$	—
$(CF_3)_2NHgSCF_3$	NOCl	Room temp.	$(CF_3)_2NNO$, CF_3SSCF_3	*9*
	Cl_2	Room temp.	$(CF_3)_2NCl$ (40), $(CF_3)_2NSCl$ (40)	—
$[(CF_3)_2NNCF_3]_2Hg$	Br_2	20°/36 hr	$(CF_3)_2NN(CF_3)Br$ (15), $[(CF_3)_2NN(CF_3)]_2$ (8)	*8*
	Cl_2	20°/3 days	$[(CF_3)_2NN(CF_3)]_2$ (5)	—
	HCl	Room temp./rapid	$(CF_3)_2NN(CF_3)H$ (100)	—
	NOCl	Room temp./rapid	$(CF_3)_2NN(CF_3)NO$ (100)	—

and $(CF_3)_2NS_2N(CF_3)_2$ (*12*). The relationships are shown by the following equations:

$$\mathrm{Hg[N(CF_3)_2]_2} \begin{cases} \rightarrow \mathrm{HgF_2 + CF_3N{=}CF_2 + (CF_3)_2NCF{=}NCF_3} \\ \\ \rightarrow \mathrm{HgS + [(CF_3)_2N]_2S + [(CF_3)_2N]_2S_2} \end{cases}$$

The mercury derivative when heated alone above 135° dissociates into HgF_2 and $CF_3N{=}CF_2$, but reforms quantitatively on cooling. In the presence of sulfur and mercuric sulfide at 165°, dimerization of the $CF_3N{=}CF_2$ takes place, apparently interfering with the recombination between HgF_2 and $CF_3N{=}CF_2$. However, dimerization does not occur in the absence of a mercuric salt.

D. PHOTOLYSIS

Prolonged irradiation of the mercurial alone gives unchanged material (36%), tetrakis(trifluoromethyl)hydrazine (53%), perfluoro-2-azapropene (15%), perfluorodimethylamine (13%), and $(CF_3)_2NN(CF_3)CF_2N(CF_3)_2$ (15%). These products could have arisen by two distinct primary decomposition modes of the mercurials (*14*), i.e.,

$$\mathrm{[(CF_3)_2N]_2Hg} \begin{cases} \rightarrow \mathrm{2(CF_3)_2N\cdot + Hg} \\ \\ \rightarrow \mathrm{2CF_3N{=}CF_2 + HgF_2} \end{cases}$$

The formation of the $(CF_3)_2N$ radical predominates, as shown by the production of $(CF_3)_2NH$ (97%) when the mercurial is irradiated in pentane. The products $CF_3N{=}CF_2$ and $(CF_3)_2NF$ must then be formed by secondary reactions of the $(CF_3)_2N$ radicals, as shown below.

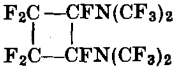
$$\mathrm{2(CF_3)_2N\cdot} \longrightarrow \mathrm{(CF_3)_2NF + CF_3N{=}CF_2}$$

$$\mathrm{2(CF_3)_2N\cdot + 2Hg} \longrightarrow \mathrm{2CF_3N{=}CF_2 + 2Hg_2F_2\ (or\ HgF_2)}$$

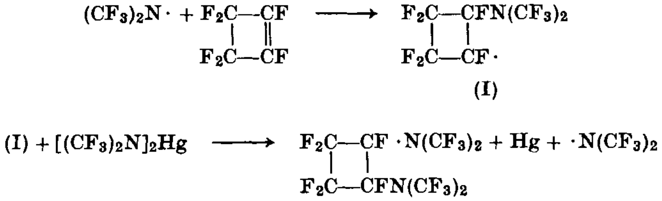
$$\mathrm{(CF_3)_2N\cdot} \xrightarrow[\text{or } HgF_2]{Hg_2F_2} \mathrm{(CF_3)_2NF}$$

The hydrazine, $(CF_3)_2NN(CF_3)_2$, is formed either by dimerization of $(CF_3)_2N$ radicals or by reaction of $(CF_3)_2N$ radicals with undissociated mercurial. The compound $(CF_3)_2NN(CF_3)CF_2N(CF_3)_2$ arises from $(CF_3)_2N$ radical addition to perfluoro-2-azapropene to give the radicals $(CF_3)_2NN(CF_3)\dot{C}F_2$ or $(CF_3)_2NCF_2\dot{N}CF_3$, followed by reaction of these with $(CF_3)_2N$ radicals or with $[(CF_3)_2N]_2Hg$.

Photolysis of a 1:1 molar mixture of the mercurial and perfluorocyclobutene (31 days) gives $(CF_3)_2NN(CF_3)_2$ (47%), $CF_3N{=}CF_2$ (13%), $(CF_3)_2NF$ (6%) and



The low yield of the last compound indicates that reaction of the $(CF_3)_2N$ radicals with the butene is slow and the secondary reactions leading to the other products have time to occur, or that the initial addition is reversible, or that the abstraction reaction (below) is not favored.



III. *N*-Halogenobis(trifluoromethyl)amines and Derivatives

A. METHODS OF SYNTHESIS

Di[bis(trifluoromethyl)amino]mercury(I) provides a convenient route to the synthesis of *N*-iodo, *N*-bromo-, and *N*-chlorobis(trifluoromethyl)-amine. Although the *N*-iodamine is formed only under mild conditions in diffuse daylight over an extended period, the *N*-chloro and *N*-bromo

$$[(CF)_2N]_2Hg + 2X_2 \rightarrow 2(CF_3)_2NX + HgX_2$$

analogs are obtained readily in high yields. The *N*-chloramine was first prepared by reacting phosphorus pentachloride with bis(trifluoromethyl)hydroxylamine (*15*).

$$(CF_3)_2NOH + PCl_5 \rightarrow (CF_3)_2NCl + POCl_3 + HCl$$

N-Fluorobis(trifluoromethyl)amine has not been prepared by reacting the mercurial(I) with fluorine. Instead it can be formed in fairly good yield by either fluorinating trimethylamine with cobaltic fluoride or by subjecting $HCONMe_2$ to electrochemical fluorination. Table IV summarizes other reactions that are now known to give *N*-fluorobis(trifluoromethyl)amine.

Interesting gradations in some physical properties of the *N*-halogenobis(trifluoromethyl)amines are shown in Table V.

TABLE IV

PRODUCTION OF *N*-FLUOROBIS(TRIFLUOROMETHYL)AMINE

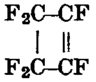
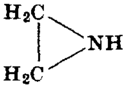
Starting materials	Conditions	Yield (%)	Ref.
$Me_3N/N_2 + CoF_2$	130°–220°	40–70	*16*
$[(CF_3)_2N]_2Hg$	$h\nu$	13	*14*
$[(CF_3)_2N]_2Hg$ + 	$h\nu$/30 days	6	*14*
$CF_3N{=}CF_2 + AgF_2$	100°	45	*17*
$CF_3N{=}CF_2 + CoF_3$	250°/20 hr	—	*17*
$(CF_3)_2NCF{=}NCF_3$	100°/24 hr	—	*17*
$(CF_3)_2NH + AgF_2$	50°/15 hr	—	*18*
$(CF_3)_2NCOF + AgF_2$	100°/18 hr	60	*18*
$HCONMe_2$	Electrochemical fluorination	38	*19*
HCONHMe	Electrochemical fluorination	11	*19*
$MeNH_2$, Me_2NH, Me_3N	Electrochemical fluorination	As a mixture with $CF_3CF_2NF_2$, 12–22%	*20*
	Electrochemical fluorination	18	*20*
$PhNMe_2 + CoF_3$	300°/24 hr	—	*21*
$NMe_3 + CoF_3$	250°	—	*22*
$HCONMe_2/H_2 + F_2$	115°–275°	12–36	*23*
$CF_3CN + NF_3 + CsF$	520°	—	*24*
$Hg(CN)_2 + KF{\cdot}2HF$	Electrolysis at 80°	—	*25*
HCN, $(CN)_2$, $MeNH_2$, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$	Jet fluorination	—	*24, 26*

TABLE V

COMPARISON OF PHYSICAL PROPERTIES OF *N*-SUBSTITUTED BIS(TRIFLUOROMETHYL)AMINES

Compound	B.p.(°C)	ν_{max} (mμ), [ϵ]	ν_{max} (cm^{-1})	ϕ(ppm)	Ref.
$(CF_3)_2NF$	−37	—	1320, 1275, 1230, 975	71.3	*9, 17*
$(CF_3)_2NCl$	−9	246[116]	1315, 1260, 1210, 968	64.1	*6, 9*
$(CF_3)_2NBr$	22	293[120]	1310, 1250, 1200, 962	60.7	*6, 9*
$(CF_3)_2NI$	57	352[124]	1305, 1245, 1185, 960	55.8	*9, 27*
$(CF_3)_2NH$	−6.7 to −6	—	—	—	*28, 29*
$(CF_3)_2NNO$	−4 to −3	—	—	—	*12*
$(CF_3)_2NNO_2$	16.4	—	—	—	*30*
$(CF_3)_2NCN$	21	—	—	—	—

B. PHOTOLYSIS

Progress in the chemistry of bis(trifluoromethyl)amino radical is facilitated by the ease of rupture of the nitrogen–halogen bond, which is certainly much less when the halogen is fluorine. *N*-Iodobis(trifluoromethyl)amine is unstable since, on standing, tetrakis(trifluoromethyl)hydrazine is formed and iodine is liberated. The *N*-bromamine undergoes similar decomposition only on photolysis. Its mode of decomposition can be shown as follows:

$$\begin{aligned} (CF_3)_2NX &\rightarrow (CF_3)_2N\cdot + X \\ 2(CF_3)_2N\cdot &\rightarrow (CF_3)_2N{-}N(CF_3)_2 \\ 2X\cdot &\rightarrow X_2 \end{aligned}$$

Many reactions which are now known to yield tetrakis(trifluoromethyl)hydrazine are shown in Table VI.

TABLE VI

FORMATION OF TETRAKIS(TRIFLUOROMETHYL)HYDRAZINE

Starting Reagents	Conditions	Yield (%)	Ref.
$CF_3N{:}CF_2/AgF_2$	100°	—	*17*
$CF_3N{:}CF_2/CoF_3$	250°/20 hr	—	*17*
$(CF_3)_2NH/AgF_2$	50°/15 hr	—	*18*
$(CF_3)_2NCOF/AgF_2$	100°/18 hr	13	*18*
$(CF_3)_2NBr$	Irradiation with Hg lamp for 5 days	—	*31*
$(CF_3)_2NBr$	100°/96 hr/dark	40	*32*
$(CF_3)_2NBr/CF_3CF{:}CFCF_3$	100°/48 hr/dark, followed by $h\nu$/168 hr	91	*32*
$(CF_3)_2NOCF_3$	$h\nu$/21 days	80	*33*
$(CF_3)_2NOCF_3/CF_3CF{:}CFCF_3$	$h\nu$/30 days	43	*14*
$(CF_3)_2NOCF_3/CF_2{:}NCF_3$	$h\nu$/35 days	55	*14*
$[(CF_3)_2N]_2Hg$	$h\nu$/30 days	53	*14*
$[(CF_3)_2N]_2Hg$	$h\nu$/31 days	47	*14*
$CF_3N{=}NCF_3$	$h\nu$/5 cm pressure	—	*34, 35*
Me_2NCOH	Electrochemical fluorination	35	*19*
	Fluorination process	14	*18, 20*

Young and Dresdner have reported that the N–N bond in tetrakis(trifluoromethyl)hydrazine is extremely stable to thermal rupture compared to the bonds in a number of substituted hydrazine (*36*). Thus, pyrolysis at 550°C over a period of 5 hr gave an 84% recovery of the hydrazine. The stability possessed by this compound is indeed remarkable since the bulky trifluoromethyl groups must cause substantial repulsions. The N–N bond appears to be unusually strengthened and shortened despite the strong nonbonded F ··· F repulsions across it. The crowding of the trifluoromethyl groups is found to flatten the two N pyramids almost to planarity and to set the dihedral angle between opposite bis(trifluoromethyl)amino groups at a value of 90°. A molecular orbital description suggests that the shorter N–N bond may be understood in terms of the enhancement of π bonding ensuing from the nearly D_{2d} symmetry imposed by steric forces (*37*) (Fig. 1).

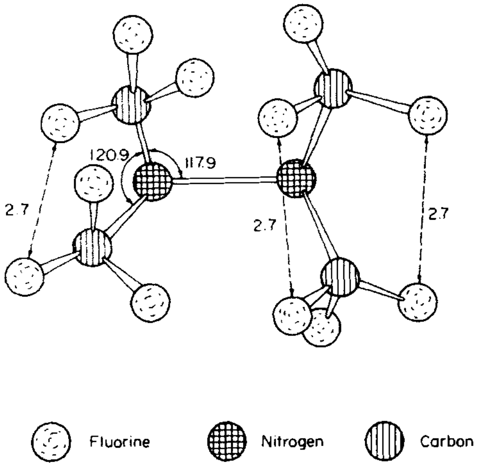


FIG. 1. Structural representation of $N_2(CF_3)_4$ (*37*).

C. REACTIONS

1. *Formation of Boron Compounds*

Bis(trifluoromethyl)amine produces no reaction with boron trifluoride (*6*), but the reactions with boron trichloride and tribromide proceed smoothly at room temperature to afford white crystalline amino derivatives, $(CF_3)_2NBX_2$ (X = Cl, Br), according to the following equations (*38*).

$$(CF_3)_2NH + BX_3 \rightarrow (CF_3)_2NH\cdot BX_3$$
$$(CF_3)_2NHBX_3 \rightarrow (CF_3)_2NBX_2 + HX$$
$$X = Cl, Br$$

The reaction with boron trichloride at 110° gives only volatile products, namely, boron trifluoride, hydrogen chloride, and 1,1-dichloro-3,3,3-

trifluoro-2-azapropene. Both bis(trifluoromethyl)aminoboron dichloride and the dibromide are white crystalline solids which undergo rapid decomposition at room temperature.

$$(CF_3)_2NBX_2 \rightarrow CF_3N{=}CX_2 + BF_3$$

2. *Reactions with Silicon Compounds*

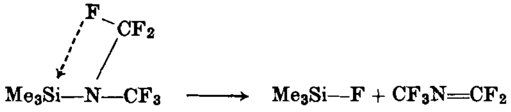
Di[bis(trifluoromethyl)amino]mercury reacts with trimethylchlorosilane at room temperature to afford trimethylfluorosilane, perfluoro-2-azapropene, and mercury chloride (*39*).

$$[(CF_3)_2N]_2Hg + 2Me_3SiCl \rightarrow 2Me_3SiF + 2CF_3N{=}CF_2 + HgCl_2$$

The interaction of *N*-chlorobis(trifluoromethyl)amine with di(trimethylsilyl)mercury proceeds vigorously at room temperature to give perfluoro-2-azapropene, trimethylfluorosilane, trimethylchlorosilane, and mercury. At −126°, the reaction gives bis(trifluoromethyl)aminotrimethylsilane, together with a substantial amount of other decomposition products.

$$2(CF_3)_2NCl + 2(Me_3Si)_2Hg \rightarrow (CF_3)_2NSiMe_3 + 2Me_3SiCl + Me_3SiF + CF_3N{=}CF_2 + 2Hg$$

The silane is unstable at room temperature, and decomposition is usually complete within 24 hours, involving probably β-elimination, a process



$$Me_3Si{-}N(CF_3){-}CF_2{-}F \longrightarrow Me_3Si{-}F + CF_3N{=}CF_2$$

rather common for silicon compounds containing either halogen or hydrogen in a position beta to silicon.

The unstable nature of the silane is of interest in that it indicates the difficulty that may be associated with the preparation of similar compounds of the lower members in the series of elements with the group.

3. *Reactions with Compounds of Group VB Elements*

a. Compounds of Nitrogen. N-Bromo- and *N*-chlorobis(trifluoromthyel)amine react with a number of unsaturated nitrogen compounds. With cyanogen chloride, the *N*-chloramine gives 1:1 addition under ultraviolet irradiation (*8*).

$$(CF_3)_2NCl + CNCl \xrightarrow{h\nu} (CF_3)_2NN{:}CCl_2$$

Nitroso derivatives are formed with both nitric oxide and nitrogen dioxide (*31*).

$$(CF_3)_2NBr + NO_2 \xrightarrow{80^\circ} (CF_3)_2NONO$$

$$(CF_3)_2NBr + NO \xrightarrow[\text{temp.}]{\text{room}} (CF_3)_2NNO$$

b. Compounds of Phosphorus, Arsenic, and Antimony. Earlier attempts to attach $(CF_3)_2N$ group(s) to phosphorus by reacting either PCl_3 or $(CF_3)_2PI$ with $[(CF_3)_2N]_2Hg$ have produced only the fluorinated derivatives, namely, PF_3 and $(CF_3)_2PF$. Other attempts involving the reactions of red phosphorus with the mercurial have been equally unsuccessful (*40*). However, when tris(trifluoromethyl)phosphine is allowed to react with either *N*-chloro- or *N*-bromobis(trifluoromethyl)amine in a 1:1 molar ratio at elevated temperatures, bis(trifluoromethyl)aminobis(trifluoromethyl)phosphine and CF_3X (X = Cl or Br) are produced quantitatively. Further stepwise substitution reactions give both the di- and trisubstituted derivatives, $[(CF_3)_2N]_nP(CF_3)_{3-n}$ ($n = 2, 3$). The overall reactions are shown by the equations (*41, 42*).

$$\begin{tikzcd}
(CF_3)_2NX + (CF_3)_3P \arrow[r] & (CF_3)_2NP(CF_3)_2 + CF_3X \arrow[d, "(CF_3)_2NBr"] \\
& {[(CF_3)_2N]_2PCF_3 + CF_3Br} \arrow[d, "(CF_3)_2NBr"] \\
& {[(CF_3)_2N]_3P + CF_3Br}
\end{tikzcd}$$

An extension of the exchange reactions to tris(trifluoromethyl)arsine gives only the mono- and disubstituted derivatives,

$$[(CF_3)_2N]_nAs(CF_3)_{3-n} \quad (n = 1, 2)$$

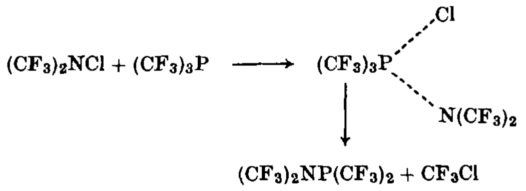
However, the reaction of tris(trifluoromethyl)stibine and *N*-chlorobis(trifluoromethyl)amine even at −20° proceeds differently. Only decomposition occurs, as shown by the equation:

$$3(CF_3)_2NCl + (CF_3)_3Sb \rightarrow 3CF_3N{=}CF_2 + 3CF_3Cl + SbF_3$$

These findings can be best explained by suggesting that an unstable intermediate, $(CF_3)_2NSb(CF_3)_2$, which is initially formed, undergoes intramolecular fluorination to give $CF_3N{=}CF_2$ and $(CF_3)_2SbF$. In view of the fact that the rate of disproportionation for $(CF_3)_2SbX$ (X = Cl, Br, I) decreases in the order $Cl > Br > I$, it is therefore expected that $(CF_3)_2SbF$ would also undergo successive disproportionation to give antimony trifluoride. The complete reactions can be represented as

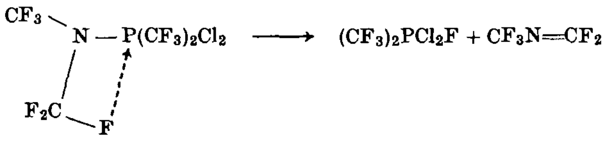
$$\begin{aligned}
(CF_3)_3Sb + (CF_3)_2NCl &\rightarrow (CF_3)_2NSb(CF_3)_2 + CF_3Cl \\
(CF_3)_2SbN(CF_3)_2 &\rightarrow (CF_3)_2SbF + CF_3N{=}CF_2 \\
2(CF_3)_2SbF &\rightarrow (CF_3)_3Sb + CF_3SbF_2 \\
2CF_3SbF_2 &\rightarrow (CF_3)_2SbF + SbF_3
\end{aligned}$$

It seems reasonable to suppose that the nonreversible reactions between, for example, *N*-chlorobis(trifluoromethyl)amine and tris-(trifluoromethyl)phosphine, involve the formation of the phosphorus(V) derivative which decomposes to give $(CF_3)_2NP(CF_3)_2$ and CF_3Cl.



