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Studies in Azide Chemistry. Part II.¹ Photolysis of 2*H*-Hexafluoropropyl and 2-Chloro-1,1,2-trifluoroethyl Azide

By R. E. Banks,* D. Berry, M. J. McGlinchey, and G. J. Moore, Chemistry Department, The University of Manchester Institute of Science and Technology, Manchester M60 1QD

U.v. irradiation of 2H-hexafluoropropyl azide yields nitrogen and 3H-hexafluoro-2-azabut-1-ene, which reacts with water to give trifluoroacetaldehyde and undergoes fluoride-initiated isomerisation to 3H-hexafluoro-2-azabut-2-ene. Photolysis of the azide in the presence of an excess of cyclohexane, methylcyclohexane, or cyclohexene yields, after hydrolysis of the initial products, N-cyclohexyl-, N-(1-methylcyclohexyl)-, and N-(cyclohex-2-enyl)αβββ-tetrafluoropropionamide, respectively. These azide decomposition reactions may be interpreted in terms of the intermediacy of 2H-hexafluoropropylnitrene, just as photolysis of 2-chloro-1,1,2-trifluoroethyl azide alone to give 3-chloro-1,1,3-trifluoro-2-azapropene and in the presence of cyclohexane to provide N-cyclohexylchlorofluoroacetamide may be rationalised in terms of 2-chloro-1,1,2-trifluoroethylnitrene. Treatment of chlorotrifluoroethylene with triethylammonium azide under the conditions used to convert perfluoropropene into 2H-hexafluoropropyl azide and perfluoropropenyl azide apparently yields only 2-chloro-1,1,2-trifluoroethyl azide.

ONLY speculative information about polyfluoroalkylnitrenes appears to exist in the literature,² and the object of this work was simply to assess the possibility of generating such species by photolysis of 2H-hexafluoropropyl and 2-chloro-1,1,2-trifluoroethyl azide. Expediency led to the choice of these particular azides, samples being available from other investigations.

Preparation of Azides.—Perfluoroalkyl azides are usually formed when polyfluoro-olefins of type CF, CFX are treated with sodium azide in ethanol or triethylammonium azide in a chlorinated solvent (Scheme 1).^{3,4} By-products may arise via ejection of fluoride from the intermediate carbanion (I).^{1,3,5}

$$N_{3} CF_{2} = CFX \longrightarrow CFX \cdot CF_{2} \cdot N_{3} \xrightarrow{H^{+}donor} CHFX \cdot CF_{2} \cdot N_{3}$$
(I)
(I)
(I)
(I)
Scheme 1 X = F, Cl, I, or CF_{3}

Thus treatment of perfluoropropene with triethylammonium azide in sym-tetrachloroethane at 0° gives

of 2H-heptafluoropropane.¹ A more convenient method of preparation of 2H-hexafluoropropyl azide involves treatment of perfluoropropene with sodium azide in ethanol,³ and, as with the perfluoropropene-triethylammonium azide reaction,¹ it was found much better from the viewpoint of both yield and convenience to carry out the reaction in a sealed vessel instead of passing the gaseous olefin into the stirred reagent at atmospheric pressure. 2H-Hexafluoropropyl azide was thus obtained in 22% yield, together with a ca. 10:1mixture (68%) of ethyl 2*H*-hexafluoropropyl ether and ethyl pentafluoropropenyl ether; the propenyl ether, not detected previously,³ was identified by treatment of the mixture of ethers with bromine in aqueous sodium bromide and subsequent isolation of ethyl a-bromotetrafluoropropionate and unchanged ethyl 2H-hexafluoropropyl ether (Scheme 2). Any perfluoropropenyl azide formed in this reaction would have decomposed under the conditions used to yield nitrogen and perfluoro-(2-methyl-2H-azirine),¹ which would have been con-

$$\begin{array}{c} \mathrm{CF}_{3}\cdot\mathrm{CF}:\mathrm{CF}_{2} & \xrightarrow{\mathrm{NaN}_{3}} & \mathrm{CF}_{3}\cdot\overline{\mathrm{CF}}\cdot\mathrm{CF}_{2}\cdot\mathrm{N}_{3} & \xrightarrow{\mathrm{EtOH}} & \mathrm{CF}_{3}\cdot\mathrm{CHF}\cdot\mathrm{CF}_{2}\cdot\mathrm{N}_{3} + \mathrm{EtO}^{-}\\ \mathrm{CF}_{3}\cdot\mathrm{CF}:\mathrm{CF}_{2} & \xrightarrow{\mathrm{EtO}^{-}} & \mathrm{CF}_{3}\cdot\overline{\mathrm{CF}}\cdot\mathrm{CF}_{2}\cdot\mathrm{OEt} & \xrightarrow{\mathrm{EtOH}} & \mathrm{CF}_{3}\cdot\mathrm{CHF}\cdot\mathrm{CF}_{2}\cdot\mathrm{OEt} + \mathrm{EtO}^{-}\\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & \\ & & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ &$$

2H-hexafluoropropyl azide (II; $X = CF_3$) (29%) together with perfluoropropenyl azide (36%) and traces

¹ Part I, R. E. Banks and G. J. Moore, J. Chem. Soc. (C),

1966, 2304. ² See, for example, R. A. Abramovitch, and B. A. Davis, *Chem. Rev.*, 1964, **64**, 149, and references quoted therein; R. E. **Provide Provide Pro** Banks and E. D. Burling, J. Chem. Soc., 1965, 6077; Middleton and C. G. Krespan, J. Org. Chem., 1966, 50, 1398; J. B. Hynes and T. E. Austin, *Inorg. Chem.*, 1966, 5, 488; J. B. Hynes, B. C. Bishop, and L. A. Bigelow, *ibid.*, 1967, 6, 417; and ref. 1. Hexafluoroazomethane reacts with *trans*-chlorocarbonylbis(methyldiphenylphosphine)iridium(I) to yield products formulated as trifluoromethylnitrene complexes (J. Ashley-Smith, M. Green, N. Mayne, and F. G. A. Stone, Chem. Comm., 1969, 409).

verted into ethyl a-ethoxy-ßßß-trifluoro-a-hydroxypropionate via reaction with ethanol.⁶ However, no nitrogen was detected, indicating efficient trapping of carbanion (I; $X = CF_3$) by ethanol.

