

70. *Fluorination of Cyanogen and Cyanogen Chloride with Metal Fluorides.*

By H. J. EMELÉUS and G. L. HURST.

Experiments on the fluorination of cyanogen by cobaltic fluoride and mercuric fluoride, and of cyanogen chloride by mercuric fluoride, manganic fluoride, and cupric fluoride, provide evidence that these reagents are specific in their reaction. Mercuric bistrifluoromethylamide can be prepared directly by fluorinating cyanogen or cyanogen chloride with mercuric fluoride. Some of its reactions are described.

THE preparation of tetrafluoro-3,4-dihydro-1,2-diazete, $\overline{\text{CF}_2 \cdot \text{N} : \text{N} \cdot \text{CF}_2}$ (I), by reaction of cyanogen with argentic fluoride at 105—115° was reported earlier.¹ Cyanogen chloride with argentic fluoride in a water-cooled reactor gives $\text{CF}_3 \cdot \text{N} : \text{N} \cdot \text{CF}_3$ in high yield,² and perfluoroalkyl cyanides also give perfluoroazoalkanes as major products.³ None of these reactions gives compounds with N-F bonds. In contrast, trifluoromethyl cyanide is converted mainly into perfluoroethane and perfluoroethylamine by cobaltic fluoride at 200—250°,⁴ and these products have also been obtained from trifluoromethyl cyanide and fluorine at 275°. Attaway and Bigelow⁵ report, however, that at *ca.* 40°, and with a low ratio of fluorine to trifluoromethyl cyanide, perfluoroazoethane is formed in place of the perfluoro-amine. These results, though not strictly comparable, suggest that the fluorinating action of metal fluorides may to some extent be specific, quite apart from

¹ Emeléus and Hurst, *J.*, 1962, 3276.

² Glemser, Schroeder, and Haeseler, *Z. anorg. Chem.*, 1955, 282, 80.

³ Young, Durrell, and Dresdner, *J. Amer. Chem. Soc.*, 1960, 82, 4553.

⁴ Coates, Harris, and Sutcliffe, *J.*, 1951, 2762.

⁵ Attaway and Bigelow, *J. Amer. Chem. Soc.*, 1959, 81, 3599.

differences in reaction conditions. The experiments described below were made to examine this point further.

Cobaltic fluoride was first used to fluorinate cyanogen under the mild conditions used with argentic fluoride.¹ There was only slight reaction below 145°, the products being identified spectroscopically as CF₄, C₂F₆, and CF₃CN; none of the cyclic diazete (I) was detected. Nearly complete fluorination occurred at 150—160° to form a mixture of CF₄, C₂F₆ (total, 65%) together with NF₂·C₂F₄·NF₂, what was probably a mixture of (CF₃)₂NF with C₂F₅·NF₂, and a trace of C₂F₅·N:N·C₂F₅. These products were identified spectroscopically and by fluorine nuclear magnetic resonance. No CF₃·CN was found, though this may have been an intermediate. These products at 150—160° are similar to those obtained with elementary fluorine, many of the more vigorous reactions of which probably proceed by a free-radical mechanism. The same may be true of the more vigorous reactions with cobaltic fluoride. Under milder conditions, where no N-F bonds are formed, it is possible that co-ordination of the nitrogen atom of the cyanide group to the metal atom in the fluorinating reagent is an essential preliminary to reaction. Presence of hydrogen in the molecule undergoing fluorination also appears to favour the formation of N-F bonds. Thus, preliminary experiments on the fluorination of hydrogen cyanide with argentic fluoride give (CF₃)₂NF and CF₃·NF₂ as major products,⁶ and the same reagent with (CF₃)₂NH under fairly vigorous conditions favours formation of (CF₃)₂NF rather than CF₃·N:N·CF₃.³ Fluorination of methyl cyanide with mercuric fluoride at 150—180° also gives compounds with N-F bonds.⁷

The reaction of other metal fluorides has been investigated. Both cyanogen and cyanogen chloride with mercuric fluoride at 240° gave a mixture of CF₃·N:CF₂ and mercuric bistrifluoromethylamide, Hg[N(CF₃)₂]₂, as the major products. The latter is known⁸ to be formed from mercuric fluoride and CF₃·N:CF₂ and, in our experiments, yields of *ca.* 15% of mercurial were readily obtained by recycling the CF₃·N:CF₂. Some cyanuric fluoride was formed, but about 80% of the cyanide was unaccounted for. It may have been present in the reactor as Hg[N(CF₃)₂]F, but no evidence for this could be obtained; separation of such a product from the large excess of mercuric fluoride would be difficult. An alternative explanation is that polymeric material remained in the reactor.