The preferential elimination of CF_3Cl as against $(CF_3)_2NCl$ may be explained on energetic ground.

Reaction of bis(trifluoromethyl)aminobis(trifluoromethyl)phosphine with chlorine at room temperature forms the addition product, $(CF_3)_2NP(CF_3)_2Cl_2$, which decomposes on standing to give perfluoro-2-azapropene and bis(trifluoromethyl)dichlorofluorophosphorane. Complete decomposition occurs on heating the dichloride at 60° for a day.



In this respect, the adduct differs from that of $(CF_3)_3PCl_2$, which can be distilled at 70°/370 mm without decomposition, but may explode violently on nearing the boiling point.

The arsenical, $(CF_3)_2NAs(CF_3)_2$, behaves quite differently with chlorine No pentavalent arsenic dichloride is obtained. With two moles of chlorine, the products isolated are CF_3Cl, $(CF_3)_2NCl$, and

$(CF_3)_2NAsCl_2$; an excess of chlorine gives only CF_3Cl, $(CF_3)_2NCl$, and $AsCl_3$ *(43)*.

$$(CF_3)_2NAs(CF_3)_2 \begin{cases} \xrightarrow{2Cl_2} (CF_3)_2NAsCl_2 + 2CF_3Cl \\ \xrightarrow{3Cl_2} AsCl_3 + 2CF_3Cl + (CF_3)_2NCl \end{cases}$$

The entry to the field of metal carbonyls is achieved through the synthesis of $(CF_3)_2NP(CF_3)_2Ni(CO)_3$ *(44)*. This compound, a colorless liquid which decomposes on fractionation, is prepared by the reaction of $(CF_3)_2NP(CF_3)_2$ with $Ni(CO)_4$ in ether. Attempts to carry out further substitution reactions have been unsuccessful.

Emeléus and Onak have discovered that the reaction between *N*-chlorobis(trifluoromethyl)amine and PF_2X ($X = F$, Cl) gives addition products *(45)*. In this reaction some perfluoro-2-azapropene is also produced, indicating that intramolecular fluorination, a feature common to many compounds containing bis(trifluoromethyl)amino group(s), has occurred. It has also been found that *N*-chlorobis(trifluoromethyl)amine reacts with bis(trifluoromethyl)phosphorus chloride and fluoride in the same manner at temperatures not greater than 20° *(46)*. While the chloride gives two phosphoranes, namely, bis(trifluoromethyl)amino-bis(trifluoromethyl)dichlorophosphorane and bis(trifluoromethyl)dichlorofluorophosphorane, the fluoride yields bis(trifluoromethyl)amino-bis(trifluoromethyl)chlorofluorophosphorane and bis(trifluoromethyl)-chlorodifluorophosphorane. Perfluoro-2-azapropene is also one of the products in both reactions. The overall reactions may be considered to proceed as follows.

$$(CF_3)_2NCl + PF_2X \rightarrow (CF_3)_2NPF_2ClX$$

$$(CF_3)_2PX + (CF_3)_2NCl \rightarrow (CF_3)_2NP(CF_3)_2XCl$$

$$(CF_3)_2NP(CF_3)_2XCl \rightarrow (CF_3)_2PXFCl + CF_3N{=}CF_2$$

$$X = F, Cl$$

The interactions with trifluoromethylphosphorus dichloride and difluoride follow a similar course. Apart from perfluoro-2-azapropene produced in these reactions, the dichloride gives bis(trifluoromethyl)-aminotrifluoromethyltrichlorophosphorane, which undergoes decomposition at room temperature to yield trifluoromethyltrichlorofluorophosphorane and perfluoro-2-azapropene. The reaction with trifluoromethylphosphorus difluoride gives the expected products, namely, bis(trifluoromethyl)aminotrifluoromethylchlorodifluorophosphorane and trifluoromethylchlorotrifluorophosphorane.

Bis(trifluoromethyl)phosphorus iodide reacts somewhat differently even at −126° to afford bis(trifluoromethyl)fluorophosphine, perfluoro-2-azapropene, and a dark brown solid which is presumably iodine monofluoride. In addition, bis(trifluoromethyl)chlorodifluorophosphorane is also formed.

4. Reactions with Compounds of Group VIB Elements

Tullock claims that the reaction of *N*-chlorobis(trifluoromethyl)-amine with sulfur heated to 350° in a pressure vessel gives $(CF_3)_2NSCl$ and $[(CF_3)_2N]_2S$ (*47*). Irradiation of a mixture of *N*-chlorobis(trifluoromethyl)amine and sulfur chloropentafluoride gives bis(trifluoromethyl)-aminopentafluorosulfur (*48*), whereas with sulfur tetrafluoride, two bis(trifluoromethyl)amino derivatives of sulfur are formed, namely, $(CF_3)_2NSF_5$ and $(CF_3)_2NSCl$, although in low yield. $(CF_3)_2NSCl$ has also been prepared from *N*-chlorobis(trifluoromethyl)amine by either heating it with sulfur (*47*) or on prolonged irradiation with sulfuryl dichloride (*13*).

N-Chloro-, *N*-bromo-, and *N*-iodobis(trifluoromethyl)amines react with selenium at room temperature. The chlor- and bromamines give products which could be explained by the equations,

$$(CF_3)_2NX + Se \rightarrow (CF_3)_2NSeX$$
$$2(CF_3)_2NX + 3Se \rightarrow [(CF_3)_2N]_2Se + Se_2X_2$$

and iodine is liberated in the reaction with the *N*-iodamine,

$$2(CF_3)_2NI + Se \rightarrow [(CF_3)_2N]_2Se + I_2$$

No derivatives containing the Se–I bond are known (*49a*).

5. Addition to Alkenes

Addition of *N*-halogenobis(trifluoromethyl)amine, $(CF_3)_2NX$ (where $X = Cl$, Br and I), to olefins has been extensively investigated. In most cases, 1:1 adducts are produced, as illustrated by the equation (*27, 31, 32, 49*),

$$(CF_3)_2NX + CH_2{=}CH_2 \rightarrow (CF_3)_2NCH_2{\cdot}CH_2X$$
$$X = Br, I$$

With unsymmetrical olefins, mixtures of isomeric products are obtained. For example,

$$(CF_3)_2NX + RCH{=}CH_2 \rightarrow (CF_3)_2NCHRCH_2X + (CF_3)_2NCH_2CHRX$$

Haszeldine and co-workers have suggested that both free radical and ionic mechanisms are operative. As to which is the overriding one depends to a great extent on the conditions under which the experiments are conducted. Thus, in general, photolyzing and heating are considered to favor chain reactions, whereas reactions carried out at low temperatures in the dark are considered to involve ionic intermediates.

Table VII summarizes the isomer ratios obtained from the reactions of *N*-halogenoamines with substituted olefins under various conditions. Thus, under ultraviolet light the *N*-chloramine reacts with trifluoroethylene to give 1:1 adducts of 2-chloro-1,2,2-trifluorobis(trifluoromethyl)ethylamine(IV) and 2-chloro-1,1,2-trifluorobis(trifluoromethyl)-

TABLE VII

REACTIONS OF *N*-HALOGENOBIS(TRIFLUOROMETHYL)AMINE WITH ALKENES

Reactants	Conditions	Products (% yield)	Ref.
$CH_3CH{:}CH_2/(CF_3)_2NCl$	−24°/dark/3 days	$(CF_3)_2NCH(CH_3)CH_2Cl$ (60) $(CF_3)_2NCH_2CH(CH_3)Cl$	*50*
$CH_2{:}CHF/(CF_3)_2NCl$	$h\nu$/30 min	1. $(CF_3)_2NCH_2CHFCl$ (95), 2. $(CF_3)_2NCHF{\cdot}CH_2Cl$ (5)	*50*
	25°/dark/10 days	1. (93), 2. (7)	*50*
$CH_2{:}CHF/(CF_3)_2NBr$	Room temp./dark/ 12 weeks	$(CF_3)_2NCH_2{\cdot}CHFBr$	*32*
$CH_2{:}CHF/(CF_3)_2NI$	$h\nu$/1 hr	3. $(CF_3)_2NCH_2{\cdot}CHFI$ (93), 4. $(CF_3)_2NCHFCH_2I$ (7), and traces of $(CF_3)_2NH$ and $CF_3N{:}CF_2$	*50*
	Gas phase/daylight/1 hr	3. (65), 4. (35)	*50*
	−24°/dark/24 hr	3. (2), 4. (98), and small amounts of $(CF_3)_2NH$, $CF_3N{:}CF_2$, and CHF_3CH_2I	
$CH_2{:}CF_2/(CF_3)_2NBr$	25°/dark/½ hr	5. $(CF_3)_2NCH_2CF_2Br$	*32*
	100°/dark/24 hr	5.	
$CF_3CF{:}CF_2/(CF_3)_2NCl$	165°/7 days	$(CF_3)_2NCF_2CFClCF_3$ (96), $(CF_3)_2NCF(CF_3)CF_2Cl$ (4), and traces of $(CF_3)_2NH$ and $CF_3N{:}CF_2$	*51*
$CF_3CF{:}CF_2/(CF_3)_2NBr$	100°/dark/24 hr	$(CF_3)_2NCF_2CFBrCF_3$	*32*
$CF_3CF{:}CF_2/(CF_3)_2NI$	$h\nu$/10 days	$(CF_3)_2NCF_2CFICF_3$, SiF_4, COF_2, $CF_3N{:}CF_2$, $(CF_3)_2NH$, and $[(CF_3)_2N]_2$	*51*
	120°/3 hr	SiF_4, $CF_3N{:}CF_2$, CF_3NCO, CO_2, COF_2, $(CF_3)_2NH$, and $[(CF_3)_2N]_2$	*51*

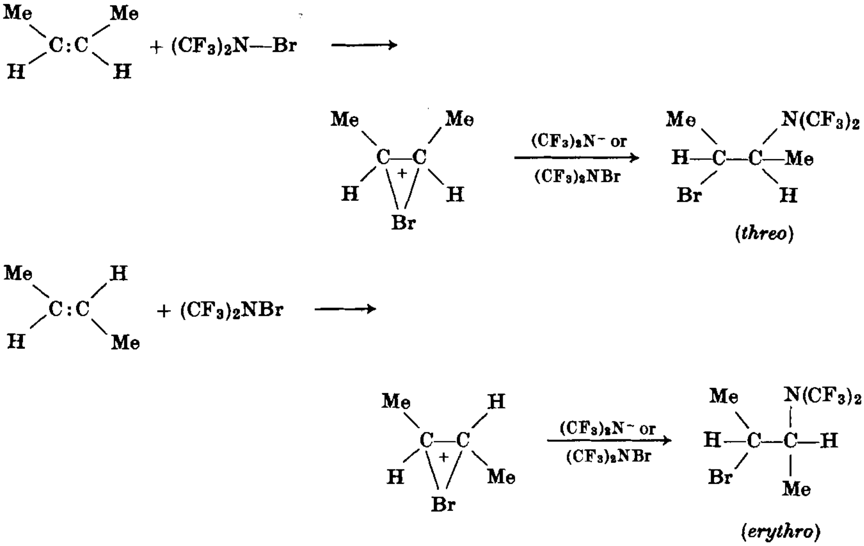
ethylamine (V) in the ratio of 87:13. The bidirectional addition involves $(CF_3)_2N$ radical as the chain carrier, as shown below.

$$(CF_3)_2NCl \xrightarrow[h\nu]{\Delta \text{ or}} (CF_3)_2N\cdot + Cl$$

$$\begin{tikzcd}
(CF_3)_2N\cdot + CF_2{:}CHF \arrow[r] & (CF_3)_2NCF_2CFH \arrow[d, "(CF_3)_2NCl"] & + & (CF_3)_2NCHFCF_2 \arrow[d, "(CF_3)_2NCl"] \\
& \text{(V)} & & \text{(IV)}
\end{tikzcd}$$

The isomeric distribution afforded by *N*-halogenoamines is similar to that given by CF_3I, also under free radical conditions, suggesting that $(CF_3)_2N$ and CF_3 radicals are of comparable electrophilicity.

Under nonradical conditions, substituted olefins which contain electropositive substituents are attacked by *N*-chloro-, *N*-bromo-, and *N*-iodobis(trifluoromethyl)amine. The reactions between the *N*-bromamine and *cis*- or *trans*-but-2-ene at −78° in the dark give stereospecific trans addition products, namely, *threo*- and *erythro*-2-bromo-1-methyl-*N*,*N*-bis(trifluoromethyl)propylamine, respectively, in high yield. The reactions are considered to involve cyclic bromonium ion intermediates, and not four-center addition, as shown below (*49*).



Similarly, an iodonium intermediate is proposed in the reaction with the *N*-iodamine at low temperatures in the dark.

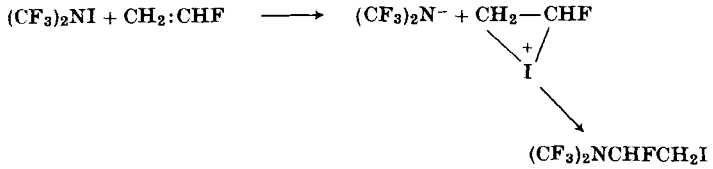
TABLE VIII

REACTIONS OF *N*-HALOGENOAMINES WITH TRIFLUOROETHYLENE (*51*)

N-Halogeno-amine	Ratio of attack on CHF and CF_2 groups			
	25°/light	UV irradiation		20°/dark
$(CF_3)_2NCl$	—	87:13 (96%)	78:22 (99%)	—
$(CF_3)_2NBr$	78:22 (95%)	—	—	77:23 (15%)
$(CF_3)_2NI$	76:24 (99%)	74:26 (93%)	—	—

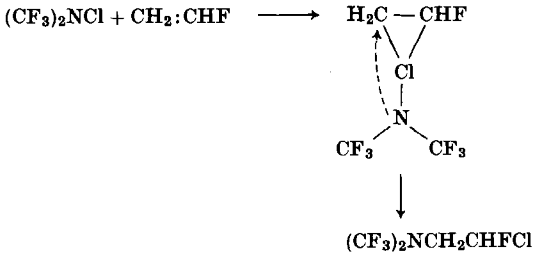
With olefins containing electronegative groups, the tendency to add the *N*-halogenoamines across the double bonds under nonradical conditions decreases in the order I > Br > Cl (*51*). This could be due to both the decrease in the availability of the π electrons of the olefins as well as the ease of expansion of coordination number of the halogen decreasing in the order I > Br > Cl. Thus, the *N*-chloramine does not react with vinyl fluoride at –24° in the dark in contrast to the reaction that has been observed with the *N*-iodamine under similar conditions. On the other hand, the *N*-halogenoamines react with olefins containing electropositive substituents even at low temperatures; with olefins containing only electronegative substituents ultraviolet or high temperature conditions are necessary to ensure addition reactions (Table VIII).

It is in the area involving the reactions with electronegative substituents under nonradical conditions where the postulated mechanisms need be restated, for it seems unlikely that free radical mechanism can be proposed for the reaction between the *N*-chloramine and vinyl fluoride at 25° in the dark (*50*). Under such conditions, the $(CF_3)_2N$ radical is unlikely to be generated. It is now proposed that under nonradical conditions, two types of reactions are possible—the unimolecular and bimolecular reactions. The former is favored when X in $(CF_3)_2NX$ is iodine or bromine and the latter is preferred when X is chlorine. The unimolecular reaction explains as in the case of the reaction between $(CF_3)_2NI$ and $CH_2{=}CHF$, the preferential attack on the CHF carbon, as shown below,



together with the presence of $(CF_3)_2NCH_2CHFI$ as a minor product.

For the bimolecular reaction involving the *N*-chloramine the mechanism can be written as follows:



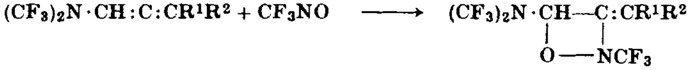
This mechanism explains the predominant amount of $(CF_3)_2NCH_2CHFCl$ as against $(CF_3)_2NCHFCH_2Cl$, thus avoiding the rather unlikely free radical pathway. The ratio of the isomers would therefore be in the same order as that expected for radical reactions. This same mechanism is operative in the reactions between $(CF_3)_2NBr$ and either $CH_2{:}CHF$ or $CH_2{:}CF_2$ at room temperature in the dark (*32*).

6. *Addition to Allenes*

Haszeldine and co-workers have reported the addition of *N*-bromobis(trifluoromethyl)amine to allene to give a mixture of olefins, namely $(CF_3)_2NCH_2{\cdot}CBr{:}CH_2$ and $(CF_3)_2NC(CH_2Br){:}CH_2$. With a twofold excess of *N*-bromamine, however, addition across both the double bonds is observed, but only one product has been isolated, $(CF_3)_3NCH_2CBr_2CH_2N(CF_3)_2$ (*27, 32*). The vapor phase reaction of the *N*-bromamine with allene in daylight is considered to proceed via free radical intermediates, while the liquid phase reaction at −78° in the dark probably proceeds via ionic intermediates. Addition to a number of bis(trifluoromethyl)-amino-substituted allenes can proceed at much lower temperatures (−78°); $[(CF_3)_2N]_2C{:}C{:}CH_2$ does not react, whereas $[(CF_3)_2NCH{:}C{:}CHN(CF_3)_2]$ affords only $[(CF_3)_2N]_2CH{\cdot}CBr{:}CHN(CF_3)_2$. A mixture of addition compounds, namely, $[(CF_3)_2N]_2CH{\cdot}CBr{:}CH_2$ and $(CF_3)_2NCH_2CBr{:}CHN(CF_3)_2$, is obtained from $(CF_3)_2NCH{:}C{:}CH_2$. In contradistinction, no addition reaction is observed with $[(CF_3)_2N]_2C{:}C{:}CHN(CF_3)_2$. Only a substitution reaction involving a displacement of the labile allenic hydrogen is noted.

$$[(CF_3)_2N]_2C{:}C{:}CHN(CF_3)_2 + (CF_3)_2NBr \rightarrow [(CF_3)_2N]_2C{:}C{:}CBrN(CF_3)_2 + (CF_3)_2NH$$

A series of bis(trifluoromethyl)amino-substituted allenes are converted to the corresponding oxazetidines, as shown below (*52*).

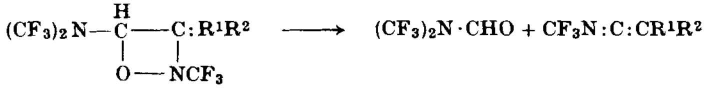


$R^1 = R^2 = H$

$R^1 = H, R^2 = (CF_3)_2N$

$R^1 = R^2 = (CF_3)_2N$

Pyrolysis of the oxazetidines by a flow method at 200°–300° gives equimolar quantities of *N*,*N*-bis(trifluoromethyl)formamide and the corresponding *N*-trifluoromethylketenimine by ring cleavage as illustrated by the equation:



$R^1 = R^2 = H$

$R^1 = H, R^2 = (CF_3)_2N$

$R^1 = R^2 = (CF_3)_2N$

This reaction serves to confirm the oxazetidine structures.

7. *Addition to Alkynes*

Only one mole of *N*-bromobis(trifluoromethyl)amine is taken up with acetylene at 50° (*31*).

$$(CF_3)_2NBr + CH{\equiv}CH \rightarrow (CF_3)_2NCH{=}CHBr$$

With a substituted acetylene, $(CF_3)_2NC{\equiv}CH$, *N*-chlorobis(trifluoromethyl)amine under the influence of ultraviolet light produces a mixture of isomers (*51*).