³ I. L. Knunyants and E. G. Bykhovskaya, Doklady Akad. Nauk S.S.S.R., 1960, 131, 1338.

⁴ I. L. Knunyants and E. G. Bykhovskaya, Zhur. Vsesoyuz. Khim. obshch. im. D.I. Mendeleeva, 1962, 7, 585.

⁵ C. S. Cleaver and C. G. Krespan, J. Amer. Chem. Soc., 1965, 87, 3716. ⁶ R. E. Banks, D. Berry, and G. J. Moore, J. Chem. Soc. (C),

^{1969, 2598.}

The reaction between chlorotrifluoroethylene and triethylammonium azide was carried out previously by passing the gaseous olefin into a warm solution of the azide in chlorobenzene,⁴ and the only product isolated was 2-chloro-1,1,2-trifluoroethyl azide (II; X = Cl) (60% yield). By analogy with perfluoropropenyl azide, which decomposes steadily at room temperature,^{1,3,5} it seemed that any 2-chloro-1,2-diffuorovinyl azide (III) formed would have decomposed into 2-chloro-2,3-difluoro-2H-azirine (IV) and nitrogen and probably gone

undetected, since the azirine (estimated b.p. $ca. -15^{\circ}$) would have been lost either by vaporisation or by hydrolysis during work-up, which involved treatment of the reaction mixture with aqueous hydrochloric acid then water [cf.1,6 the conversion of perfluoro-(2-methyl-2Hazirine), b.p. -15.5° , into trifluoropyruvic acid by water]. However, formation of the unsaturated azide is now

J. Chem. Soc. (C), 1970

may be interpreted in terms of the greater basicity of the anion $\overline{C}FCI \cdot CF_2 \cdot N_3$ compared with $CF_3 \cdot \overline{C}F \cdot CF_2 \cdot N_3$ (from the stability viewpoint, the former suffers from Coulombic repulsion between chlorine 3p and carbon 2p filled orbitals⁸), which reduces the opportunity for elimination of β -fluorine as fluoride. The possibility that perfluoropropenyl azide arises via dehydrofluorination of 2H-hexafluoropropyl azide by triethylamine liberated during the reaction between perfluoropropene and triethylammonium azide was not investigated; 2H-hexafluoropropyl azide has been found inert towards hot aqueous alkali.3,5

Photolysis of Azides.-2H-Hexafluoropropyl azide decomposes at temperatures above 200° to give 3*H*-hexafluoro-2-azabut-1-ene (VI) in high yield (86% based on 95% conversion at $270-280^{\circ}$ in platinum), a reaction reported originally by Russian investigators,9 who postulated the intermediacy of 2H-hexafluoropropylnitrene (V) (Scheme 3).

Irradiation of 2H-hexafluoropropyl azide with u.v. light also yields 3H-hexafluoro-2-azabut-1-ene (73%) yield based on 87% conversion of the azide in silica during 24 hr.), together with nitrogen (85%), tar, silicon tetrafluoride, and traces of compounds identified

$$\begin{array}{c|c} CF_{3} \cdot CHF \cdot CF_{2} \cdot N_{3} & \xrightarrow{h\nu} & CF_{3} \cdot CHF \cdot N : CF_{2} & \xrightarrow{SiO_{2}} & CF_{3} \cdot CHF \cdot N CO + SiF_{4} \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & &$$

SCHEME 5

discounted because when the procedure used to convert perfluoropropene into a mixture of 2*H*-hexafluoropropyl azide and perfluoropropenyl azide¹ was applied to chlorotrifluoroethylene only 2-chloro-1,1,2-trifluoroethyl azide (50%) was isolated, and no evidence was obtained for the production of 2-chloro-1,2-difluorovinyl azide. Assuming that carbanions are generated in reactions between polyfluoro-olefins and triethylammonium azide (as generally accepted for other nucleophilic reactions of such olefins, and established for some⁷), this result

7 R. E. Banks, 'Fluorocarbons and their Derivatives,' Oldbourne, London, 1964.

⁸ J. Burdon, Tetrahedron, 1965, 21, 3373.
 ⁹ I. L. Knunyants, E. G. Bykhovskaya, and V. N. Frosin, Doklady Akad. Nauk S.S.S.R., 1960, 132, 357.
 ¹⁰ D. A. Barr and R. N. Haszeldine, J. Chem. Soc., 1955, 2532;

1956, 3428.

by i.r. spectroscopy as an isocyanate and a secondary amine, presumably derived from the azabutene by reaction with silica or traces of moisture ($cf.^{10}$ analogous reactions of perfluoro-2-azapropene) (Scheme 4). Reaction of 3H-hexafluoro-2-azabut-1-ene with an excess of water at room temperature converts it completely into trifluoroacetaldehyde, presumably as in Scheme 5. Treatment of 3H-hexafluoro-2-azabut-1-ene with anhydrous potassium fluoride at room temperature converts it rapidly into 3*H*-hexafluoro-2-azabut-2-ene (VII), an isomerisation not without precedent; ¹¹ and the same change occurs slowly when the azabut-1-ene is stored in

¹¹ R. E. Banks, M. G. Barlow, R. N. Haszeldine, and M. K. McCreath, *J. Chem. Soc.*, 1965, 7203; P. H. Ogden and R. A. Mitsch, *J. Amer. Chem. Soc.*, 1967, **89**, 5007; P. H. Ogden, *J. Chem. Soc.* (C), 1967, 2302; P. H. Ogden, *J. Org. Chem.*, 1968, 02, 0216 33, 2518.

