238. *Trifluoromethanesulphenyl Pseudohalides.*

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Trifluoromethanesulphenyl cyanide, thiocyanate, selenocyanate, and isocyanate have been prepared and characterised. The hydrolysis of the isocyanate and of a dimeric form has been investigated and the structures of the products are discussed. Ammonia and amines react with the isocyanate to form the corresponding urea derivatives. The isocyanate trimerises at 100° without the necessity of a catalyst.

Reaction between trifluoromethanesulphenyl chloride and silver cyanide, thiocyanate, selenocyanate, or cyanate occurs readily and quantitatively, to yield the corresponding trifluoromethanesulphenyl pseudohalides. The cyanide so prepared is slowly hydrolysed by water but is rapidly decomposed by dilute alkali, yielding fluoride, carbonate, cyanate, and sulphide, a reaction which indicates attack on the S–C bond, with initial formation of the thiol, $CF_3{\cdot}SH$, and the cyanate ion, corresponding with the hydrolysis of organo-thiocyanates.[1] Fluorine nuclear magnetic resonance studies of the cyanide gave a chemical shift of 38·8 p.p.m., whereas, for a number of compounds containing the $CF_3{\cdot}S{\cdot}N$ group the shift is 51 ± 3 p.p.m. This indicates that the cyanide has the normal rather than the iso-structure, which is consistent with the nature of the hydrolysis products. Trifluoromethanesulphenyl thiocyanate was unstable above room temperature and decomposed quantitatively to bistrifluoromethyl disulphide and polythiocyanogen. It was, however, stable to water but was hydrolysed by dilute alkali to a complex mixture of products which were not fully identified. This behaviour also parallels that of organo-sulphenyl thiocyanates.[2] The selenocyanate, $CF_3{\cdot}S{\cdot}SeCN$, was stable up to about 300°: decomposition at 500° yielded selenium quantitatively. Phenylsulphenyl selenocyanate decomposes at a lower temperature (175°) according to the equation $Ph{\cdot}S{\cdot}SeCN \longrightarrow (PhS)_2 + (CN)_2 + Se_3(CN)_2 + Se$.

Reaction of trifluoromethanesulphenyl chloride with silver cyanate gave trifluoromethanesulphenyl isocyanate as the major product (*ca.* 75%), but, in addition, a second product (*ca.* 25%) proved to be a dimer. Hydrolysis of the monomer with water at room temperature gave *NN'*-bis(trifluoromethanesulphenyl)urea and carbon dioxide quantitatively. The intermediate carbamic acid, $CF_3{\cdot}S{\cdot}NH{\cdot}CO_2H$, was not isolated though, in the analogous hydrolysis of organo-isocyanates, this has been done.[3] Reaction of trifluoromethanesulphenyl isocyanate with ammonia, methylamine, dimethylamine, aniline, and diphenylamine gave the products $CF_3{\cdot}S{\cdot}NH{\cdot}CO{\cdot}NH_2$, $CF_3{\cdot}S{\cdot}NH{\cdot}CO{\cdot}NHMe$, $CF_3{\cdot}S{\cdot}NH{\cdot}CO{\cdot}NMe_2$, $CF_3{\cdot}S{\cdot}NH{\cdot}CO{\cdot}NHPh$, and $CF_3{\cdot}S{\cdot}NH{\cdot}CO{\cdot}NPh_2$ corresponding to addition across the N=C bond, as in the case of organo-isothiocyanates.[4]

