

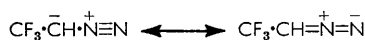
366. Carbene Chemistry. Part I. Reactions of Fluoroalkyl-diazo-compounds.*

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2,2,2-Trifluorodiazaoethane readily undergoes photolysis to yield nitrogen and trifluoromethylcarbene, $\text{CF}_3\cdot\dot{\text{C}}\text{H}$, which (i) rearranges to produce trifluoroethylene, (ii) reacts with 2,2,2-trifluorodiazaoethane to produce *cis*- and *trans*-1,1,1,4,4,4-hexafluorobut-2-ene, or (iii) reacts with trifluoroethylene to give 1,1,2-trifluoro-3-trifluoromethylcyclopropane. The diazoethane also reacts with *cis*- or *trans*-hexafluorobut-2-ene to produce a pyrazoline, and it can yield a polymer if its concentration is high. Photolysis of 2,2,3,3,4,4,4-heptafluorodiazao-n-butane similarly yields nitrogen and the carbene $\text{C}_3\text{F}_7\cdot\dot{\text{C}}\text{H}$, rearrangement of which involves migration of a C_2F_5 group to form the olefin $\text{C}_2\text{F}_5\cdot\text{CH}:\text{CF}_2$ rather than migration of fluorine to give the olefin $\text{C}_2\text{F}_5\cdot\text{CF}:\text{CHF}$. Polytrifluoromethylcarbene (polyhexafluorobut-2-ene) has good thermal stability and chemical resistance; a preferred, possibly isotactic, form has m. p. $>310^\circ$ and is thermally stable in air at 290° .

As part of a study of the reactions of carbenes and methylenes, the preparation and reactions of two polyfluoroalkylcarbenes, $\text{CF}_3\cdot\dot{\text{C}}\text{H}$ and $\text{C}_3\text{F}_7\cdot\dot{\text{C}}\text{H}$, have been investigated. Each can be generated by photolysis of the corresponding diazo-compound.

2,2,2-Trifluorodiazaoethane, a bright yellow liquid b. p. $11\cdot7^\circ$, was prepared by nitrosation of 2,2,2-trifluoroethylamine.¹ The trifluoromethyl group imparts stability comparable with that of diazoacetic ester, and, with care, the pure trifluorodiazaoethane can be stored and manipulated without undue danger. Its infrared spectrum shows a strong band at $4\cdot70\ \mu$, and the shift to shorter wavelength, compared with unsubstituted diazoalkanes and diazoacetic ester,² shows that the structure involving the $\text{N}=\text{N}$ bond is of importance:



Its ultraviolet spectrum is similar to that of other diazo-alkanes,³ with a weak maximum at $397\ \text{m}\mu$ ($\epsilon\ 5\cdot0$) and increasing absorption below $284\ \text{m}\mu$.

The products from the irradiation of 2,2,2-trifluorodiazaoethane in a silica vessel depend on the initial pressure of the diazo-alkane. When the liquid diazo-alkane was present (vapour pressure *ca.* 2.5 atm.), whether the liquid phase was shielded from the radiation or not, the products were: trifluoroethylene (10%), *cis*- (6%) and *trans*-1,1,1,4,4,4-hexafluorobut-2-ene (13%), nitrogen (74%), polytrifluoromethylcarbene (7%), 3,4,5-tris-trifluoromethyl-2-pyrazoline (40%), and 1,1,2-trifluoro-3-trifluoromethylcyclopropane (1%). Only a small amount of involatile liquid remained unidentified.

When no liquid diazo-alkane was present during photolysis, and the initial pressure was 0.47 atm., the yield of 3,4,5-tris-trifluoromethyl-2-pyrazoline and of polytrifluoromethylcarbene dropped to almost zero; reduction of initial pressure to 0.11 atm. led to a further increase in the yield of trifluoroethylene at the expense of the butenes, as follows (yield at 0.47 atm. given first): trifluoroethylene, 22 and 32%; *cis*-1,1,1,4,4,4-hexafluorobut-2-ene, 20 and 22%; *trans*-hexafluorobut-2-ene, 41 and 26%.

* Preliminary report, Fields and Haszeldine, *Proc. Chem. Soc.*, 1960, 22.

¹ Gilman and Jones, *J. Amer. Chem. Soc.*, 1943, **65**, 1458.

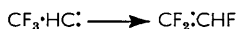
² Crawford, Fletcher, and Ramsay, *J. Chem. Phys.*, 1951, **19**, 406; Yates, Shapiro, Yoda, and Fugger, *J. Amer. Chem. Soc.*, 1957, **79**, 5756.