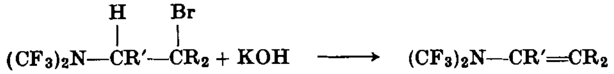
$$(CF_3)_2NCl + (CF_3)_2NC{\equiv}CH \xrightarrow{h\nu} (CF_3)_2NCCl{=}CHN(CF_3)_2 + [(CF_3)_2N]_2C{=}CHCl$$

IV. Bis(trifluoromethyl)amino-Substituted Organic Compounds

A. UNSATURATED BIS(TRIFLUOROMETHYL)AMINO DERIVATIVES

1. *Synthesis by Dehydrohalogenation*

Dehydrohalogenation of a number of bis(trifluoromethyl)amino derivatives has demonstrated that it can be adopted as a general method for the synthesis of unsaturated derivatives. Thus, the olefin, acetylene, and allene derivatives have been prepared by this method using mainly potassium hydroxide as a dehydrohalogenating reagent. In one instance, a zinc–ethanol mixture has been employed (*53*). Most of these reactions have been conducted under relatively mild conditions. The nature of the reaction products depends to a large extent on the derivatives under investigation. Most saturated bromo or iodo derivatives produce only olefins, as shown below (*27*, *53*, *54*).



$$(CF_3)_2N\text{—}\overset{\overset{H}{|}}{C}R'\text{—}\overset{\overset{Br}{|}}{C}R_2 + KOH \longrightarrow (CF_3)_2N\text{—}CR'{=}CR_2$$

On heating *erythro*-Me[$(CF_3)_2N$]CH·CHMeBr and *threo*-Me[$(CF_3)_2N$]CH·CHMeBr with potassium hydroxide, *cis*-MeCH:CMe[$N(CF_3)_2$] and *trans*-MeCH:CMe[$N(CF_3)_2$] are formed, respectively. With a dibromide derivative where the bromine atoms reside on the β-position of a substituted propene, the final product could be an allene.

$$(CF_3)_2NCH_2\cdot CBr_2\cdot CH_2N(CF_3)_2 + KOH \rightarrow (CF_3)_2NCH{:}C{:}CHN(CF_3)_2$$

Several allenic compounds containing bis(trifluoromethyl)amino groups have been derived from the substituted bromopropenes. For example,

$$(CF_3)_2NCH_2\cdot CBr{:}CH_2 + KOH \rightarrow (CF_3)_2NCH{:}C{:}CH_2$$

Acetylenic bonds can be formed from the same reaction using bromoethylene derivatives, as illustrated below (*54*).

$$(CF_3)_2NCH{:}CHBr + KOH \rightarrow (CF_3)_2NC{\equiv}CH$$

2. *Reactivity*

Compounds containing bis(trifluoromethyl)amino group(s) bonded to carbon are relatively more stable to heat and hydrolysis when compared to those compounds where bis(trifluoromethyl)amino groups are bonded to other elements. Thus, addition reactions have been observed

TABLE IX

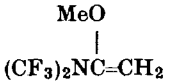
ADDITION REACTIONS OF $(CF_3)_2NCR{:}CR_2$

Olefin	Reagent	Product (% yield)	Ref.
$(CF_3)_2NCF{:}CF_2$	Br_2	$(CF_3)_2NCFBrCF_2Br$ (98)	*53*
$(CF_3)_2NCF{:}CF_2$	HBr/$h\nu$	$(CF_3)_2NCHF\cdot CF_2Br$	*53*
$(CF_3)_2NCH{:}CH_2$	HBr/$AlBr_3$	$(CF_3)_2NCHBr\cdot CH_3$ (94)	*27*
$(CF_3)_2NCH{:}CH_2$	HBr/$h\nu$/96 hr	$(CF_3)_2NCH_2CH_2Br$ (88) $(CF_3)_2NCHBrCH_3$ (6)	*27*
$(CF_3)_2NCH{:}CH_2$	CF_3I/$h\nu$	$(CF_3)_2NCHICH_2CF_3$ (46)	*54*
		$(CF_3)_2NCH_2\cdot CH_2CF_3$ (22)	*54*
		$(CF_3)_2NCH{:}CHCF_3$ (22)	*54*
$(CF_3)_2NCH{:}CH_2$	Br_2	$(CF_3)_2CHBrCH_2Br$	*54*

for bis(trifluoromethyl)aminoethylene, bis(trifluoromethyl)aminotrifluoroethylene, and bis(trifluoromethyl)aminoacetylene without breaking up the $(CF_3)_2N-C$ moiety (see Tables IX and X).

TABLE X

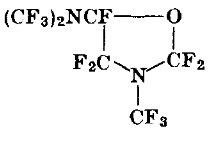
REACTIVITY OF $(CF_3)_2NC{\equiv}CH$

Reagent	Conditions	Product (% yield)	Ref.
$HBr/AlBr_3$	Dark	$(CF_3)_2NCBr{=}CH_2$ (95)	*55*
$Br_2/AlBr_3$	7 hr	*trans*-$(CF_3)_2NCBr{=}CBr_2$ (95), *cis*-$(CF_3)_2NCBr{=}CBr_2$ (22)	*55*
	3 weeks	Ratio of trans:cis is 36:64	
HBr	$h\nu$/liquid phase	$(CF_3)_2N{\cdot}CBr{:}CH_2$ (53), *trans*-$(CF_3)_2NCH{:}CHBr$ (32), *cis*-$(CF_3)_2NCH{:}CHBr$ (9)	*55*
$H_2SO_4/HgSO_4$	Room temp.	$(CF_3)_2NCOCH_3$	
H_2/Raney Ni	—	$(CF_3)_2NCH{:}CH_2$	*27*
MeOH	Acid catalyzed at 95°	Decomposition	*27*
MeOH	Basic condition	 $(CF_3)_2N\overset{\overset{MeO}{\vert}}{C}{=}CH_2$ (56), *cis*-$(CF_3)_2NCH{:}CHOMe$ (28), $(CF_3)_2NC(OMe)_2CH_3$ (3)?	*55*
KOBr	Alkaline	$(CF_3)_2N{\cdot}C{\equiv}CBr$ (89)	*55*

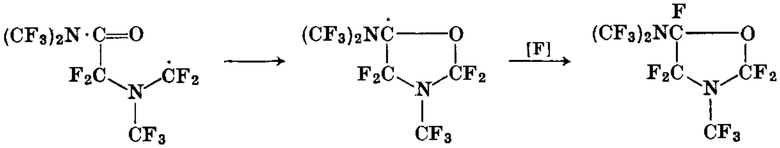
B. SATURATED BIS(TRIFLUOROMETHYL)AMINO DERIVATIVES

1. Synthesis by Electrochemical Fluorination

The electrochemical fluorination of the methyl ester of *N*,*N*-dimethylglycine $(CH_3)_2NCH_2{\cdot}CO_2CH_3$ and the corresponding dimethylamide $(CH_3)_2NCH_2{\cdot}CON(CH_3)_2$, both derivatives of glycine, afford the expected product, i.e., the acid fluoride of *N*,*N*-bis(trifluoromethyl)difluoroglycine $[(CF_3)_2NCF_2COF]$, albeit in only 6% yield. It is hydrolyzed to the parent acid, and the nitrogen atom in this acid is inert and completely nonbasic (*30*). The by-products of the dimethylamide derivatives are perfluorotrimethylamine, $[(CF_3)_3N]$, *N*,*N*-bis(trifluoromethyl)carbamoyl fluoride, $[(CF_3)_2N{\cdot}COF]$, and an oxazolidine derivative.



The first two of these must presumably have been produced by the same carbon–carbon bond cleavage, although the yield of the amine (2%) is less than that of the carbamoyl fluoride derivative (7%). The oxazolidine could have arisen from a simple cyclization reaction such as



This could also have occurred at any stage in the fluorination. Such cyclizations are a very common feature of electrochemical fluorinations.

The electrochemical fluorination of a series of carbamic acid derivatives (Table XI) with the general structure $(R\cdot CH_2)_2\cdot NCOM$ (R = H, alkyl; M = H, Cl, alkyl, NR_2) affords bis(trifluoromethyl)carbamyl fluoride, $[(CF_3)_2N\cdot COF]$, as the major product in yields ranging from 4–37%; and the best yields are obtained from the carbamyl chloride (R = H, M = Cl) (*56*).

TABLE XI

ELECTROCHEMICAL FLUORINATION OF SOME $(RCH_2)_2NCOM$ COMPOUNDS (*56*)

Organic starting material	Products (% yield)
$HCON(CH_3)_2$	$(CF_3)_2NCOF$
$(CH_3)_2NCOCl$	$(CF_3)_2NCOF$
$(C_2H_5)_2NCOCl$	$CF_2OCF_2CF_2NC_2F_5$ as well $(CF_3)_2NCOF$ depending on experimental conditions
$(C_4H_9)_2NCOCl$	$(CF_3)_2NCOF$, $CF_2OCF(C_2F_5)CF_2NC_4F_9$
$O(CH_2CH_2)_2NCOCl$	$(CF_3)_2NCOF$, $O(CF_2CF_2)_2NCOF$
$CF_3CON(CH_3)_2$	CF_3COF, $(CF_3)_2NCOF$, $CF_3CON(CF_3)_2$
$(CH_3)_2NCON(CH_3)_2$	$(CF_3)_2NCOF$, $(CF_3)_2NCON(CF_3)_2$

Bis(trifluoromethyl)carbamoyl fluoride gives esters with alcohols, and apparently hydrolyzes to the free acid which resembles the non-fluorinated analog in its stability. Pyrolysis of the fluoride at 575°C gives perfluoro-2-azapropene, $CF_3N{=}CF_2$.

The yield of the fluoride from dimethylcarbamyl chloride is dependent on the concentration as tabulated below (*56*, *57*).

Concentration of $(CH_3)_2NCOCl$	Yield (%) of $(CF_3)_2NCOF$
0.5 mole%	24
3.5 mole %	6
Higher concentration	$(CF_3)_2NCOCl$ (considerable amount)

The yield is also influenced by temperature, current, and voltage. Unlike other acid chlorides (*58*, *59*), it reacts very sluggishly with hydrogen fluoride. This could account for its formation.

Perfluoroamide products from *N*,*N*-dimethylformamide, *N*,*N*-dimethyltrifluoroacetamide, and tetramethyl urea have been obtained in yields of 5.5 and 2%, respectively (*56*). Fluorination of dimethylformamide with elementary fluorine produces a small amount of bis(trifluoromethyl)carbamoyl fluoride and *N*-fluorobis(trifluoromethyl)amine; the latter is not formed in the electrochemical process.

2. *Bis(trifluoromethyl)amine*

Bis(trifluoromethyl)amine, a colorless liquid, can be readily prepared by the addition of hydrogen fluoride to perfluoro-2-azapropene (*29*). Several methods are also known which lead to the formation of this secondary amine, as summarized in Table XII. It boils at about −6°,

TABLE XII

FORMATION OF BIS(TRIFLUOROMETHYL)AMINE

Reactants	Conditions	Other products	Ref.
$HF/CF_3N{:}CF_2$	100°/15 hr	—	*6*
	150°/15 hr	—	*29*
	Room temp./immediate	—	*53, 61*
$HF/(CN)_2$	200°–450°	—	*62*
HF/XCN (X = halide)	200°–450°	—	*62*
$HF/CCl_3N{:}CCl_2$	30°–35°	—	*63*
$HCl/CF_3N{:}CF_2$	20°/44 hr	$CF_3N{=}CCl_2$	*53*
$C_2H_5OH/CF_3N{:}CF_2$	Room temp./40 min	$CF_3NHCOOC_2H_5$	*64*
$(CF_3)_2NCOF$	400°/18 hr	—	*6*
ICN/IF_5	—	—	*28*
$(CF_3)_2NCl/H_2O$	Room temp./30 min	—	*13*
$(CF_3)_2NOH/PCl_5$	50°/21 hr, then 20°/20 hr	—	*15, 65*
$(CF_3)_2NBr/CH(CH_3)_2C_2H_5$	$h\nu$/4 days	—	*32*
$[(CF_3)_2N]_2Hg$	$h\nu$/30 days	—	*14*
$[(CF_3)_2N]_2Hg/CH(CH_3)_2C_2H_5$	$h\nu$/14 days	—	*32*
Electrolysis of $Hg(CN)_2$ in an electrolyte of $KF \cdot 2HF$	—	—	*25*

12 degrees lower than dimethylamine. This is due to the highly electronegative trifluoromethyl groups which cause a marked decrease in the electron density at the nitrogen atom. The resultant effect is a decrease in hydrogen bonding. A significant reduction in its basicity is demonstrated by its lack of reactivity with either hydrogen chloride or boron trifluoride (*6*). It does not react with acid chlorides or trifluoroacetic anhydride.

In contrast to its unreactivity toward the usual amine reagents, it is entirely destroyed by exposure to water and aqueous acids or bases. Its decomposition under these conditions has been suggested to proceed by an initial loss of HF and subsequent hydrolysis of perfluoro-2-azapropene, according to the following equation (*29*).

$$\begin{tikzcd} (CF_3)_2NH \arrow[r, "-HF"] & CF_3N{:}CF_2 \arrow[r, "H_2O"] & CF_3N{=}C{=}O \arrow[d, "H_2O"'] \\ & & F^- + CO_2 + NH_3 \end{tikzcd}$$

Facile elimination of hydrogen fluoride is also encountered in its reactions with inorganic halides such as PCl_3. Compounds of the type $(CF_3)_2NMCl_2$ are not obtained; rather, the products are MF_3, HCl, and $CF_3N{=}CCl_2$. The proposed mechanisms are as shown below (*6*).

$$\begin{array}{rcl} (CF_3)_2NH & \rightarrow & CF_3N{:}CF_2 + HF \\ 3HF + MCl_3 & \rightarrow & MF_3 + 3HCl \\ CF_3N{:}CF_2 + HCl & \rightarrow & CF_3NHCF_2Cl \\ & & \downarrow \\ & & CF_3N{:}CFCl + HF \\ CF_3N{:}CFCl + HCl & \rightarrow & CF_3NHCFCl_2 \\ & & \downarrow \\ & & CF_3N{:}CCl_2 + HF \end{array}$$

Although boron trichloride has been reported to follow the above course, Greenwood and Hooten have reported the isolation of the amino-derivatives, $(CF_3)_2NBX_2$, with boron trichloride and tribromide, according to the following equations (*38*).

$$\begin{array}{rcl} (CF_3)_2NH + BX_3 & \rightarrow & (CF_3)_2NH\cdot BX_3 \\ (CF_3)_2NHBX_3 & \rightarrow & (CF_3)_2NBX_2 + HX \\ & X = Cl, Br & \end{array}$$

Both bis(trifluoromethyl)aminoboron dichloride and dibromide are white crystalline solids which undergo rapid decomposition at room temperature according to the equation:

$$(CF_3)_2NBX_2 \rightarrow CF_3N{:}CX_2 + BF_3$$

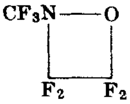
Although the reaction between bis(trifluoromethyl)amine and potassium fluoride at about 150° yields CF_3NHCOF (*66*), its reaction with argentic fluoride causes fission of the N–H bond to afford HF and $(CF_3)_2NN(CF_3)_2$ (*18*).

3. *Some Perfluoroalkyl Tertiary Amines,* $(CF_3)_2NR$

Perfluoroalkyl tertiary amines such as $(CF_3)_3N$ and $(CF_3)_2NC_2F_5$ have been prepared by methods involving either the electrochemical process or cobaltic fluoride. However, perfluoro-2-azapropene reacts with RSF_5 to afford $(CF_3)_2NR$ (R = CF_3 and C_2F_5) in fairly good yields. These and a few other methods are summarized in Table XIII.

TABLE XIII

FORMATION OF $(CF_3)_2NR$

Starting materials	Conditions	Yield (%)	Ref.
R = CF_3			
$(CH_3)_2NCH_2COOCH_3$	Electrochemical fluorination	—	*30*
$(CH_3)_2NCOH$	Electrochemical fluorination	5	*19*
$(CH_3)_2NH$ or $(CH_3)_3N$	Fluorination process	11–15	*20*
$(CH_3)_3N/HF$	Electrolysis	—	*67, 68*
HCN, CH_3NH_2, or $NH_2CH_2CH_2NH_2$	Jet fluorination	—	*69*
$(CH_3)_3N/CoF_3$	250°	6	*22, 70*
$CF_3N:CF_2/CF_3SF_3$	540°/1 atm	Quite good yield	*71*
$CF_3N:CF_2/(CF_3)_2NOCF_3$	hν/35 days	22	*14*
	hν/11 days	12	*72*
R = C_2F_5			
$(CH_3)_2NC_2H_5/CoF_3$	250°	—	*19, 70*
$CF_3N:CF_2/C_2F_5SF_5$	400°/12 atm	46	*71*

Both the amines are poor Lewis bases by virtue of the highly electronegative perfluoroalkyl substituents. Therefore, numerous salts formed by trialkylamines have no counterparts for the perfluoroanalogs.

The structure of tris(fluoromethyl)amine has been established by Livingston and Vaughan (*73, 74*). The structural parameters as compared with trimethylamine reveal some interesting features (Table XIV).

TABLE XIV

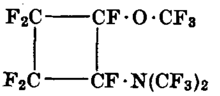
COMPARISON OF STRUCTURAL PARAMETERS

Molecule	CN (Å)	CF (Å)	CNC (deg)	FCF (deg)
$(CF_3)_3N$	1.47 + 0.01	—	108 ± 4	—
$(CF_3)_3N$	1.43 ± 0.03	1.32 ± 0.03	114 ± 3	108.5 ± 2

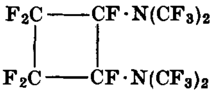
The CF_3 groups in tris(trifluoromethyl)amine are similar to those in tetrakis(trifluoromethyl)hydrazine. The C–N bonds are slightly shorter than in trimethylamine, in keeping with the usual trend. There is deviation at the nitrogen from a tetrahedral to a planar structure, but the effect is less than is encountered in $(CF_3)_2NN(CF_3)_2$. This is certainly due to the steric stress introduced by the bulky CF_3 groups. The closest approach of fluorine atoms attached to different carbon atoms is less than the limiting value of 2.70 Å.

C. PYROLYSIS OF BIS(TRIFLUOROMETHYL)AMINO DERIVATIVES

1. *Cyclobutanes* (*53*)

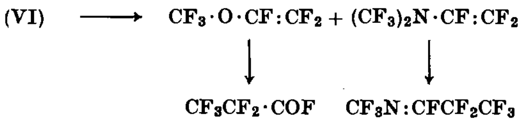


(VI)



(VII)

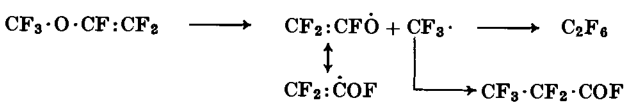
Pyrolysis of compounds (VI) and (VII) in a platinum tube under optimum conditions of 600° with a contact time of 1 sec/1–2 mm proceeds as follows (*75*).



$$\begin{tikzcd} \text{(VI)} \arrow[r] & CF_3\cdot O\cdot CF{:}CF_2 \arrow[d] & + & (CF_3)_2N\cdot CF{:}CF_2 \arrow[d] \\ & CF_3CF_2\cdot COF & & CF_3N{:}CFCF_2CF_3 \end{tikzcd}$$

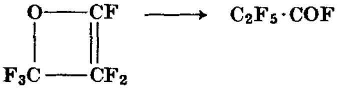
$$\text{(VII)} \longrightarrow (CF_3)_2NCF{:}CF_2 \longrightarrow CF_3N{:}CFCF_2CF_3$$

Pentafluoropropionyl fluoride could be formed either via the thermal rearrangement of the vinyl ether,



$$\begin{tikzcd} CF_3\cdot O\cdot CF{:}CF_2 \arrow[r] & CF_2{:}CF\dot{O} \arrow[d, leftrightarrow] & + & CF_3\cdot \arrow[r] \arrow[dr] & C_2F_6 \\ & CF_2{:}\dot{C}OF & & & CF_3\cdot CF_2\cdot COF \end{tikzcd}$$

or via a 4-center intramolecular rearrangement,



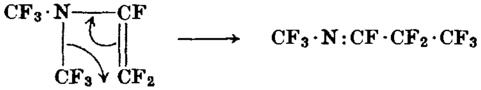
2. *Polyfluorovinylamines* (*53*)

The rearrangement of the perfluoro(*N*,*N*-dimethylvinylamine) to perfluoro-2-azapentene at 600° and contact time of about 7 sec could proceed by a radical process (*A*) or by an intramolecular process (*B*).

Reaction (*A*) $(CF_3)_2N\cdot CF{:}CF_2 \longrightarrow CF_3N\cdot CF{:}CF_2 + CF_3\cdot$

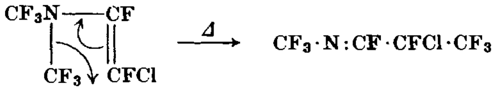
$$CF_3\dot{N}\cdot CF{:}CF_2 \longleftrightarrow CF_3\cdot N{:}CF\cdot CF_2\cdot \xrightarrow{CF_3\cdot} CF_3N{:}CF\cdot CF_2\cdot CF_3$$

Reaction (*B*)



In the presence of a large excess of toluene and at 610°, with a contact time of 0.66 sec, perfluoro(*N*,*N*-dimethylvinylamine) affords perfluoro-2-azapentene (46% yield), fluoroform (31%), 1,1-difluoroethylene (38%), and the breakdown products, COF_2, CF_3NCO, and SiF_4. The presence of fluoroform indicates the attack of CF_3 radical generated on toluene.

