664. *Perfluoroalkyl Derivatives of Nitrogen. Part IV.* The Synthesis, Properties and Infrared Spectra of Perfluoroalkyl* iso*Cyanates and Carbamates.*

By D. A. Barr and R. N. Haszeldine.

Trifluoromethyl and heptafluoropropyl *iso*cyanate have been synthesised (*a*) by the Curtius reaction, (*b*) by controlled hydrolysis of perfluoro(methylenealkylamines), and (*c*) by reaction of perfluoro(methylenealkylamines) with silica. Perfluoroalkyl carbamates are prepared from the *iso*cyanates by reaction with an alcohol, or by reaction of the alcohol with the perfluoro(methylenealkylamine). Reactions of the perfluoroalkyl *iso*cyanates and carbamates which lead to partial breakdown of the perfluoroalkyl group have been examined. Assignments are made for the $\nu_{a(NCO)}$ and $\nu_{s(NCO)}$ vibrations of the *iso*cyanate group which can thus be distinguished spectroscopically from the nitrile group. Assignments are also made for the C:O, N–H stretching, and N–H deformation vibrations in *N*-alkyl-, *N*-aryl-, and *N*-perfluoroalkylcarbamates.

The Hofmann degradation of amide to amine : [1]

$$R{\cdot}CO{\cdot}NH_2 + NaOBr \longrightarrow R{\cdot}NH_2 + CO_2 + NaBr$$

is said to fail when R is a perfluoroalkyl group such as CF_3, C_2F_5, or C_3F_7.[2,3] Trifluoroacetamide was considered to yield hexafluoroethane,[2] and the higher homologues a perfluoroalkyl bromide.[3] Consideration of the reactions of fluorine compounds and of the mechanism of the Hofmann reaction made these results irreconcilable to us. We have therefore re-examined the issue and wish to clarify and correct some of the earlier results.

The present communication is concerned with the synthesis and reactions of perfluoroalkyl *iso*cyanates and carbamates, since these compounds are the intermediates in the normal Hofmann degradation of amide to amine. Our interpretation of the Hofmann reaction with perfluoroalkyl amides is to be reported in Part V of this series, and correlated with the Curtius reaction with perfluoroalkanecarboxylic acids and with the results of Hofmann

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* Part III, preceding paper.

[1] Hofmann, *Ber.*, 1881, **14**, 2725.

[2] Gryszkiewicz-Trochimowski, Sporzynski, and Wnuk, *Rec. Trav. chim.*, 1947, **66**, 426.

[3] Husted and Kohlhase, *J. Amer. Chem. Soc.*, 1954, **76**, 5141.

and Curtius reactions with derivatives of carboxylic acids containing polar groups other than perfluoroalkyl groups.

Perfluoroalkyl iso*Cyanates*.—Trifluoromethyl *iso*cyanate and heptafluoropropyl *iso*cyanate were prepared by three routes: (*a*) the Curtius reaction with a perfluoroacyl halide:

$$R_F\cdot COCl \longrightarrow R_F\cdot CON_3 \longrightarrow R_F\cdot NCO + N_2$$

(*b*) controlled hydrolysis of the perfluoro(methylenealkylamine):

$$R_F\cdot N\colon CF_2 + H_2O \longrightarrow R_F\cdot NCO + 2HF$$

and (*c*) reaction of the perfluoro(methylenealkylamine) with silica at 160—200°:

$$R_F\cdot N\colon CF_2 \longrightarrow R_F\cdot NCO + SiF$$

This last method is not of great practical value but illustrates the reactivity of the difluoromethylene-fluorine atoms.