Kirkbride and Norrish, *J.*, 1933, 119; Adamson and Kenner, *J.*, 1937, 1551; Wolf, *Z. phys. Chem. (Leipzig)*, 1932, **B17**, 46.

These results can be accommodated by a scheme in which the primary reaction is the formation of trifluoromethylcarbene:



In the absence of nucleophiles, the electron-deficient trifluoromethylcarbene rearranges by migration of fluorine from β - to α -carbon, with formation of a double bond:



The probability of collision of the $\text{CF}_3\cdot\text{HC}\cdot$ with another molecule (*e.g.*, of unchanged 2,2,2-trifluorodiazoethane) decreases with decrease in initial pressure, and rearrangement to give trifluoroethylene thus increases.

Reaction of trifluoromethylcarbene with the trifluorodiazoethane is considered to be the main route to the hexafluorobutenes, rather than a reaction second-order in trifluoromethylcarbene such as dimerisation. Other studies⁴ showed that dimerisation of methylene or of ethylidene formed by photolysis of the respective ketens is insignificant. The *trans*:*cis* ratio of the hexafluorobutenes also varies with initial reactant pressure (Table). Irradiation of pure *cis*- and of pure *trans*-hexafluorobut-2-ene under similar

trans:*cis* Ratio of hexafluorobutenes.

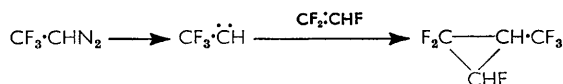
Experiment	1	2	3	4 *	5 †
Initial pressure of $\text{CF}_3\cdot\text{CHN}_2$ (atm.)	2.4	0.47	0.11	0.35	0.12
Total hexafluorobut-2-ene (%)	19	61	48	63	52
<i>trans</i> : <i>cis</i> Ratio	2.1	2.1	1.2	1.3	1.1

* Irradiation in Pyrex ($\lambda > 3000 \text{ \AA}$). † With a four-fold excess of trifluoroethylene.

conditions showed that the *cis*-isomer is more readily converted into the *trans*-isomer than the converse. This effect could account for the slight excess of the *trans*-isomer found in experiments 3—5 even if the isomers were formed with equal probability, but some process must occur in experiments 1 and 2 which specifically favours the formation of the *trans*-isomer.

The change in the *trans*:*cis*-ratio of but-2-ene produced in the photolysis of diazoethane at various pressures has recently been interpreted in terms of initial formation of an excited *trans*-but-2-ene;⁵ the change in isomer ratio is much greater than that observed for the hexafluorobutenes although the highest pressure used was much lower (*ca.* 0.5 atm.) and only radiation of longer wavelength was used.

1,1,2-Trifluoro-3-trifluoromethylcyclopropane was first isolated from the photolysis product by gas chromatography, and synthesised separately:



Tris(trifluoromethyl)pyrazoline, the major component of a complex mixture boiling between 117 and 137°, was isolated by large-scale gas chromatography. It absorbed in the infrared at 2.92 μ (N-H) and 6.17 μ (C=N) and was, therefore, assigned the Δ^2 -structure. This structure is also in accord with the stability of the pyrazoline to heat and to ultra-violet radiation, both of which would be expected to decompose a 1-pyrazoline.⁶

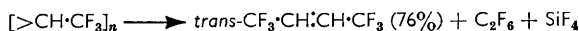
The residue from the photolyses at pressures >1 atm. consisted of a viscous brown

⁴ Kistiakowsky and Rosenberg, *J. Amer. Chem. Soc.*, 1950, **72**, 321; Kistiakowsky and Mahan, *ibid.*, 1957, **79**, 2412.

⁵ Frey, *J.*, 1962, 2293.

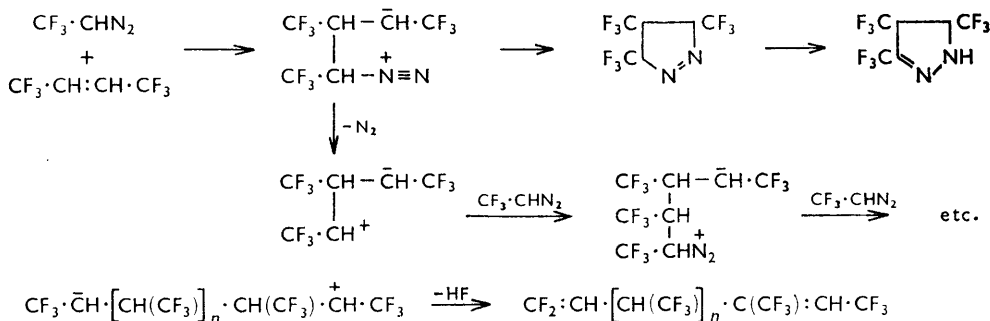
⁶ McGreer, Wing Wai, and Carmichael, *Canad. J. Chem.*, 1960, **38**, 2410; Kocsis, Ferrini, Arigoni, and Jeger, *Helv. Chim. Acta*, 1960, **43**, 2178.