The dimer $(CF_3{\cdot}S{\cdot}NCO)_2$ is believed to be *NN*-bis(trifluoromethanesulphenyl)carbamoyl isocyanate, $(CF_3{\cdot}S)_2N{\cdot}CO{\cdot}NCO$. Its infrared spectrum shows strong absorptions at 2260 cm.$^{-1}$, corresponding with absorption at 2269 cm.$^{-1}$ in organo-isocyanates.[5] There is no absorption above 3000 cm.$^{-1}$, showing that no N–H or NH_2 group is present. There is also a doublet at 1755, 1738 cm.$^{-1}$, associated with a C=O group, and other features are in accord with the presence of $CF_3{\cdot}S$ groups. Hydrolysis with water occurs quantitatively, to give carbon dioxide and an isomer of *NN'*-bis(trifluoromethanesulphenyl)urea. This could be the asymmetrical disubstituted compound $(CF_3{\cdot}S)_2N{\cdot}CO{\cdot}NH_2$ or the isourea $CF_3{\cdot}S{\cdot}NH{\cdot}C({:}NH){\cdot}O{\cdot}S{\cdot}CF_3$. The spectrum of the deuterated compound, prepared from the dimer and deuterium oxide, shows the first of these formulæ to be correct. The bands at 3480—3280 cm.$^{-1}$ in the hydrogen compound are assigned to sym. and asym. N–H

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[1] Tarbell and Harnish, *Chem. Rev.*, 1951, **49**, 79.

[2] Lecher and Simon, *Ber.*, 1921, **54**, 632; Lecher and Wittwer, *Ber.*, 1922, **55**, 1474.

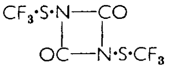
[3] van Hoogstraten, *Rec. Trav. chim.*, 1932, **51**, 414.

[4] Wurtz, *Annalen*, 1849, **71**, 326; 1851, **80**, 347; Hofmann, *ibid.*, 1850, **74**, 14.

[5] Davison, *J.*, 1953, 3712.

stretching vibrations of the NH_2 group and are found in urea,[6] primary amides,[7] and trifluoromethanesulphenylurea. The band at 1604 cm.$^{-1}$ can also be assigned to the NH_2 deformation band and is found in the spectrum of urea at 1606 cm.$^{-1}$. Replacement of hydrogen by deuterium shifts the 3480—3280 cm.$^{-1}$ absorptions to 2590—2430 cm.$^{-1}$ and in deuterated urea to 2604—2421 cm.$^{-1}$. The displaced 1604 cm.$^{-1}$ absorption in the deuterated compound is masked by strong absorption at 1200—1100 cm.$^{-1}$ due to the C–F stretching vibration. The symmetrically disubstituted urea has a completely different spectrum, especially at 3500—3000 and around 1600 cm.$^{-1}$. Above 3000 cm.$^{-1}$ it has only one strong absorption, at 3280 cm.$^{-1}$, which is shifted to 2440 cm.$^{-1}$ in the deuterated compound. In the 1600 cm.$^{-1}$ region it shows no absorption apart from a band of medium intensity at 1507 cm.$^{-1}$, which is shifted on deuteration but may be assigned to a N–H deformation rather than a deformation of the amino-group. Other features of the spectrum are consistent with the asymmetrical formulation.

A cyclic formulation (A) of the dimer is excluded by the infrared spectrum and also by the fact that hydrolysis would give the symmetrical disubstituted urea. Phenyl isocyanate gives such a compound in the presence of triphenylphosphine or a tertiary amine as catalyst,[8] but with alkali-metal formates or acetates as catalyst gives a cyclic trimer.[9] Trifluoromethanesulphenyl isocyanate trimerises in absence of a catalyst at 100° to tris(trifluoromethanesulphenyl) isocyanurate. Fluorine nuclear magnetic resonance measurements on the trimer show two absorptions of similar intensity, at 48·2 and 48·8 p.p.m. This observation suggests the presence of two geometrical isomers, one with all the trifluoromethanesulphenyl groups in the plane of the ring and one with one of the groups out of the plane. The scale model of the proposed structure showed that free rotation about the N–S bond would be sterically hindered.


(A)

Experimental

Trifluoromethanesulphenyl chloride was prepared from bis(trifluoromethylthio)mercury and chlorine.[10] In several reactions in which it was used it was contaminated with small amounts of bistrifluoromethyl disulphide, complete removal of which was more readily achieved from the products than from the starting material. All other starting materials were prepared and purified by known methods.