The synthesis of trifluoromethyl and heptafluoro-*n*-propyl *iso*cyanate by a conventional Curtius reaction gave but little difficulty; the perfluoroacyl azides decompose smoothly but more slowly than their alkyl analogues. The preparation of heptafluoropropyl *iso*cyanate has been described in a patent,[4] but it was there predicted that trifluoroacetyl azide would be dangerously explosive and that it could not be employed to make trifluoromethyl *iso*cyanate; we find no marked difference between the trifluoromethyl and the heptafluoropropyl compound. It has been suggested several times [3,4,5] that there is an inherent difference between trifluoromethyl compounds on the one hand, and pentafluoroethyl, heptafluoropropyl, etc., compounds on the other which is " a change in kind and not in degree of reactivity " [4] so that there is " a transition point in the physical and chemical properties in the series ".[5] Thus the compounds CF_3–Z (Z = CON_3, $CO\cdot NH_2$, or CO_2H) have been reported as showing large chemical differences from the compounds C_2F_5–Z and C_3F_7–Z, and this has led to a belief that many trifluoromethyl derivatives cannot be made even though the pentafluoroethyl or heptafluoropropyl derivatives are known. This belief in a change in kind is founded upon wrong evidence, *e.g.*, (*a*) the apparent failure to prepare trifluoromethyl *iso*cyanate and (*b*) the reported products of the Hofmann reaction with trifluoroacetamide. There are sometimes minor differences in physical properties from those predicted for trifluoromethyl compounds, *e.g.*, the increment in boiling point between a CF_3 and a C_2F_5 derivative is often different from what it is between a C_2F_5 and a C_3F_7 derivative; such differences are of minor import, however, and are reflected in slight or moderate changes in the degree of reactivity of the compounds, *e.g.*, trifluoroiodomethane yields a Grignard derivative less readily than heptafluoroiodopropane,[6] but the difference in reactivity is never such that the heptafluoropropyl compound can exist whilst the trifluoromethyl compound cannot.

Use of carefully controlled conditions enables perfluoro(methylene-*n*-propylamine) to be hydrolysed to heptafluoropropyl *iso*cyanate in almost theoretical yield,[7,8] and application of similar conditions to perfluoro(methylenemethylamine) would doubtless give yields of trifluoromethyl *iso*cyanate higher than reported here (50%).

The perfluoroalkyl *iso*cyanates are considerably more volatile than their unsubstituted analogues (cf. $CF_3\cdot NCO$, b. p. −36°; $CH_3\cdot NCO$, b. p. 44°), an effect often found in fluorine chemistry.

N-*Perfluoroalkylcarbamates*.—Perfluoroalkyl *iso*cyanates react in normal fashion with water, aqueous alkali, or ethanol; that the products expected by analogy with alkyl *iso*cyanate reactions are not always isolated is caused not by the failure of the –NCO group to react in conventional manner, but by the instability of the $-CF_2\cdot NH-$ group when present in a medium of high dielectric constant. If this principle is borne in mind there

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[4] Ahlbrecht and Husted, U.S.P. 2,617,817; *Chem. Abs.*, 1953, **47**, 8774.
[5] Husted and Ahlbrecht, *J. Amer. Chem. Soc.*, 1953, **75**, 1605.
[6] Haszeldine, *J.*, 1952, 3423; 1953, 1748; 1954, 1273.
[7] Barr and Haszeldine, *J.*, 1955, 1881.
[8] *Idem*, Part II, *J.*, 1955, 2532; Part III, preceding paper.

is nothing anomalous in the *iso*cyanate reactions, and clear predictions for other reactions can be made.

Heptafluoropropyl *iso*cyanate reacts with water, to give heptafluoropropylcarbamic acid (I) which is decarboxylated to heptafluoropropylamine (II); the last product cannot be isolated as such from an aqueous medium, since rapid decomposition and elimination of hydrogen fluoride yields pentafluoropropionitrile (III), which can be isolated. Further hydrolysis takes place if the reaction mixture is kept, particularly in presence of the acid produced by fluoride liberation, giving pentafluoropropionamide (IV) and thence ammonium pentafluoropropionate (V), both of which have been detected. Decomposition of the $-CF_2{\cdot}NH-$ system is probably sufficiently rapid to prevent its reaction with heptafluoropropyl *iso*cyanate to give a disubstituted urea, *e.g.*, $(C_3F_7{\cdot}NH)_2CO$, but even if formed this would be unstable in an aqueous medium and would yield pentafluoro-propionitrile, -propionamide, and, ultimately, -propionate.

Aqueous sodium hydroxide similarly converts heptafluoropropyl *iso*cyanate into sodium pentafluoropropionate.