liquid, soluble in ether, and a hard, brittle, insoluble solid. The liquid contained several components and was not examined. The solid, originally transparent, became white and opaque when washed with ether, and was insoluble in water and common organic solvents. Its pyrolysis *in vacuo* at 800°:

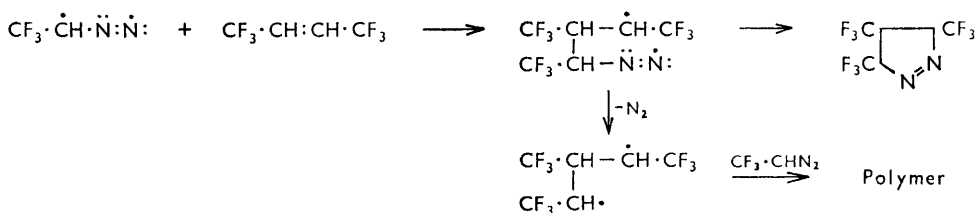


is in accord with the proposed polytrifluoromethylcarbene (polyhexafluorobut-2-ene) structure rather than with polytrifluoroethylene, which would also have the same analysis. The high yield of *trans*-hexafluorobut-2-ene suggests that hexafluorobutene units “unzip” from the polymer as does tetrafluoroethylene from pyrolysing polytetrafluoroethylene.⁷

The pyrazoline and the polymer are formed in quantity only when the initial concentration of the trifluorodiazomethane is high. They could arise from initial nucleophilic attack by the diazo-alkane on hexafluorobutene followed by ring-closure to give the pyrazoline, or elimination of nitrogen to give a carbonium ion and thence the polymer:

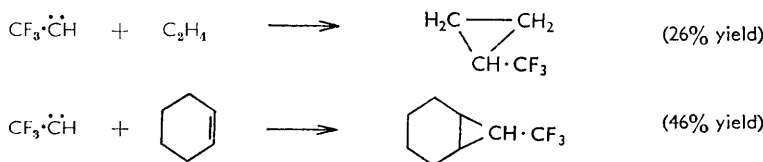


Alternatively, and probably preferred under the conditions used, the excited di-radical form of the diazo-alkane could yield pyrazoline and polymer:



The formation of pyrazolines on irradiation of mixtures of diazomethane and fluoro-olefins has been interpreted in terms of similar di-radical forms.⁸

The ready reaction of the carbene with hydrocarbon olefins, *e.g.*,



suggests that it reacts in the electrophilic singlet state (carbene) rather than in the triplet

⁷ Madorsky, Hart, Straus, and Sedlak, *J. Res. Nat. Bur. Stand.*, 1953, **51**, 327.

⁸ Misani, Speers, and Lyon, *J. Amer. Chem. Soc.*, 1956, **78**, 2801.

state (di-radical). In accord with this is the low yield (9%) of 1,1,2-trifluoro-3-trifluoromethylcyclopropane obtained by irradiation of 2,2,2-trifluorodiazethane and trifluoroethylene; there is no "dark" reaction. Trifluoroethylene, which is not sensitive to electrophilic attack, thus acts mainly as an inert gas during the photolysis of the trifluorodiazethane (Table).

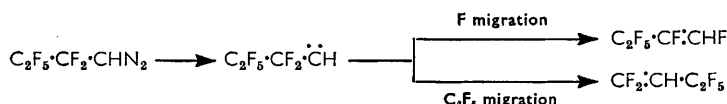
1,2,3-Tris(trifluoromethyl)cyclopropane, which might have resulted from attack of trifluoromethylcarbene on the hexafluorobutenes, was not detected as a photolysis product of 2,2,2-trifluorodiazethane. Separate experiments showed that photolysis at room temperature or thermal degradation at 340° of the pyrazoline gave only mixtures of unidentified products, and not tris(trifluoromethyl)cyclopropane.

Polytrifluoromethylcarbene.—The relatively high decomposition point (220–235°) for the polymer obtained by photolysis of 2,2,2-trifluorodiazethane at superatmospheric pressure makes a polymer of type $[\text{CH}(\text{CF}_3)\cdot\text{CH}(\text{CF}_3)]_n$ of interest as a possible industrial product. Attempts were made to improve its yield and quality, in particular its m. p., which varied with the experimental conditions used.