2-Chloro-1,2-difluorovinylbis(trifluoromethyl)amine, on pyrolysis under similar conditions to those above, produced 4-chlorooctafluoro-2-azapent-2-ene (51%), together with a mixture consisting mainly of hexafluoroethane, silicon tetrafluoride, and carbonyl fluoride.



A radical process is also operative although to a lesser extent.

$$(CF_3)_2N\cdot CF{:}CFCl \xrightarrow{\Delta} CF_3\cdot\dot{N}\cdot CF{:}CFCl + CF_3\cdot$$

$$CF_3\cdot\dot{N}\cdot CF{:}CFCl \longrightarrow CF_3\cdot N{:}CF\cdot CFCl\cdot \xrightarrow{CF_3\cdot} CF_3N{:}CF\cdot CFClCF_3$$

V. Bis(trifluoromethyl)carbamyl Fluoride, $(CF_3)_2NCOF$

Although bis(trifluoromethyl)carbamyl fluoride (VIII) has been prepared independently by reacting perfluoro-2-azapropene or bis(trifluoromethyl)amine with perfluorophosgene in the presence of cesium fluoride (*76*), the major procedure lies in the electrochemical fluorination of compounds such as $(CH_3)_2NCOCl$, $(CH_3)_2NCOH$, $(C_2H_5)_2NCOCl$, $(CH_3)_2NCOCH_3$, $(CH_3)_2NCOCF_3$, $O(CH_2CH_2)_2NCOCl$, $(CH_3)_2NCON(CH_3)_2$, $(CH_3)_2NCH_2COOMe$, and $(CH_3)_2NCH_2CON(CH_3)_2$ (*56*, *77*, *78*). All these compounds have in common the structure $(RCH_2)_2N{-}C$, where R is hydrogen or alkyl, and it is probable that any starting material containing this structural arrangement will afford the carbonyl fluoride as one of the products. As is expected from this process other fragmentation products are formed, the best yield of the perfluorocarbonyl fluoride (37%) being obtained from dimethylcarbonyl chloride under conditions of minimum concentration and voltage.

Bis(trifluoromethyl)carbamyl chloride can be prepared by electrochemical fluorination of dimethylaminocarbamyl chloride (*76*). The bromo and chloro derivatives of compound (VIII) have also been obtained by reacting *N*-bromo- and *N*-chlorobis(trifluoromethyl)amine with carbon monoxide, respectively (*31*, *80*).

Bis(trifluoromethyl)carbamyl fluoride resists hydrolysis with water at room temperature, but reacts destructively with aqueous base or water at elevated temperatures. It does not undergo simple halogen exchange with $AlCl_3$, $SnCl_4$, or $SiCl_4$ (*56*). Pyrolysis of the carbamyl fluoride in the presence of nitrogen gives $CF_3N{:}CF_2$ in 96% yield (*56*, *77*), but the pyrolytic product is $(CF_3)_2NCF{=}NCF_3$ if the experiment is conducted in the presence of activated charcoal (*17*). The reaction with argentic fluoride at 100°C gives $(CF_3)_2NF$ and COF_2. In the presence of an alcohol, the corresponding ester is formed (*56*).

$$(CF_3)_2NCOF + ROH \rightarrow (CF_3)_2NCOOR$$

VI. Bis(trifluoromethyl)amino-Substituted Inorganic Compounds

A. *N*-NITROSOBIS(TRIFLUOROMETHYL)AMINE

N-Nitrosobis(trifluoromethyl)amine, whose reported b.p. is −3° to −4°, is fairly unstable at room temperature (*12*). It is extremely sensitive to traces of moisture and is attacked by mercury at room temperature.

Several good preparative methods for the nitroso derivative as reported in the literature are summarized in Table XV. In the method involving the catalytic oxidation of perfluoro-2-azapropene, Young *et al.* suggest that formation of nitrosyl fluoride is the intermediate step, followed by addition to excess perfluoro-2-azapropene, as shown below (*12*).

$$\mathrm{CF_3N{:}CF_2 + O_2 \xrightarrow{RhF} 2COF_2 + NOF}$$

$$\mathrm{CF_3N{=\!=}CF_2 + NOF \longrightarrow (CF_3)_2NNO}$$

The ease of addition of nitrosyl fluoride to perfluoro-2-azapropene can be explained as being due to the formation of the resonance-stabilized nitronium intermediate (*77*).

$$\mathrm{CF_3{-\!-}\overset{\ominus}{N}{-\!-}CF_3 \leftrightarrow CF_3N{=\!=}CF_2\overset{\ominus}{F}}$$

B. *N*-NITROBIS(TRIFLUOROMETHYL)AMINE

The *N*-nitramine is a stable colorless liquid. Two important methods of synthesis have emerged, namely, the oxidation of bis(trifluoromethyl)-amine by nitric acid in the presence of trifluoroacetic anhydride (*6*, *82*) and the addition of NO_2F to perfluoro-2-azapropene (*77*). A few other reactions also give the nitroamine though in much reduced yield, as shown in Table XV.

TABLE XV

PREPARATION OF *N*-NITROSO- AND *N*-NITROBIS(TRIFLUOROMETHYL)AMINE

Reagents	Conditions	Yield (%)	Ref.
$(CF_3)_2NNO$			
$(CF_3)_2NBr/NO$	Room temp.	—	*31*
$[(CF_3)_2N]_2Hg/NOCl$	—	—	*81*
$CF_3N{=}CF_2/O_2/RbF$	325°–500°	40–60	*12*
$CF_3N{=}CF_2/NOF$	Room temp.	—	*77*
$(CF_3)_2NNO_2$			
$CF_3NO/(CF_3)_2NONO$	$h\nu$	—	*82*
$(CF_3)_2NH/(CF_3CO)_2O/70°\ HNO_3$	50°/1 hr	93	*6, 82*
$(CF_3)_2NONO$	78°/14 days or 78°/14 days/O_2	6	*82*
$[(CF_3)_2N]_2Hg/ClNO_2$	—	—	*81*
$(CF_3)_2NNO/H_2O_2/(CF_3CO)_2O$	Room temp.	—	*12*
$CF_3N{=}CF_2/NO_2F$	Room temp.	92	*77*

VII. Bis(trifluoromethyl)nitroxyl and Its Derivatives

A. METHODS OF SYNTHESIS

Trifluoronitrosomethane, a key material to the formation of bis-(trifluoromethyl)nitroxyl, can be prepared by numerous methods (*4*). Of these, the most convenient practical method involving the ultraviolet irradiation of a mixture of trifluoromethyl iodide and nitric oxide in the presence of mercury was established by Haszeldine (*83*, *84*).

$$CF_3I + NO \xrightarrow[h\nu]{Hg} CF_3NO$$

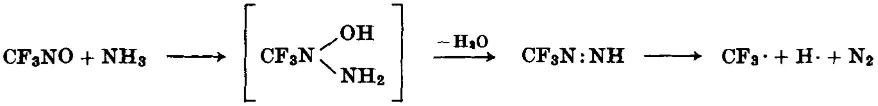
The next step proceeds by dimerization of trifluoronitrosomethane to *o*-nitrosobis(trifluoromethyl)hydroxylamine, which probably involves radical intermediates (*82*).

$$\begin{aligned} CF_3NO &\xrightarrow{h\nu} CF_3\cdot + NO \\ CF_3\cdot + CF_3NO &\longrightarrow (CF_3)_2NO\cdot \\ (CF_3)_2NO\cdot + NO &\longrightarrow (CF_3)_2NONO \\ &\text{or} \\ (CF_3)_2NO\cdot + CF_3NO &\longrightarrow (CF_3)_2NONO + CF_3\cdot \end{aligned}$$

Dimerization is reversible, and the equilibrium $(CF_3)_2NONO \rightleftharpoons 2CF_3NO$ lies well to the left. Photolysis of *o*-nitrosobis(trifluoromethyl)hydroxylamine also causes breakdown by way of $(CF_3)_2N$ radicals, leading to the formation of the compounds $CF_3N:CF_2$ and $(CF_3)_2NNO_2$. Hydrolysis by aqueous hydrochloric acid of *o*-nitrosobis(trifluoromethyl)hydroxylamine gives an almost quantitative yield of bis(trifluoromethyl)hydroxylamine.

$$\begin{gathered} (CF_3)_2NONO + HCl/H_2O \\ \text{or } 10\%\ NaOH \\ \text{or } MeOH \rightarrow (CF_3)_2NOH \end{gathered}$$

A more useful method of preparation that can be carried out on a larger scale and in a shorter time consists of interacting equimolar volumes of gaseous ammonia and trifluoronitrosomethane at atmosphere pressure and ambient temperature. The formation of the hydroxylamine is considered to proceed via radical reactions. It is suggested that the trifluoromethyl radical and hydrogen atom, which are thought to be formed by the decomposition of trifluoromethylazohydride, attack the trifluoronitrosomethane, as shown by the reaction scheme (*85*):



$$CF_3NO + NH_3 \longrightarrow \left[CF_3N\begin{matrix} OH \\ NH_2 \end{matrix} \right] \xrightarrow{-H_2O} CF_3N{:}NH \longrightarrow CF_3\cdot + H\cdot + N_2$$

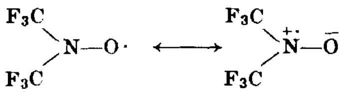
$$CF_3NO + H\cdot \longrightarrow CF_3\dot{N}{-}OH$$

$$CF_3\dot{N}OH + \cdot CF_3 \longrightarrow (CF_3)_2NOH \xrightarrow{H_2O} (CF_3)_2NOH\cdot H_2O$$

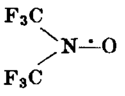
The oxidation of bis(trifluoromethyl)hydroxylamine to the nitroxyl cannot be brought about with chlorine even in the presence of ultraviolet light (*15*). This can, however, be achieved by the reaction with fluorine, argentous oxide, argentic oxide, potassium permanganate in glacial acetic acid, or by using an electrochemical method (*85–88*). The reaction with argentic oxide at room temperature gives a 100% conversion within a few hours.

B. STABILITY

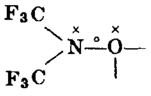
The stability of bis(trifluoromethyl)nitroxyl to dimerization has been attributed to its hybrid structures [(*a*) and (*b*)]. It has also been represented by a structure with three electron bond N∸O, i.e., with a σ bond and one electron between the nitrogen and oxygen atoms. The bond order of one and a half is consistent with its physical data such as bond length and N–O stretching vibration when compared to other related compounds as shown in Table XVI. Linnett's double quartet theory describes adequately the stability of this kind of bond [see (*d*)].



(*a*) (*b*)



(*c*)



(*d*)

TABLE XVI

PHYSICAL DATA OF BIS(TRIFLUOROMETHYL)NITROXYL AND RELATED COMPOUNDS

Molecules	Bond length (Å)	No. of electrons in N–O bond	IR (cm^{-1})	Ref.
NO	1.151	5	1876	*89*
CF_3NO	1.171	4	1595	*90*, *90a*, *91*
$(CF_3)_2NO$	1.26	3	1395(?)	*92*

The stable nature of bis(trifluoromethyl)nitroxyl cannot be ascribed to steric hindrance, but is believed to result from the strongly electronegative character of the trifluoromethyl groups. Evidence for some delocalization of the unpaired electron in the six fluorine atoms is given by its nine-line symmetrical electron spin resonance pattern (*86*). Unlike the non-fully-fluorinated nitroxyls such as dimethylnitroxyl (*93*), diethylnitroxyl (*94*), or the aromatic nitroxyls (*95*, *96*), bis(trifluoromethyl)nitroxyl shows a distinct difference in that it does not undergo disproportionation even at elevated temperatures (*97*).

C. STRUCTURE OF BIS(TRIFLUOROMETHYL)NITROXYL

The physical parameters of $(CF_3)_2NO$ are strikingly different from those of CF_3NO which has a long CN bond, a short NO bond, and a large FCF angle. It resembles $(CF_3)_2NN(CF_3)_2$ in that the CF and CN bond lengths are almost the same, and the angles between the CNC plane and the N–X bond is small in both compounds (see Table XVII). The greater deviation from planarity for the nitroxyl can be explained since the oxygen atom is smaller than the nitrogen atom. The shortest O ··· F contact found (2.53 Å) is about 0.2 Å shorter than the van der Waals distance. This is similar to the F ··· F nonbonded contacts in $(CF_3)_2NN(CF_3)_2$, also 0.2 Å less than the van der Waals distance (Fig. 2).

TABLE XVII

COMPARISON OF BOND LENGTHS (Å) AND ANGLES (°)

Bond	$(CF_3)_2NO$ (*92*)	$(CF_3)_2NN(CF_3)_2$ (*37*)	CF_3NO (*90*)
r(C–F)	1.320 ± 0.004	1.325 ± 0.005	1.321 ± 0.004
r(C–N)	1.441 ± 0.008	1.433 ± 0.007	1.555 ± 0.015
r(N–X)[a]	1.26 ± 0.03	1.40 ± 0.02	1.171 ± 0.008
F–C–F	109.8 ± 1.0	108.2 ± 0.5	111.9 ± 0.4
C–N–C	120.9 ± 2.0	121.2 ± 1.5	—
C–N–X	117.9 ± 0.6	119.0 ± 1.5	121.0 ± 1.6
θ[b]	21.9 ± 3	9 ± 5	—

[a] X = O or N.

[b] θ = angle between the CNC plane and the NX bond.

A comparison of the structures of various nitroxyls reveals a number of interesting features. The deviation from planarity at the N atom appears to be small, and zero for di(*t*-butyl)- and di(*p*-methoxybenzyl)-nitroxyls. In all cases except di(*p*-methoxybenzyl)nitroxyl, the oxygen makes close O ··· C or O ··· F contacts (see Table XVIII). This observation can be attributed to steric factors.

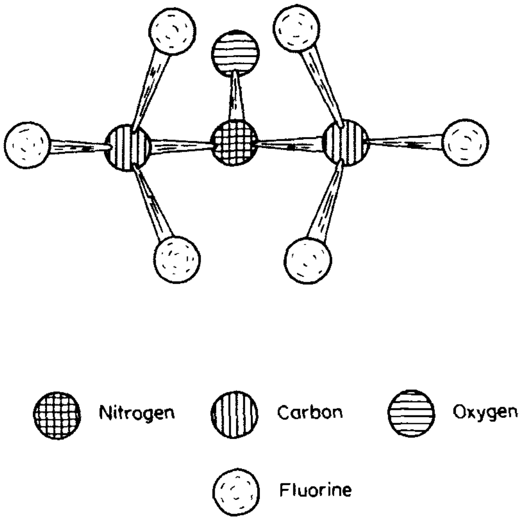


FIG. 2. The structure of bis(trifluoromethyl)nitroxyl.

TABLE XVIII

COMPARISON OF DISTANCES AND ANGLES IN NITROXYLS

Bond	$(CF_3)_2NO$	$(t\text{-}Bu)_2NO$ (*98*)	$(p\text{-}MeOC_6H_4CH_2)_2NO$ (*99*)	Ferrocenyl-*t*-butylnitroxyl (*99*)
r(C–N)	1.441 ± 0.008	1.512 ± 0.020	1.44 ± 0.05	—
r(N–O)	1.26 ± 0.03	1.28 ± 0.03	1.23 ± 0.05	1.20
C–N–C	120.9 ± 2.0	136 ± 3	124 ± 5	—
C–N–O	117.2 ± 0.6	112 ± 2	118 ± 3	—
θ[a]	21.9 ± 3	0	0	small

[a] θ = angle between the CNC plane and the N–O bond.

D. ORGANIC DERIVATIVES

1. *Addition Reactions*

Bis(trifluoromethyl)nitroxyl undergoes addition reactions with ethylene and polyhalogenated olefins, and the yields of the products are generally high (*85*, *100*, *101*). The rate of addition depends on the nature of the olefins and can be described by a first-order equation. The reaction scheme is as follows (*102*).

$$(CF_3)_2NO\cdot + CF_2{=}CXY \xrightarrow{\text{slow}} (CF_3)_2NOCF_2CXY\cdot$$

$$(CF_3)_2NOCF_2CXY\cdot + (CF_3)_2NO\cdot \xrightarrow{\text{fast}} (CF_3)_2NOCF_2CXYON(CF_3)_2$$

$$X = F,\ Y = H, F, Cl, Br, CF_3$$

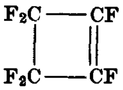
$$X = Y = H$$

$$X = Y = CF_3$$

On the basis of rate values and activation energies, the reactivities of olefins with the nitroxyl decreases in the following order:

$$CF_2{=}CF_2 > CF_2{=}CFCl > CF_2{=}CFBr >$$

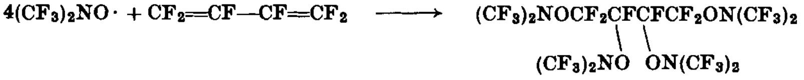
$$CF_2{=}CFH > CF_3{-}CF{=}CF_2 > CF_2{=}CH_2 > (CF_3)_2C{=}CF_2 >$$



In the reaction with hexafluorobutadiene at room temperature, only one product is formed, namely, $(CF_3)_2NOCF_2CF{=}CFCF_2ON(CF_3)_2$ (*100*). The structure is confirmed by the absence of an IR C=C stretching vibration, which would have been present for an unsymmetrical isomer. Thus, this reaction involving a 1,2-shift in the double bond may be shown by the scheme,

$$\begin{array}{lcl} (CF_3)_2NO\cdot + CF_2{=}CF{-}CF{=}CF_2 & \longrightarrow & (CF_3)_2NOCF_2CF{-}CF{=}CF_2 \\ & & \qquad\downarrow \\ & & (CF_3)_2NOCF_2CF{=}CFCF_2\cdot \\ (CF_3)_2NOCF_2CF{=}CFCF_2\cdot + (CF_3)_2NO\cdot & \longrightarrow & (CF_3)_2NOCF_2CF{=}CFCF_2ON(CF_3)_2 \end{array}$$

Under more drastic conditions (250°), however, complete addition to both the double bonds is observed.



$$4(CF_3)_2NO\cdot + CF_2{=}CF{-}CF{=}CF_2 \longrightarrow (CF_3)_2NOCF_2\underset{ON(CF_3)_2}{\underset{|}{C}}F\underset{ON(CF_3)_2}{\underset{|}{C}}FCF_2ON(CF_3)_2$$

In the presence of a mixture of $CF_2{=}CF_2$ and NO, the nitroxyl undergoes interactions which can be described by the following equations.

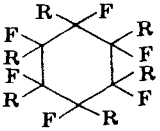
$$(CF_3)_2NO + CF_2{=}CF_2 \rightarrow (CF_3)_2NOCF_2CF_2\cdot$$
$$(CF_3)_2NOCF_2CF_2\cdot + NO \rightarrow (CF_3)_2NOCF_2CF_2NO$$
$$(CF_3)_2NO\cdot + NO \rightarrow (CF_3)_2NONO$$
$$(CF_3)_2NOCF_2CF_2\cdot + (CF_3)_2NO\cdot \rightarrow (CF_3)_2NOCF_2CF_2ON(CF_3)_2$$

Formulation of 2:1 adducts from the reactions of the nitroxyl and olefins as nitroxyalkanes and not as amine oxides [e.g., $(CF_3)_2NOCF_2CF_2ON(CF_3)_2$ and not as $(CF_3)_2N^+(O^-)CF_2CF_2N^+(O^-)(CF_3)_2$] is based on nuclear magnetic resonance and mass spectra measurements, as well as the failure to deoxygenate them by hot iron; the adducts give mass spectra that do not show peaks due to $(P{-}16)^+$ or $(P{-}32)^+$ ions, contrary to what would be expected if they contain oxygen atoms coordinated to nitrogen (*101*).

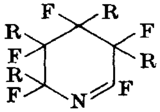
The reactions between bis(trifluoromethyl)nitroxyl and isobutene, 2-methylbut-1-ene, and 2-methylbut-2-ene at room temperature yield predominantly 2:1 nitroxyl:olefin adducts. By contrast, hydrogen abstraction predominates in the case of 3-methylbut-1-ene to afford the isomeric bis(trifluoromethyl)nitroxyalkanes, namely, $(CF_3)_2NOCMe_2CH{:}CH_2$ and $Me_2C{:}CHCH_2ON(CF_3)_2$, in 32 and 60% yield, respectively (*103*).

