# Bis(trifluoromethyl)aminotrimethylsilane

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Bis(trifluoromethyl)aminotrimethylsilane, $(CF_3)_2N{\cdot}SiMe_3$, which is unstable at room temperature, has been prepared and characterised.

REACTION of *N*-halogenobis(trifluoromethyl)amine with various mercurials gives bis(trifluoromethyl)amino-derivatives.[1]

$$(CF_3)_2NBr + Me_2Hg \longrightarrow (CF_3)_2N{\cdot}HgMe + MeBr$$

Reaction of chlorotrimethylsilane and di[bis(trifluoromethyl)amino]mercury, however, gave no bis(trifluoromethyl)amino-derivatives,

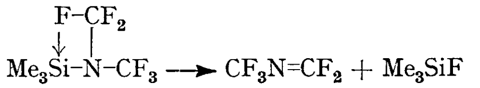
$$[(CF_3)_2N]_2Hg + 2Me_3SiCl \longrightarrow 2Me_3SiF + 2CF_3N{=}CF_2 + HgCl_2$$

At room temperature *N*-chlorobis(trifluoromethyl)amine reacted very vigorously with bis(trimethylsilyl)mercury to give perfluoro-2-azapropene, fluorotrimethylsilane, trimethylchlorosilane, and mercury. At −126°, however, the reaction gave the new compound bis(trifluoromethyl)aminotrimethylsilane (16%), together with substantial amount of fluorotrimethylsilane, chlorotrimethylsilane, perfluoro-2-azapropene, and mercury.

$$2(CF_3)_2NCl + 2(Me_3Si)_2Hg \longrightarrow (CF_3)_2N{\cdot}SiMe_3 + 2Me_3SiCl + Me_3SiF + CF_3N{=}CF_2 + 2Hg$$

The $^1H$ n.m.r. spectrum of bis(trifluoromethyl)aminotrimethylsilane showed a single peak ($\tau$ 9·25), and the $^{19}F$ n.m.r. spectrum gave a single line [48·8 p.p.m. (w.r.t. $CCl_3F$)]. The i.r. spectrum indicated the presence of both bis(trifluoromethyl)amino- and trimethylsilyl groups which further confirmed the structure. The parent ion was present in the cracking pattern.

The compound was unstable at room temperature, and decomposition was usually complete within 24 hr., giving perfluoro-2-azapropene and fluorotrimethylsilane. This behaviour is similar to that of $CF_3{\cdot}S{\cdot}SiH_3$ which decomposes to $SiH_3F$ and $SCF_2$;[2] the mechanism for both decompositions probably involves $\gamma$-elimination,



$$Me_3Si{-}N(CF_2{-}F){-}CF_3 \longrightarrow CF_3N{=}CF_2 + Me_3SiF$$

a process quite common for silicon compounds containing either a β-halogen[3] or hydrogen.[4]

Since $Me_2N{\cdot}SiMe_2$ reacts with phosphorus pentafluoride to give $Me_2N{\cdot}PF_4$,[5] a study of the analogous reaction of $(CF_3)_2N{\cdot}SiMe_2$ was undertaken in the hope that a method of forming bis(trifluoromethyl)amino–phosphorus bond might be discovered. Instead, the products isolated were perfluoro-2-azapropene, fluorotrimethylsilane, and unchanged phosphorus pentafluoride. The instability of bis(trifluoromethyl)aminotrimethylsilane has prevented its chemical properties being fully investigated.

## EXPERIMENTAL

All the reactions were carried out in a vacuum system. The identity of all known compounds was confirmed by i.r. spectroscopy on a Perkin-Elmer Infracord spectrometer. The $^{19}F$ n.m.r. spectrum was recorded at −35° and 40 Mc./sec. on a Varian Associates V4300B spectrometer; the $^1H$ n.m.r. spectrum was recorded at 60 Mc./sec. on a Perkin-Elmer R-10 instrument. The variation of vapour pressure with temperature of the new compound was investigated in an all-glass apparatus to avoid problems of tap-grease absorption with the temperature below 20°. The mass spectrum was measured on an AEI MS 9 operating at an ionisation voltage of 70 ev. The new silicon compound was degraded for analysis by sodium in liquid ammonia.