The perfluoroalkyl *iso*cyanates react normally with anhydrous alcohols to give alkyl *N*-perfluoroalkylcarbamates (urethanes), *e.g.*, ethyl *N*-heptafluoro-*n*-propylcarbamate (VI). The carbamates have also been synthesised by reaction of perfluoro(methylenealkylamines) with a *limited* amount of ethanol, *e.g.*,

$$CF_3{\cdot}N{:}CF_2 \xrightarrow{EtOH} CF_3{\cdot}NH{\cdot}CO_2Et$$

The hydrogen fluoride produced reacts with perfluoro(methylenemethylamine), to give bistrifluoromethylamine, thus showing that the high temperatures used earlier [8] for the preparation of this amine are not essential.

The *iso*cyanate is probably immediately formed as intermediate when a perfluoro(methylenealkylamine) reacts with an alcohol, although addition of ethanol to the N:C bond followed by loss of hydrogen fluoride and ultimate formation of ethyl ether constitutes a less likely alternative route to the *iso*cyanate, *e.g.*,

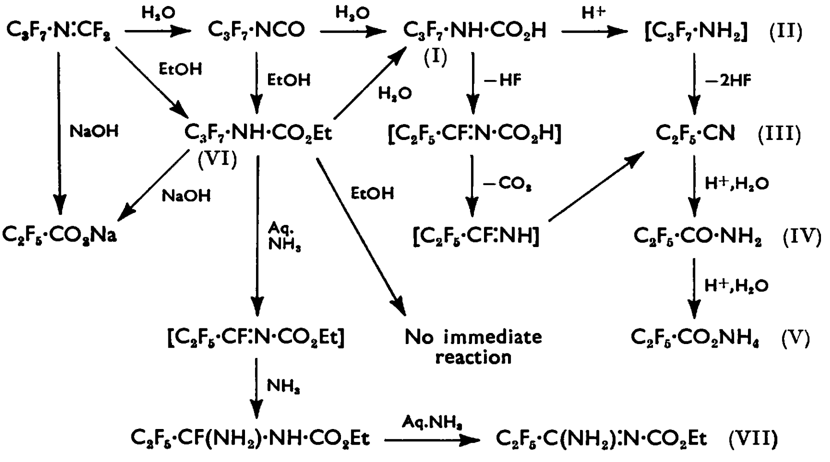
$$(a)\qquad C_3F_7{\cdot}N{:}CF_2 \longrightarrow C_3F_7{\cdot}NCO + 2HF \longrightarrow C_3F_7{\cdot}NH{\cdot}CO_2Et$$

or

$$(b)\quad C_3F_7{\cdot}N{:}CF_2 \longrightarrow C_3F_7{\cdot}NH{\cdot}CF_2{\cdot}OEt \longrightarrow C_3F_7{\cdot}N{:}CF{\cdot}OEt \longrightarrow C_3F_7{\cdot}NH{\cdot}CF(OEt)_2$$

$$C_3F_7{\cdot}NH{\cdot}CF(OEt)_2 \longrightarrow C_3F_7{\cdot}N{:}C(OEt)_2 \longrightarrow C_3F_7{\cdot}N{:}C{:}O + Et_2O$$

This formation of ethyl perfluoroalkylcarbamates almost quantitatively from perfluoro(methylenealkylamines) is in accord with the formation of the *iso*cyanates by controlled aqueous hydrolysis, and shows that N=C fission is not the initial step (cf. Part I) of the hydrolysis or alcoholysis of perfluoro(methylenealkylamines); the reactivity of the difluoromethylene-fluorine atoms [7] is the key factor.



The *N*-perfluoroalkylcarbamates are low-melting solids which are readily soluble, and stable, in an excess of ethanol at room temperature, thus showing that the $-CF_2 \cdot NH-$ system can exist in a polar solvent provided that acid or base is absent. They decompose slowly when kept for several hours in alcoholic solution; under these conditions perfluoro-(methylenemethylamine) reacted with an excess of anhydrous methanol to give dimethyl ether, dimethyl carbonate, and ammonium fluoride.[7] The carbamates are insoluble in cold water and react with it only after several minutes or when shaken. Ethyl heptafluoropropylcarbamate, when allowed to react slowly with water, yields a solid which is probably *N*-heptafluoropropylcarbamic acid (I). Aqueous base rapidly converts ethyl heptafluoropropylcarbamate into sodium pentafluoropropionate.