Pyrex at room temperature, presumably through the agency of traces of fluoride ion formed by hydrolysis of the starting material by adventitious moisture on the glass (silicon tetrafluoride is also produced) (Scheme 6).

$$F_{3} \cdot CHF \cdot N = CF_{2} \cdot F \longrightarrow CF_{3} \cdot CH - N \cdot CF_{3} \longrightarrow CF_{3} \cdot CH : N \cdot CF_{3} + F$$

$$(VI) \qquad F_{2} \qquad (VII)$$

$$Scheme 6$$

In an attempt to provide some support for the obvious ¹² rationale that u.v. irradiation of 2*H*-hexa-fluoropropyl azide generates 2*H*-hexafluoropropylnitrene, dilute solutions of the azide in cyclohexane and in cyclohexene were photolysed in silica; these substrates, particularly cyclohexane, are well known traps for non-fluorinated nitrenes. Since α -fluorine atoms in an

U.v. irradiation of a 100:1 molar mixture of cyclohexane and 2H-hexafluoropropyl azide for 56 hr. gave nitrogen (91% based on 98% conversion of the azide), silicon tetrafluoride, traces of 3H-hexafluoro-2-azabut-2-ene and the compounds believed to be CF₃·CHF·NCO and CF_3 ·CHF·NH·CF₃, tar, and N-cyclohexyl- $\alpha\beta\beta\beta$ -tetrafluoropropionamide (X) (g.l.c.-estimated yield >30%; isolated pure in 18% yield). Similar photolysis of a dilute solution of the azide in cyclohexene provided the same volatile products in almost identical yields, together with bicyclohex-2-enyl, a small amount of unidentified high-boiling material (not CF3. CHF.CO.NH2; see later), tar, and N-(cyclohex-2-enyl)- $\alpha\beta\beta\beta$ -tetrafluoropropionamide (XI) (estimated yield ca. 30%). Neither the photolysis in cyclohexane nor that in cyclohexene appeared to be proceeding by a radical-chain process, since when the u.v. lamp was switched off

$$CF_{3} \cdot CF: CF_{2} + RNH_{2} \xrightarrow{\text{ether}} CF_{3} \cdot CHF \cdot C(:NR) \cdot NHR \xrightarrow{\text{HCl aq.}} CF_{3} \cdot CHF \cdot CO \cdot NHR (66\%)$$

Scheme 7 R = cyclohexyl

amine containing the group R^1R^2N ·CF₂ undergo ready nucleophilic displacement when R^1 is a hydrocarbon entity and R^2 hydrogen or $R^{1,7,13}$ it was realised from the outset that isolation of products such as (VIII) and (IX) would prove difficult owing to their susceptibility towards attack by moisture, which would convert them into the corresponding amides (X) and (XI). Thus, no



effort was made to exclude moisture during work-up of reaction mixtures, and final products were treated with aqueous methanol to complete the conversions (VIII) nitrogen evolution ceased but commenced again when the irradiation was re-started; and no reaction (e.g., triazoline formation) seemed to occur between 2H-hexafluoropropyl azide and cyclohexene in the dark at room temperature during 4 weeks. Thus photo-activation of the azide seems essential.

These results can be rationalised in terms of either a ' nitrene mechanism ',¹⁴ involving generation of 2*H*-hexafluoropropylnitrene and subsequent insertion into a C-H bond of cyclohexane or a favoured allylic C-H bond of cyclohexene, or an 'activated azide mechanism '¹⁴ (Scheme 8). Since bicyclohex-2-enyl is formed from cyclohexene alone under the photolysis conditions employed, no conclusions can be drawn from its presence in the reaction involving 2*H*-hexafluoropropyl azide. However, the absence in the products from both photolyses of αH -tetrafluoropropionitrile (XII; see Scheme 8), evidence for which and for the related αH -tetrafluoropropionamide was sought by g.l.c. and i.r. analysis with the aid of authentic samples, militates against the 'azide



 \longrightarrow (X) and (IX) \longrightarrow (XI); authentic samples of amides were prepared from perfluoropropene by standard methods,⁷ e.g. Scheme 7.

¹² For recent reviews of decomposition reactions of azides see G. L'Abbé, *Chem. Rev.*, 1969, **69**, 345 and T. L. Gilchrist and C. W. Rees, 'Carbenes, Nitrenes, and Arynes,' Nelson, London, 1969. mechanism.' From a deductive viewpoint, formation of N-cyclohexyl- $\alpha\beta\beta\beta$ -tetrafluoropropionamide (X) is good

¹³ N. N. Yarovenko and M. A. Raksha, *Zhur. obshchei Khim.*, 1959, **29**, 2159; L. H. Knox, E. Velarde, S. Berger, D. Cuadriello, and A. D. Cross, *J. Org. Chem.*, 1964, **29**, 2187; J. Kopecký, J. Šmejkal, and M. Hudlický. *Chem. and Ind.*, 1969, 271.

¹⁴ W. Lwowski, Angew. Chem. Internat. Edn., 1967, 6, 897.

