# 227. *Preparation of Carbamyl Fluorides by the Action of Anhydrous Hydrogen Fluoride on* iso*Cyanates.*

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Anhydrous hydrogen fluoride reacts with phenyl *iso*cyanate to give *phenylcarbamyl fluoride*. The reaction is reversed on heating or on treatment with water. Similar results have been obtained with a series of aliphatic and aromatic mono- and di-*iso*cyanates. Phenyl cyanide and phenyl *iso*thiocyanate do not form stable adducts with hydrogen fluoride.

The simple aliphatic and aromatic *iso*cyanates are powerful lachrymators and are very readily hydrolysed by water. Attention has been directed to the preparation of compounds which would be free from these defects but would react with amines in a similar way to the *iso*cyanates, and in the course of this work the previously unknown alkyl- and aryl-carbamyl fluorides, NHR·CO·F, have been prepared.

The preparation of carbamyl fluoride itself by the action of anhydrous hydrogen fluoride on cyanic acid at −80° has been described by Linhard and Betz (*Ber.*, **1940**, **73**, **177**), and *N*-substituted carbamyl chlorides have been prepared by several authors both from the amines and from the *iso*cyanates. The chlorides, however, dissociate very readily and it was hoped that the fluorides would be more stable.

Phenyl *iso*cyanate reacted readily with anhydrous hydrogen fluoride at room temperature to give a quantitative yield of *phenylcarbamyl fluoride*, the constitution of which was proved by analysis and by its reaction with aqueous ammonia to form phenylurea and ammonium fluoride. It was non-lachrymatory and fairly stable to heat, but evolved hydrogen fluoride on heating above 100°. On treatment with water, the carbamyl fluoride decomposed rapidly, producing a strong odour of phenyl *iso*cyanate and depositing carbanilide. This indicated that the decomposition was not a true hydrolysis of the acid fluoride to the carbamic acid, but simply a dissociation into phenyl *iso*cyanate and hydrogen fluoride, resulting from the ease of hydration of hydrogen fluoride. This was confirmed by the failure of the carbamyl fluoride to react with aqueous 40% hydrofluoric acid, hydrolysis being completely suppressed.

p-*Tolyl-*, *hexadecyl-*, p-*nitrophenyl-*, *hexamethylene-bis-*, and m-*phenylene-bis-carbamyl fluorides* were similarly prepared from the corresponding *iso*cyanates and di-*iso*cyanates. They were all crystalline solids, closely resembling phenylcarbamyl fluoride in their reactions. Elementary analysis of these compounds was complicated by their attacking glass, and although satisfactory C, H, and N analyses were generally obtained, the fluorine figures were almost invariably less than calculated; this is considered to be due to the known difficulty of determining organically combined fluorine and not to the presence of impurities.

Attempts to prepare benziminofluoride and phenylthiocarbamyl fluoride by the action of anhydrous hydrogen fluoride on phenyl cyanide and on phenyl *iso*thiocyanate were unsuccessful.

## EXPERIMENTAL.

Microanalyses by Mr. E. S. Morton. M. p.'s are uncorrected.

*Phenylcarbamyl Fluoride*, $NHPh\cdot CO\cdot F$.—Anhydrous hydrogen fluoride (25 c.c.) was measured into a nickel tube cooled in solid carbon dioxide, and cautiously diluted with an equal volume of dry ether. A solution of phenyl *iso*cyanate (24 g.) in dry ether (25 c.c.) was then added from a dropping funnel during 15 minutes; the reaction tube was closed with a rubber bung carrying a calcium chloride drying tube, removed from the bath and allowed to stand at 20° for 2 hours. The ether and excess hydrofluoric acid were removed by heating under reduced pressure at 40°, this operation being very slow owing to the formation of an HF–ether complex. On pouring into a platinum basin and allowing to stand in a desiccator, the residue solidified to a mass of crystals, m. p. 30—31°. This was dissolved in carbon tetrachloride (30 c.c.), filtered, cooled in an ice–salt mixture and diluted with an equal volume of pentane; the colourless needles which separated were washed with pentane. *Phenylcarbamyl fluoride* had m. p. 32° (Found: N, 10·35; F, 12·2. $C_7H_6ONF$ requires N, 10·1; F, 13·65%). By treatment with concentrated aqueous ammonia, phenylcarbamyl fluoride gave ammonium fluoride (identified by testing with cerium nitrate in dilute acetic acid) and phenylurea, m. p. 147°. On treating the carbamyl fluoride with water, a strong odour of phenyl *iso*cyanate was noticed and a white precipitate slowly separated; the final products were hydrofluoric acid and carbanilide, m. p. 235—236°.