Ahlbrecht and Husted[4] described the reaction of heptafluoropropyl *iso*cyanate with methanol and *o*-bromophenol to give urethanes (carbamates); they also noted that aqueous ammonia and methyl heptafluoropropylcarbamate gave a solid, m. p. 104—106°, believed to have formula (VII). The formation of a compound of this type is best visualised as involving elimination of hydrogen fluoride, followed by nucleophilic addition of ammonia and loss of a second molecule of hydrogen fluoride as shown. A similar process would account for the formation of the solid, m. p. 156—158°, believed[4] to be $C_2F_5 \cdot C(NH_2){:}N \cdot CO \cdot NH_2$, on reaction of heptafluoropropyl *iso*cyanate with aqueous ammonia.

Infrared Spectra of Perfluoroalkyl iso*Cyanates and Carbamates.*—The interaction of the pseudo-symmetrical vibrations $\nu_{C=O}$ and $\nu_{C=N}$ in cyanic acid[9] and in methyl *iso*cyanate[10] is considered to give one very strong anti-symmetrical absorption $\nu_{a(NCO)}$ at *ca.* 4·4 μ and a weak symmetrical absorption $\nu_{s(NCO)}$ at *ca.* 7·4 μ. Davison[11] examined eight *iso*cyanates for these stretching vibrations and showed that $\nu_{a(NCO)}$ gives a characteristic absorption at 4·41 μ. Nitriles absorb in the same region, but at slightly longer wavelength (4·44 μ). Assignment of the $\nu_{s(NCO)}$ vibration must only be tentative in the 7·4 μ region, since bands associated with methyl and methylene deformations cause ambiguity, although a band at 7·26 μ in methyl *iso*cyanate was so assigned.[10] Unambiguous assignment of $\nu_{s(NCO)}$ usually cannot be made, however, and the possible value of this vibration to distinguish *iso*cyanates from nitriles is thus lost.

The infrared spectra of the perfluoroalkyl *iso*cyanates $CF_3 \cdot NCO$ and $C_3F_7 \cdot NCO$ are of interest in this connection, since there is no question of interference by C–H absorptions. Trifluoromethyl *iso*cyanate shows a doublet for $\nu_{a(NCO)}$ like cyanic acid and at much the same wavelength (see Table). Heptafluoropropyl *iso*cyanate shows only a single peak at 4·37 μ. The perfluoroalkyl *iso*cyanates thus show a small but definite shift to shorter wavelength for $\nu_{a(NCO)}$ relative to alkyl or aryl *iso*cyanates; such shifts are often observed on introduction of fluorine into a molecule.[12]

Heptafluoropropyl *iso*cyanate shows two bands, at 6·80 and 7·40 μ, which might be assigned to $\nu_{s(NCO)}$, but since trifluoromethyl *iso*cyanate shows a strong band at 6·84 μ and only a weak band at 7·50 μ, preference is given to the 6·80 or 6·84 μ band. The strength of this band is noteworthy, since it is considerably more powerful than in alkyl *iso*cyanates. A somewhat similar change in extinction coefficient was observed[13] with bis(perfluoroalkyl)-amines such as $(CF_3)_2NH$, where the N–H deformation vibration appears as a strong band at 6·65 μ; in unsubstituted dialkylamines the N–H deformation vibration is very weak or absent.

Perfluoroalkanenitriles show the C⋮N stretching vibration at 4·41 μ, *i.e.*, at slightly longer wavelength than the stretching vibration of the –NCO group. Distinction between perfluoroalkyl *iso*cyanates and related nitriles thus cannot be made with certainty on grounds of band position alone, but clear distinction is possible if the intensity of absorption is also considered, since the C⋮N vibration is much weaker than the –NCO vibration; the presence of a strong band at 6·8 μ confirms a perfluoroalkyl *iso*cyanate structure.

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[9] Herzberg and Reid, *Discuss. Faraday Soc.*, 1950, **9**, 92.
[10] Eyster and Gillette, *J. Chem. Phys.*, 1940, **8**, 369.
[11] Davison, *J.*, 1953, 3712.
[12] Haszeldine, *Nature*, 1951, **168**, 1028.
[13] Barr and Haszeldine, *J.*, 1955, 4169.