Manganic fluoride gave no detectable products containing N-F bonds in its reaction with cyanogen chloride. Free chlorine was formed, together with CF₃·N:CF₂, though the yield of the latter was smaller than with argentic fluoride.² Cupric fluoride resembled mercuric fluoride to some extent; at 290—300° it gave an 85% yield of cyanuric fluoride from cyanogen chloride, and approximately 3·5% of CF₃·N:CF₂. At 415—450° the yield of the former dropped to *ca.* 50% while that of the latter rose to *ca.* 10%. These experiments with different fluorides do not provide a basis for discussing reaction mechanisms, especially in view of the minor products formed, not all of which have been identified. They appear to demonstrate, however, that the course of the reaction is determined to a considerable extent by the fluoride used, a fact which is also implicit in the work of earlier investigators.

Experiments were made on the reaction of mercuric fluoride on several halogen-containing compounds (CH₃I, PCl₃, Cu₂I₂, CNCl, and I₂). In each case the mercurial behaved as a fluorinating agent and liberated CF₃·N:CF₂. Reaction of the mercurial with excess of copper powder at 170° gave a good yield of (CF₃)₂N·CF·N·CF₃. There was no evidence for the formation of CuN(CF₃)₂, which might have been expected by analogy of the reaction between bistrifluoromethylthiomercury and copper, which yields trifluoromethylthiocopper, Cu(S·CF₃).⁹

⁶ G. L. Hurst, unpublished observation.

⁷ Hückel, *Nachr. Akad. Wiss., Göttingen, Math.-Physik, Kl.*, 1946, 36 (*Chem. Abs.*, 1949, 43, 6793d); Nerdel, *Naturwiss.*, 1952, 59, 209.

⁸ Young, Durrell, and Dresdner, *J. Amer. Chem. Soc.*, 1959, 81, 1587.

⁹ Man, Coffman, and Muettterties, *J. Amer. Chem. Soc.*, 1959, 81, 3575.

EXPERIMENTAL

The reactor was a copper tube (2.5 × 60 cm.) fitted at each end with standard tapers for attachment to Pyrex traps. The fluorides were prepared in this tube in quantities of 1—2 moles from the chlorides, with a fluorine flow of *ca.* 14 g./hr. Towards the end of the reaction the tube temperature was raised to the following values: AgCl, 200°; CoCl₂, 270°; MnCl₂, 270°; HgCl₂, 100°; CuCl and CuCl₂, 200—400°. Cyanogen and cyanogen chloride were prepared and purified by standard methods.¹⁰ The material to be fluorinated was held in a trap at just below its b. p. and the vapour was carried in dry nitrogen (2—3 bubbles/sec.) over the heated fluoride spread evenly in the reactor. Products were collected in a trap cooled in liquid nitrogen, and separated by fractional condensation in the vacuum system. Infrared spectra, used in identifying most of the products, were recorded (in sodium chloride) in the region 4000—670 cm.⁻¹ with a Model 137 Infracord spectrometer.

Fluorination of Cyanogen with Cobaltic Fluoride.—Only slight reaction occurred at 105—125°. Unreacted cyanogen was removed with 10% aqueous sodium hydroxide. The separated product showed infrared peaks at 1100—1300 cm.⁻¹ (C-F) but the strong peak at 781 cm.⁻¹ due to tetrafluoro-3,4-dihydro-1,2-azete was absent. Cyanogen (4.5 g.) passed over cobaltic fluoride (228 g.) at 150—160° gave a product (12.4 g.) which gave a fraction (7.9 g.; *M*, 116) not condensed at -131°, and identified spectroscopically as a mixture of CF₄ and C₂F₆ with small amounts of SiF₄ and COF₂. Carbonyl fluoride was also observed in the most volatile fraction from later reactions. A fraction condensed at -112° (*M*, 172) yielded, on re-fractionation, a product (2.5 g.) of *M*, 171. This showed only a single peak in the gas chromatogram and had an approximately linear log *p*-1/*T* plot (b. p. -34°). The formula C₂F₇N was tentatively assigned. Perfluorodimethylamine (b. p. -37°) was identified spectroscopically¹¹ but strong peaks were present which were not due to this compound. The fluorine nuclear magnetic resonance (n.m.r.) spectrum showed five resonance peaks with chemical shifts (δ, relative to trichlorofluoromethane) of -15.7 (very broad), 70.8 (doublet), 81.2 (triplet), 87.1 (broad), and 118.8 p.p.m., the relative areas being 100, 80, 130, 10, and 90. The peaks at 70.8 and 87.1 p.p.m. were assigned to (CF₃)₂NF, the doublet being attributed to the CF₃ group and the peak at 87.1 p.p.m. to the NF group. The remaining peaks were assigned, respectively, to NF₂, CF₃, and CF₂ groups in the isomeric compound C₂F₅·NF₂ (b. p. -34°). These tentative assignments are consistent with data recorded for analogous compounds.^{3,5,12,13} A less volatile fraction of the product (*M*, 205) was identified as perfluoroethylenediamine (*M*, 205). The n.m.r. spectrum showed two peaks, at δ 116.2 (triplet) and -16.7 p.p.m., reported values being 116.5 and -15.9 p.p.m.¹³ Gas chromatography showed *ca.* 3% of an impurity associated with weak n.m.r. peaks at 83.6 and 112.9 p.p.m. These are in fair agreement with shifts of 84.2 and 113.7 p.p.m. found for C₂F₅·N:N·C₂F₅.¹⁴