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evidence for the generation of 2*H*-hexafluoropropylnitrene by photolysis of 2*H*-hexafluoropropyl azide, because well-established cases are known of insertion into C-H bonds of cyclohexane or alkylcyclohexanes by nitrenes generated photochemically (and thermally) from azides.¹⁵ Photolysis of 2*H*-hexafluoropropyl azide in methylcyclohexane solution yields a mixture of *N*-(methylcyclohexyl)- $\alpha\beta\beta\beta$ -tetrafluoropropionamides containing mainly the isomer derived from attack at the tertiary C-H bond, which is not inconsistent with a ' nitrene mechanism.' ^{14,16} Hastelloy-B Heli-pak wire coils $(0.036 \times 0.07 \times 0.07$ in.), to give 2*H*-hexafluoropropyl azide (4.74 g., 24.6 mmoles, 22%), b.p. 51°, with the same i.r. spectrum as an analytical sample ¹ [λ_{max} (vapour) 3.38w (C-H str.), 4.63s (N₃ asym. str.), 7.25s, 7.33m,sh, 7.75vs, 7.93s, 8.15s,sh, 8.27vs, 8.42s, 9.00m,br, 9.26m, 9.51m, 11.25m, 11.45m,sh, 11.81m, 12.53m, 13.27m, 14.06m,sh, 14.17m, and 14.33m,sh µm.] and δ [CF₃·CO₂H interchange; CF₃(1)·CHF(2)·CF₂(3,4)·N₃] -1.07 [CF₃, d ($|J_{1,2}|$ 10.8) of t ($|J_{1,3}| \approx |J_{1,4}| \approx 9.5$) of d ($|J_{1,H}|$ 5.8 Hz)], +7.96 (CF₂, complex m), and +135.5 [CHF, d ($|J_{gem-H,F}|$ 44.0) of t ($|J_{2,3}| \approx |J_{2,4}| \approx 13.5$ Hz) of q] p.p.m. (relative intensities 3:2:1), τ 5.28 [doublet of



Photolysis of 2-chloro-1,1,2-trifluoroethyl azide alone gave nitrogen quantitatively (based on azide converted) but only a low yield (19%) of 3-chloro-1,1,3-trifluoro-2-azapropene (XIII) and much tar. A trapping experiment with cyclohexane yielded *N*-cyclohexylchlorofluoroacetamide (14%) (XIV), which is presumed to arise via 2-chloro-1,1,2-trifluoroethylnitrene (Scheme 9).

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer spectrophotometer model 21 or 257, n.m.r. spectra with a Perkin-Elmer R10 instrument operating at 35° and 60 (¹H) or $56\cdot46$ (¹⁹F) MHz, and mass spectra with an AEI MS2H or MS9 spectrometer. Molecular weights were determined by Regnault's method unless stated otherwise.

Triethylammonium azide was prepared and used essentially as described by others.⁵

CAUTION. Several violent explosions have occurred during our work with acyclic polyfluorinated azides (including one when a sample was heated too rapidly during combustion analysis) and constant use of robust face shields, blast screens, and guard tubes, where appropriate, is considered essential.

2H-Hexafluoropropyl Azide.—The azide was prepared by reaction of perfluoropropene with triethylammonium azide in sym-tetrachloroethane, as described previously,¹ or with sodium azide in ethanol as follows.

Perfluoropropene (16.74 g., 111.6 mmoles) was condensed in vacuo on to absolute ethanol (40 ml.) and sodium azide (8.47 g., 130.4 mmoles) contained in a cold (-196°) Dreadnought glass tube (300 ml.). The tube was sealed in vacuo, placed in a stout steel guard tube, warmed to room temperature, and shaken vigorously for 14 hr. The volatile product was pumped into a cold (-196°) trap and then distilled through a Podbielniak column (30.0 \times 0.8 cm.) packed with sextets $(|J_{1,\rm H}| \approx |J_{3,\rm H}| \approx |J_{4,\rm H}| \approx 6.0 \text{ Hz})]$, a mixture (0.9 g.), b.p. 52—60°, shown by i.r. spectroscopy to contain 2*H*-hexafluoropropyl azide, ethyl 2*H*-hexafluoropropyl ether, and ethyl pentafluoropropenyl ether, and ethyl 2*H*-hexafluoropropyl ether (14.97 g., 76.37 mmoles) containing (by i.r. spectroscopy) a small amount of ethyl pentafluoropropenyl ether, b.p. 60—65°.