The infrared spectra of perfluoroalkylcarbamates are interesting (see Table). These compounds are hydrogen-bonded in the liquid or solid state, since the C:O and N–H stretching vibrations of ethyl *N*-heptafluoropropylcarbamate, for example, move markedly to shorter wavelength when the compound is in the vapour phase. The spectrum of the liquid carbamate shows both free (2·90 μ) and bonded (3·07 μ) N–H vibrations. The C:O stretching vibration is at a distinctly longer wavelength than that for esters of perfluoroalkanecarboxylic acids (5·55—5·60 μ) such as ethyl heptafluorobutyrate, but at an appreciably shorter wavelength than that for ethyl *N*-methylcarbamate.

Infrared spectra.

iso*Cyanates.*

		$\nu_{a(NCO)}$	$\nu_{s(NCO)}$
CF_3·NCO (D.M.S.) *	v	4·33 4·40} doublet	6·84
C_3F_7·NCO (D.M.S.)	v	4·37	6·80
Ph·NCO	v	4·40	[a]
,, (D.M.S.) ...	l	4·40	[a]
HNCO [9]	v	4·37 4·42} doublet	7·54
CH_3·NCO [10]	v	4·48 [b]	7·26
CH_3·$[CH_2]_{17}$·NCO [11]	N	4·44	[a]
$[CH_2]_6(NCO)_2$ [11]	N	4·44	[a]

Nitriles.

		$\nu_{C\equiv N}$			$\nu_{C\equiv N}$
CF_3·CN ...	v	4·40	CCl_3·CN...	l	4·45
C_2F_5·CN...	v	4·41	CH_2Cl·CN	l	4·44
C_3F_7·CN...	v	4·41	—	—	—

Carbamates (*urethanes*).

		N–H stretch.	N–H deform.	C:O
CF_3·NH·CO_2Et ...	N	3·07	6·50	5·79
C_3F_7·NH·CO_2Et ...	l	2·90, 3·07	6·51	5·73
	v	2·91	6·67	5·62
CH_3·NH·CO_2Et ...	l	3·00	6·49	5·88
	s	2·98, 2·88	6·49, 6·60	5·79
CH_2Ph·NH·CO_2Et	N		[c]	5·92
	s	[c]	[c]	5·74
Ph·NH·CO_2Et	N	3·04	6·54	5·81, 5·88, 5·74
	s	2·91	6·57	5·74
NH_2·CO_2Et	N	[c]	[c]	5·92
	s	[c]	[c]	5·77
CH_3·N(NO)·CO_2Et	l	—	—	5·71
	s	—	—	5·71
C_3F_7·NH·CO_2H ...	N	3·14	6·49	5·62

* Spectra thus marked have been offered for the D.M.S. scheme to Messrs. Butterworths, 88 Kingsway, London, W.C., to whom application should be made.

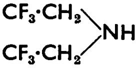
v = vapour, l = liquid film, N = Nujol mull, s = solution in CCl_4. [a] Assignment uncertain. [b] Accuracy doubtful. [c] Not examined, or assignment doubtful.

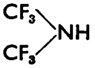
The infrared spectra of ethyl *N*-methyl-, *N*-benzyl-, and *N*-phenyl-carbamate also reveal strong hydrogen bonding in the liquid or solid (see Table). Ethyl *N*-methylcarbamate shows a shift in the N–H stretching vibration of 0·12 μ, and in the C:O stretching vibration of 0·09 μ when dissolved in carbon tetrachloride. Ethyl *N*-benzylcarbamate shows a similar shift in the C:O vibration. The spectrum of ethyl *N*-phenylcarbamate shows the bonded carbonyl group as a doublet at 5·81 and 5·88 μ, and the " free " carbonyl group is present as a weak side band at 5·74 μ; only one strong band, at 5·74 μ, appears when the compound is dissolved in carbon tetrachloride. Ethyl carbamate also shows strong hydrogen bonding. That the shifts in the N–H and C:O vibrations reported above are caused by intermolecular hydrogen bonding of the –N–H····O=C– type is supported by the infrared spectrum of *N*-methyl-*N*-nitrosourethane which shows unbonded C:O absorption at 5·71 μ both as a liquid and in solution.