Cyanogen (4.13) with cobalt trifluoride at 135—145° produced little reaction. The most volatile fraction of the product (0.35 g.; *M*, 88) contained CF₃·CN (*v*_{max.} 1215 vs and 2270s cm.⁻¹, corresponding with published data¹⁴). The infrared spectrum of the fraction condensed at -131° was identical with that of the corresponding fraction from the reaction at 105—125°. There was no spectroscopic evidence for C₂F₅·NF₂, NF₂·C₂F₄·NF₂, or tetrafluoro-1,2-diazete.

Fluorination of Cyanogen Chloride and Cyanogen with Mercuric Fluoride.—In a typical experiment cyanogen chloride (15.9 g.) was passed over mercuric fluoride (300 g.) at 290—300° (3 hr.). Fractionation of the product (5.0 g.) gave material (0.16 g.) which passed a trap cooled to -131° and was shown spectroscopically to contain COF₂, SiF₄, and CF₃·N:CF₂. The fraction condensed at -131° was perfluoro-2-azapropene (2.5 g.; *M*, 131. Calc for C₂F₅N: *M*, 133), the infrared spectrum of which was identical with that of a specimen prepared from mercuric perfluorodimethylamide. A trace of (CF₃)₂NH was detected spectroscopically¹⁵ in an intermediate fraction. The product condensed at -80° gave, on further fractionation,

¹⁰ Brauer, "Handbuch der Präparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart, 1960.

¹¹ Young, Tsoukalas, and Dresdner, *J. Amer. Chem. Soc.*, 1958, **80**, 3604.

¹² Muller, Lauterbur, and Svatos, *J. Amer. Chem. Soc.*, 1957, **79**, 1807; Hynes and Bigelow, *ibid.*, 1962, **84**, 2751; Hynes, Bishop, Bandyopadhyay, and Bigelow, *ibid.*, 1963, **85**, 83.

¹³ Robson, McLoughlin, and Hynes, *J. Amer. Chem. Soc.*, 1961, **83**, 5010.

¹⁴ Bigelow, Hynes, and Bishop, preprints, Second International Symposium on Fluorine Chemistry, Estes Park, Colorado, 1962, p. 138.

¹⁵ Barr and Haszeldine, *J.*, 1955, 4169.

mercuric perfluorodimethylamide (1.5 g.), m. p. 17—18°. It was analysed for mercury by titrating an acid solution of the product from aqueous hydrolysis with potassium thiocyanate. Carbon and nitrogen were determined by weighing the $\text{CF}_3\cdot\text{N}\cdot\text{CF}_2$ formed in the quantitative reaction with Cu_2I_2 (see below) (Found: C, 9.3; Hg, 39.4; N, 10.9. Calc. for $\text{C}_4\text{F}_{12}\text{HgN}_2$: C, 9.5; Hg, 39.9; N, 11.1%). The average yield of mercurial was increased to 15% (on the cyanogen) if the $\text{CF}_3\cdot\text{N}\cdot\text{CF}_2$ was re-cycled over the same bed of mercuric fluoride. The yield varied little if the temperature was varied in the range 240—320°. A small amount of cyanuric fluoride (>10% of the wt. of mercurial) was isolated in the fractionation. The reaction was similar with cyanogen in place of cyanogen chloride. Cyanogen (5.10 g.), in a single pass over mercuric fluoride at 240—250°, gave 1.5 g. of purified mercurial.