A solution of bromine (25 g.) in aqueous sodium bromide (26 g. in 250 ml.) was added dropwise, with stirring, to the b.p. $60-65^{\circ}$ fraction (50.0 g.) from several experiments until the colouration due to bromine persisted. The product was shaken with mercury and the organic layer was dried $(MgSO_4)$ and distilled, to give ethyl 2H-hexafluoropropyl ether (42.7 g., 218 mmoles) (Found: C, 30.7; H, 3.2%; M, 193. Calc. for C₅H₆F₆O: C, 30.6; H, 3.1%; M, 196), b.p. 64° (lit., 3 64°), δ [CF₃·CO₂H interchange; CF₃(1)·CHF(2)·- $CF_2(3,4) \cdot O \cdot C_2H_5 = -0.8 [CF_3, d (|J_{1,2}| 10.4) \text{ of } d (|J_{1,4}| 9.5) \text{ of }$ d ($|J_{1,3}|$ 8.8) of d ($|J_{1,H}|$ 5.9 Hz)], +5.6 [CF₂, AB-type q ($|J_{3,4}|$ 149.5), each member split into d ($|J_{2,3}|$ 11.7, $|J_{2,4}|$ 12.3) of q of d ($|J_{3,H}|$ 4.6, $|J_{4,H}|$ 6.9)], and +137.5 [CHF, d ($|J_{gem-H,F}|$ 43.8 Hz) of t of q] p.p.m. (relative intensities 3 : 2 : 1), τ 5 23 [CHF, d ($|J_{H,F}|$) of d of q of d], 5 93 (CH₂, q), and 8.70 (CH₃, t), and ethyl α -bromotetrafluoropropionate (7.2 g., 28.5 mmoles), b.p. 50°/42 mm.Hg., λ_{max} 5.66s µm. (C:O str.), with a correct analysis [Found: C, 23.5; H, 2.0%; M (mass spec.), 253. Calc. for C₅H₅BrF₄O₂: C, 23.7; H, 2.0%; M, 253] but showing weak impurity bands in its n.m.r. spectra which otherwise clearly revealed its identity: δ (CF₃·CO₂H interchange) +1.0 (CF₃, d (|J| 8.8) Hz) and +58.0 (CFBr, 1:3:3:1 quartet) p.p.m. (relative intensities 3:1), τ 5.56 (CH₂, q) and 8.64 (CH₃, t). The impurity was probably ethyl 1,2-dibromopentafluoropropyl ether, and gave rise to weak absorptions at -11.0, -4.0, and +55.5 p.p.m. (relative intensities 1:3:1) in the ¹⁹F spectrum.

2H-Hexafluoropropyl azide was also prepared on a 40 g. scale (20% yield) by passing perfluoropropene (150 g.) during 12 hr. into a vigorously stirred suspension of sodium azide (46 g.) in absolute ethanol (400 ml.) contained in a

¹⁵ W. Lwowski and T. W. Mattingly, J. Amer. Chem. Soc., 1965, **87**, 1947; G. T. Tisue, S. Linke, and W. Lwowski, *ibid.*, 1967, **89**, 6303; A. G. Anastassiou, H. E. Simmons, and F. D. Marsh, *ibid.*, 1965, **87**, 2296; A. G. Anastassiou, *ibid.*, 1967, **89**, 3184; A. G. Anastassiou and J. N. Shepelavy, *ibid.*, 1968, **90**, 492.

¹⁶ A. G. Anastassiou and H. E. Simmons, J. Amer. Chem. Soc., 1967, 89, 3177; A. G. Anastassiou, *ibid.*, p. 3184; see also D. S. Breslow, E. I. Edwards, R. Leone, and P. von R. Schleyer, *ibid.*, 1968, 90, 7097, and references quoted therein.

stainless steel autoclave (1 l.) equipped with a high-speed magnetic stirrer.

2-Chloro-1,1,2-trifluoroethyl Azide.-Chlorotrifluoroethylene (15.6 g., 134 mmoles) was condensed in vacuo into a cold (-196°) Pyrex tube (300 ml.) containing triethylammonium azide (30.0 g., 208 mmoles) in sym-tetrachloroethane (150 ml.). The tube was placed in a steel guard and shaken vigorously while it warmed to $ca. 0^{\circ}$; the guard and tube were then stored in an ice-bath for 64 hr. The volatile product was pumped from the cold (0°) tube and combined with the product from a duplicate experiment; the combined product [from 31.2 g. (268 mmoles) C₂F₃Cl] was fractionated, in vacuo, to give chlorotrifluoroethylene (1.3 g., 11 mmoles, 4% recovery) (Found: M, 116. Calc. for $C_2F_3Cl: M, 116.5$) and a colourless liquid (31.2 g.) that was expanded into an evacuated bulb (20 l.) and left at 20°/111 mm.Hg overnight; no change in pressure occurred and no nitrogen was produced, so the material was condensed and distilled in a small Vigreux still to give 2-chloro-1,1,2-trifluoroethyl azide (20.8 g., 130 mmoles, 50% based on C₂F₃Cl consumed) (Found: C, 14.7; H, 1.0; N, 26.0%; M, 158. Calc. for $C_2HClF_3N_3$: C, 15.0; H, 0.6; N, 26.3%; *M*, 159·5), b.p. 57°/752 mm.Hg, λ_{max} (vapour) 3·34w (C–H str.), 4·62s (N₃ asym. str.), 7·36m, 7·73s, 7·94s, 8·09s, 9.08s, 9.38s, 10.60w, 10.70w (doublet), 11.14w, 11.57s, 12.21s, 13.08m, 14.36m, sh, 14.44m, and 14.53m, sh. µm., $\delta(CF_3 \cdot CO_2 H \text{ interchange}) + 12 \cdot 0 br [CF_2, d of d (|J_{OF_2, H}| ca.$ 4.0) showing signs of further splitting owing to the asymmetric carbon centre] and +76.5 [CHFCl, d ($|J_{gem-H,F}|$ 49.0) of t ($|J_{CF, CF_4}|$ 14.1 Hz)] (relative intensities 2:1), δ (benzene interchange) +0.5 (CHFCl, d of t) p.p.m.

