Organosilicon Chemistry. Part IV.[1] The Reaction of Trimethylsilane with Trifluoronitrosomethane

By **A. C. Delany, R. N. Haszeldine,*** and **A. E. Tipping**, Chemistry Department, The University of Manchester Institute of Science and Technology

The photolytic and platinum-catalysed reactions between trimethylsilane and trifluoronitrosomethane have been investigated. Gas-phase photolysis gives a 1 : 1 adduct believed to be *N*-trifluoromethyl-*O*-trimethylsilylhydroxylamine, and *NN*-bistrifluoromethyl-*O*-trimethylsilylhydroxylamine, in good yield. When both the gas and liquid phases are irradiated the major product is *NN*-bistrifluoromethyl-*O*-trimethylsilylhydroxylamine. The platinum-catalysed reaction gives the same 1 : 1 adduct, in high yield.

Pyrolysis of the 1 : 1 adduct at 100° gives mainly trimethylfluorosilane; hydrolysis yields carbon dioxide, trimethylfluorosilane, and hexamethyldisiloxane. Hydrolysis of *NN*-bistrifluoromethyl-*O*-trimethylsilylhydroxylamine gives *NN*-bistrifluoromethylhydroxylamine and hexamethyldisiloxane.

Few free-radical additions to trifluoronitrosomethane have so far been reported. Those which involve trifluoromethyl [2,3] or bistrifluoromethylnitroxide [4] radical addition are believed to occur by initial radical attack on the nitrogen atom of trifluoronitrosomethane. In the present work the reaction between trimethylsilane and trifluoronitrosomethane has been investigated under both photolytic and platinum-catalysed conditions. The gas-phase photolysis of an equimolar mixture of trimethylsilane and trifluoronitrosomethane gave recovered silane (7%), nitrogen (9%), hexafluoroazoxymethane (4%), trimethylfluorosilane (15%), *NN*-bistrifluoromethyl-*O*-trimethylsilylhydroxylamine (I) (28%), a 1 : 1 adduct (II) (43%), and small amounts of hexamethyldisiloxane, various unidentified components, a non-volatile oil, and a non-volatile solid. Irradiation of both gas and liquid phases enhanced the yield of (I) at the expense of (II). The yields of the silicon-containing products are based on silane used, whereas the yields of nitrogen and hexafluoroazoxymethane are based on the nitroso-compound.

$$\underset{\text{(I)}}{(CF_3)_2N{\cdot}O{\cdot}SiMe_3} \qquad \underset{\text{(II)}}{CF_3{\cdot}NH{\cdot}O{\cdot}SiMe_3}$$

$$\underset{\text{(III)}}{CF_3{\cdot}N(OH){\cdot}SiMe_3}$$

The instability of the 1 : 1 adduct (II) made a definite structural determination difficult, but the mass spectrum showed a strong band at *m*/*e* 84 ($CF_3{\cdot}NH^+$) and bands at *m*/*e* 147 and 131 due to the breakdown of hexamethyldisiloxane. Unless the *m*/*e* 84 peak arises by rearrangement of the breakdown products from (III) in the mass spectrometer, this evidence suggests that the 1 : 1 adduct has structure (II), in which the $CF_3{\cdot}NH$ group and $Me_3Si{\cdot}O$ group are present, rather than (III). On this basis the 1 : 1 adduct probably arises from initial trimethylsilyl radical attack on the oxygen atom of trifluoronitrosomethane:

$$CF_3{\cdot}NO + Me_3Si{\cdot} \longrightarrow CF_3{\cdot}\dot{N}{\cdot}O{\cdot}SiMe_3 \xrightarrow{Me_3SiH} CF_3{\cdot}NH{\cdot}O{\cdot}SiMe_3 + Me_3Si{\cdot}$$