The fact that only 2:1 nitroxyl–olefin adducts are obtained shows that the nitroxyl is an excellent free radical scavenger, a conclusion that is underlined by the formation of only the compound $(CF_3)_2NOCF_2CF_2ON(CF_3)_2$ when the nitroxyl and tetrafluoroethylene are mixed in the molar ratio of 1:10. With an excess of an equimolar mixture of ethylene and tetrafluoroethylene, the nitroxyl combines almost exclusively (98%) with the perfluoroolefin, pointing to its strong nucleophilic character, $(CF_3)_2\overset{+\cdot}{N}{-}O^-$.

The nitroxyl undergoes addition reaction with hexafluorobenzene to give a 6:1 adduct (IX) (*102*).



(IX)



(X)

R = $(CF_3)_2NO$

Similarly, pentafluoropyridine yields 2,3,4,5 tetrakis[bis(trifluoromethyl)nitroxy]-2,3,4,5,6-pentafluoropyridine (X). The C:N bonds are resistant to radical attack (*104*).

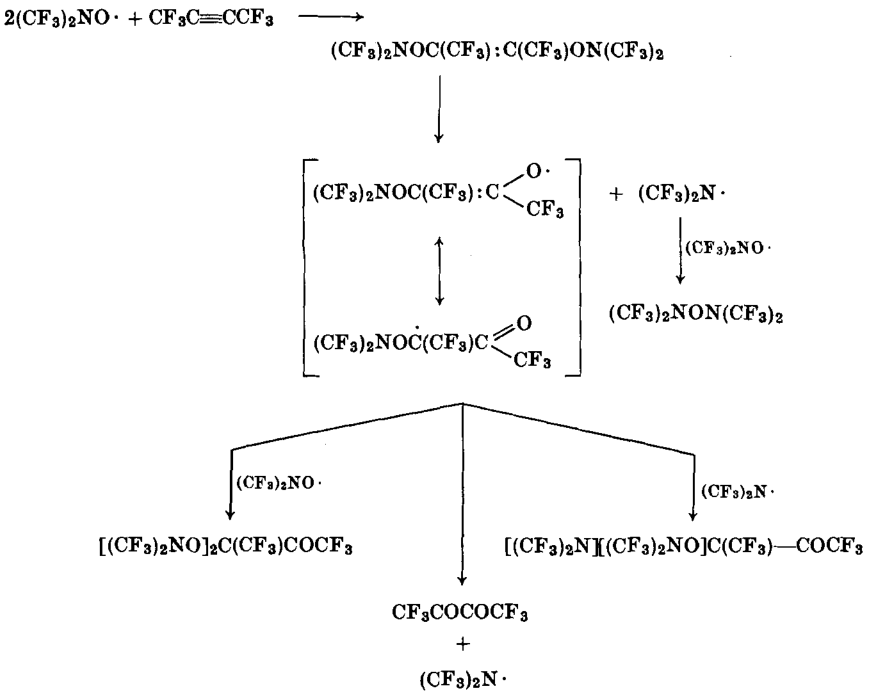
Reactions with acetylene and a number of substituted acetylenes give a wide range of products which are listed in Table IX. A plausible

TABLE XIX

REACTIONS OF $(CF_3)_2NO$ WITH SUBSTITUTED ACETYLENES (*105*)

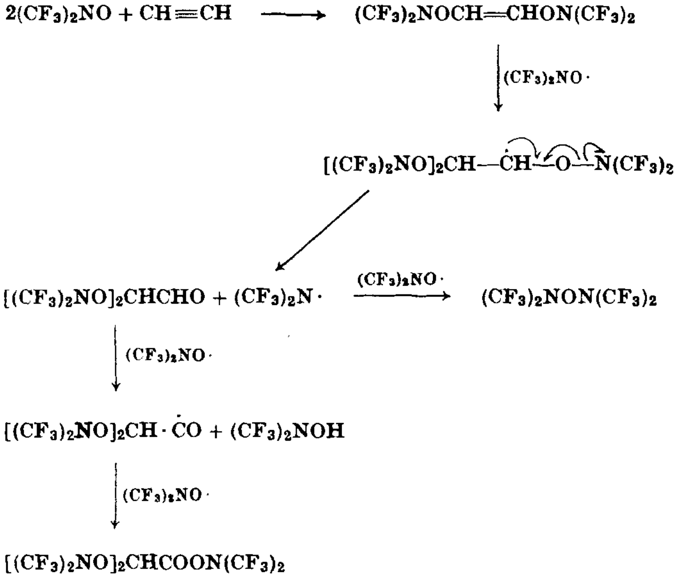
Acetylene	Conditions	Products
$CF_3C\equiv CCF_3$	85°/48 hr	$CF_3COCOCF_3$, $[(CF_3)_2NO]_2C(CF_3)COCF_3$, $[(CF_3)_2N][(CF_3)_2NO]C(CF_3)COCF_3$, $(CF_3)_2NON(CF_3)_2$
$C_6F_5C\equiv CC_6F_5$	—	$C_6F_5COCOC_6F_5$, $(CF_3)_2NON(CF_3)_2$
$CF_3C\equiv CF$	—	CF_3COCOF, $(CF_3)_2NON(CF_3)_2$, $[(CF_3)_2NO]_2C(CF_3)COF$, $[(CF_3)_2N][(CF_3)_2NO]C(CF_3)COF$
$CH\equiv CH$	—	$(CF_3)_2NOH$, $(CF_3)_2NON(CF_3)_2$, $[(CF_3)_2NO]_2CHCOON(CF_3)_2$
$CF_3C\equiv CH$	—	$CF_3COCH[ON(CF_3)_2]_2$, $CF_3COCH[N(CF_3)_2][ON(CF_3)_2]$

mechanism is suggested to account for the products obtained with hexafluorobut-2-yne, as shown below (*105*).



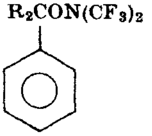
The formation of perfluorobiacetyl $R_F\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}R'_F$ occurs with a number of substituted acetylenes, $R_FC{:}CR'_F$ (R_F = a fluorocarbon group; $R'_F = F$ or R_F).

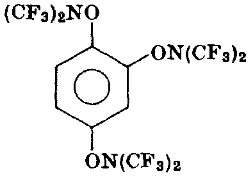
The reactions with acetylene, CH≡CH, are outlined in the following course.



2. *Substitution Reactions*

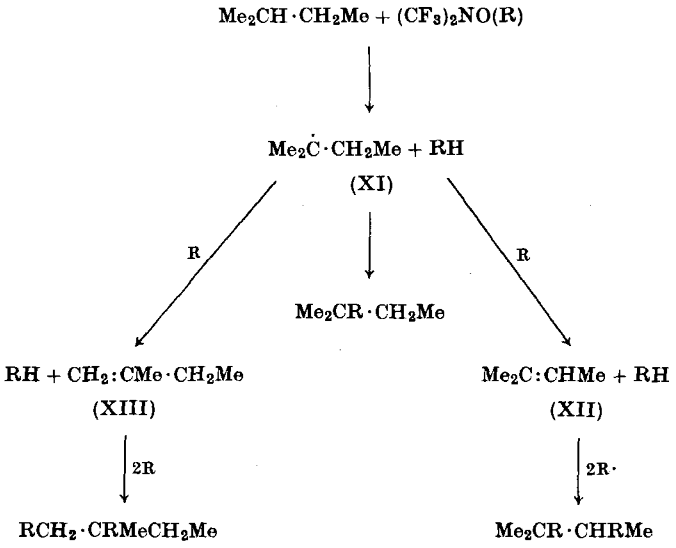
Bis(trifluoromethyl)nitroxyl is rather unusual when compared to other nitroxyls containing hydrocarbon groups in that it behaves as an excellent hydrogen abstractor and a scavenger. As such, it facilitates substitution reactions with organic compounds. The reaction of the nitroxyl with chloroform affords $(CF_3)_2NOCCl_3$ (*87*). With $PhCHR_2$ ($R = H, CH_3$), $PhCR_2ON(CF_3)_2$ is produced (*101*). The attack is at the benzylic carbon, and the benzene nucleus remains unscathed. However, with benzene alone 1,2,4-tri[bis(trifluoromethyl)nitroxy] benzene is





formed, which on alkaline hydrolysis gives 1,2,4-trihydroxybenzene from methanol (*111*, *120*).

Alkanes. Although methane resists attack by bis(trifluoromethyl)-nitroxyl, other alkanes undergo essentially hydrogen abstraction followed by an intermediate scavenging of the radical generated by the nitroxyl (*103*). The ease of hydrogen abstraction increases in the order tertiary hydrogen > secondary hydrogen > primary hydrogen, as illustrated by its reactions with isopentane.



The tertiary hydrogen is postulated to be attacked initially, followed by abstraction of hydrogen atoms at positions beta to the tertiary carbon of the intermediate (XI), leading to the formation of intermediate olefins (XII) and (XIII). Their respective ratio (1:3.2) is governed by both the statistical probability of encounter of the nitroxyl with a β-hydrogen (secondary H: tertiary H is 1:3) and the energy requirements for the respective abstractions.

The formation of the carbonyl derivatives is always accompanied by perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane). Thus, the reactions with ethane and neopentane give $MeCO_2N(CF_3)_2$ and $Me_3CCO_2N(CF_3)_2$, respectively, apart from the diazapentane.

In the reactions with a series of alkanes (Table XX), it is noted that the molar ratio of di- to monosubstituted product increases as the number of C–H bonds adjacent to the site of the initial hydrogen abstraction increases.

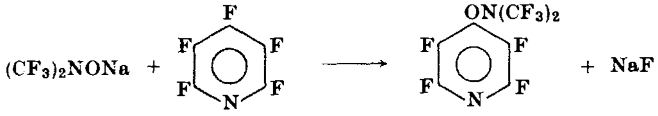
TABLE XX

REACTIONS OF $(CF_3)_2NO$ WITH ALKANES

Alkane	Radical	No. of C–H	Molar ratio: $\frac{1,2\text{-}[(CF_3)_2NO]_2R^2}{(CF_3)_2NOR^1}$
C_2H_6	CH_3CH_2	3	0.15
C_3H_8	$(CH_3)_2CH$	6	0.4
t-C_4H_{10}	$(CH_3)_3C$	9	1.3
i-C_5H_{12}	$(CH_3)_2CCH_2CH_3$	8	1.2

3. Reactions with Sodium, Mercury, and Cesium Derivatives

Haszeldine *et al.* have shown that sodium bis(trifluoromethyl)-nitroxide reacts in the normal way with CH_3I, COF_2, and CF_3COCl to give $(CF_3)_2NOCH_3$, $[(CF_3)_2NO]_2CO$, and $(CF_3)_2NOCOCF_3$, respectively. With perfluoropyridine, however, substitution at the 4-fluorine is observed (*106*).



Mercury di[bis(trifluoromethyl)nitroxide] reacts in a similar manner with CH_3I and $COCl_2$ (*107*).

Acyl or allyl chlorides react readily with bis(trifluoromethyl)-hydroxylamine in the presence of cesium fluoride at room temperature to give good yields of the respective nitroxy derivatives. The use of tetramethyl sulfone as a solvent is necessary in the reaction with allyl chloride (*108*).

$$CH_2{=}CHCH_2Cl + (CF_3)_2NOH + CsF \xrightarrow[\text{10 hr}]{\text{room temp.}} CH_2{=}CHCH_2ON(CF_3)_2 + HCl$$

The reaction of the solid adduct, $[(CF_3)_2NOH]_n \cdot CsF$, with halides such as COX_2 or RCOX can be formulated thus (*109*).

$$[(CF_3)_2NOH]_nCsF + nR_fCOX \rightarrow n(CF_3)_2NOCOR_f + CsF \cdot nHX$$

4. *Polymerization*

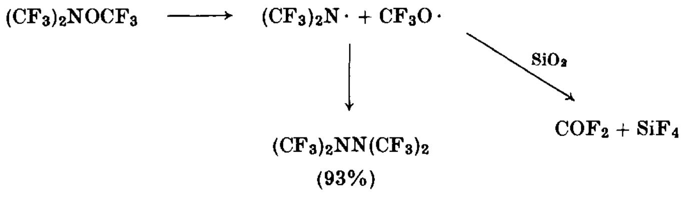
When perfluorobutadiene is left to stand for 1 week at 60° in the presence of bis(trifluoromethyl)nitroxyl, it undergoes homopolymerization to yield 3–5% poly(perfluorobutadiene). Infrared evidence indicates the existence of a copolymer of perfluoro-1,4- and perfluoro-1,2-butadiene. The copolymer structure was further confirmed by comparison of the ^{19}F NMR spectrum of perfluorobutadiene with that of poly(perfluorobutadiene) in hexafluorobenzene, which indicated that the end part $CF{=}CF_2$ formed by 1,2-addition of polymerization gives a signal at a lower field than that of $CF{=}CF$ formed by 1,4-polymerization (*110*).

5. *Photolysis*

a. $(CF_3)_2NO$. Photolysis of bis(trifluoromethyl)nitroxyl at ordinary temperature and pressure causes a 60% conversion to the stable dimer, $(CF_3)_2NOON(CF_3)_2$ (*111*), and smaller amounts of other products such as $(CF_3)_2NONO$ and $(CF_3)_2NOCF_3$ are also formed. The reactions can be rationalized as follows.

$$\begin{aligned}
(CF_3)_2NO\cdot + \cdot ON(CF_3)_2 &\xrightarrow{h\nu} (CF_3)_2NOON(CF_3)_2\\
(CF_3)_2NO\cdot &\xrightarrow{h\nu} 2CF_3\cdot + NO\\
(CF_3)_2NO\cdot + NO &\longrightarrow (CF_3)_2NONO\\
(CF_3)_2NO\cdot + CF_3\cdot &\longrightarrow (CF_3)_2NOCF_3
\end{aligned}$$

b. $(CF_3)_2NOCF_3$. Prolonged irradiation (Hanovia S500 lamp) of tris(trifluoromethyl)hydroxylamine gives perfluorotetramethylhydrazine in high yield and the breakdown products can be accounted for by the following equations (*112*).



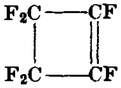
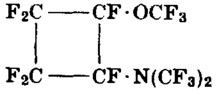
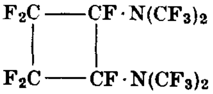
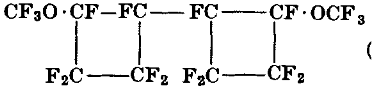
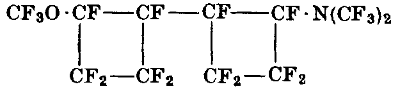
$$\begin{tikzcd}
(CF_3)_2NOCF_3 \arrow[r] & (CF_3)_2N\cdot + CF_3O\cdot \arrow[d] \arrow[dr, "SiO_2"] & \\
& \begin{matrix}(CF_3)_2NN(CF_3)_2\\(93\%)\end{matrix} & COF_2 + SiF_4
\end{tikzcd}$$

Decomposition proceeds by cleavage of the relatively weak N–O bond.

Photolysis of tris(trifluoromethyl)hydroxylamine in the presence of several unsaturated compounds produces products, which are summarized in Table XXI.

TABLE XXI

PHOTOLYTIC INTERACTIONS OF $(CF_3)_2NOCF_3$ WITH UNSATURATED ORGANIC COMPOUNDS (*14*)

Ratio of $(CF_3)_2NOCF_3$ to unsaturated compounds	Time (days)	Products (% yield)
 1:1 ratio	30	 (*a*) (26)  (*b*)  (*c*) (30)  (*d*)
2:1 ratio	30	(*a*) (45); (*b*) (16); (*c*) (21); $(CF_3)_2NN(CF_3)_2$ (7); (*d*) (5)
$CF_3CF{:}CFCF_3$ 1:1 ratio	30	$(CF_3)_2NN(CF_3)_2$ (43)
$CF_3N{:}CF_2$ 1:1 ratio	35	$(CF_3)_2NCF_2N(CF_3)OCF_3$ (10), $(CF_3)_2NN(CF_3)_2$ (55), $(CF_3)_2NN(CF_3)CF_2OCF_3$ (4), $(CF_3)_3N$ (37)

6. *Pyrolysis*

a. $(CF_3)_2NO$. Bis(trifluoromethyl)nitroxyl is stable at temperatures up to 200° (111). A large part of the compound decomposes at 350° with a contact time of 2 min. The pyrolysis products are perfluorodiazomethane, tris(trifluoromethyl)hydroxylamine, and nitrogen oxides. The reactions can be described by the following equations (*111*).

$$(CF_3)_2NO\cdot \rightarrow 2CF_3\cdot + NO$$

$$2(CF_3)_2NO\cdot \rightarrow (CF_3)_2N\cdot + NO_2 + 2CF_3\cdot$$

$$(CF_3)_2N\cdot \rightarrow CF_3N{=}NCF_3 + 2CF_3\cdot$$

$$(CF_3)_2NO\cdot + CF_3\cdot \rightarrow (CF_3)_2NOCF_3$$

Hot iron deoxyfluorinates bis(trifluoromethyl)nitroxyl to perfluoro-2-azapropene (*101*).

b. $(CF_3)_2NOCOCF_3$. Pyrolysis in a platinum-lined autoclave at 220° yields *tris*(trifluoromethyl)amine (33%), tris(trifluoromethyl)hydroxylamine (30%), carbon dioxide, and carbon monoxide (*106*).

c. $(CF_3)_2NOCF_3$. Pyrolysis is essentially complete at 775° to give approximately equimolar amounts of perfluoro-2-azapropene (39%) and *N*-fluorobis(trifluoromethyl)amine (35%), together with carbonyl fluoride and silicon tetrafluoride (*112*), according to the equations,

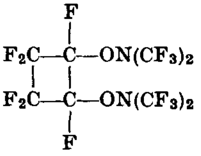
$$(CF_3)_2NOCF_3 \rightarrow (CF_3)_2N\cdot + CF_3O\cdot$$
$$2(CF_3)_2N\cdot \rightarrow (CF_3)_2NF + CF_3N{=}CF_2$$

The bis(trifluoromethyl)amino radical disproportionates under these conditions rather than dimerizes as in the photochemical reaction. Small quantities of perfluoromethane and perfluoroethane are also formed. *N*-Fluorobis(trifluoromethyl)amine is itself only 22% decomposed under these conditions.

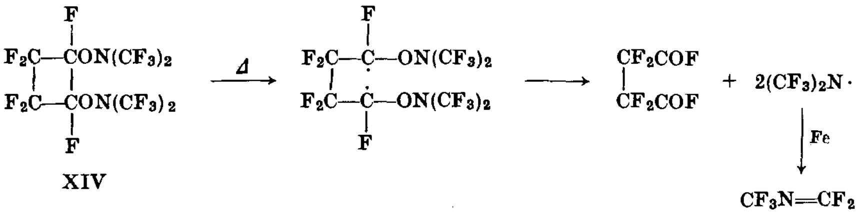
$$(CF_3)_2NF \longrightarrow (CF_3)_2N\cdot \xrightarrow{SiO_2} \underset{(77\%\ \text{yield})}{CF_3N{:}CF_2} + SiF_4$$

$$CF_3N{:}CF_2 \xrightarrow{SiO_2} \underset{(9\%)}{CF_3NCO} + SiF_4$$

d.