Reactions of 2H-Hexafluoropropyl Azide.-(a) Pyrolysis. A slow stream of dry nitrogen was bubbled through 2Hhexafluoropropyl azide (2.00 g., 10.4 mmoles) and thence through a platinum tube (100 imes 1 cm.) heated at 270-280° over 56 cm. of its length. After 6 hr. the supply of azide was exhausted, and the pyrolysate, collected in two traps cooled to -72 and -183° , respectively, was subjected to repeated trap-to-trap fractional condensation in vacuo, to give (i) $(-63^{\circ} \text{ trap})$ 2H-hexafluoropropyl azide (0.11 g., 0.57 mmoles, 5% recovery) containing (by i.r. spectroscopy) traces of compounds tentatively identified as CF3 CHF NCO [$\lambda_{max.}$ 4.38 and 6.83 $\mu m.$ (asym. and sym. N-C-O str., respectively)] and CF_3 ·CHF·NH·CF₃ [λ_{max} . 2.89 and 6.56 µm. (N-H str. and def., respectively)] derived from hydrolysis of 3H-hexafluoro-2-azabut-1-ene; (ii) $(-95^{\circ} \text{ trap})$ 3*H*-hexafluoro-2-azabut-1-ene (1·40 g., 8·48 mmoles; 86% based on azide consumed) (Found: C, 22.0; H, 0.6; N, 8.7%; M, 166. Calc. for C₃HF₆N: C, 21.8; H, 0.6; N, 8.5%; M, 165), λ_{\max} 3.35vw (C-H str.) and 5.54s (C.N str.) μ m., δ (CF₃-CO₂H interchange) -35.4 and -22.8 (N:CF₂, two very broad humps), +10.0 (CF₃), and +95.2br (CHF, d, $|J_{\text{H},\text{F}}|$ 48.0 Hz) p.p.m. (relative intensities 1:1:3:1; and (iii) (-196° trap) a mixture (0.05 g.) shown by i.r. spectroscopy to comprise silicon tetrafluoride and unidentified material containing C-F bonds.

When the pyrolysis was repeated at 205-210 and $250-260^{\circ}$, 3H-hexafluoro-2-azabut-1-ene was obtained in 78 (based on 14% consumption of the azide) and 82% (31% consumption) yield, respectively.

(b) Photolysis alone. 2H-Hexafluoropropyl azide (3.00 g., 15.5 mmoles), sealed in a silica ampoule (300 ml.), was irradiated for 24 hr. with u.v. light from a 500 w Hanovia lamp placed 20 cm. distant. Nitrogen (0.37 g., 13.2 mmoles, 85%) (Found: M, 27. Calc. for N₂: M, 28) (show-

ing no i.r. absorption) was removed from the ampoule and collected in a cold (-196°) trap filled with activated charcoal, and the condensable volatile product was fractionated, to give 2*H*-hexafluoropropyl azide (0.39 g., 2.02 mmoles, 13% recovery) contaminated with compounds tentatively identified by i.r. spectroscopy [as in (a)] as CF₃·CHF·NCO and CF₃·CHF·NH·CF₃, 3*H*-hexafluoro-2-azabut-1-ene (1.63 g., 9.88 mmoles, 73% based on azide consumed), and silicon tetrafluoride containing unidentified C-F compounds (0.13 g.). An involatile red-brown tar (0.3 g.) (Found: C, 28.3; H, 3.3; N, 6.0%) showing strong i.r. absorptions in the C-H and C-F str. regions was recovered from the inner walls of the reaction vessel.

(c) Photolysis in cyclohexane. 2H-Hexafluoropropyl azide (7.72 g., 40.0 mmoles) was divided into three equal portions and each was condensed in vacuo into one of three cold (-196°) silica tubes (300 ml.) between which had been equally divided 336 g. (4.00 moles) of cyclohexane. The tubes were sealed, warmed to room temperature (no nitrogen evolution was observed), and irradiated for 56 hr. as in (b); evolution of nitrogen was clearly observed, but ceased if the lamp was switched off, and a red-brown tar formed on the inner walls of the tubes. The gaseous product was freed from nitrogen (0.99 g., 35.4 mmoles, 91% based on azide consumed) (Found: M, 28. Calc. for N₂: M, 28) and shown by a combination of fractionation and i.r. analysis to contain 2H-hexafluoropropyl azide (0.19 g., 0.98 mmoles, 2% recovery), traces of 3H-hexafluoro-2-azabut-2-ene, CF3-CHF•NCO, and CF₃•CHF•NH•CF₃, and silicon tetrafluoride. The liquid product was poured from the tubes, leaving a red-brown tarry residue with an i.r. spectrum very similar to that of the tar obtained by photolysis of 2H-hexafluoropropyl azide alone, and evaporated at reduced pressure to remove cyclohexane; the pale-yellow semi-solid residue was recrystallised from aqueous methanol to yield N-cyclohexyl- $\alpha\beta\beta\beta$ -tetrafluoropropionamide (1.59 g., 7.01 mmoles, 18%) [Found: C, 47.8; H, 5.7; N, 6.0%; M (mass spec.), 227. $C_9H_{13}F_4NO$ requires C, 47.6; H, 5.7; N, 6.2%; M, 227], as white crystals, m.p. 88–89°, λ_{max} (mull) 3.02 (N-H str.), 5.99 (CO str.), and 6.43 (N-H def.) μ m., which had the same g.l.c. retention time (2m. silicone oil MS550-Celite; 150°) and i.r. spectrum as an authentic sample (the m.p. of which it did not depress) prepared as described later. The yield of the propionamide was estimated to be at least 30% by g.l.c. analysis (column as before) of the crude pale vellow product.

(d) Photolysis in methylcyclohexane. The previous experiment was repeated with 5.00 g. (25.9 mmoles) of 2H-hexafluoropropyl azide and 215.6 g. (2.20 moles) of methyl-cyclohexane divided equally between two silica tubes (300 ml.) and with a 67 hr. irradiation period. A red tar with an i.r. spectrum identical with that of the tar formed in the photolysis with cyclohexane was obtained, and the gaseous product contained nitrogen (19.0 mmoles, 72%), silicon tetrafluoride, and traces of 2H-hexafluoropropyl azide and 3H-hexafluoro-2-azabut-2-ene. The liquid product was evaporated under reduced pressure to remove methylcyclohexane, leaving an oily yellow residue that was sublimed *in vacuo* (bath temp. 160°) to give a pale yellow solid which was shown by elemental analysis, i.r. spectroscopy, and g.l.c. (2 m. silicone oil MS550-Celite at 160° and 2 m.