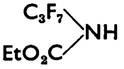
The strong band at 6·50 μ in the spectrum of ethyl *N*-trifluoromethylcarbamate, and a similar band in the spectrum of ethyl *N*-heptafluoropropylcarbamate as liquid (6·51 μ) or vapour (6·67 μ) is assigned to the N–H deformation vibration. Ethyl *N*-methylcarbamate, ethyl *N*-phenylcarbamate, and heptafluoropropylcarbamic acid also show bands in this region and a similar assignment is made; the benzene-ring absorption is at 6·26 μ. Several bands appear in the spectra of solutions of ethyl *N*-benzylcarbamate and ethyl carbamate in the 6·3—6·6 μ region; the strongest of these (6·45 μ) is probably the N–H deformation vibration, but this assignment is less certain than for the examples discussed above.

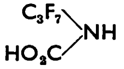
The N–H deformation vibration is not normally visible in secondary alkylamines, but it is markedly increased in intensity when the amine contains fluorine, *e.g.*, in $(CF_3{\cdot}CH_2)_2NH$ and $(CF_3)_2NH$.[13] It appears to be a general phenomenon that attachment of an electronegative group to nitrogen enhances the intensity of the N–H deformation band. The annexed compounds all contain at least one strongly electronegative group attached to the

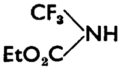
N–H group, and all show a band near 6·65 μ when the compound is in the vapour phase or solution (*i.e.*, non-bonded N–H) or at 6·5—6·6 μ for a bonded N–H group (values given in parentheses). It will be noted that the N–H deformation vibration is at a longer wavelength when the N–H group is " free " than when it is hydrogen-bonded (*e.g.*, $C_3F_7{\cdot}NH{\cdot}CO_2Et$, see Table); this shift is the opposite of that found for the N–H stretching vibration.

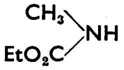

6·67 μ

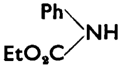

6·65 μ

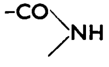

6·67 μ


(6·49 μ)


(6·50 μ)


6·60 μ


6·57 μ


6·4—6·6 μ

The only other assignment which is plausible for the band appearing near 6·65 μ is the stretching vibration of the C–N bond; this would imply partial double bond character of the C–N link. The situation is similar to that prevailing for the amide I and amide II bands of substituted amides (see ref. 14 for a discussion) except that the possibility of keto-enol tautomerism can be eliminated. The absence of a strong band near 6·65 μ in the spectra[7,8,13] of compounds such as $(CF_3{\cdot}CH_2)_2N{\cdot}NO$, $(CF_3{\cdot}CH_2)_2N{\cdot}NO_2$, $CF_3{\cdot}NO_2$, $C_3F_7{\cdot}NO_2$, $CF_3{\cdot}NO$, $C_3F_7{\cdot}NO$, $CF_3{\cdot}N{:}N^+(O^-){\cdot}CF_3$, or $(CF_3)_2N{\cdot}O{\cdot}NO$, however, suggests that the 6·65 μ band in the compounds $(CF_3{\cdot}CH_2)_2NH$, $(CF_3)_2NH$, $CF_3{\cdot}NH{\cdot}CO_2Et$, and $C_3F_7{\cdot}NH{\cdot}CO_2Et$ is best assigned to the N–H deformation vibration.

EXPERIMENTAL

See earlier Parts for details of the preparation of starting materials and the techniques used.

Trifluoromethyl iso*Cyanate*.—(a) *From trifluoroacetyl chloride.* Trifluoroacetyl chloride (0·920 g., 7·0 mmole), dry sodium azide (1·0 g., 15 mmole), and anhydrous mesitylene (40 ml.) were sealed in a 200 ml. Pyrex tube, then shaken vigorously for 30 min. in a boiling-water bath; shaking was continued after removal of the tube from the bath until it reached room temperature. Nitrogen was detected when the reaction vessel was opened, and fractionation of the volatile products gave trifluoroacetyl chloride (0·340 g., 2·6 mmole; 37%) and some trifluoromethyl *iso*cyanate. The remainder of the products were transferred from the Pyrex tube to a flask fitted with reflux condenser leading to a trap cooled in liquid oxygen. The flask was then slowly heated to 165° during which process bubbles of gas were evolved from the solid present, and material collected in the cold trap; the flask was finally kept at 165° for 2 hr. Fractionation of the products of the cold trap gave a mixture (1·4 mmole) of trifluoromethyl *iso*cyanate (80%) and trifluoroacetyl chloride (20%), analysed by molecular-weight and infrared-spectral determinations. The combined impure trifluoromethyl *iso*cyanate was kept in a 10 ml. tube with dry silver cyanide (0·5 g.) for 7 days at 20°; under these conditions trifluoroacetyl halides are converted into trifluoroacetyl cyanide dimer (W. C. Francis, unpublished results). Refractionation then gave *trifluoromethyl* iso*cyanate* (0·125 g., 1·13 mmole; 26%) (Found: C, 21·6; N, 12·8%; *M*, 111. C_2ONF_3 requires C, 21·6; N, 12·6%; *M*, 111). The low yield is attributed to handling losses on the scale used rather than to any inherent difficulty in the reaction, and there is no doubt that the yield could be improved substantially. The vapour pressure of trifluoromethyl *iso*cyanate determined over the range $-78°$ to $-45°$ is given by $\log_{10} p(\text{mm.}) = 7{\cdot}838 - 1176/T$, whence the b. p. is calculated as $-36{\cdot}0°$, the latent heat of vaporisation is 5380 cals./mole, and Trouton's constant is 22·7.