Preparation of Trifluoromethanesulphenyl Cyanide.—Trifluoromethanesulphenyl chloride (2·5 g., 18·3 mmoles) reacted in a sealed tube with dry silver cyanide (8 g., 59·8 mmoles) at room temperature (1 hr.). *Trifluoromethanesulphenyl cyanide* was isolated from the product by fractional condensation at −80° (Found: S, 26·0; F, 44·4%; *M*, 127. C_2F_3NS requires S, 25·2; F, 44·85%; *M*, 127). Vapour pressures (−47° to +21°) were given by $\log_{10} p$ (mm.) = $8{\cdot}395 - 1704/T$. The extrapolated b. p. was 36°, the m. p. −70°, the latent heat of vaporisation 7660 cal./mole, and Trouton's constant 24·8.

After trifluoromethanesulphenyl cyanide (0·563 g.) had been heated with water (1 g.) at 100° for 3 hr., 0·383 g. was recovered. The aqueous solution contained fluoride and sulphide. Sulphur and carbon dioxide were also formed. The solution gave ammonia when heated with alkali. Hydrolysis by 10% alkali was rapid and complete at room temperature. The hydrolysate contained fluoride, sulphide, polysulphide, and carbonate. Cyanide and thiocyanate were absent. Cyanate was detected by liberation of ammonia with alkali after acid hydrolysis, sulphide having first been removed with cadmium carbonate.

Preparation of Trifluoromethanesulphenyl Thiocyanate.—Trifluoromethanesulphenyl chloride (3 g., 22 mmoles) and silver thiocyanate (10 g., 60·3 mmoles) in a sealed tube at room temperature (2 hr.) gave, after removal of a trace of bistrifluoromethyl disulphide present in the

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[6] Stewart, *J. Chem. Phys.*, 1957, **26**, 248.

[7] "The Chemistry of Penicillin," Princeton Univ. Press, N.J., 1949, p. 390.

[8] Hofmann, *Ber.*, 1871, **4**, 246; Raiford and Freyermuth, *J. Org. Chem.*, 1943, **8**, 230.

[9] Hofmann, *Ber.*, 1885, **18**, 764.

[10] Haszeldine and Kidd, *J.*, 1953, 3225.

starting material by distillation at $-60°$, *trifluoromethanesulphenyl thiocyanate*, which distilled at $-20°$ (Found: *M*, 150—163. $C_2F_3NS_2$ requires *M*, 159). The m. p. was $-35·5°$. It decomposed in a few hours at room temperature to polythiocyanogen and bistrifluoromethyl disulphide. This reaction was used in the analysis. A sample (0·761 g., 4·8 mmoles) in a sealed tube (14 days) gave thiocyanogen (0·277 g.) (Found: C, 20·4; N, 22·4; S, 54·5. Calc. for CNS: C, 20·7; N, 24·2; S, 55·1%). The infrared spectrum was identical with that of an authentic specimen. The other product was bistrifluoromethyl disulphide (0·483 g.) (Found: *M*. 200. Calc. for $C_2F_6S_2$: *M*, 202). The identity was checked by the infrared spectrum. The weights of these two products expected for the reaction $2CF_3{\cdot}S{\cdot}SCN = CF_3{\cdot}S{\cdot}S{\cdot}CF_3 + 2(SCN)$ were 0·483 and 0·277 g., respectively. The thiocyanate was hydrolysed very slowly by water and rapidly by 10% aqueous alkali, but the products were not identified.

Preparation of Trifluoromethanesulphenyl Selenocyanate.—Trifluoromethanesulphenyl chloride (5·24 g., 39·2 mmoles) containing a little of the disulphide reacted in a sealed tube (1 hr.) with silver selenocyanate (11 g., 51·7 mmoles). After removal of disulphide, *trifluoromethanesulphenyl selenocyanate* was isolated by distillation at $-30°$ (Found: C, 10·6; S, 14·7; Se, 37·4%; *M*, 207. C_2F_3NSSe requires C, 11·65; S, 15·5; Se, 38·2%; *M*, 206). Vapour pressures ($-10°$ to $+40°$) were given by $\log_{10} p(\text{mm.}) = 7·322 - 1741/T$. The b. p. was 119°, the m. p. $-67°$, the latent heat of vaporisation 8170 cal./mole, and Trouton's constant 20·8. The selenocyanate (0·101 g.), heated in a sealed tube at 500° for 6 hr., gave selenium (0·0395 g.). Other products, identified by their infrared spectra, were carbon dioxide, carbonyl sulphide, and silicon tetrafluoride.