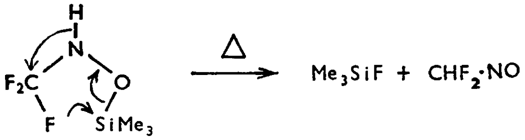
Aqueous hydrolysis of (II) gave carbon dioxide, trimethylfluorosilane (*ca.* 40%), hexamethyldisiloxane (*ca.* 48%), and fluoride and ammonium ions:

$$CF_3{\cdot}NH{\cdot}O{\cdot}SiMe_3 + H_2O \longrightarrow CF_3{\cdot}NH{\cdot}O^- + H_2\overset{+}{O}{\cdot}SiMe_3 \longrightarrow (Me_3Si)_2O$$

$$CF_3{\cdot}NH{\cdot}O^- \xrightarrow{H_2O} NH_3,\ CO_2,\text{ and }HF$$

$$Me_3Si{\cdot}O{\cdot}SiMe_3 + HF \longrightarrow Me_3SiF + Me_3SiOH$$

Pyrolysis of (II) at 100° gave trimethylfluorosilane (80%), nitrogen (4%), a mixture of gaseous fluorohydrocarbons, carbon dioxide, trifluoromethylisocyanate, and an unidentified white solid. The major product, trimethylfluorosilane, probably arises by initial nucleophilic



Scheme

---

[1] Part III, R. Fields, R. N. Haszeldine, and R. E. Hutton, *J. Chem. Soc.* (*C*), 1967, 2559.

[2] J. Jander and R. N. Haszeldine, *J. Chem. Soc.*, 1954, 912.

[3] R. N. Haszeldine and B. J. H. Mattinson, *J. Chem. Soc.*, 1957, 1741.

[4] R. E. Banks, R. N. Haszeldine, and M. J. Stevenson, *J. Chem. Soc.* (*C*), 1966, 601.

attack of fluorine on silicon (Scheme), rather than by initial loss of hydrogen fluoride:

$$CF_3\cdot NH\cdot O\cdot SiMe_3 \xrightarrow{\Delta} CF_2{:}N\cdot O\cdot SiMe_3 + HF$$

$$CF_2{:}N\cdot O\cdot SiMe_3 + HF \longrightarrow CF_2{:}N\cdot OH + Me_3SiF$$

since silicon tetrafluoride would be expected as a by-product from the hydrogen fluoride in glass vessels.

NN-Bistrifluoromethyl-*O*-trimethylsilylhydroxylamine (I) was unambiguously synthesised from *O*-nitrosobistrifluoromethylhydroxylamine in 50% yield.

$$(CF_3)_2N\cdot OH + Me_3SiCl \longrightarrow (CF_3)_2N\cdot O\cdot SiMe_3 + HCl$$

The other main product was hexamethyldisiloxane. Hydrolysis of (I) gave the hydroxylamine $(CF_3)_2N\cdot OH$ (90%) and hexamethyldisiloxane (85%).

The mode of formation of (I) is not immediately apparent, but it may arise *via* the known, stable nitroxide radical, $(CF_3)_2N\cdot O\cdot$,[5] or *via* the dimer $(CF_3)_2N\cdot O\cdot NO$.

Platinum Catalysis.—Reaction between an equimolar mixture of trimethylsilane and trifluoronitrosomethane in the dark (5 days), in the presence of hexachloroplatinic acid hydrate which had previously been reduced with trimethylsilane, gave nitrogen (5%), hexafluoroazoxymethane (1%), trimethylfluorosilane (10%), (II) (74%), (I) (16%), and small amounts of a non-volatile oil and hexamethyldisiloxane.

Platinum-catalysed additions of silanes to olefins have been much investigated and are thought to involve a complex of the silane with platinum[6,7] which may or may not also involve a molecule of olefin.[8] A possible reaction scheme to account for the formation of (II) is as follows.

$$Me_3SiH + Pt \rightleftharpoons Me_3Si\cdot PtH \xrightleftharpoons{Me_3SiH}$$

$$[Me_3Si]_2PtH_2 \xrightarrow{CF_3\cdot NO} CF_3\cdot NH\cdot O\cdot Pt[SiMe_3]_2H$$

$$CF_3\cdot NH\cdot O\cdot Pt[SiMe_3]_2H \longrightarrow CF_3\cdot NH\cdot O\cdot SiMe_3 + Me_3Si\cdot PtH$$

EXPERIMENTAL

Reactants and products were manipulated, where possible, in a conventional vacuum-system to avoid contamination with air or moisture. The products were separated either by repeated fractional distillation *in vacuo* or by preparative-scale g.l.c. The identities of products were established by molecular weight determination (Regnault's method), i.r. spectroscopy (Perkin-Elmer spectrophotometer model 21 with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R10 spectrometer operating at 56·46 Mc./sec. for ^{19}F and at 60·0 Mc./sec. for ^1H), mass spectrometry (A.E.I. MS/2H spectrometer), and g.l.c. (Perkin-Elmer Fraktometer models 116, 154B, and 452). All irradiations were carried out at a distance of 6 in. from a Hanovia S.500 u.v. lamp.