p-*Tolylcarbamyl fluoride* was obtained in quantitative yield from *p*-tolyl *iso*cyanate as described above for the phenyl analogue. By crystallisation from benzene, it was obtained in colourless prisms, m. p. 58° (Found: C, 63·45; H, 5·0; N, 9·25; F, 10·7. $C_8H_8ONF$ requires C, 62·75; H, 5·2; N, 9·15; F, 12·4%). On treatment with water it gave *pp'*-ditolylurea, m. p. 262°, and, with aqueous ammonia, *p*-tolylurea, m. p. 186°.

p-*Nitrophenylcarbamyl Fluoride*.—Anhydrous hydrofluoric acid (20 c.c.) was charged into a nickel tube cooled in solid carbon dioxide, and *p*-nitrophenyl *iso*cyanate (12 g.) was added over 15 minutes. The mixture was allowed to stand at 20° for 2 hours and the excess hydrogen fluoride was then driven off by a current of dry nitrogen at 40°. The yellow crystalline residue, p-*nitrophenylcarbamyl fluoride*, was purified by crystallisation from dry ether, giving colourless needles (5·5 g.), m. p. 141°, which rapidly turned yellow on standing and which decomposed to give a high-melting solid on heating to a temperature slightly above the m. p. (Found: C, 44·9; H, 2·75; N, 15·5; F, 10·25. $C_7H_5O_3N_2F$ requires C, 45·6; H, 2·7; N, 15·25; F, 10·35%). On treatment with water this carbamyl fluoride gave *pp'*-dinitrodiphenylurea, m. p. 310°.

n-*Hexadecylcarbamyl fluoride*, $NHC_{16}H_{33}\cdot CO\cdot F$, was obtained in quantitative yield from *n*-hexadecyl *iso*cyanate by the procedure described above for the phenyl analogue. Crystallisation of the crude product from light petroleum (b. p. 60—80°) gave colourless plates, m. p. 98° (Found: N, 5·2; F, 5·7. $C_{17}H_{34}ONF$ requires N, 5·1; F, 6·9%). On treatment with concentrated aqueous ammonia, this carbamyl fluoride gave *n*-hexadecylurea, m. p. 109° (cf. Buck *et al.*, *J. Amer. Chem. Soc.*, 1938, **60**, 461).

*Hexamethylene-di-*(*carbamyl fluoride*) was prepared from hexamethylene di*iso*cyanate as described above for the phenyl analogue. Crystallisation from benzene gave colourless needles, m. p. 75° (Found: C, 46·25; H, 6·85; N, 13·4; F, 16·75. $C_8H_{14}O_2N_2F_2$ requires C, 46·15; H, 6·75; N, 13·45; F, 18·25%). A solution in dioxan, poured into excess of concentrated aqueous ammonia, gave a precipitate of hexamethylenediurea, m. p. 195—196°.

m-*Phenylene-di-*(*carbamyl Fluoride*).—A solution of *m*-phenylene di*iso*cyanate (20 g.) in dry ether (100 c.c.) was allowed to react with a solution of anhydrous hydrofluoric acid (20 c.c.) in dry ether (20 c.c.) as described above for phenyl *iso*cyanate. The ether and excess hydrogen fluoride were distilled off under reduced pressure at 40°, leaving a white powder having an indefinite m. p.; m-*phenylene-di-*(*carbamyl fluoride*) is readily soluble in dioxan and only slightly soluble in benzene and in ether (Found: N, 13·75; F, 15·2. $C_8H_6O_2N_2F_2$ requires N, 14·0; F, 17·0%). A dioxan solution gave a precipitate of *m*-phenylene-di-urea, m. p. 302°, on pouring into excess concentrated aqueous ammonia. Treatment of the carbamyl fluoride with water gave a high-melting polymer.

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