Preparation of Trifluoromethanesulphenyl Isocyanate.—Trifluoromethanesulphenyl chloride (3·5 g., 2·56 mmoles) and silver cyanate (10 g., 6·65 mmoles) in a sealed tube at room temperature (1 hr.) gave two products after removal of bistrifluoromethyl disulphide present in the starting material. The first, volatile in a vacuum at $-20°$, was *trifluoromethanesulphenyl isocyanate* (Found: *M*, 142. C_2OF_3NS requires *M*, 143). Analysis was based on the quantitative hydrolysis, described below. Vapour pressures ($-42°$ to $+20°$) were given by $\log_{10} p(\text{mm.}) = 7·741 - 1458/T$. The b. p. was 27°, the m. p. $-97°$, the latent heat of vaporisation 6350 cal./mole, and Trouton's constant 21·2. Trifluoromethanesulphenyl isocyanate (0·535 g.) and water (0·895 g.) in a sealed tube at room temperature gave carbon dioxide (0·084 g.) (Found: *M*, 43·6) (further identified by its infrared spectrum) and NN′-*bis(trifluoromethanesulphenyl)urea* (0·482 g.) (Found: C, 13·8; N, 11·2; S, 24·4%; *M*, 252. $C_3H_2F_6N_2OS_2$ requires C, 13·8; N, 10·8; S, 24·6%; *M*, 260). The m. p. was 182°. The theoretical weights of the two products from the equation $2CF_3{\cdot}S{\cdot}NCO + H_2O = (CF_3{\cdot}S{\cdot}NH)_2CO + CO_2$ are 0·082 and 0·486 g., respectively.

The second reaction product (*ca.* 25% of the whole) was a liquid, which was separated by distillation in vacuum at room temperature and purified by fractional condensation; it was a *dimer* of trifluoromethanesulphenyl isocyanate [Found: C, 17·2; N, 10·2; S, 22·1%; *M*, 302. $(CF_3{\cdot}S{\cdot}NCO)_2$ requires C, 16·8; N, 9·8; S, 22·4%; *M*, 286]. It was very sensitive to hydrolysis. A sample (0·380 g.) sealed with excess of water gave carbon dioxide (0·061 g.) (identified by its infrared spectrum) and the asymmetrical isomer, NN-*bis(trifluoromethanesulphenyl)urea* (0·332 g.) (Found: C, 13·7; H, 0·98; N, 11·2; S, 23·8%; *M*, 254. $C_3H_2F_6N_2OS_2$ requires C, 13·8; H, 0·8; N, 10·8; S, 24·6%; *M*, 260). The m. p. was 43°. The weights of hydrolysis products for the equation $(CF_3{\cdot}S{\cdot}NCO)_2 + H_2O = (CF_3{\cdot}S)_2N{\cdot}CO{\cdot}NH_2 + CO_2$ are 0·061 and 0·332 g., respectively. Spectroscopic evidence for the identity of the urea derivative is given elsewhere.

Trimerisation of Trifluoromethanesulphenyl Isocyanate.—A sample, heated in a sealed tube at 100° for 4 hr., gave a white *trimer*, m. p. 111° [Found: C, 16·8; N, 10·1; S, 22·2%; *M*, 441. $(CF_3{\cdot}S{\cdot}NCO)_3$ requires C, 16·8; N, 9·8; S, 22·4%; *M*, 429].