Trifluoronitrosomethane was prepared as described previously,[9] trimethylchlorosilane (commercially available) was purified by fractional distillation, and trimethylsilane was prepared (80%) by the reduction of trimethylchlorosilane with lithium aluminium hydride.

Ultraviolet-Initiated Reaction of Trifluoronitrosomethane with Trimethylsilane.—Trifluoronitrosomethane (1·238 g., 12·41 mmoles) and trimethylsilane (0·925 g., 12·47 mmoles) were sealed in a silica tube (150 ml.) and the gas phase was irradiated until the blue colour of the nitroso-compound had disappeared (18 hr.). The products were (*a*) nitrogen (0·015 g., 0·54 mmole, 9% based on $CF_3\cdot NO$) (Found: *M*, 27. Calc. for N_2: *M*, 28), identified by mass spectrometry, (*b*) a volatile fraction (1·96 g.), and (*c*) a non-volatile residue (*ca.* 0·2 g.).

Fraction (*b*) was shown by g.l.c. (4 m. silicone oil at 70°) to contain ten components, separated by g.l.c. into (i) a mixture of four unidentified components (0·16 g., 0·27 mmole; *M*, 60); (ii) hexafluoroazoxymethane (0·049 g., 0·27 mmole, 4% based on $CF_3\cdot NO$) (Found: *M*, 180. Calc. for $C_2F_6N_2O$: *M*, 182); (iii) trimethylsilane (0·61 g., 0·82 mmole, 7%) (Found: *M*, 74. Calc. for $C_3H_{10}Si$: *M*, 74); (iv) trimethylfluorosilane (0·160 g., 1·74 mmoles, 14% based on Me_3SiH consumed) (Found: *M*, 90. Calc. for C_3H_9FSi: *M*, 92); (v) *N*-trifluoromethyl-*O*-trimethylsilylhydroxylamine (II) (0·865 g., 5·00 mmoles, 43% based on Me_3SiH), pure by g.l.c. on several columns, but decomposing steadily when kept in glass, and for which a satisfactory analysis was not obtained (Found: C, 26·7; H, 5·0; N, 9·0%; *M*, 169. Calc. for $C_4H_{10}F_3NOSi$: C, 27·7; H, 5·8; N, 8·1%; *M*, 173), b.p. 39°/720 mm. (decomp.), $\lambda_{max.}$ 2·72vw, 2·96w, 5·42w, 6·84m, 7·30s, 7·60vs, 7·86vs, 8·20vs, 8·46vs, 9·75s, 10·90s, and 12·14m μ, *m/e* (principal peaks) 159 ($C_3H_8F_3NOSi^+$, 1·2%), 147 ($C_5H_{15}OSi_2^+$, 3·0%), 131 ($C_4H_{11}OSi_2^+$, 2·1%), 84 (CHF_3N^+, 3·5%), 83 (CF_3N^+, 18·4%), 81 (CHF_2NO^+, base peak), 77 ($C_2H_6FSi^+$, 49·0%), 73 ($C_3H_9Si^+$, 6·8%), 69 (CF_3^+, 78·5%), 65 (CHF_2N^+, 21·6%), 62 (CH_3FSi^+, 20·4%), 51 (CHF_2^+, 17·5%), 50 (CF_2^+, 5·7%), 49 ($CFSi^+$, 6·8%), 47 (FSi^+, 12·7%), 46 ($C_2H_3F^+$, 10·7%), 44 (CH_4Si^+, 8·1%), 32 (CHF^+, 6·6%), 31 (CF^+, 12·6%), and 30 (H_2Si^+, 18·5%); the ^{19}F n.m.r. spectrum showed a broad singlet at 7·4 p.p.m. to low field of external reference trifluoroacetic acid, and the ^1H n.m.r. spectrum showed a broad singlet (intensity 1) at 0·8 p.p.m. and a singlet (intensity 9) at 6·83 p.p.m. to high field of external reference benzene; (vi) *NN*-bistrifluoromethyl-*O*-trimethylsilylhydroxylamine (I) (0·771 g., 3·20 mmoles, 28% based on Me_3SiH), pure by g.l.c. but labile, and for which a satisfactory analysis was not obtained (Found: C, 26·4; H, 4·3; N, 5·1%; *M*, 238. Calc. for $C_5H_9F_6NOSi$: C, 24·9; H, 3·7; N, 5·8%; *M*, 241), b.p. 69°/720 mm., $\lambda_{max.}$ 2·76vw, 3·40w, 4·12w, 6·96w, 7·18m, 7·64vs, 7·90vs, 8·20vs, 9·34s, 9·56s, 10·30vs, 11·02w, 11·74s, 12·00w, 12·54w, 13·20w, and 14·00—14·22s (triplet) μ, *m/e* (principal peaks) 169 ($C_2HF_6NO^+$, 6·5%), 150 ($C_2HF_5NO^+$, 8·1%), 149 ($C_2F_5NO^+$, 2·7%), 147 ($C_5H_{15}OSi_2^+$, 25·6%), 81 (CHF_2NO^+, 11·6%), 77 ($C_2H_6FSi^+$, 4·8%), 73 ($C_3H_9Si^+$,