2,2,2-Trifluorodiazethane was not polymerised by gold(III) chloride, colloidal gold, or copper stearate. Boron trifluoride etherate decomposed it, but without formation of solid polymer of high m. p. Concentrated sulphuric acid exploded the diazo-alkane at low temperature. Thermal decomposition at 120° gave a 59% yield of solid polymer together with the pyrazoline; after removal of polymer of low molecular weight, by heating in air at 140°, no further loss of weight occurred in air until 250°. A solution of cuprous iodide in ether containing methylamine also gave a solid polymer (ca. 29% yield) but with a low m. p. (132–145°). Free-radical initiation of polymerisation by dimethyl $\alpha\alpha'$ -azodiisobutyrate also gave solid polymer, m. p. 220–270°, in 18% yield.

The best polymer was produced by storing pure 2,2,2-trifluorodiazethane in a sealed Dreadnought tube in the dark at room temperature for 2–3 years. Two-thirds of the diazoethane reacted, and a polymer (38% yield) thermally stable at 290° in air and with m. p. ca. 320° was isolated. Its infrared spectrum was much sharper than that of any of the other polymers. Pyrolysis of the polymer again gave *trans*-hexafluorobut-2-ene in 61% yield. It is possible that the slow polymerisation, catalysed by a weak ionic catalyst such as glass, yielded the more crystalline isotactic polyhexafluorobut-2-ene (polytrifluoromethylcarbene).

Photolysis of 2,2,3,3,4,4,4-Heptafluorodiazobutane.—The ease with which trifluoromethylcarbene rearranges to trifluoroethylene is surprising in view of the stability of the trifluoromethyl group and the strength of its C–F bond. Indeed, this is the first migration of fluorine from CF_3 to be observed under mild conditions. Heptafluorodiazobutane was studied to determine whether fluorine or the perfluoroethyl group would migrate after formation of the carbene:

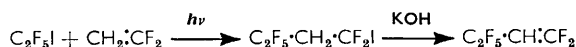


Photolysis of the vapour at low pressure with radiation of wavelength $>3000 \text{ \AA}$ (Pyrex vessels) gave $\text{C}_3\text{F}_7\cdot\text{CH}:\text{CH}\cdot\text{C}_3\text{F}_7$ (47%), $\text{C}_2\text{F}_5\cdot\text{CH}:\text{CF}_2$ (31%), and nitrogen (95%), together with involatile material (11% by weight of starting material). 1,1,3,3,4,4,4-Heptafluorobut-1-ene shows strong absorption at 5.69μ , in agreement with the $\text{CH}:\text{CF}_2$ stretching vibration for the compounds $\text{CF}_3\cdot\text{CH}:\text{CF}_2$ (5.63μ) and $\text{C}_3\text{F}_7\cdot\text{CH}:\text{CF}_2$ (5.69μ).⁹ The compound $\text{CF}_3\cdot\text{CF}:\text{CHF}$ absorbs strongly at 5.74μ ,¹⁰ and replacement of CF_3 by C_2F_5 would move the absorption to still longer wavelength.

⁹ Haszeldine and Steele, *J.*, 1954, 923, and unpublished results.

¹⁰ Haszeldine and Steele, *J.*, 1953, 1592.

1,1,3,3,4,4,4-Heptafluorobut-1-ene was synthesised¹¹ as follows:



A perfluoroalkyl radical is known^{9,11} to attack only the methylene group of 1,1-difluoroethylene (vinylidene difluoride). The ultraviolet spectrum of the iodo-compound produced is also in accord with the presence of a CF_2I group (λ_{max} , 271 m μ) and distinguishes it from a compound containing a $\text{CF}_2\text{CH}_2\text{I}$ group (λ_{max} , 260–263 m μ).¹² Dehydroiodination was best effected (93% yield) by use of dry powdered potassium hydroxide rather than alcoholic potassium hydroxide.

Photolysis of the heptafluorodiazobutane at higher pressure with radiation of wavelength >2000 Å (silica vessels) caused an increase in the amount of involatile material (23% by weight of starting material) at the expense of the heptafluorobutene (15% yield).

The liquid photolysis product, 1,1,1,2,2,3,3,6,6,7,7,8,8,8-tetradecafluoro-oct-4-ene $\text{C}_8\text{H}_2\text{F}_{14}$, was assigned the structure by analogy with the product from photolysis of the trifluorodiazethane. The weakness of absorption in the 5.5–6.0 μ region suggests that it may be the *trans*-isomer.