Reactions of Trifluoromethanesulphenyl Isocyanate.—(*a*) *With ammonia.* Trifluoromethanesulphenyl isocyanate (0·5 g.) was shaken with an excess of ammonia in a sealed tube for 1 hr. The product, after removal of ammonia at $-40°$, was *trifluoromethanesulphenylurea* (Found: C, 15·2; H, 2·0; N, 18·5. $C_2H_3F_3N_2OS$ requires C, 15·0; H, 1·8; N, 17·5%). The m. p. was 102—104°. The compound was soluble in ether and acetone but insoluble in carbon disulphide, benzene, or carbon tetrachloride.

(*b*) *With methylamine.* Trifluoromethanesulphenyl isocyanate (0·5 g.) and methylamine (1·5 g.) gave, after removal of the excess of amine, N-*methyl*-N′-*trifluoromethanesulphenylurea* (Found: C, 21·4; H, 3·05; N, 16·8. $C_3H_5F_3N_2OS$ requires C, 20·6; H, 2·9; N, 16·05%), soluble in ether and acetone but insoluble in water. The m. p. was 140° (sublimes).

(*c*) *With dimethylamine.* The isocyanate (0·5 g.) and dimethylamine under the same conditions gave NN-*dimethyl*-N′-*trifluoromethanesulphenylurea* (Found: C, 25·7; H, 4·2; N, 15·7. $C_4H_7F_3N_2OS$ requires C, 25·5; H, 3·7; N, 14·9%), only slightly soluble in acetone. The m. p. was 126°.

(*d*) *With aniline.* The reaction was carried out in carbon disulphide (15 ml.) with the isocyanate (0·3 g.) and aniline (1 g.) at room temperature. The precipitate of N-*phenyl*-N′-*trifluoromethanesulphenylurea* was filtered off, washed with carbon disulphide, and dried in a vacuum (Found: C, 40·7; H, 3·0; N, 12·4. $C_8H_7F_3N_2OS$ requires C, 40·6; H, 3·0; N, 11·8%). It was soluble in chloroform, ether, and acetone and insoluble in water. The m. p. was 179° (decomp.).

(*e*) *With diphenylamine.* The isocyanate (0·3 g.) and diphenylamine in carbon disulphide (20 ml.) gave NN′-*diphenyl*-N-*trifluoromethanesulphenylurea* (Found: C, 53·9; H, 3·8; N, 8·6. $C_{14}H_{11}F_3N_2OS$ requires C, 53·9; H, 3·5; N, 9·0%). The m. p. was 157°. The compound was soluble in acetone but insoluble in water.

Infrared Spectra.—Measurements were made on a Perkin-Elmer model 21 double-beam spectrometer and an Infracord instrument (for the potassium bromide region), with sodium chloride or potassium bromide prisms. Solids were examined as Nujol or hexachlorobutadiene mulls, liquids as films, and vapours in a 10 cm. cell with sodium chloride windows. The following were recorded:

$(CF_3{\cdot}S{\cdot}OCN)_2$: 2370w, 2260s, 2180m, 1800w, 1755s, 1738s, 1527 vw, 1512vw, 1465m, 1430s, 1326s, 1185vw,br, 1150vs,br, 1110vs,br, 955m, 876w, 757s, 736m,sh, 728m, 603m, 590m, 570w, 540w, 489m, 478m, 433w.

$(CF_3{\cdot}S{\cdot}OCN)_3$: 1744s, 1483w, 1334s, 1323s, 1217m, 1199m, 1159s, 1130s, 1098m, 760w, 744m, 737m,sh, 720w, 656w, 595vw, 568w, 540vw, 532vw, 468m, 447w, 437w, 400s.

$CF_3{\cdot}S{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}S{\cdot}CF_3$: 3280s, 3190m,sh, 2925w, 1728w, 1679w, 1507m, 1480w, 1370m, 1206—1185s,br, 1173s, 1127s, 1107s, 936m, 822m, 751m, 670s,br, 562m, 537w,br, 469s, 428m.

$(CF_3{\cdot}S)_2{\cdot}N{\cdot}CO{\cdot}NH_2$: 3480s, 3350s, 3290s, 3200m, 1763w, 1727s, 1687s, 1604s, 1353s, 1175s,sh, 1155vs,br, 1104s, 955s, 935m,sh, 753s, 656m, 566m, 493s,br, 475s,br.