Apiezon–Celite at 157°) to be a 9:11:63:17 (ratio of g.l.c. peak areas) mixture of N-(methylcyclohexyl)- $\alpha\beta\beta\beta$ -tetra-fluoropropionamides (0.88 g., 3.65 mmoles, 14%) [Found: C, 49.5; H, 6.4; N, 5.7%; M (mass spec.), 241. Calc. for C₁₀H₁₅F₄NO: C, 49.8; H, 6.2; N, 5.8%; M, 241], λ_{max} . (mull) 3.03 (N–H str.), 5.95 (C:O str.), and 6.45 (N–H def.) μ m., and with a 'fingerprint region' pattern very similar to that found in the i.r. spectrum of N-cyclohexyl- $\alpha\beta\beta\beta$ -tetrafluoropropionamide. The major component of the mixture had the same g.l.c. retention time as an authentic sample of N-(1-methylcyclohexyl)- $\alpha\beta\beta\beta$ -tetrafluoropropionamide later.

(e) Photolysis in cyclohexene. No reaction occurred when a solution of 2H-hexafluoropropyl azide (5.0 g.) in cyclohexene $(21 \cdot 2 g)$ was stored in the dark at room temperature for 4 weeks. However, photolysis (500 w Hanovia u.v. lamp; 56 hr.) of 2H-hexafluoropropyl azide (7.72 g., 40.0 mmoles) in cylohexene (328 g., 4.00 moles) [solution equally divided between three silica ampoules (each 300 ml.)] gave nitrogen (1.02 g., 36.4 mmoles, 91%), small amounts of 2H-hexafluoropropyl azide, 3H-hexafluoro-2-azabut-2-ene, CF₃·CHF·NCO, CF₃·CHF·NH·CF₃, and silicon tetrafluoride, and a liquid that was evaporated in vacuo to remove cyclohexene, leaving a pale yellow oily residue (3.9 g.) containing [by i.r. spectroscopy and g.l.c. (2 m. silicone oil MS550-Celite, 150°)] almost equimolar amounts of bicyclohex-2-enyl $\mathit{N-}(cyclohex-2\text{-}enyl)-\alpha\beta\beta\beta\text{-}tetrafluoropropionamide}$ and (estimated yield ca. 30%) (authentic samples of both were available) together with a small amount of an unknown component with a longer g.l.c. retention time than either. The pale yellow residue slowly deposited crystals when stored at room temperature, and the whole sample was treated with aqueous methanol to provide N-(cyclohex-2-enyl)- $\alpha\beta\beta\beta$ tetrafluoropropionamide (1.47 g., 6.53 mmoles, 16%), recrystallisation of which from aqueous methanol gave an analytical sample [Found: C, 47.8; H, 5.2; N, 6.2%; M (mass spec.), 225. Calc. for C₉H₁₁F₄NO: C, 48.0; H, 4.9; N, 6.2%; *M*, 225], m.p. and mixed m.p. 59-60°. A film of brown tar streaked with buff-coloured material coating the inner walls of the reaction vessel was not investigated.

Reactions of 3H-Hexafluoro-2-azabut-1-ene.—(a) Isomerisation. 3H-Hexafluoro-2-azabut-1-ene (0.21 g., 1.27 mmole) was stored in a Pyrex ampoule (5 ml.) at room temperature for 8 weeks. Fractionation of the volatile product gave silicon tetrafluoride (0.13 mmole), identified by i.r. spectroscopy, and 3H-hexafluoro-2-azabut-2-ene (0.14 g., 0.85 mmole, 67%) [Found: C, 22.2; H, 0.6; N, 8.6%; M (mass spec.), 165. C₃HF₆N requires C, 21.8; H, 0.6; N, 8.5%; M, 165], b.p. 17.0° (isoteniscope), λ_{max} 5.84 µm. (C:N str.), δ (CF₃·CO₂H interchange; 10% w/v in CHCl₃) -12.6br (N·CF₃, s) and -5.8 (CF₃·CH, m) p.p.m. (relative intensities 1:1), δ (benzene interchange) -1.6br p.p.m. (m).

3*H*-Hexafluoro-2-azabut-1-ene (0.26 g., 1.58 mmole) was condensed *in vacuo* into a cold (-196°) Pyrex tube (5 ml.) containing anhydrous potassium fluoride (0.10 g., 1.72mmole). The tube was sealed, warmed to room temperature, and left for 1 hr. The volatile product was shown by i.r. spectroscopy to be 3*H*-hexafluoro-2-azabut-2-ene (0.18g., 1.09 mmole, 70%).

(b) Hydrolysis. 3H-Hexafluoro-2-azabut-1-ene (0.35 g., 2.12 mmoles) was shaken with water (10 ml.) in a Pyrex ampoule (20 ml.) at room temperature overnight. The product was treated with a solution of 2,4-dinitrophenyl-hydrazine in 6N-sulphuric acid to yield the 2,4-dinitrophenylhydrazone of trifluoroacetaldehyde (0.33 g., 1.19)

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mmole, 56%) (Found: C, 34.6; H, 1.9; N, 20.1. Calc. for $C_8H_5F_3N_4O_4$: C, 34.5; H, 1.8; N, 20.2%), m.p. and mixed m.p. 149—150° (from 50% aqueous ethanol) (lit.,¹⁷ 149.7—151.0°).