Fluorination of Cyanogen Chloride with Manganic Fluoride.—Reaction was very incomplete at 20—80°. The products identified spectroscopically were CF_4 , CF_3Cl , COF_2 , SiF_4 , $\text{CF}_3\cdot\text{N}\cdot\text{N}\cdot\text{CF}_3$, and traces of unidentified products containing C-F bonds. Reaction of cyanogen chloride (6.4 g.) with manganese trifluoride at 160—190° gave a most volatile fraction (0.37 g.; *M*, 77.5) containing CF_4 , CF_3Cl , SiF_4 , and COF_2 . The fraction at -131° (4.0 g.; *M*, 108) contained chlorine and $\text{CF}_3\cdot\text{N}\cdot\text{N}\cdot\text{CF}_3$. Chlorine was removed by treatment with an excess of iodine and distilling off the $\text{CF}_3\cdot\text{N}\cdot\text{N}\cdot\text{CF}_3$ (2.38 g.; *M*, 163. Calc. for $\text{C}_2\text{F}_8\text{N}_2$: *M*, 166), identified spectroscopically. Other fractions contained unreacted cyanogen chloride, a little cyanuric fluoride, identified spectroscopically, and traces of unidentified products.

Reaction of Cyanogen Chloride with Cupric Fluoride. Cyanogen chloride (7.21 g.) was passed over cupric fluoride (181 g.) at 290—300° (2 hr.). The most volatile fraction (0.1 g.) contained COF_2 , SiF_4 , and $\text{CF}_3\cdot\text{N}\cdot\text{CF}_2$. A fraction condensed at -131° (0.27 g.; *M*, 120) was impure $\text{CF}_3\cdot\text{N}\cdot\text{CF}_2$. No extraneous infrared peaks were observed at 1100—1300 cm^{-1} , showing that the impurity was probably CNCl rather than a compound with C-F bonds. An unidentified fraction (0.15 g.; *M*, 101) separated in a trap cooled to -112°. The main product (4.3 g.), which separated at -85°, was identified spectroscopically as cyanuric fluoride.¹⁶ Cyanogen chloride (17.0 g.), passed over cupric fluoride at 450—460°, gave cyanuric fluoride (6.3 g.).

Reactions of Mercuric Bistrifluoromethylamide.—(a) *With methyl iodide.* The mercurial (0.577 g.) and methyl iodide (0.324 g.), in a sealed tube at 80° (1 hr.), gave methyl fluoride (0.589 g.; *M*, 34.1) and perfluoro-2-azapropene (0.245 g.; *M*, 133), showing the main reaction to be:



(b) *With phosphorus trichloride.* The mercurial (0.472 g.) and phosphorus trichloride (0.127 g.) reacted in a sealed tube at room temperature to give phosphorus trifluoride (0.036 g.; *M*, 88.5) and perfluoro-2-azapropene (0.216 g.; *M*, 134), which were characterised spectroscopically. The solid residue (2.45 g.) was identified qualitatively as mercuric chloride.

(c) *With cuprous iodide.* The mercurial (0.552 g.) and dry cuprous iodide (1.38 g.) reacted at 50—80° (9 hr.) to give perfluoro-2-azapropene (0.285 g.), shown spectroscopically to contain a trace of $(\text{CF}_3)_2\text{N}\cdot\text{CF}\cdot\text{N}\cdot\text{CF}_3$.¹⁷

(d) *With cyanogen chloride.* The mercurial (0.601 g.) and cyanogen chloride (0.153 g.) reacted at 100—120° (12 hr.) to give slightly impure perfluoro-2-azapropene (0.263 g.; *M*, 130) and cyanuric fluoride (0.020 g.). Other trace products were not identified.

(e) *With iodine.* The mercurial (0.679 g.) and iodine (1.18 g.), heated together at 100° (1 hr.), gave perfluoro-2-azapropene (0.234 g.; *M*, 133). Unreacted mercurial (0.25 g.) was recovered.

(f) *With copper.* The mercurial (0.611 g.) and copper powder (10 g.), heated at 170° (48 hr.), gave as the main product $(\text{CF}_3)_2\text{N}\cdot\text{CF}\cdot\text{N}\cdot\text{CF}_3$ (0.249 g.; *M*, 263. Calc. for $\text{C}_4\text{F}_{10}\text{N}_2$: *M*, 266). The infrared spectrum was that published.¹⁶ Unreacted mercurial (0.064 g.) was recovered. A trace of $\text{CF}_3\cdot\text{N}\cdot\text{CF}_2$ was also identified spectroscopically in the product after fractionation.

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UNIVERSITY CHEMICAL LABORATORY,
LENSFIELD ROAD, CAMBRIDGE.

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¹⁶ Seel and Ballreich, *Chem. Ber.*, 1959, **92**, 344.

¹⁷ Nauptschain, Braid, and Lawlor, *J. Org. Chem.*, 1958, **23**, 323.