(b) *From perfluoro(methylenemethylamine) by reaction with water.* Perfluoro(methylenemethylamine) (0·067 g., 0·50 mmole) in a sealed 5 ml. ampoule was inserted in a 3 l. flask which was evacuated. Water vapour (0·037 g., 2·0 mmole) was then admitted to the flask, and the tip of the ampoule was broken. This rapid mixing of the reactants in the vapour phase caused immediate reaction. After 24 hr. at 20° fractionation of the volatile products *in vacuo* gave unchanged perfluoro(methylenemethylamine) (0·32 mmole, 64%) identified by means of its

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[14] Randall, Fowler, Fuson, and Dangl, " Infrared Determination of Organic Structures," van Nostrand Co., New York, 1949.

infrared spectrum, silicon tetrafluoride, a small amount of carbon dioxide, and trifluoromethyl *iso*cyanate (*ca.* 50% based on $CF_3\cdot N{:}CF_2$ used). The last compound was identified by means of the characteristic bands in its infrared spectrum at 4·33, 4·40 μ (doublet), 6·83, 8·30, 8·62, 8·66 (doublet), and 14·10 μ.

(c) *From perfluoro(methylenemethylamine) by reaction with silica.* Perfluoro(methylenemethylamine) (0·050 g., 0·38 mmole) and silica powder (0·5 g.), sealed in a 5 ml. silica tube and heated at 200° (75 hr.), gave unchanged perfluoro(methylenemethylamine) (90%), silicon tetrafluoride, and trifluoromethyl *iso*cyanate (*ca.* 90% based on $CF_3\cdot N{:}CF_2$ used).

Ethyl N-*Trifluoromethylcarbamate.*—Perfluoro(methylenemethylamine) (1·00 g., 7·5 mmole) and anhydrous ethanol (0·322 g., 7·0 mmole), sealed in a small Pyrex tube in absence of air or moisture and shaken rapidly (40 min.), gave, after fractionation *in vacuo*, *ethyl* N-*trifluoromethylcarbamate* (0·37 g., 31%) (Found: C, 30·6; H, 3·6; N, 8·8. $C_4H_6NF_3O_2$ requires C, 30·6; H, 3·8; N, 8·9%), m. p. 28·5—29·0°, and bistrifluoromethylamine (0·58 g., 51%). The latter was identified by means of its infrared spectrum.

Heptafluoro-n-*propyl* iso*Cyanate.*—*From heptafluorobutyryl chloride.* The chloride (1·65 g., 7·1 mmole), anhydrous toluene (7 ml.), and dry sodium azide (1·2 g., 18 mmole) were sealed in a 200 ml. Pyrex tube in absence of air, then kept at −22° (10 min.) before being allowed to warm slowly to 20° (2 hr.). The tube was shaken overnight at room temperature, then heated at 110° (2 hr.). Fractionation of the volatile products *in vacuo* gave heptafluoro-*n*-propyl *iso*cyanate (1·22 g., 5·8 mmole; 82%), b. p. 24·5° (isoteniscope) (Found: C, 22·8; N, 6·4%; *M*, 212. Calc. for C_4ONF_7: C, 22·7; N, 6·6%; *M*, 211). Ahlbrecht and Husted[4] report b. p. 25°/740 mm. See also Part III.[8]

