Reactions of Trichloronitrosomethane

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Trichloronitrosomethane reacts with silver(I) fluoride to give O-nitrosobistrifluoromethylhydroxylamine, and with silver(I) fluoride in dimethylformamide to give hexafluoroazoxymethane. With sodium fluoride in dimethylform-amide it yields dimethyltrifluoromethylamine.

THE direct preparation of trichloronitrosomethane from chloroform ¹ has prompted further investigation of its reactions. Except for its oxidation to trichloronitromethane, its reduction to dichloroformaldehyde oxime, and its thermal decomposition,² little work on the reactions of trichloronitrosomethane has been published. Some reactions of the nitroso-compound with fluorinating agents are now reported.

Existing preparations of fluorocarbon and chlorofluorocarbon derivatives of nitrogen are mostly costly and often lengthy. The use of trichloronitrosomethane as a substrate for fluorination offered a new route to these compounds. It has now been found that trichloronitrosomethane and fluorinating agents constitute a highly reactive system, and the products found depend upon the conditions of the reaction and the fluorinating agent used.

Sodium fluoride suspended in dimethylformamide has been reported as a reagent for substitutive fluorination under mild conditions.³ Nitrosyl chloride, which is the most reactive final product of the thermal decomposition of trichloronitrosomethane,² has been used in a reaction in which dimethylformamide was the solvent,⁴ and presumably does not react with the amide. When sodium fluoride in dimethylformamide was treated with trichloronitrosomethane, however, a 12% yield of dimethyltrifluoromethylamine,^{5,6} could be separated, showing that the dimethylformamide had been involved in reaction. The dimethyltrifluoromethylamine was formed slowly at 40° and more rapidly at 80°.

Some more detailed spectroscopic data for dimethyltrifluoromethylamine than those previously reported,^{5,6} are given in the Experimental section. The formation of the observed metastable ions in the mass spectrum must involve considerable rearrangements. The breakdown Scheme, in which an asterisk indicates that the appropriate metastable transitions were observed, accounts for the recorded spectrum.



Breakdown of $CF_3N(CH_3)_2$ in the mass spectrometer, where each species was observed as a singly charged cation SCHEME

When a solution of trichloronitrosomethane in dimethylformamide reacted with silver(1) fluoride instead of with sodium fluoride, the yield of dimethyltrifluoromethylamine was much lower (1.6%), and hexafluoroazoxymethane was the chief fluorocarbon product isolated (10.5%) yield). Trifluoronitrosomethane is known to undergo a disproportionation reaction in the presence of bases,⁷ to give hexafluoroazoxymethane and trifluoronitromethane [reaction (1)]. The relative amounts

$$3CF_3NO \xrightarrow{\text{Base}} CF_3N(O):NCF_3 + CF_3NO_2 \quad (1)$$

of the azoxy-compound and the nitro-compound formed are not stoicheiometric, however, and may be affected by the presence of reducing or oxidising agents in the reaction mixture.⁸ In the present case, carbon dioxde ⁶ F. S. Fawcett, C. W. Tullock, and D. D. Coffman, J. Amer.

Chem. Soc., 1962, **84**, 4275.

⁷ R. N. Haszeldine and J. Jander, J. Chem. Soc., 1954, 919.
 ⁸ A. Ya. Yakubovich, V. A. Ginsburg, S. P. Makarov, V. A. Shpanskii, N. F. Privezentseva, L. L. Martynova, B. V. Kir'yan, and A. L. Lemke, Proc. Acad. Sci. (U.S.S.R.), 1961, 140, 1069.

¹ B. W. Tattershall, preceding paper.

 ² W. Prandtl and K. Sennewald, Chem. Ber., 1929, 62, 1754.
 ³ C. W. Tullock and D. D. Coffman, J. Org. Chem., 1960, 25, 2016.

 ⁴ P. Tarrant and D. E. O'Connor, J. Org. Chem., 1964, 29, 2012.
 ⁵ R. J. Harder and W. C. Smith, J. Amer. Chem. Soc., 1961, 83, 3422.

J. Chem. Soc. (A), 1970

was observed, which may have been formed by the oxidation of dimethylformamide.