$CF_3{\cdot}S{\cdot}NH{\cdot}CO{\cdot}NH_2$: 3450s, 3310m,sh, 3260s, 1675s, 1605m,br, 1570w, 1475s,br, 1353m, 1175s, 1140m, 1116s, 1019m, 869w, 752m, 635m,br, 565m, 483s,br, 469s,br.

$CF_3{\cdot}S{\cdot}NH{\cdot}CO{\cdot}NHMe$: 3315s, 3250s, 2930w, 1657s, 1638m,sh, 1185m, 1562w, 1470m, 1427m, 1260w, 1175s, 1145s, 1125s, 1114s,sh, 963w, 890w, 755m, 720s, 670—640s,br, 565m, 473s, 455s.

$CF_3{\cdot}S{\cdot}NH{\cdot}CO{\cdot}NMe_2$: 3260s, 2960w, 2800vw, 2520vw, 2080vw, 1670s, 1535w, 1495s, 1445vs, 1413m, 1353m, 1267w, 1220vw, 1183m, 1148s, 1125s, 1065vw, 1020vw, 895vw, 845w, 840w, 763m, 750m, 720m, 635s, 611m, 564m, 553w, 539w, 525w, 502w, 493w, 468s.

$CF_3{\cdot}S{\cdot}NH{\cdot}CO{\cdot}NHPh$: 3260s,br, 3120w, 3040w, 2900w,br, 1647vs, 1596s, 1560vs, 1500m, 1472s, 1447m, 1365m,sh, 1311m, 1290m, 1255m, 1190s, 1168s, 1153m,sh, 1130vs, 1077w, 1049m, 1029w, 932m, 903w, 769m, 755w, 716m, 687m, 655m,br, 595w, 560w, 495m, 470m, 403w.

$CF_3{\cdot}S{\cdot}NH{\cdot}CO{\cdot}NPh_2$: 3190s, 2930w, 2850w, 1686s, 1590w, 1489m, 1435m,sh, 1432s, 1394m, 1311m, 1299m, 1277m, 1270m, 1200w, 1178w, 1157m, 1115s, 1069w, 1046w, 1030vw, 1020w, 957w, 904vw, 871vw, 832vw, 804vw, 756m, 749m, 696m,sh, 690m, 662w, 645w,br, 620w, 512w, 502w, 469w, 450w, 420—405w,br.

Fluorine Nuclear Magnetic Resonance Spectra.—Measurements were made on a Varian Associates V-4300 B spectrometer with a flux stabiliser at 40 Mc./sec., the sample spinning technique being used. Chemical shifts recorded in p.p.m. with a 10—20% solution in acetone (*a*) or dioxan (*b*), with trichlorofluoromethane as an internal standard, were: $CF_3{\cdot}SCl$, 49·8; $CF_3{\cdot}S{\cdot}CN$, 38·8; $CF_3{\cdot}S{\cdot}NCO$, 52·6; $CF_3{\cdot}S{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}S{\cdot}CF_3$, (*a*) 53·1; $(CF_3{\cdot}S)_2N{\cdot}CO{\cdot}NH_2$, (*a*) 51·5; $CF_3{\cdot}S{\cdot}NH{\cdot}CO{\cdot}NH_2$, (*b*) 53·2; $CF_3{\cdot}S{\cdot}NH{\cdot}CO{\cdot}NHMe$, (*a*) 53·9; $CF_3{\cdot}S{\cdot}NH{\cdot}CO{\cdot}NMe_2$, (*b*) 53·0; $CF_3{\cdot}S{\cdot}NH{\cdot}CO{\cdot}NHPh$, (*a*) 53·3; $CF_3{\cdot}S{\cdot}NH{\cdot}CO{\cdot}NPh_2$, (*a*) 52·4; $(CF_3{\cdot}S{\cdot}NCO)_3$, (*a*) 48·2, 48·8; $(CF_3{\cdot}S)_2N{\cdot}CO{\cdot}NCO$, 52·0.

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