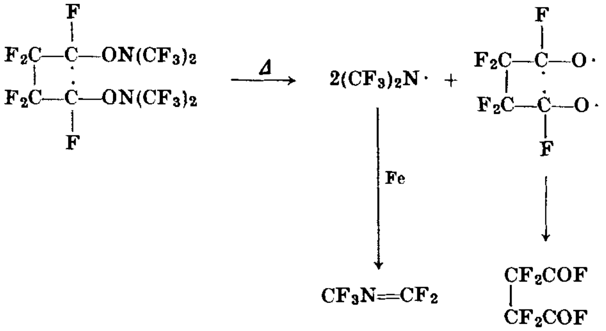


It has been reported that the adducts from the nitroxyl and ethylene, tetrafluoroethylene and perfluoropropene undergo no change at all when heated at 210° for 3 hr with hot iron powder. Under these conditions, however, the adduct from perfluorocyclobutene does not undergo deoxygenation, but breaks down to give high yields of perfluoromethylenemethylamine and perfluorosuccinyl fluoride (*101*). Plausible mechanisms proposed could be:



XIV

and/or



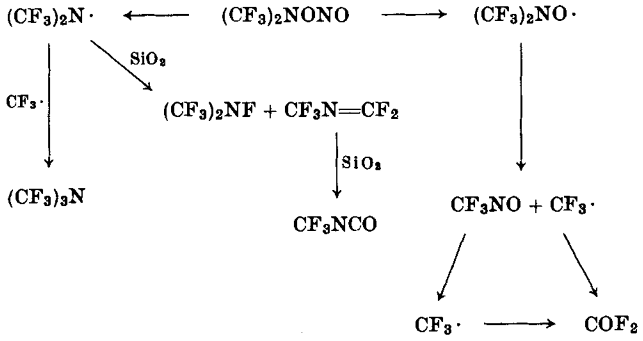
e. $(CF_3)_2NONO$. At 80°, *o*-nitrosobis(trifluoromethyl)hydroxylamine is converted to $(CF_3)_2NNO_2$, $(CF_3)_2NOCF_3$, CF_3NCO, CF_3NO_2, and $(CF_3)_2NN(CF_3)_2$. A free radical mechanism is suggested for the rearrangement of the *o*-nitroso compound into the *N*-nitro compound (*82*).

$$(CF_3)_2NONO \rightleftharpoons (CF_3)_2N\cdot + NO_2 \rightarrow (CF_3)_2NNO_2$$

Other products which are formed have been accounted for by the following reaction scheme.

$$\begin{tikzcd}
(CF_3)_2N\cdot \arrow[r] & (CF_3)_2NN(CF_3)_2 & & & & \\
(CF_3)_2N\cdot \arrow[r, "SiO_2"] & CF_3N{=}CF_2 \arrow[r, "SiO_2"] & CF_3NCO & & & \\
(CF_3)_2NONO \arrow[r] & NO + (CF_3)_2NO\cdot \arrow[r] \arrow[d, "CF_3\cdot"] & CF_3NO \arrow[d, "NO_2"] & + & CF_3\cdot \arrow[r, "NO_2"] \arrow[d, "SiO_2"] & CF_3NO_2 \\
 & (CF_3)_2NOCF_3 & CF_3NO_2 & & COF_2 &
\end{tikzcd}$$

Pyrolytic breakdown of *o*-nitrosobis(trifluoromethyl)hydroxylamine at 730° can be interpreted by assuming that intermediates such as bis(trifluoromethyl)amino and bis(trifluoromethyl)nitroxyl radicals are formed, presumably by the initial cleavage of N–O and NO–N bonds (*112*). The formation of the products can be explained by the following scheme.



E. INORGANIC DERIVATIVES

1. *Group IIIB Compounds*

Tri[bis(trifluoromethyl)nitroxy]boron can be formed either by reacting boron trichloride with di(bistrifluoromethylnitroxy)mercury(II) or by reacting boron tribromide with bis(trifluoromethyl)hydroxylamine (*113*, *114*).

$$3[(CF_3)_2NO]_2Hg + 2BCl_3 \rightarrow 2[(CF_3)_2NO]_3B + 3HgCl_2$$
$$3(CF_3)_2NOH + BBr_3 \rightarrow [(CF_3)_2NO]_3B + 3HBr$$

It reacts with ammonia or tertiary amines at 25° or below to give thermally stable adducts in high yields.

$$[(CF_3)_2NO]_3B + \text{Base} \rightarrow \text{Base}\cdot B[ON(CF_3)_2]_3$$
$$\text{Base} = (CH_3)_3N,\ C_5H_5N,\ \text{or } NH_3$$

With dimethylamine, a typical Lewis acid–base adduct does not form, but rather $(CF_3)_2NOH$ and dimethylaminodi[bis(trifluoromethyl)-nitroxy]boron are produced quantitatively.

$$B[ON(CF_3)_2]_3 + (CH_3)_2NH \rightarrow (CH_3)_2NB[ON(CF_3)_2]_2 + (CF_3)_2NOH$$

Hydrolysis of tri[bis(trifluoromethyl)nitroxy]boron with water is complete, giving boric acid and bis(trifluoromethyl)hydroxylamine.

2. *Group IVB Compounds*

Silicon derivatives can be readily obtained by reacting the nitroxyl with the appropriate silanes containing at least one Si–H bond. This reaction is dependent on both the hydrogen-abstracting and radical-scavenging properties of the nitroxyl (*87*, *115*).

$$(CF_3)_2NO\cdot + (CH_3)_nCl_{3-n}SiH \rightarrow (CH_3)_nCl_{3-n}Si\cdot + (CF_3)_2NOH$$
$$(CF_3)_2NO\cdot + (CH_3)_nCl_{3-n}Si\cdot \rightarrow (CH_3)_nCl_{3-n}SiON(CF_3)_2$$
$$n = 0, 1, 2, 3$$

Sodium bis(trifluoromethyl)nitroxide has been reported to give high yields of $(CH_3)_3SiON(CF_3)_2$ with trimethylchlorosilane (*106*). Di[bis(trifluoromethyl)nitroxy]mercury has been utilized for the preparation of a series of silicon and germanium derivatives. Its unusual behavior is that it can act as both a halogen and a hydrogen abstractor (*113*, *116*).

$$2[(CF_3)_2NO]_2Hg + GeCl_4 \rightarrow Ge[ON(CF_3)_2]_4 + 2HgCl_2$$
$$4[(CF_3)_2NO]_2Hg + GeH_4 \rightarrow Ge[ON(CF_3)_2]_4 + 4(CF_3)_2NOH + 4\,Hg$$

In situations where both the halogen and a hydrogen are directly bonded to silicon, the reactions are less specific. Both the bonds are equally susceptible to cleavage. For example,

$$7[(CF_3)_2NO]_2Hg + 2SiH_3Br \rightarrow 2[(CF_3)_2NO]_4Si + 6(CF_3)_2NOH + HgBr_2 + 6Hg$$

The reaction between trimethylstannane and the nitroxyl is violent and is accompanied by a flash, depositing a black residue (*115*).

3. *Group V B Compounds*

Bis(trifluoromethyl)nitroxyl reacts instantly with nitric oxide to give a quantitative yield of the corresponding *O*-nitroso derivative (*86*, *104*).

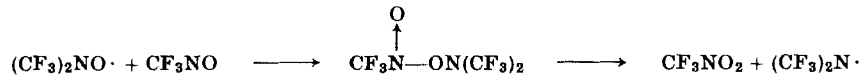
$$(CF_3)_2NO\cdot + NO \rightarrow (CF_3)_2NONO$$

With nitrogen dioxide, bis(trifluoromethyl)nitroxyl is reported to form a compound believed to be the oxygen-substituted adduct, *O*-nitrobis(trifluoromethyl)hydroxylamine.

O-Nitrosobis(trifluoromethyl)hydroxylamine is reported to be formed in the reaction between bis(trifluoromethyl)nitroxyl and trifluoronitrosomethane (*101*). In this case, apparently, a radical reaction occurs in which trifluoromethyl radicals are formed, which then attack trifluoronitrosomethane to afford the nitroxyl.

$$(CF_3)_2NO + CF_3NO \rightarrow (CF_3)_2NONO + \cdot CF_3$$
$$CF_3NO + \cdot CF_3 \rightarrow (CF_3)_2NO\cdot$$

Formation of perfluoro(2,4-dimethyl-3-oxa-2,4-diazopentane) is also reported to occur from the same reaction, which can similarly be explained by the following radical sequence.



$$(CF_3)_2NO\cdot + CF_3NO \longrightarrow CF_3\overset{\overset{O}{\uparrow}}{N}\text{—}ON(CF_3)_2 \longrightarrow CF_3NO_2 + (CF_3)_2N\cdot$$

$$(CF_3)_2NO\cdot + (CF_3)_2N\cdot \longrightarrow (CF_3)_2NON(CF_3)_2$$

Bis(trifluoromethyl)nitroxyl reacts vigorously with phosphorus trichloride at room temperature to yield two products, namely, $(CF_3)_2NOPCl_4$ and $(CF_3)_2NOPCl_2$ (*111*). The former can also be obtained from phosphorus pentachloride and *o*-nitrosobis(trifluoromethyl)-hydroxylamine, according to the equation,

$$(CF_3)_2NONO + PCl_5 \rightarrow (CF_3)_2NOPCl_4 + NOCl$$

With phosphorus trifluoride, no phosphorus derivatives of the nitroxyl are produced. Instead, the reaction gives a mixture of products, namely, $(CF_3)_2NOON(CF_3)_2$, POF_3, and $CF_3N{=}CF_2$. A clearer picture emerges in the reactions with trifluoromethyl-substituted phosphines. Thus, a series of phosphines $(CF_3)_2PX$ ($X = CF_3$, F, Cl, and Br) undergoes oxidative addition reactions with bis(trifluoromethyl)nitroxyl to afford the corresponding phosphoranes (*117*).

$$(CF_3)_2PX + 2(CF_3)_2NO\cdot \rightarrow [(CF_3)_2NO]_2P(CF_3)_2X$$

Of all these compounds, only the bromophosphorane appears to be unstable. Bromine is given off on long standing. The reaction with an equimolar quantity of bis(trifluoromethyl)iodophosphine proceeds differently, giving bis(trifluoromethyl)nitroxybis(trifluoromethyl)phosphine and iodine.

$$(CF_3)_2PI + (CF_3)_2NO\cdot \rightarrow (CF_3)_2NOP(CF_3)_2 + \tfrac{1}{2}I_2$$

The phosphine can also be obtained from the mercurial.

$$2(CF_3)_2PI + [(CF_3)_2NO]_2Hg \rightarrow 2(CF_3)_2PON(CF_3)_2 + HgI_2$$

The mercurial has certainly been a good starting point to obtain other phosphorus derivatives such as $[(CF_3)_2NO]_3PO$ and $[(CF_3)_2NO]_3PS$. An interesting synthetic approach is to utilize both the hydrogen-abstracting and hydrogen-scavenging properties of the nitroxyl to obtain both the phosphine and the phosphorane derivatives. For example,

$$\begin{tikzcd}
(CF_3)_2PH + 2(CF_3)_2NO\cdot \arrow[r] & (CF_3)_2P\cdot + (CF_3)_2NOH \arrow[d, "(CF_3)_2NO"] \\
& (CF_3)_2NOP(CF_3)_2 \arrow[d, "2(CF_3)_2NO"] \\
& [(CF_3)_2NO]_3P(CF_3)_2
\end{tikzcd}$$

With bis(trifluoromethyl)arsine, only the trivalent arsenic derivative is afforded, in almost quantitative yield.

$$\begin{tikzcd}
(CF_3)_2AsH + (CF_3)_2NO\cdot \arrow[r] & (CF_3)_2As\cdot + (CF_3)_2NOH \arrow[d, "(CF_3)_2NO\cdot"] \\
& (CF_3)_2NOAs(CF_3)_2
\end{tikzcd}$$

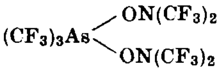
The above reactions indicate that the rate of scavenging of $(CF_3)_2P$ and $(CF_3)_2As$ radicals by the nitroxyl is faster than the rate of coupling.

A series of reactions of tris(trifluoromethyl)arsine with the nitroxyl have established that further stepwise substitution reactions lead to di- and tri[bis(trifluoromethyl)nitroxy]arsenic derivatives, and the overall reactions are represented by the following equations.

$$\begin{tikzcd}
& (CF_3)_2NOAs(CF_3)_2 + (CF_3)_2NOCF_3 \arrow[d, "\text{room temp.}"', "(CF_3)_2NO\cdot"] \\
(CF_3)_2NO\cdot + (CF_3)_3As \arrow[ur, "\text{room temp.}", "(2/1)"'] \arrow[r, "\text{room temp.}", "(4/1)"'] \arrow[dr, "70^\circ", "(6/1)"'] & {[(CF_3)_2NO]_2AsCF_3 + (CF_3)_2NOCF_3} \arrow[d, "\text{room temp.}"', "(CF_3)_2NO\cdot"] \\
& {[(CF_3)_2NO]_3As + (CF_3)_2NOCF_3}
\end{tikzcd}$$

Two possible mechanisms can be proposed for the radical exchange reactions. First, a pentacovalent arsenic derivative can be postulated.

$$(CF_3)_3As + 2(CF_3)_2NO\cdot \longrightarrow$$



$$(CF_3)_3As\begin{cases} ON(CF_3)_2 \\ ON(CF_3)_2 \end{cases}$$

(XV)

Second, the reaction could also proceed by addition of one mole of the nitroxyl to give a radical intermediate (XVI), followed by the elimination of a trifluoromethyl radical. The formation of only tris(trifluoromethyl)-hydroxylamine instead of hexafluoroethane can be attributed to the effective scavenging ability of the nitroxyl. The reactions can be represented as follows.

$$(CF_3)_2NO\cdot + (CF_3)_3As \rightarrow (CF_3)_2NO\dot{A}s(CF_3)_3(XVI) \rightarrow (CF_3)_2NOAs(CF_3)_2 + \cdot CF_3$$

$$(CF_3)_2NO\cdot + \cdot CF_3 \rightarrow (CF_3)_2NOCF_3$$

It is likely that the reactions proceed by both mechanisms via a pentacovalent and an arsenic radical intermediate (XVI).

Tri[bis(trifluoromethyl)nitroxy]arsine can also be prepared in 76% yield by the reaction of the nitroxyl with arsenic metal. Except for this compound, both the mono- and the di[bis(trifluoromethyl)nitroxy] derivatives are liquids. They are all susceptible to attack by moisture. Hydrolysis of the compounds $(CF_3)_2AsON(CF_3)_2$ and $CF_3As[ON(CF_3)_2]_2$ by 20% sodium hydroxide at 110° cleaves the CF_3–As bond to give a quantitative yield of trifluoromethane, which can be used to provide additional confirmation of the composition of the compounds.

All the arsenic derivatives react readily with hydrogen chloride, cleaving the As–O bonds.

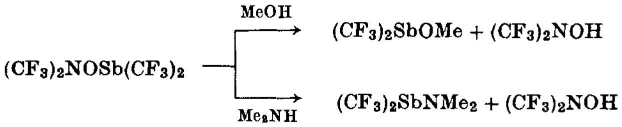
$$[(CF_3)_2NO]_nAs(CF_3)_{3-n} + nHCl \rightarrow (CF_3)_{3-n}AsCl_n + n(CF_3)_2NOH$$

Arsenic trichloride does not react with the radical even at temperatures up to 100°C, but in the presence of sufficient iodine to convert all the chlorine into ICl, it was converted rapidly into $[(CF_3)_2NO]_2AsCl$. The influence of stoichiometric amounts of iodine in promoting the reaction of the radical with these chlorides may be due to its combination with free chlorine, which is known to react with $[(CF_3)_2NO]_3As$ to reform $AsCl_3$.

The reaction of bis(trifluoromethyl)nitroxyl with tris(trifluoromethyl)stibine at room temperature gives an intractable white solid. Carried out at −40°C in a 2:1 ratio, bis(trifluoromethyl)nitroxybis(trifluoromethyl)stibine (XVII) and tris(trifluoromethyl)hydroxylamine are formed, as shown by the following equation (*118*).

$$(CF_3)_2NO + (CF_3)_3Sb \rightarrow (CF_3)_2NOSb(CF_3)_2 + (CF_3)_2NOCF_3$$

Compound (XVII) releases bis(trifluoromethyl)hydroxylamine and bis(trifluoromethyl)chlorostibine easily with hydrogen chloride. With dimethylamine and methanol, the reactions proceed in a similar manner.



$$(CF_3)_2NOSb(CF_3)_2 \xrightarrow{MeOH} (CF_3)_2SbOMe + (CF_3)_2NOH$$

$$(CF_3)_2NOSb(CF_3)_2 \xrightarrow[Me_2NH]{} (CF_3)_2SbNMe_2 + (CF_3)_2NOH$$

4. Group VIB Compounds

The reactions of bis(trifluoromethyl)hydroxylamine with some halides of sulfur in the presence of cesium fluoride give stable sulfur derivatives of the general formula $(CF_3)_2NOX$, where X represents SO_2F, $SO_3N(CF_3)_2$, $S(O)ON(CF_3)_2$, $SON(CF_3)_2$, $S(O)F$, and $SSON(CF_3)_2$ (*114*) (see Table XXII).

TABLE XXII

REACTIONS OF $(CF_3)_2NOH$ IN THE PRESENCE OF CsF

Reactants	Temp. (°C)/hr	Products
SO_2F_2	25/1	$(CF_3)_2NOSO_2F$, $[(CF_3)_2NO]_2SO_2$
SOF_2	Room temp./4	$[(CF_3)_2NO]_2SO$
	−100/0.33	$(CF_3)_2NOSOF$, $[(CF_3)_2NO]_2SO$, SOF_2
S_2Cl_2	−20/18	$[(CF_3)_2NO]_2S_2$, $[(CF_3)_2NO]_2S$, $[(CF_3)_2N]_2S$
SCl_2	−20/18	$[(CF_3)_2NO]_2S$
SF_4	—	$[(CF_3)_2N]_2O$, $(CF_3)_2NOS(O)F$, SOF_2
CF_3OSO_2F	0/2	$[(CF_3)_2NO]_2CO$, COF_2, SO_2F_2, $(CF_3)_2NOSO_2F$, $[(CF_3)_2NO]_2SO_2$

Liquid bis(trifluoromethyl)nitroxyl converts tetrasulfur tetranitride quantitatively at room temperature into a stable, white crystalline solid, tetrathiazyl tetra[bis(trifluoromethyl)nitroxide], $[NSON(CF_3)_2]_4$ (*60, 60a, 60b*) (Fig. 3). It is also formed by reacting the nitroxyl with either $N_4S_4H_4$ or $N_3S_3Cl_3$ at room temperature. The tetramer is not wetted by water and is not attacked at room temperature by gaseous or concentrated hydrochloric or nitric acid. Complete breakdown occurs at 60°

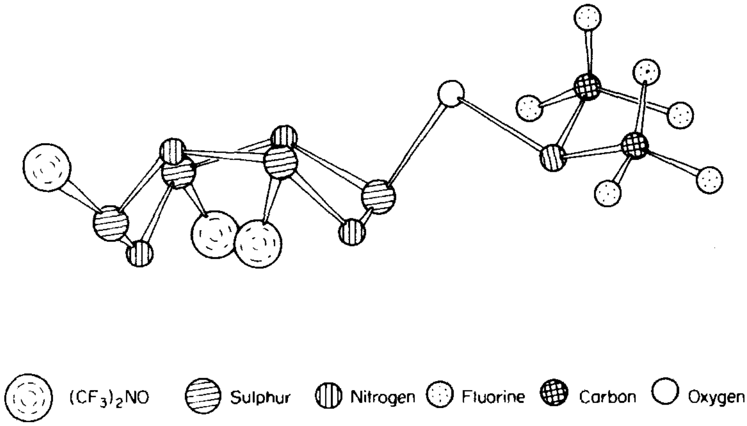


FIG. 3. Tetrathiazyl tetra[bis(trifluoromethyl)nitroxide], showing one of the bis(trifluoromethyl)nitroxy substituents.

with 10% aqueous sodium hydroxide. A complex decomposition occurs at 60°–80° *in vacuo*, and about 30% of bis(trifluoromethyl)nitroxyl is retrieved.

Thiazyl fluoride, NSF, reacts with di[bis(trifluoromethyl)nitroxy]-mercury to afford thiazyl bis(trifluoromethyl)nitroxide, $NSON(CF_3)_2$, in good yield. It undergoes spontaneous polymerization to give the trimer trithiazyl tri[bis(trifluoromethyl)nitroxide], $[NSON(CF_3)_2]_3$. Unlike the tetramer, both the monomer and trimer are readily hydrolyzed and they react with hydrogen chloride to form $(CF_3)_2NOH$ and $N_3S_3Cl_3$. The greater reactivity of the trimer has been attributed to its geometry resembling that of $N_3S_3Cl_3$, in which all the halogen atoms are on the same side of the N_3S_3 ring (*60*, *69*).

The crystal structure of the tetramer shows that the geometry of the $N_4S_4O_4$ moiety is very similar to that reported for $N_4S_4F_4$ (*78*), the parameters being given in Table XXIII.