In the absence of solvents, sodium fluoride effected hardly any fluorination of trichloronitrosomethane; the chief reaction then was the known pyrolysis of the nitrosocompound to give nitrosyl chloride. Silver(I) fluoride, however, reacted readily with neat trichloronitrosomethane; several products, formed in low yield, could be neither separated nor identified, but the main product was O-nitrosobistrifluoromethylhydroxylamine, (CF₃)₂-NONO, which is a dimer of trifluoronitrosomethane, and has previously been found as the product of u.v. irradiation of trifluoronitrosomethane,^{9,10} or of its reaction with nitric oxide.¹¹ It has not been ascertained whether the trichloronitrosomethane reacted to give chlorocarbon intermediates, which were then fluorinated, or whether it was first fluorinated to trifluoronitrosomethane, which then reacted further. In both the fluorinations using silver fluoride, a trace of trifluoronitrosomethane was found.

Prandtl and Sennewald² reported that although neat trichloronitrosomethane decomposes thermally over several months at room temperature, it is rapidly pyrolysed at its normal b.p. (57°), approximately according to equation (2). The present author has confirmed

 $3 \operatorname{CCl}_3 \cdot \operatorname{NO} \longrightarrow \operatorname{CCl}_3 \cdot \operatorname{N:CCl}_2 + \operatorname{CCl}_3 \cdot \operatorname{NO}_2 + \operatorname{NOCl} \quad (2)$

that these products are formed under the described conditions. Some of the fluorinations described here, however, were carried out at temperatures as high as 80°, so it was thought desirable to examine the pyrolysis of the nitroso-compound in solution.

Chloroform was chosen as solvent, since the nitrosocompound can be produced by the photochemical nitrosation of chloroform with nitrosyl chloride, as an inseparable mixture with chloroform,¹ and pyrolysis of such a mixture might be a useful preparation of dichloromethylene(trichloromethyl)amine. The scale of the experiment and the concentration of the nitroso-compound were chosen to simulate the product of the preparation from chloroform. The nitroso-compound decomposed steadily during ca. 4 h, when the mixture was heated under reflux at atmospheric pressure. The quantity of chlorocarbon-nitrogen products was insufficient for them to be separated by distillation at reduced pressure with a fractionation column, and complete separation could not be effected by highvacuum methods. Dichloromethylene(trichloromethyl)amine was identified as a chief product, as had been found in pyrolysis of the neat liquid, but perhaps because of the milder conditions employed both for the pyrolysis and in the attempted separation, other products could be detected.

The peak of highest m/e value of a series of O-containing peaks in the mass spectrum of the products, corresponded to $C_3Cl_5N_2O^+$ (confirmed by mass measurement). In chlorocarbon compounds of this type, a parent ion is rarely observed, but rather the ion of highest m/e which is observed contains one chlorine atom less than the parent substance. If this were so in this case, the substance responsible for the spectrum would be of molecular formula $C_3Cl_6N_2O$. In the light of the fragmentation pattern observed, and the intense absorption at 1835 cm⁻¹ (C-O stretching frequency for a carbonyl group in a strained ring) in the i.r. spectrum of the product, the

presence of a compound $Cl_3C \cdot \dot{N} \cdot C(O) \cdot \dot{N} \cdot CCl_3$ may be postulated. The analogous di-t-butyldiaziridinone has been reported ¹² to have high thermal stability, and to show i.r. absorptions at 1926sh, 1880, 1862, and 1800sh cm^{-1} (in CCl_4).

EXPERIMENTAL

Compounds were manipulated in a Pyrex glass vacuum system, the stopcocks of which were lubricated with Kel-F No. 90 grease. Pressures were measured by use of a Pyrex spiral gauge. I.r. spectra were measured with Perkin-Elmer 125 or 457 spectrophotometers, n.m.r. spectra with a Bruker HFX5-90 MHz spectrometer, and mass spectra with an A.E.I. MS 9 spectrometer.

Trichloronitrosomethane, prepared from trichloromethanesulphenyl chloride 2,13 was purified by vacuum fractionation (M = 148.6). Silver(I) fluoride was prepared by the method of Anderson and Bak.¹⁴ Dimethylformamide was heated at 120° with calcium hydride under nitrogen, then purified by vacuum fractionation.

Reaction of Trichloronitrosomethane with Fluorinating Agents.—(a) With silver(I) fluoride. A mixture of dried silver(1) fluoride (9.55 g, 75.3 mmol) and trichloronitrosomethane (0.751 g, 5.06 mmol) in a glass ampoule (30 ml) was heated at 40° for 8.5 h. The volatile products were a complex mixture which could be only partially separated by vacuum fractionation. Trifluoronitrosomethane (estimated yield < 2%) and O-nitrosobistrifluoromethylhydroxylamine were identified by their i.r. spectra. Yield of the O-nitrosohydroxylamine: ca. 20% by ¹⁹F n.m.r. absorption intensity measurements.