Ethyl N-*Heptafluoro*-n-*propylcarbamate.*—Heptafluoro-*n*-propyl *iso*cyanate (0·45 g., 2·14 mmole) and anhydrous ethanol (0·098 g., 2·1 mmole) were sealed in a 30 ml. Pyrex tube in absence of air or moisture, then set aside at room temperature for 2 hr. Only traces of the reactants remained, and distillation of the liquid product gave only *ethyl* N-*heptafluoro*-n-*propylcarbamate* (0·49 g., 91%) (Found: C, 28·5; H, 2·3; N, 5·4. $C_6H_6O_2NF_7$ requires C, 28·0; H, 2·3; N, 5·5%), b. p. 55—58°/9 mm., m. p. (sealed tube) 10—11°.

The carbamate (0·056 g., 0·22 mmole) was unchanged when kept in anhydrous ethanol (2 ml.) in absence of air or moisture at 20° for 16 hr. and was recovered in 80% yield.

Hydrolysis of Ethyl N-*Heptafluoro*-n-*propylcarbamate.*—(a) *By water.* The carbamate (0·032 g., 0·125 mmole) in a sealed fragile glass tube was inserted into a larger tube containing water (1 ml., 55 mmole). The tube was then sealed and shaken vigorously to break the inner tube and allow rapid mixing. The globules of the carbamate slowly disappeared without evolution of gas, and white crystals appeared (30 min.). The crystals, which were separated and dried *in vacuo* over phosphoric anhydride, are believed to be of *N*-heptafluoropropylcarbamic acid (0·015 g., 52%), since infrared spectroscopic examination showed a fluoro-acid carbonyl band at 5·62 μ (cf. $CF_3\cdot CO_2H$ 5·56 μ), N–H stretching absorption at 3·14 μ, and N–H deformation vibration at 6·49 μ. The spectroscopic examination also showed that the solid was not pentafluoropropionamide or ethyl heptafluoropropylcarbamate.

(b) *By aqueous alkali.* The carbamate (0·080 g., 0·31 mmole) and 10% aqueous sodium hydroxide (1 ml.) were shaken in a small sealed tube. The globules of the carbamate disappeared rapidly and when, after 3 hr., the tube was opened, ammonia was detected as gaseous product. The aqueous solution was neutralised (dilute nitric acid), then evaporated to dryness with silver nitrate (1 g.). Extraction with ether, followed by evaporation to dryness, yielded silver pentafluoropropionate (0·070 g., 84%), identified by means of its infrared spectrum. A blank experiment showed that about 80% of sodium pentafluoropropionate can be recovered from aqueous solution as silver salt by this procedure, and if allowance is made for this, the yield of sodium pentafluoropropionate is quantitative within experimental error.

Reaction of Perfluoro(methylene-n-*propylamine) with Ethanol.*—(a) *With an excess of perfluoro(methylenepropylamine).* Perfluoro(methylene-*n*-propylamine) (0·345 g., 1·48 mmole) and anhydrous ethanol (0·061 g., 1·33 mmole) were sealed in a 5 ml. Pyrex tube, shaken, and warmed rapidly to room temperature. After 15 min. the volatile material present was entirely unchanged perfluoro(methylene-*n*-propylamine) (0·100 g., 0·43 mmole; 39%). Fractionation of the liquid product gave only ethyl *N*-heptafluoro-*n*-propylcarbamate [0·150 g., 0·58 mmole; 58% based on perfluoro(methylenepropylamine) used], identified by means of its infrared spectrum.

(b) *With an excess of ethanol.* Perfluoro(methylenepropylamine) (0·253 g., 1·08 mmole) and anhydrous ethanol (4 ml., 70 mmole) were sealed in a 5 ml. tube and set aside at room temperature for 1·5 hr. Ethyl carbonate, ammonium fluoride, and ethyl heptafluoropropylcarbamate were identified in the distilled liquid products by means of their infrared spectra; carbon dioxide was not detected.

Spectra.—Spectra were recorded by a Perkin-Elmer Model 21 spectrophotometer with rock-salt optics. A 10 cm. gas cell was used for vapour spectra, and sealed cells for liquid samples.

One of us (D. A. B.) is indebted to Imperial Chemical Industries Limited, Plastics Division, for a maintenance allowance.

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[*Received, March* 20*th*, 1956.]