---

[5] W. D. Blackley and R. R. Reinhard, *J. Amer. Chem. Soc.*, 1965, **87**, 802; S. P. Makarov, A. Ya Yakubovich, S. S. Dubov, and A. N. Medvedev, *Doklady Akad. Nauk S.S.S.R.*, 1965, **160**, 1319.

[6] J. W. Ryan and J. L. Speier, *J. Amer. Chem. Soc.*, 1964, **86**, 895.

[7] R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisher, *J. Amer. Chem. Soc.*, 1961, **83**, 4385.

[8] A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, 1965, **87**, 16.

[9] A. H. Dinwoodie and R. N. Haszeldine, *J. Chem. Soc.*, 1965, 1675.

3·2%), 69 (CF_3^+, base peak), and 66 ($CH_2F_2N^+$, 3·8%); the ^{19}F n.m.r. spectrum showed a singlet at 8·1 p.p.m. to low field from external reference trifluoroacetic acid, and the ^1H spectrum showed a singlet at 6·86 p.p.m. to high field from external reference benzene; and (vii) hexamethyldisiloxane (*ca.* 0·05 g., 0·3 mmole, 5%) which was not separated but identified by its g.l.c. retention time.

Platinum-catalysed Reaction of Trifluoronitrosomethane with Trimethylsilane.—Hexachloroplatinic acid hydrate (0·025 g.) was dissolved in methyl alcohol (10 ml.) and the solution was poured into a blackened Pyrex tube (610 ml.). Removal of the methanol left a thin film of hexachloroplatinic acid which was reduced by leaving it in contact with trimethylsilane at just less than 1 atm. pressure for 48 hr. The trimethylsilane was then removed and trifluoronitrosomethane (1·06 g., 10·71 mmoles) and trimethylsilane (0·79 g., 10·68 mmoles) were added. The reaction, as measured by the pressure fall, was *ca.* 90% complete within 48 hr., although a trace of trifluoronitrosomethane (blue colour) remained until the 5th day, and the products were (i) nitrogen (0·007 g., 0·26 mmole, 5% based on $CF_3\cdot NO$), (ii) hexafluoroazoxymethane (0·009 g., 0·05 mmole, 1% based on $CF_3\cdot NO$), (iii) unchanged trimethylsilane (0·007 g., 0·10 mmole, 1%), (iv) trimethylfluorosilane (0·092 g., 1·02 mmoles, 10% based on Me_3SiH consumed), (v) (II) (1·30 g., 7·90 mmoles, 74%), (vi) (I) (0·20 g., 0·87 mmole, 8% based on Me_3SiH consumed), (vii) a small amount of hexamethyldisiloxane (*ca.* 0·15 g., 0·1 mmole, 2%), and an ether-soluble oil (0·05 g.).