(b) With silver(1) fluoride in dimethylformamide. Trichloronitrosomethane (0.752 g, 5.06 mmol) and dimethylformamide (4.54 g, 62.1 mmol) were condensed onto dried silver(I) fluoride (8.41 g, 66.3 mmol) in a glass ampoule (30 ml); this was sealed, and the mixture was heated at 40° for 10 h, with occasional mixing of the reagents by means of an electric vibrator. The volatile products were partially separated by vacuum fractionation and codistillation; 15 unchanged trichloronitrosomethane and dimethylformamide were returned to the reaction ampoule containing the involatile products and the mixture was further heated at 80° for 3 h. Then the product retained by a trap at -45° in a vacuum fractionation was mainly dimethylformamide, and was discarded. The more volatile products from both

- ¹³ W. Prandtl and W. Dollfus, Chem. Ber., 1932, 65, 754.
 ¹⁴ F. A. Andersen and B. Bak, Acta Chem. Scand., 1953, 7, 236.
 ¹⁵ G. H. Cady and D. P. Siegwarth, Analyt. Chem., 1959, 31,
- 618.

<sup>J. Jander and R. N. Haszeldine, J. Chem. Soc., 1954, 696.
R. N. Haszeldine and B. J. H. Mattinson, J. Chem. Soc.,</sup>

^{1957, 1741.}

¹¹ D. A. Barr, R. N. Haszeldine, and C. J. Willis, J. Chem.

Soc., 1961, 1351. ¹² F. D. Greene and J. C. Stowell, J. Amer. Chem. Soc., 1964, 86, 3569.

stages of the reaction were further separated by codistillation, to give trifluoronitrosomethane (0.080 mmol, 1.6% yield), hexafluoroazoxymethane (0.27 mmol, 10.5% yield, and dimethyltrifluoromethylamine (0.080 mmol, 1.6% yield). A mixture (3.39 mmol, M = 44.5) of carbon dioxide, nitrous oxide, and traces of trifluoronitromethane and trifluoromethyl isocyanate remained unseparated; its mass spectrum showed that it was mainly carbon dioxide, rather than nitrous oxide. All the products were identified by their i.r. spectra; in addition, mass spectra were observed for CF₃NCO [m/e: 111(C₂F₃NO⁺); 92 (C₂F₂NO⁺); 69 (CF₃⁺); 64 (CF₂N⁺); and 50 (CF₂⁺)] and for CF₃N(O):NCF₃ [m/e: 162.9922 (calc. for C₂F₅N₂O⁺: 162.9931); 113 (CF₃-N₂O⁺); 99 (CF₃NO⁺); 69 (CF₃⁺); 50 (CF₂⁺); 44 (N₂O⁺); and 30 (NO⁺)].

(c) With sodium fluoride. A mixture of trichloronitrosomethane (0.768 g, $5 \cdot 17$ mmol) and dried sodium fluoride (2.52 g, $60 \cdot 0$ mmol) was heated in a glass ampoule (30 ml) at 40° for $5 \cdot 5$ h. The i.r. spectrum of the volatile products showed only nitrosyl chloride, unchanged trichloronitrosomethane, and a trace of chlorotrifluoromethane.

(d) With sodium fluoride in dimethylformamide. Trichloronitrosomethane (0.762 g, 5.13 mmol) and dimethylformamide (3.82 g, 52.2 mmol) were condensed onto dried sodium fluoride (2.30 g, 54.9 mmol) in a glass ampoule (40 ml), which was then sealed and heated at 40° for 7 h. After the i.r. spectrum of the volatile products had been recorded, heating was continued at 80° for $5 \cdot 2$ h, when the blue colour of the nitroso-compound had almost disappeared. Vacuum fractionation of the volatile products then yielded dimethyltrifluoromethylamine (0.624 mmol, 12.1% yield; M =111.3), identified spectroscopically 5,6 (see below). The more volatile products were partially separated by codistillation, and were estimated to contain carbon dioxide (3.14 mmol) and nitrous oxide (0.58 mmol). The lessvolatile products contained carbon tetrachloride, besides dimethylformamide and unchanged trichloronitrosomethane; this mixture was not successfully separated by distillation.

Spectroscopic Data for Dimethyltrifluoromethylamine..... I.r. spectrum of the gas. v: 3021m, 2984m, 2974sh,w, 2908m, 2870m, 2825m, 1494m, 1488m, 1480m, 1472sh,w, 1460m, 1344s, 1278s, 1200s, 1088vs, and 974m cm⁻¹.