TABLE XXIII

COMPARING PARAMETERS OF ISOMERIC $(NSOR)_4$

Compound	Bond length in the ring (Å)		NSN (°)	SNS (°)	NSO (°)
$[NSON(CF_3)_2]_4$	1.62	1.56	111.8	123.4	107.9 88.9
$(NSOF)_4$	1.66	1.54	111.7	123.9	106.2 91.5

5. *Metalation*

So far, bis(trifluoromethyl)nitroxyl is known to react directly with tin (*85*), lead (*85*), arsenic (*87*), selenium, tellurium (*79*), sodium (*106*), potassium (*119*), and mercury (*107*) and the metal derivatives can be formulated as shown.

$[(CF_3)_2NO]_2M$ $[(CF_3)_2NO]_4M'$ $[(CF_3)_2NO]_2Hg$ (?) $[(CF_3)_2NO]_3As$ $(CF_3)_2NOM''$

$M = Sn, Pb$ $M' = Se, Te$ $M'' = Na, K$

The sodium derivative can also be prepared from sodium iodide and the nitroxyl. Cesium iodide, however, takes up two moles of the radical to form a light-sensitive buff-colored solid, $CsI[ON(CF_3)_2]_2$, which is analogous to $CsICl_2$ (*116*).

The derivatives of sodium, tin, and lead are crystalline, ionic solids, whereas the arsenic, selenium, and tellurium derivatives are molecular compounds. The mercurial is believed to be polymeric, involving tetracoordination. The sodium and mercurial derivatives are important intermediates in metathetical reactions, and their uses have been explained in previous sections.

Sodium bis(trifluoromethyl)nitroxide can also be prepared by treating a solution of *N*,*N*-bis(trifluoromethyl)hydroxylamine in tetrahydrofuran with an equimolar amount of powdered sodium hydroxide in the presence of Linde molecular sieve type 4H at 0°–20° (*106*). Evaporation of the solvent leaves behind a white solid which is difficult to free from tetrahydrofuran and which reacts rapidly with water, regenerating *N*,*N*-bis(trifluoromethyl)hydroxylamine and sodium hydroxide.

Sodium bis(trifluoromethyl)nitroxide if formed by passing gaseous bis(trifluoromethyl)hydroxylamine over sodium wire at 20°/50 mm is contaminated by sodium fluoride and this method can lead to violent explosion. However, no explosion occurs if excess hydroxylamine is reacted with a sodium mirror (*106*).

F. *N*,*N*-BIS(TRIFLUOROMETHYL)HYDROXYLAMINE

N,*N*-Bis(trifluoromethyl)hydroxylamine, the first member of fluorocarbon hydroxylamine series, was discovered by Haszeldine and Mattinson in 1957 by treating *o*-nitrosobis(trifluoromethyl)hydroxylamine with hydrochloric acid, methanol, or 10% sodium hydroxide (*15*). A later method reported by Makarov *et al.* in 1965, in which trifluoronitrosomethane and ammonia are reacted together (*85*), is a better one.

N,*N*-Bis(trifluoromethyl)hydroxylamine is a very weak acid with a dissociation constant of 1.5×10^{-9} in aqueous solution (*120*). It forms a

TABLE XXIV

FORMATION AND PHYSICAL DATA OF BIS(TRIFLUOROMETHYL)-HYDROXYLAMINE ADDUCTS (*121*)

Adduct	Physical state	M.p. (°C)	Yield (%)
$(CF_3)_2NOH, NH_3$	Liquid	—	94
$(CF_3)_2NOH \cdot MeNH_2$	Solid	28.0–28.5	~99
$[(CF_3)_2NOH \cdot Me_2NH$	Solid	35.0	~98
$[(CF_3)_2NOH]_2Me_3N$	Solid	28.0–28.5	98
$(CF_3)_2NOH \cdot EtNH_2$	Liquid	—	>99
$[(CF_3)_2NOH]_2Et_2NH$	Solid	41.5–42.5	~98
$(CF_3)_2NOH \cdot Et_3N$	Liquid	—	~93

well-defined 1:1 adduct with a molecule of water, and the latter can be readily removed with phosphorus pentoxide (*85*). With a variety of simple organic amines, it forms a series of weakly associated adducts which are liquids or low melting, sublimable, crystalline solids at room temperature (Table XXIV). These adducts are partially dissociated in the gas phase (*121*).

At −183°, *N*,*N*-bis(trifluoromethyl)hydroxylamine forms a solid adduct with cesium or potassium fluoride. At room temperature, the potassium fluoride adduct has an equilibrium vapor pressure of 4 mm. For the cesium fluoride adduct the value is 0.5–1 mm. The cesium fluoride adduct melts at 70°. On the basis that two moles of *N*,*N*-bis(trifluoromethyl)hydroxylamine combines with one mole of cesium fluoride the reaction probably occurs as follows.

$$n(CF_3)_2NOH + CsF \rightarrow [(CF_3)_2NOH]_nCsF$$
$$(n \leqslant 2)$$

Metathetical reactions involving cesium or potassium salts with a number of halides are discussed in previous sections.

G. TRIS(TRIFLUOROMETHYL)HYDROXYLAMINE

The formation of tris(trifluoromethyl)hydroxylamine has been reported in several instances, as summarized in Table XXV. Among the preparative methods, photolysis of a mixture of $(CF_3)_2NO$ and CF_3I or flow pyrolysis of CF_3NO at high temperatures seem to render fairly good yields. A free radical mechanism can be proposed for both reactions.

TABLE XXV

FORMATION OF $(CF_3)_2NOCF_3$

Starting material	Conditions	Yield (%)	Ref.
CF_3NO/N_2F_4	—	—	*122*
$(CF_3)_2NO$	$h\nu$/6 hr	—	*123*
CF_3NO	Flow pyrolysis at 400°/3 mm with contact time of 3 sec; or pyrolysis at 250°–300° with contact time of 1–2 min	66	*124* *125*
$(CF_3)_2NO/CF_3I$	$h\nu$/4 hr	84	*101*
$CF_3C(O)ONO$	Thermal decomposition	5	*126*
CF_3NO/AgF_2	129°	23	*126*
$CF_3NO/AgF_2/F_2$	24°	55	*126*

Tris(trifluoromethyl)hydroxylamine is stable to at least 200°C even in the presence of elemental fluorine.

Intense irradiation of tris(trifluoromethyl)hydroxylamine gives mainly $(CF_3)_2NON(CF_3)_2$, whereas weaker irradiation gives mainly $(CF_3)_2NON(CF_3)_2$ and a smaller amount of $(CF_3)_2NN(CF_3)OCF_3$. The formation of the products is rationalized in terms of free radical reactions involving an initial cleavage of the N–O bond in the hydroxylamine to give $(CF_3)_2N$ and CF_3O radicals (*33, 112*):

$$(CF_3)_2NOCF_3 \xrightarrow{h\nu} (CF_3)_2N\cdot + CF_3O\cdot$$

$$(CF_3)_2N\cdot \longrightarrow (CF_3)_2NN(CF_3)_2$$

$$(CF_3)_2N\cdot + (CF_3)_2NOCF_3 \begin{array}{l} \longrightarrow (CF_3)_2NN(CF_3)_2 + CF_3O\cdot \\ \longrightarrow (CF_3)_2NN(CF_3)(OCF_3) + CF_3\cdot \\ \longrightarrow (CF_3)_2NON(CF_3)_2 + CF_3\cdot \end{array}$$

$$CF_3O\cdot + SiO_2 \longrightarrow COF_2 + SiF_4$$

The formation of radicals such as $(CF_3)_2N\cdot$ and $CF_3O\cdot$ involving the cleavage of N–O bond is confirmed by the nature of products that are afforded as a result of the photolysis of $(CF_3)_2NOCF_3$ with several olefins and perfluoro-2-azapropene. The results of such reactions are summarized in Table XXI.

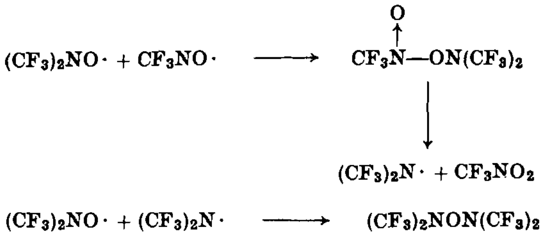
H. PERFLUORO(2,4-DIMETHYL-3-OXA-2,4-DIAZAPENTANE), $(CF_3)_2NON(CF_3)_2$

Several reactions are now known which lead to the formation of $(CF_3)_2NON(CF_3)_2$. It is formed in 73% yield by irradiating gaseous tris(trifluoromethyl)hydroxylamine (1.7 atm) with Hanovia S·500 ultraviolet lamps for 28 days (*33*). The mechanism that has been proposed involves the attack of $(CF_3)_2N\cdot$ on the oxygen of $(CF_3)_2NOCF_3$ with displacement of a CF_3 radical, leading to the formation of the compound, as illustrated below.

$$(CF_3)_2NOCF_3 \xrightarrow{h\nu} (CF_3)_2N\cdot + CF_3O\cdot$$

$$(CF_3)_2N\cdot + (CF_3)_2NOCF_3 \longrightarrow (CF_3)_2NON(CF_3)_2 + CF_3\cdot$$

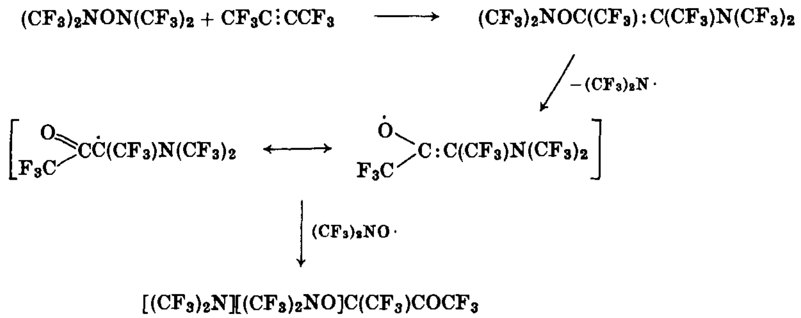
The interaction between $(CF_3)_2NO$ and CF_3NO gave a 99% conversion (*101*). The reactions of $(CF_3)_2NO$ with various substituted acetylenes also give $(CF_3)_2NON(CF_3)_2$ in yields ranging from 26–55% (*105*). The product obtained from the reaction between tin and bis(trifluoromethyl)-nitroxyl which was originally thought to be $(CF_3)_2NOON(CF_3)_2$ (*111*) is now established as $(CF_3)_2NON(CF_3)_2$ (*128*).



$$(CF_3)_2NO\cdot + CF_3NO\cdot \longrightarrow CF_3\overset{O\uparrow}{N}{-}ON(CF_3)_2 \longrightarrow (CF_3)_2N\cdot + CF_3NO_2$$

$$(CF_3)_2NO\cdot + (CF_3)_2N\cdot \longrightarrow (CF_3)_2NON(CF_3)_2$$

$(CF_3)_2NON(CF_3)_2$ undergoes reactions with perfluorobut-2-yne, and the mechanism scheme suggested is indicated below (*105*).



Its reactions with tetrafluoroethylene gives only $(CF_3)_2NOCF_2CF_2N(CF_3)_2$. Both these reactions with unsaturated perfluoroorganic compounds reflect the relative ease of cleavage of the N–O bond in $(CF_3)_2NON(CF_3)_2$.

VIII. Spectroscopic Properties

A. INFRARED SPECTRA

Infrared spectroscopy has been extensively employed to establish the presence of compounds containing bis(trifluoromethyl)amino and bis(trifluoromethyl)nitroxy groups. As such, it is an important diagnostic tool. Characteristic peaks due to the presence of these groups can be assigned as follows:

ν(C–F)	1200–1400 cm^{-1}	usually three peaks of strong to very strong intensity
δ(C–F)	705– 730 cm^{-1}	one peak of medium to strong intensity
ν(C–N)	960– 980 cm^{-1}	one peak of strong intensity
ν(N–O)	990–1070 cm^{-1}	one peak of strong intensity

The N–O stretching vibration of alkyl- or aryl-substituted nitroxyls are located in the region of 1340–1370 cm^{-1} (*1*), which is not detected at all in the spectrum of bis(trifluoromethyl)nitroxyl. This band is probably masked by those due to the C–F stretching vibrations. A shift of the N–O stretching vibration is observed for all bis(trifluoromethyl)nitroxy derivatives, which can be taken as indicative of compound formation.

B. NUCLEAR MAGNETIC RESONANCE SPECTRA

To maintain some form of consistency, the values of the chemical shift are given with respect to the standard CCl_3F. Where CF_3COOH has been used as a standard in the original paper, conversion can be effected by the equation $\phi = CF_3COOH + 78.5$.

1. *Bis(trifluoromethyl)amino Derivatives*

a. $(CF_3)_2N$-Substituted Alkanes. ^{19}F Nuclear magnetic resonance spectroscopy is useful not only in confirming the presence of bis(trifluoromethyl)amino groups in a large number of derivatives, but also in determining the structures of some derivatives. For example, the products arising from the interaction between $(CF_3)_2NCl$ and $CF_3CF{:}CF_2$ consist of two isomers which have been assigned as $(CF_3)_2NCF_2CFClCF_3$ and $(CF_3)_2NCF(CF_3)CF_2Cl$, whereas $(CF_3)_2NCF_2CFICF_3$ is the structure adopted for the product given by the addition of $(CF_3)_2NI$ to $CF_3CF{:}CF_2$. Their ^{19}F NMR data are provided in Table XXVI.

The magnetically nonequivalence of trifluoromethyl groups in a series of *N*,*N*-bis(trifluoromethyl)alkylamines has been demonstrated (*131*). The ^{19}F NMR spectra of these compounds of the general formula $(CF_3)_2NR$ (where R is a substituted ethyl group) show a single resonance due to trifluoromethyl groups at normal temperature, and two coupled absorptions of equal intensity ($J_{CF_3CF_3}$ ca. 10 Hz) at lower temperatures. These observations have been explained on the basis that inversion at the nitrogen is restricted, with contributions from hindered rotation about the N–C(R) bond. The free energies that have been derived from the series of compounds for coalescences, $G_c^{\#}$, ranges from 8.4–15.8 kcal

TABLE XXVI

NMR DATA FOR BIS(TRIFLUOROMETHYL)AMINO DERIVATIVES

Compound	Group	Type	Chemical shift (ppm)	Coupling constant (Hz)
$(CF_3)_2N–CFF–CFCl–CF_3$	X	br. q.	54.5	AX BX GX = 15.2
X AB G P	P	t of q	80.5	AP BP = 12.1 GP = 6.2
	A	q	88.8	AB = 241, AC = 10.0
	B	q	88.8	BG = 2.4
	G	Complex	139.0	
$(CF_3)_2N–CF(CF_3)–CFFCl$	X		93.1	
X G P AB	P		76.6	
	AB	q	65.8	
	G		2.8	
$(CF_3)_2N–CFF–CFI–CF_3$	X	q of q	59.7	AX BX GX = 15.5
X AB G P				PX = 2.0
	P		75.3	
	AB	Multiplet	75.5	AB = 243
	G		10.7	

mole^{-1}; and these values are associated in part with steric hindrance from substituents at the α-carbon of the substituted ethyl group (R). Thus, for compounds with a single halogen at the α-carbon, $G_c^{\#}$, increases with increasing size of the halogen. Changing substituents on the β-carbon has a much smaller effect.

b. $(CF_3)_2N$-Substituted Olefins and Acetylene. For a series of *N*,*N*-bis(trifluoromethyl)vinylamines, the fluorine chemical shifts appear in the region ranging from −18.8 to −21.4 ppm (*55*). The band due to $(CF_3)_2N$ group is somewhat broadened, probably because of ^{14}N quadrupolar relaxation. No coupling is obtained with the geminal, cis, or trans protons.

In ^1H NMR, however, spectral coupling between the olefinic protons and the fluorine nuclei is well defined, and the values recorded are given below:

F···H (geminal)	1.5–1.9 Hz
F···H (cis)	0.7–0.8 Hz
F···H (trans)	0.5 Hz

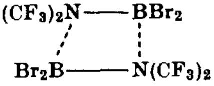
Substantial coupling between the protons and fluorine through three or four bonds is obtained, whereas coupling through five bonds is either small or not observed.

In $(CF_3)_2NC\vdots CH$, a coupling constant of 0.6 Hz is obtained in the ^1H NMR spectrum.

c. $(CF_3)_2N$–Mercury. The fluorine chemical shifts of compounds of the type $(CF_3)_2NHgR$ [$R = (CF_3)_2N$, CH_3, SCF_3] appear at about 48 ppm. There is no coupling between the fluorine nuclei and ^{199}Hg, unlike the presence of ^{199}Hg–^1H coupling in $(CF_3)_2NHgCH_3$.

The band due to the $(CF_3)_2N$ group in $[(CF_3)_2NNCF_3]_2Hg$ is located at 66.9 ppm, possessing a weak coupling (1.9 Hz) with the NCF_3 fluorine.

d. $(CF_3)_2N$–Boron. ^{11}B NMR studies of bis(trifluoromethyl)aminoboron dibromide suggest that it is dimeric, involving 4-coordinate boron and nitrogen (*38*).



The chemical shift is comparable to that for dimeric dimethylaminoboron dibromide, as shown by the ^{11}B chemical shifts.

	Monomer[a]	Dimer[a]
$(CH_3)_2NBBr_2$	−7·7	+11·8
$(CF_3)_2NBBr_2$	—	+7·0

[a] w.r.t. trimethyl borate.

e. $(CF_3)_2N$–Phosphorus and $(CF_3)_2N$–Arsenic. The chemical shifts of fluorine of $(CF_3)_2N$ in many phosphorus and arsenic derivatives fall in the normal range, i.e., 48 to 55 ppm. In trivalent compounds of the type $[(CF_3)_2N]_nM(CF_3)_{3-n}$ ($M = P$ and As $n = 1, 2$), the fluorines in $(CF_3)_2N$ groups couple with distant fluorines, the coupling constant ranging from 3.5 to 5.5 Hz; and coupling with phosphorus gives rise to distinct doublets (J ca. 14–24 Hz).

As expected, only phosphorus gives 5-coordinate derivatives containing $(CF_3)_2N$ groups. The structures of several phosphoranes have been elucidated by means of their ^{19}F NMR spectra. The fluorines in $(CF_3)_2N$ groups couple weakly with phosphorus (0.5–4 Hz), and in a number of compounds such coupling is not observed. Coupling with fluorine directly bonded to phosphorus is strong (10–15 Hz). Thus, $(CF_3)_2NPF_3Cl$ has been characterized mainly by its ^{19}F NMR spectrum, giving the following parameters: At −70°, a typical trifluorophosphorane spectrum is observed with: $J_{P-F(axial)} = 930$ Hz; $\phi_{F(axial)} = -16.9$ ppm; $J_{F(axial)-F(equat.)} = 95$ Hz; $J_{P-F(equat.)} = 1030$ H_z; $\phi_{F(equat.)} = +55.8$ ppm; $J_{CF_3-F(P)} = 10.8$ Hz; $J_{CF_3-P} = 2.3$ Hz; $\phi_{CF_3} = +55.3$ ppm.

At room temperature, only a broad doublet is observed because of a rapid exchange process.

f. Sulfur Derivatives. The chemical shifts of the $(CF_3)_2N$ fluorine in divalent derivatives of sulfur appear at 54 to 59 ppm. Weak coupling with distant protons in $(CF_3)_2NSCH_3$ and give rise to distant fluorines in $(CF_3)_2NSCF_3$ quartets (*11*). In $(CF_3)_2NSF_5$, the only derivative of hexavalent sulfur, the spectral pattern is of the AB_4X_6 type, where coupling of the $(CF_3)_2N$ fluorine with the equatorial fluorine is stronger than with the apical fluorine (*48*).

2. *Bis(trifluoromethyl)nitroxy Derivatives*

Unlike bis(trifluoromethyl)amino derivatives, ^{19}F NMR spectra due to bis(trifluoromethyl)nitroxy groups are generally simpler since one resonance ranging from 67–85 ppm with respect to CCl_3F is obtained. Only in a limited number of compounds is F ··· F coupling observed, as illustrated in Table XXVII (*101, 105*).