Comparison Reactions.—The following reactions were carried out. (*a*) Trifluoronitrosomethane (0·66 g., 6·7 mmoles) and trimethylsilane (0·50 g., 6·7 mmoles) were sealed in a silica tube (80 ml.) and irradiated with both the gas and liquid phases exposed to the radiation. (*b*) Trifluoronitrosomethane (1·15 g., 11·6 mmoles) and trimethylsilane (0·86 g., 11·6 mmoles) were sealed in a silica tube (140 ml.) and the gas phase was irradiated. (*c*) Trifluoronitrosomethane (0·87 g., 8·75 mmoles), trimethylsilane (0·65 g., 8·75 mmoles), and the reduced platinum catalyst (0·025 g. of hexachloroplatinic acid hydrate) were sealed in a Pyrex tube (105 ml.) and left in the dark. (*d*) Trifluoronitrosomethane (1·42 g., 14·35 mmoles) and trimethylsilane (1·06 g., 14·35 mmoles) were sealed in a silica tube (175 ml.) and kept in the dark. The relative abundances of the products in these reactions were established by partial separation into various fractions and then g.l.c. and mass spectrographic analysis of each fraction. The results are shown in the Table.

Hydrolysis of N-*Trifluoromethyl*-O-*trimethylsilylhydroxylamine.*—The hydroxylamine (0·044 g., 0·25 mmole) reacted immediately with purified degassed water (0·5 ml.) to give hexamethyldisiloxane (*ca.* 0·010 g., *ca.* 0·06 mmole, *ca.* 48%), trimethylfluorosilane (*ca.* 0·009 g., *ca.* 0·10 mmole, *ca.* 40%), and carbon dioxide (0·004 g., 0·09 mmole).

Comparison reactions

	U.v.*	U.v.†	Pt-catalysed	Dark reaction ‡
Pressure (atm.)	4	4	4	4
Temp.	30°	30°	22°	22°
Time (days) ...	4	5	3	180
Ratio (I) : (II)...	3·0	1·0	0·1	
Ratio N_2	6·5 :	1·8 :	1·0	
Ratio Me_3SiF ...	2·5 :	1·5 :	1·0	

* Both the liquid and gas phases irradiated. † Only gas phase irradiated. ‡ Only unchanged reactants were recovered.

Pyrolysis of N-*Trifluoromethyl*-O-*trimethylsilylhydroxylamine.*—The hydroxylamine (0·250 g., 1·45 mmoles), sealed in a Pyrex tube (20 ml.) and heated at 100° (12 hr.), gave nitrogen (0·001 g., 0·03 mmole, 4%), a mixture (0·027 g., 0·40 mmole; *M*, 68) shown by i.r. spectroscopy to contain carbon dioxide, trifluoromethylisocyanate, possibly trifluoromethane, and various unidentified components, and trimethylfluorosilane (0·107 g., 1·16 mmoles, 80%) (Found: *M*, 90. Calc. for C_3H_9FSi: *M*, 92). A white solid which encrusted the walls of the tube was not identified.

Hydrolysis of NN-*Bistrifluoromethyl*-O-*trimethylsilylhydroxylamine.*—The hydroxylamine (0·101 g., 0·42 mmole) reacted with purified degassed water (0·5 ml.) to give hexamethyldisiloxane (0·029 g., 0·18 mmole, 86%) and bistrifluoromethylhydroxylamine (0·064 g., 0·38 mmole, 90%) (Found: *M*, 168. Calc. for C_2HF_6NO: *M*, 169).

Reaction of Trimethylchlorosilane with NN-*Bistrifluoromethylhydroxylamine.*—The silane (0·131 g., 1·20 mmoles) and the hydroxylamine (0·202 g., 1·20 mmoles), prepared by the hydrolysis of *O*-nitroso-*NN*-bistrifluoromethylhydroxylamine,[2,3] gave, after 1 hr., *NN*-bistrifluoromethyl-*O*-trimethylsilylhydroxylamine (0·145 g., 0·60 mmole, 50%) (Found: *M*, 238, Calc. for $C_5H_9F_6NOSi$: *M*, 241), hexamethyldisiloxane (0·045 g., 0·28 mmole, 46%), and a mixture of hydrogen chloride, silicon tetrafluoride, and trifluoromethyl isocyanate.

We thank Imperial Chemical Industries Limited, Nobel Division, for a gift of trimethylchlorosilane.

[8/762 *Received, May* 31*st*, 1968]