N.m.r. spectra. The amine was dissolved in a mixture of carbon tetrachloride with known quantities of dichlorodifluoromethane and of tetramethylsilane, in a sealed tube. The ¹H n.m.r. showed a quartet, J = 0.92 Hz, at $\tau = 7.48$. The ¹⁹F n.m.r. showed an unresolved peak, sufficiently broad to include a septet with J = 0.92 Hz, at 62.85 p.p.m. to higher field from CCl₂F₂. The absorptions due to com-¹⁶ E. Kühle, B. Anders, and G. Zumach, Angew. Chem. Internat. Edn., 1967, **6**, 649. pound and to standard were integrated in each spectrum and, from the measured quantities of the standards, the ratio of protons to fluorine atoms was found to be ca. 2.

Mass spectrum [m/e (relative intensity), assigned formula]: 114 (1.7), ${}^{12}C_{2}{}^{13}CH_{6}F_{3}N^{+}$; 113.0456 (45.3), calc. for $C_{3}H_{6}F_{3}N^{+}$ 113.0452; 112 (100), $C_{3}H_{5}F_{3}N^{+}$; 94 (16.3), $C_{3}H_{6}F_{2}N^{+}$; 78.0158 (25.2), calc. for $C_{2}H_{2}F_{2}N^{+}$ 78.0155; 69 (16.6), CF_{3}^{+} ; 60.0251 (25.3), calc. for $C_{2}H_{3}FN^{+}$ 60.0250; 50 (2.1), CF_{2}^{+} ; 44 (1.3), $C_{2}H_{6}N^{+}$; 43 (4.2), $C_{2}H_{5}N^{+}$; 42 (13.8), $C_{2}H_{4}N^{+}$; 41 (3.0), $C_{2}H_{3}N^{+}$; 40 (1.7), $C_{2}H_{2}N^{+}$; 33 (8.5), $CH_{2}F^{+}$; and 31 (1.5), CF^{+} . Metastable ions gave peaks at 54.2, 38.3, and 32.2, corresponding to 112 \longrightarrow 78 + 34, 94 \longrightarrow 60 + 34, and 112 \longrightarrow 60 + 52, respectively.

Pyrolysis of Trichloronitrosomethane (in Chloroform).— A solution of trichloronitrosomethane (3.35 g, 22.6 mmol) in chloroform (13.0 g) was heated under reflux from a water condenser; gas passing this was lead to a trap at -196° to which a constant pressure (*ca.* 1 atm) of nitrogen was applied. A 20 cm column packed with glass beads was interposed between condenser and heated pot. The residual liquid had become almost colourless after 4 h, and heating was increased so that any involatile pyrolysate trapped in the column packing was washed down.

The gaseous product was shown by its i.r. spectrum to be chiefly nitrosyl chloride, with some carbonyl chloride. The less volatile residue (15.30 g) was vacuum fractionated to remove chloroform and the residual liquid was subjected to molecular distillation; complete separation was not effected. One component was identified as dichloromethylene(trichloromethyl)amine (ca. 0.7 g, 3.3 mmol), on the basis of its i.r. spectrum [bands at 1638s (C=N stretching frequency for an -N=CCl₂ compound ¹⁶), 1020m, 936s, 801m, 777s, and 619m cm⁻¹] and its mass spectrum $[m/e: 178 (C_2Cl_4N^+); 143 (C_2Cl_3N^+); 117 (CCl_3^+);$ 96 (CCl_2N^+); 82 (CCl_2^+); and 61 ($CClN^+$)], in which peak assignments were confirmed by the observation of the appropriate chlorine isotope patterns. Another, less volatile component underwent molecular distillation slowly at 50°, and showed a characteristic strong i.r. absorption at 1835 cm⁻¹. The mass spectrum of this fraction, besides showing the fragments listed above for CCl₃N:CCl₂, showed a series of ions containing oxygen, which may have been fragments from a single compound (the number of chlorine atoms indicated by the isotope patterns is shown in parentheses): m/e: 254.8404 (5 Cl), calc. for $C_3^{35}Cl_5N_2O^+$ 254.8453; 124 (2 Cl), C₂Cl₂NO⁺; 89 (1 Cl), C₂ClNO⁺; and 63 (1 Cl), CClO⁺. A weak pattern was also observed at m/e = 229 (5 Cl), and assigned to C₂Cl₅NO⁺.

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