*Reaction of* N-*Chlorobis(trifluoromethyl)amine with Bis(trimethylsilyl)mercury.*—In a typical experiment, *N*-chlorobis(trifluoromethyl)amine (0·658 g., 3·50 mmoles) was introduced into an ampoule containing bis(trimethylsilyl)mercury (1·25 g., 3·61 mmoles). The mixture was warmed from −196 to −126°. Vigorous reaction soon occurred accompanied by precipitation of a grey solid which later was confirmed to contain mercury. The ampoule was maintained at this temperature for 15 min. and then at −64° for a further 2 hr. Fractionation of the volatile products gave bis(trifluoromethyl)aminotrimethylsilane (0·243 g., 1·17 mmoles), (Found: F, 48·9%; *M*, 223. Calc. for $C_5H_9F_6NSi$: F, 50·7%; *M*, 225). The chief bands in the i.r. spectrum were at 2930w, 1320vs, 1275vs, 1200m,sh, 1175vs, 1140w, 1070w, 9639, 910w, 856vs, 765w, and 703w cm.$^{-1}$. Vapour pressures (−30 to 10°) are represented by $\log_{10}p$ (mm.) = 7·055 − (1470/$T$) giving the derived boiling point as 80°, the latent heat of vaporisation as 6·74 kcal. mole$^{-1}$, and Trouton constant as 19·1. The mass spectral cracking pattern showed the following cationic species: *m/e* (intensity, ion) 226 (0·04, $C_5H_9F_6NSi$), 225 (0·3, $C_5H_9F_6NSi$), 210 (0·09, $C_4H_6F_6NSi$), 133 (3·0, $C_2F_5N$), 114 (100·0, $C_2F_4N$), 92 (1·2, $C_3H_9FSi$), 85 (0·02, $SiF_3$), 81 (0·9, $CH_3F_2Si$), 77 (56·0, $C_2H_6FSi$), 73 (11·0, $C_3H_9Si$), 69 (10·0, $CF_3$), 66 (0·3, $SiF_2$), 63 (3·5, $CFH_3Si$), 59 (0·9, $C_2H_6Si$), 58 (0·4, $C_2H_5Si$), and 50 (0·9, $CF_2$). Perfluoro-2-azapropene (0·311 g., 2·34 mmoles) was collected at a −196° trap. The other volatile compounds were chlorotrimethylsilane and fluorotrimethylsilane (0·533 g.; *M*, 102) which were difficult to separate quantitatively by vacuum

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fractionation. The identities were confirmed from their molecular weights and i.r. spectra of pure samples of each component isolated.

*Decomposition of Bis(trifluoromethyl)aminotrimethylsilane.*—Bis(trifluoromethyl)aminotrimethylsilane (0·553 g., 2·46 mmoles) was set aside at room temperature for 19 hr. Fractionation of the products gave perfluoro-2-azapropene (0·295 g., 2·22 mmoles) trapped at −196°, fluorotrimethylsilane (0·202 g., 2·19 mmoles) trapped at −126°, and unchanged $(CF_3)_2NSiMe_3$ (0·053 g., 0·24 mmoles).

*Reaction of Bis(trifluoromethyl)aminotrimethylsilane with Phosphorus Pentafluoride.*—Phosphorus pentafluoride (0·160 g., 1·27 mmoles) and bis(trifluoromethyl)aminotrimethylsilane (0·129 g., 0·573 mmoles) in an ampoule cooled in ether slush was left to warm slowly overnight (11 hr.), and then maintained at room temperature for a further 24 hr. Fractionation of the products gave unchanged phosphorus pentafluoride (0·148 g., 1·18 mmoles), perfluoro-2-azapropene (0·077 g., 0·580 mmoles), and fluorotrimethylsilane (0·054 g., 0·587 mmoles).

*Reaction of Chlorotrimethylsilane with Di[bis(trifluoromethyl)amino]mercury.*—Chlorotrimethylsilane (0·241 g., 2·21 mmoles) and di[bis(trifluoromethyl)amino]mercury (0·557 g., 1·10 mmoles) were set aside at room temperature for 7 days. Fractionation of the products gave perfluoro-2-azapropene (0·293 g., 2·20 mmoles), fluorotrimethylsilane (0·205 g., 2·23 mmoles), and mercuric chloride (0·253 g., 0·97 mmoles).

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