TABLE XXVII

NMR DATA FOR BIS(TRIFLUOROMETHYL)NITROXY DERIVATIVES

Compound	Group	Type	Chemical shift (ppm)	Coupling constant (Hz)
$(CF_3)_2NO{-}CF_3$	X	q	65.7	XP = 5.0
X P	P	sep	67.6	
$(CF_3)_2NO{-}CF_2CF_2{-}ON(CF_3)_2$	X	t	77.6	XA = 7.7
X A	A	sep	77.0	
B				
$(CF_3)_2NO{-}CF_2{-}CF{-}CF_3$	X	t	70.0	XA = 7.9
|				
X A $ON(CF_3)_2$	Y	d	69.7	YB = 9.9
y				

C. ELECTRON SPIN RESONANCE SPECTRA

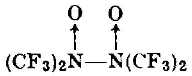
The existence of bis(trifluoromethyl)nitroxyl as a free radical carrying a lone electron is demonstrated by its electron spin resonance studies.

Dilute solutions of the nitroxyl in both CCl_4 (*85*) and CCl_3F (*86*) give a nine-line symmetrical ESR pattern with relative intensities of 1 : 6 : 20.5 : 40 : 50 : 40 : 20.5 : 6 : 1, which corresponds very closely with the theoretical expectation of 1 : 7 : 22 : 41 : 50 : 41 : 22 : 7 : 1 for the six equivalent fluorine atoms of two trifluoromethyl groups attached to nitrogen. At very low concentrations, however, the central peaks are observed to split into triplets, the splitting for nitrogen and fluorine being 9.3 and 8.2 gauss, respectively. A g value of 2.0046 is obtained. Further examination of the ESR spectra of the nitroxyl measured over a temperature range of 163° to 297°K shows that the fluorine and nitrogen hyperfine splitting can be expressed by the equations

$$a^{\mathrm{F}} = (9.327 - 0.0036\ T)\ \text{gauss}$$
$$a^{\mathrm{N}} = (8.776 - 0.0023\ T)\ \text{gauss}$$

where T is the temperature in degrees Kelvin (*129*). These equations show that as the temperature is decreased, a^{F} increases and a^{N} decreases. Thus, at the lower temperatures, the favorable configurations are weighted more heavily, leading to a greater configuration of the fluorine p orbitals with the nitrogen p orbital, and hence a larger transfer of spin to the fluorine atoms. These results seem to confirm that there is some delocalization of the unpaired electron on to the six fluorine atoms, which, as first suggested by Blackley and Reinhard, contributes to the stability of the nitroxyl radical.

When the gaseous nitroxyl radical assumes a yellow form solid at low temperatures, it becomes diamagnetic. Makarov *et al.* (*85*, *130*) suggest that it is a dimer having the configuration



$$(CF_3)_2\overset{\overset{\displaystyle O}{\uparrow}}{N}-\overset{\overset{\displaystyle O}{\uparrow}}{N}(CF_3)_2$$

According to Blackley and Reinhard, dimerization at low temperatures follows the equilibrium

$$2(CF_3)_2NO \rightleftharpoons [(CF_3)_2NO]_2$$

which give the equilibrium constant for dimerization as $K_e = X/(B - 2X)^2$, where B is the initial concentration of radical and X the concentration of dimer. From the values of K_e at temperatures ranging from 232° to 126°K as obtained by ESR measurements, the derived heat of dimerization is -2.5 kcal mole^{-1}.

REFERENCES

1. Forrester, A. R., Hay, J. M., and Thomson, R. H., "Organic Chemistry of Stable Radicals." Academic Press, New York, 1968.
2. Rozantsev, E. G., "Free Nitroxyl Radicals." Plenum, New York, 1970.
3. Rozantsev, E. G., and Sholle, V. D., *Int. J. Methods Syn. Org. Chem.* **1**, 190 (1971).
4. *Fluorine Chem. Rev.* **1**, 4 (1967).
5. IUPAC, "Nomenclature of Organic Compounds." Butterworth, London, 1969.
6. Young, J. A., Tsoukalas, S. N., and Dresdner, R. D., *J. Amer. Chem. Soc.* **80**, 3604 (1958).
7. Emeléus, H. J., and Hurst, G. L., *J. Chem. Soc.* 396 (1964).
8. Dobbie, R. C., and Emeléus, H. J., *J. Chem. Soc., A* 933 (1966).
9. Dobbie, R. C., and Emeléus, H. J., *J. Chem. Soc., A* 367 (1966).
10. Young, J. A., Durrell, W. S., and Dresdner, R. D., *J. Amer. Chem. Soc.* **84**, 2105 (1962).
11. Emeléus, H. J., and Tattershall, B. W., *J. Inorg. Nucl. Chem.* **28**, 1823 (1966).
12. Young, J. A., Tsoukalas, S. N., and Dresdner, R. D., *J. Amer. Chem. Soc.* **82**, 396 (1960).
13. Emeléus, H. J., and Tattershall, B. W., *J. Chem. Soc.* 5892 (1964).
14. Haszeldine, R. N., and Tipping, A. E., *J. Chem. Soc. C* 1241 (1967).
15. Haszeldine, R. N., and Mattinson, B. J. H., *J. Chem. Soc.* 1741 (1957).
16. Emeléus, H. J., and Thompson, J., *J. Chem. Soc.* 3080 (1949).
17. Young, J. A., Durrell, W. S., and Dresdner, R. D., *J. Amer. Chem. Soc.* **81**, 1587 (1959).
18. Young, J. A., Durrell, W. S., and Dresdner, R. D., *J. Amer. Chem. Soc.* **82**, 4553 (1960).
19. Attaway, J. A., Groth, R. H., and Bigelow, L. A., *J. Amer. Chem. Soc.* **81**, 3599 (1959).
20. Gervasi, J. A., Brown, M., and Bigelow, L. A., *J. Amer. Chem. Soc.* **78**, 1679 (1956).
21. Haszeldine, R. N., *J. Chem. Soc.* 1966 (1950).
22. Haszeldine, R. N., *J. Chem. Soc.* 102 (1951).
23. Avonda, F. P., Gervasi, J. A., and Bigelow, L. A., *J. Amer. Chem. Soc.* **78**, 2798 (1956).
24. Dresdner, R. D., Tlumac, F. N., and Young, J. A., *J. Amer. Chem. Soc.* **82**, 5831 (1960).
25. Engelbrecht, A., Mayer, E., and Pupp, Chr., *Monatsh.* **95**, 633 (1964).
26. Robson, P., McLoughlin, V. C. R., Hynes, J. B., and Bigelow, L. A., *J. Amer. Chem. Soc.* **83**, 5010 (1961).
27. Alexander, E. S., Haszeldine, R. N., Newlands, M. J., and Tipping, A. E., *J. Chem. Soc., C* 796 (1968).
28. Ruff, O., and Willenberg, W., *Ber.* **73**, 724 (1940).
29. Barr, D. A., and Haszeldine, R. N., *J. Chem. Soc.* 2532 (1955).
30. Young, J. A., and Dresdner, R. D., *J. Amer. Chem. Soc.* **80**, 1889 (1958).
31. Emeléus, H. J., and Tattershall, B. W., *Z. Anorg. Allgem. Chem.* **327**, 147 (1964).
32. Haszeldine, R. N., and Tipping, A. E., *J. Chem. Soc.* 6141 (1965).
33. Haszeldine, R. N., and Tipping, A. E., *J. Chem. Soc., C* 1236 (1966).

34. Pritchard, G. O., Pritchard, H. O., Schiff, H. I., and Trotman-Dickenson, A. F., *Trans. Faraday Soc.* **52**, 849 (1956).

35. Pritchard, G. O., and Pritchard, H. O., *Chem. Ind.* (*London*) 564 (1955).

36. Young, J. A., and Dresdner, R. D., *J. Org. Chem.* **28**, 833 (1963).

37. Bartell, L. S., and Higginbotham, H. K., *Inorg. Chem.* **4**, 1346 (1965).

38. Greenwood, N. N., and Hooton, K. A., *J. Chem. Soc.*, *A* 751 (1966).

39. Ang, H. G., *J. Chem. Soc. A* 2734 (1968).

40. Dobbie, R. C., Ph.D. Thesis, Cambridge University (1966).

41. Ang, H. G., and Emeléus, H. J., *Chem. Commun.* 460 (1966).

42. Ang, H. G., and Emeléus, H. J., *J. Chem. Soc.*, *A* 1334 (1968).

43. Ang, H. G., *J. Inorg. Nucl. Chem.* **31**, 3311 (1969).

44. Ang, H. G., *J. Organometal Chem.* **19**, 245 (1969).

45. Emeléus, H. J., and Onak, T., *J. Chem. Soc.*, *A* 1291 (1966).

46. Ang, H. G., *J. Fluorine Chem.* **2**, 183 (1972).

47. Tullock, C. W., U.S. Patent 3,121,112 (1964); *Chem. Abstr.* **40**, 13143 (1964).

48. Dobbie, R. C., *J. Chem. Soc.*, *A* 1555 (1966).

49. Barlow, M. G., Fleming, G. L., Haszeldine, R. N., and Tipping, A. E., *J. Chem. Soc.*, *C* 2744 (1971).

49a. Dobbie, R. C., and Emeléus, H. J., *J. Chem. Soc.* 5894 (1964).

50. Fleming, G. L., Haszeldine, R. N., and Tipping, A. E., *J. Chem. Soc.*, *C* 3829 (1971).

51. Fleming, G. L., Haszeldine, R. N., and Tipping, A. E., *J. Chem. Soc.*, *C* 3833 (1971).

52. Coy, D. H., Haszeldine, R. N., Newlands, M. J., and Tipping, A. E., *Chem. Commun.* **7**, 456 (1970).

53. Haszeldine, R. N., and Tipping, A. E., *J. Chem. Soc.*, *C* 398 (1968).

54. Freear, J., and Tipping, A. E., *J. Chem. Soc.*, *C* 1096 (1968).

55. Freear, J., and Tipping, A. E., *J. Chem. Soc.*, *C* 411 (1969).

56. Young, J. A., Simmons, T. C., and Hoffmann, F. W., *J. Amer. Chem. Soc.* **78**, 5637 (1956).

57. Young, J. A., and Dresdner, R. D., *J. Org. Chem.* **23**, 1576 (1958).

58. Simons, J. H., "Fluorine Chemistry," Vol. 1, p. 225. Academic Press, New York, 1950.

59. Scholberg, N. M., and Brice, H. G., U.S. Patent 2,717,871 (1955).

60. Emeléus, H. J., and Poulet, R. J., *J. Fluorine Chem.* **1**, 13 (1971).

60a. Emeléus, H. J., Forder, R. A., Poulet, R. J., and Sheldrick, G. M. *Chem. Commun.* **22**, 1483 (1970).

60b. Forder, R. A., and Sheldrick, G. M., *J. Fluorine Chem.* **1**, 23 (1971).

61. Makarov, S. P., Shpanskii, V. A., Shchekatikhim, A. I., Filatov, A. S., Martynova, C. L., Pavlovskaya, I. V., Golovaneva, A. F., and Yakubovich, A. Ya., *Dokl. Akad. Nauk. SSSR* **142**, 596 (1962); *Chem. Abstr.* **57**, 4528f (1962).

62. Tullock, C. W., *Chem. Abstr.* **59**, P5022d (1963).

63. Petrov, K. A., and Neimgsheva, A. A., *Zh. Obshch. Khim.* **29**, 2169 (1959); *Chem. Abstr.* **54**, 10912d (1960).

64. Barr, D. A., and Haszeldine, R. N., *J. Chem. Soc.* 3428 (1956).

65. Haszeldine, R. N., and Mattinson, B. J. H., *Chem. Ind.* (*London*) 81 (1956).

66. Petrov, K. A., and Neimysheva, A. A., *Zh. Obshch. Khim.* **29**, 2695 (1959); *Chem. Abstr.* **54**, 10912c (1960).

67. Kauck, E. A., and Simons, J. H., U.S. Patent 2,616,927 (1952).

68. Kauck, E. A., and Simons, J. H., British Patent 666,733 (1952).

69. Glemser, O., and Richert, H., *Z. Anorg. Allgem. Chem.* **1**, 362 (1961).
70. Haszeldine, R. N., *Research* (London) **3**, 430 (1950).
71. Dresdner, R. D., *J. Amer. Chem. Soc.* **79**, 69 (1957).
72. Banks, R. E., Haszeldine, R. N., and Sutcliffe, H., *J. Chem. Soc.* 4066 (1964).
73. Livingston, R. L., and Vaughan, G., *J. Amer. Chem. Soc.* **78**, 4866 (1956).
74. Vaughan, G., Univ. Microfilms Publ. No. 9900, *Dissertation Abstr.* **14**, 1942 (1954).
75. Barr, D. A., Haszeldine, R. N., and Willis, C. J., *J. Chem. Soc.* 1351 (1961).
76. Fawcett, F. S., Tullock, C. W., and Coffman, D. D., *J. Amer. Chem. Soc.* **84**, 4275 (1962).
77. Andreades, S., *J. Org. Chem.* **27**, 4163 (1962).
78. Wieger, G. A., and Vos, A., *Acta Crystallogr.* **16**, 152 (1963).
79. Ang, H. G., Coombes, J. S., and Sukhoverkhov, V., *J. Inorg. Nucl. Chem.* **31**, 878 (1969).
80. Tullock, C. W., U.S. Patent 3,052,723 (Cl 260-583) (1962); *Chem. Abstr.* **58**, 10090d (1963).
81. Makarov, S. P., Shpanskii, V. A., Grinsburg, V. A., Shchekatikhin, A. I., Filatov, A. S., Martynova, L. L., Pavlovskaya, I. V., Golovaneva, A. F., and Yakubovich, A. Ya., *Dokl. Akad. Nauk SSR* **142**, 596 (1962); *Chem. Abstr.* **57**, 4528 (1962).
82. Dinwoodie, A. H., and Haszeldine, R. N., *J. Chem. Soc.* 1675 (1965).
83. Haszeldine, R. N., *Nature* (*London*) **168**, 1028 (1951).
84. Haszeldine, R. N., *J. Chem. Soc.* 2075 (1953).
85. Makarov, S. P., Yakubovich, A. Ya., Dubov, S. S., and Medvedev, A. N., *Proc. Acad. Sci. USSR., Chem. Soc.* **160**, 195 (1965).
86. Blackley, W. D., and Reinhard, R. R., *J. Amer. Chem. Soc.* **87**, 802 (1965).
87. Ang, H. G., *Chem. Commun.* **21**, 1320 (1968).
88. Tomilov, A. P., Smirnov, Yu. D., and Videiko, A. F., *Electrokhimiya* **2** (5), 603 (1966); *Chem. Abstr.* **65**, 3343 (1966).
89. Pauling, L., "The Nature of the Chemical Bond," p. 343. Cornell Univ. Press, New York, 1960.
90. Davis, M. I., Boggs, J. E., Coffey, D., and Hanson, H. P., *J. Phys. Chem.* **69**, 3727 (1965).
90a. Hanson, A. W., *Acta. Cryst.* **6**, 32 (1953).
91. Banus, J., *J. Chem. Soc.* 3755 (1953).
92. Glidewell, C., Rankin, D. W. H., Robiette, A. G., Sheldrick, G. M., and Williamson, S. M., *J. Chem. Soc. A* 478 (1971).
93. Chapelet-Letourneux, G., Lemaire, H., and Rassat, A., *Bull. Soc. Chim. Fr.* 3283 (1965).
94. Coppinger, G. M., and Swallen, J. D., *J. Amer. Chem. Soc.* **83**, 4900 (1961).
95. Forrester, A. R., and Thomson, R. H., *Nature* (*London*) **203**, 74 (1964).
96. Tokumaru, K., Sakuragi, H., and Simamura, O., *Tetrahedron Lett.* 3945 (1964).
97. Iwamura, M., and Inamoto, N., *Bull. Chem. Soc. Jap.* **43**, 860 (1970).
98. Andersen, B., and Andersen, P., *Acta Chem. Scand.* **20**, 2728 (1966).
99. Forrester, A. R., Hepburn, S. P., Dunlop, R. S., and Mills, H. H., *Chem. Commun.* 698 (1969).
100. Makarov, S. P., Englin, M. A., and Mel'nikova, A. V., *J. Gen. Chem. USSR* **39**, 507 (1969).
101. Banks, R. E., Haszeldine, R. N., and Stevenson, M. J., *J. Chem. Soc., C* 901 (1966).

102. Mel'nikova, A. V., Baranaev, M. H., Makarov, S. P., and Englin, M. A., *J. Gen. Chem. USSR* **40**, 350 (1970).

103. Banks, R. E., Haszeldine, R. N., and Justin, B., *J. Chem. Soc., C* 2777 (1971).

104. Banks, R. E., Cheng, W. M., Haszeldine, R. N., and Shaw, G., *J. Chem. Soc., C* 55 (1970).

105. Banks, R. E., Haszeldine, R. N., and Myerscough, T., *J. Chem. Soc., C* 1951 (1971).

106. Banks, R. E., Haszeldine, R. N., and Hyde, D. L., *Chem. Commun.* **8**, 413 (1967).

107. Emeléus, H. J., Shreeve, J. M., and Spaziante, P. M., *Chem. Commun.* **20**, 1252 (1968).

108. Nash, L. L., Babb, D. P., Couville, J. J., and Shreeve, J. M., *J. Inorg. Nucl. Chem.* **30**, 3373 (1968).

109. Babb, D. P., and Shreeve, J. M., *Inorg. Chem.* **6**, 351 (1967).

110. Toy, M. S., and Lawson, D. D., *J. Polym. Sci., Part B* **6**, 639 (1968).

111. Makarov, S. P., Englin, M. A., Videiko, A. F., Tobolin, V. A., and Dubov, S. S., *Dokl. Akad. Nauk SSSR* **168** (2), 344 (1966); *Proc. Acad. Sci. USSR, Chem. Sect.* **168**, 483 (1966).

112. Dinwoodie, A. H., and Haszeldine, R. N., *J. Chem. Soc.* 1681 (1965).

113. Emeléus, H. J., Shreeve, J. M., and Spaziante, P. M., *J. Chem. Soc., A* 431 (1969).

114. Lott, J. A., Babb, D. P., Pullen, K. E., and Shreeve, J. M., *Inorg. Chem.* **7**, 2593 (1968).

115. Ang, H. G., and Syn, Y. C., unpublished results.

116. Emeléus, H. J., Spaziante, P. M., and Williamson, S. M., *Chem. Commun.* 768 (1969).

117. Ho, K. F., M.Sc. Thesis, University of Singapore (1970).

118. Ang, H. G., Ho, K. F., Khoo, K. G., and Syn, Y. C., *6th Int. Symp. Fluorine Chem.* (1971).

119. Ang, H. G., unpublished results.

120. Makarov, S. P., Videiko, A. F., Nikolaeva, T. V., and Englin, M. A., *Zh. Obshch. Khim.* **37**, 1975 (1967); *J. Gen. Chem. USSR* **37**, 1875 (1967).

121. Flaskerud, G. G., and Shreeve, J. M., *Inorg. Chem.* 8, 2065 (1969).

122. Medvedev, A. N., Smirnov, K. N., Dubov, S. S., and Ginsburg, V. A., *Zh. Obshch. Khim.* **38**, 2462 (1968); *Chem. Abstr.* **70**, 46737 (1969).

123. Makarov, S. P., Videiko, A. F., Tobolin, V. A., and Englin, M. A., *Zh. Obshch. Khim.* **37**, 1528 (1967); *Chem. Abstr.* **68**, 12361 (1968).

124. Banks, R. E., Barlow, M. G., Haszeldine, R. N., McCreath, M. K., and Sutcliffe, H., *J. Chem. Soc.* 7209 (1965).

125. Yakubovich, A. Ya., Makarov, S. P., Ginsburg, V. A., Privezentseva, N. F., and Martynova, L. L., *Dokl. Akad. Nauk SSSR* **141**, 125 (1961); *Chem. Abstr.* **56**, 11429 (1962).

126. Shreeve, J. M., *Sci. Tech. Aerospace Rep.* **3**, 723 (1965).

127. Shreeve, J. M., and Babb, D. P., *J. Inorg. Nucl. Chem.* 87, 802 (1965).

128. Banks, R. E., *6th. Int. Symp. Fluorine Chem.* (1971).

129. Scheidler, P. J., and Holton, J. R., *J. Amer. Chem. Soc.* **88**, 371 (1966).

130. Makarov, S. P., Yakubovich, A. Ya., Dubov, S. S., and Medvedev, A. N., *Zh. Vsaes. Khim. Obshch.* **10**, 106 (1965); *Chem. Abstr.* **62**, 16034g (1966).

131. Barlow, M. G., and Cheung, K. W., *Chem. Commun.* 870 (1969).