Photolysis of 2-Chloro-1,1,2-trifluoroethyl Azide.—(a) Alone. The azide (3.00 g., 18.8 mmoles), sealed in a silica tube (300 ml.), was irradiated for 24 hr. with u.v. light from a 500 w Hanovia lamp placed 10—15 cm. distant, to give nitrogen (17.1 mmoles, 91%), silicon tetrafluoride, 2-chloro-1,1,2-trifluoroethyl azide (1.50 mmole, 8%), 3-chloro-1,1,3-trifluoro-azapropene (3.35 mmoles, 19% based on azide consumed) (Found: M, 133. C₂HF₃CIN requires M, 131.5), λ_{max} . (vapour) 5.49 µm. (C:N str.), traces of material believed to be chlorofluoromethyl isocyanate (showing i.r. absorptions at 4.38 and 6.95 µm. attributed to asym. and sym. N–C–O str., respectively), and much red tar containing (Lassaigne fusion) carbon, nitrogen, chlorine, and fluorine.

(b) In the presence of cyclohexane. Equal amounts of 2-chloro-1,1,2-trifluoroethyl azide (5.40 g., 33.8 mmoles total) were condensed in vacuo into two silica tubes (300 ml.) each containing 126 g. (3.00 moles total) of cyclohexane and cooled to -196° . The tubes were sealed and irradiated as in (a) for 48 hr. while being shaken vigorously. Work-up as in other trapping experiments gave nitrogen (26.6 mmoles, 79%), silicon tetrafluoride, cyclohexane, and N-cyclohexylchlorofluoroacetamide (0.91 g., 4.70 mmoles, 14%), finally isolated by sublimation $(66-70^{\circ}/ca. 20 \text{ mm.Hg})$ as a white solid, m.p. and mixed m.p. 67°, 8 (CF3 •CO2H interchange; 50% w/v in CCl₄) $+65\cdot6$ p.p.m. (CHFCl, d, $|J_{gem-H,F}|$ 51 Hz), with the same i.r. spectrum and g.l.c. retention time (2 m. silicone oil MS550–Celite, 150°) as an authentic sample prepared as described later.

Preparation of Amides.---(a) N-Cyclohexyl-αβββ-tetrafluoropropionamide. Perfluoropropene (10.05 g., 66.99 mmoles) was condensed in vacuo into a cold (-196°) Dreadnought glass tube (300 ml.) containing cyclohexylamine (32.2 g., 325.3 mmoles) in ether (100 ml.). The tube was sealed and warmed to room temperature; a white precipitate, presumably cyclohexylamine hydrofluoride, appeared. The tube was shaken vigorously for 15 min. and then stored at room temperature overnight. The product was filtered and the filtrate was evaporated at reduced pressure; the yellow oily residue was treated with dilute hydrochloric acid, to yield a pale yellow solid that was recrystallised from aqueous ethanol to give N-cyclohexyl- $\alpha\beta\beta\beta$ -tetrafluoropropionamide (10.10 g., 44.49 mmoles, 66%) [Found: C, 47.6; H, 5.9; N, 6.5%; M (mass spec.), 227. Calc. for C₉H₁₃F₄NO: C, 47.6; H, 5.7; N, 6.2%; M, 227] as white crystals, m.p. 89–90°, λ_{max} (mull) 3.02 (N-H str.), 6.00 (CO str.), and 6.43 (N-H def.) μ m., 8 (CF₃·CO₂H interchange; benzene soln.) -1.8 [CF₃, d ($|J_{CF_3,CF}|$ 11.3) of d ($|J_{vic-H,F}|$ 6.4 Hz)], and $+125\cdot2\left[\mathrm{CH}F,\mathrm{d}\left(\left|J_{gem-\mathrm{H},\,\mathrm{F}}\right|45\cdot5\,\mathrm{Hz}
ight)
ight)$ of q with further fine splitting] p.p.m. (relative intensities 3:1), 7 3.7 (NH, very broad hump), 5.05 (CHF, d of q), 6.25 (CH-N, broad hump), and 7.9-8.9 (ring CH₂ protons, complex).

(b) Others. In a similar manner, N-cyclohexylchlorofluoroacetamide (80% yield) [Found: C, 49.8; H, 7.0; N, 7.15%; M (mass spec.), 193.5. C₈H₁₃CIFNO requires C, 49.6; H, 6.7; N, 7.2%; M, 193.5], m.p. 67°, λ_{max} (melt) 3.07 (N-H str.), 5.97 (C:O str.), and 6.45 (N-H def.) μ m., N-(1-methylcyclohexyl)- $\alpha\beta\beta\beta$ -tetrafluoropropionamide (48% yield) [Found: M (mass spec.), 241. Calc. for C₁₀H₁₅F₄NO: M, 241], λ_{max} (mull) 3.03 (N-H str.), 5.95 ¹⁷ H. Shechter and F. Conrad, J. Amer. Chem. Soc., 1950, 72, 3371. (C:O str.), and 6·45 (N–H def.) µm., and N-(cyclohex-2-enyl)- $\alpha\beta\beta\beta$ -tetrafluoropropionamide (49% yield) [Found: C, 47·9; H, 5·2; N, 6·2%; *M* (mass spec.), 225. C₉H₁₁F₄NO requires C, 48·0; H, 4·9; N, 6·2%; *M*, 225], m.p. 59–60° (finally purified by sublimation at 60–70°/1–2 mm.Hg.), λ_{max} (mull) 3·03 (N–H str.), 6·00 (C:O str.), and 6·46 (N–H def.) µm., were prepared from chlorotrifluoroethylene–

cyclohexylamine, perfluoropropene-1-amino-1-methylcyclohexane, and perfluoropropene-3-aminocyclohexene, respectively.

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