Rearrangement of the carbene $\text{R}_\text{F}\text{CF}_2\text{HC:}$ thus occurs by migration of the R_F group, rather than of fluorine. This is the first instance of migration of part of a perfluoroalkyl group involving fission of a strong $\text{F}_2\text{C}-\text{CF}_2$ bond under relatively mild conditions.

EXPERIMENTAL

Hanovia S.500 ultraviolet lamps were used unless stated otherwise. Gas chromatography was carried out on a Perkin-Elmer 154B or 116 instrument. Columns (4 mm. internal diameter) were packed with 40% by wt. of dinonyl phthalate or silicone MS550 oil on Celite, and were at room temperature unless otherwise stated. The carrier gas was nitrogen.

2,2,2-Trifluoroethylamine Hydrochloride.—Trifluoroacetamide (49.0 g., 0.43 mole) in anhydrous ether (300 ml.) was added slowly (4 hr.) to a well-stirred, ice-cold slurry of lithium aluminium hydride (42.0 g., 1.11 moles) in anhydrous ether (600 ml.) under dry nitrogen, and the mixture was refluxed (2 hr.), and cooled to 0°. Anhydrous ether (100 ml.) was added to wash any dry hydride from the tap-funnel, and then water (100 g.) was added slowly (2 hr.), with constant vigorous stirring. After about one third of the water had been added, the then very viscous mixture was diluted with ether (200–300 ml.) and addition of the water was continued. A large excess of water was avoided. The ether was decanted and the residual solid was washed with ether (3 \times 500 ml.). The combined extracts were dried (MgSO_4) and saturated with dry hydrogen chloride. The precipitate of 2,2,2-trifluoroethylamine hydrochloride was dried *in vacuo* (P_2O_5) (43.7 g., 75%) (Found: C, 17.8; H, 3.6; N, 10.2. Calc. for $\text{C}_2\text{H}_5\text{ClF}_3\text{N}$: C, 17.7; H, 3.7; N, 10.3%). Reduction of the amide with lithium aluminium hydride is preferred to catalytic hydrogenation of the nitrile, as it is more convenient and reproducible, and yields are better (75–80% consistently).

It has been reported¹³ that explosions occur during this reduction, but provided that the conditions given above were followed precisely, and particular care was taken to ensure that water did not come into contact with lithium aluminium hydride which had dried out after being splashed on to the walls of the vessel, no difficulties were experienced during the present work.

2,2,2-Trifluorodiazethane.—Sodium nitrite (7.5 g., 0.11 mole) was added to an ice-cold solution of 2,2,2-trifluoroethylamine hydrochloride (13.5 g., 0.10 mole) in water (50 ml.) and di-n-butyl ether (50 ml.). The mixture was shaken vigorously whilst being warmed to room temperature (10 min.), cooled in ice, and the yellow ethereal layer decanted, washed with 5% aqueous sodium carbonate, and dried (MgSO_4) in the dark. The extraction was repeated (3 \times 50 ml.), with successively longer reaction periods at room temperature.

¹¹ Haszeldine and Steele, *J.*, 1955, 3005.

¹² Haszeldine and Osborne, *J.*, 1956, 61.

¹³ Reid and Smith, *Chem. Eng. News*, 1951, 29, 3042; Hine, Wiesboeck, and Ghirardelli, *J. Amer. Chem. Soc.*, 1961, 83, 1219.

The diazoethane was distilled from the solution at 1 mm. at room temperature, and separated from residual dibutyl ether by repeated fractional condensation *in vacuo* to give 2,2,2-trifluorodiazaoethane (7.78 g., 71%) (Found: C, 21.6; H, 1.0; N, 25.4%; *M*, 111. $C_2HF_3N_2$ requires C, 21.8; H, 0.9; N, 25.5%; *M*, 110), b. p. (isoteniscope) $11.7 \pm 0.5^\circ$. Its vapour pressure is given by $\log_{10} p$ (mm.) = $7.951 - 1442/T$, whence $L_v = 6.61$ kcal. mole⁻¹, and Trouton's constant = 23.2 cal. mole⁻¹ deg.⁻¹. Gilman and Jones¹ report b. p. $13-13.5^\circ/752$ mm. "by immersing the bulb of the thermometer in the boiling liquid" for an unanalysed sample. The vapour of the diazo-compound has λ_{\max} 397 m μ (ϵ 5.0), λ_{\min} 284 ($\epsilon < 0.2$).

The product was occasionally contaminated with 1-2% of 1-chloro-2,2,2-trifluoroethane formed by reaction of the diazo-compound with hydrogen chloride. Removal of the chloro-compound (b. p. 6.9°) by distillation was impracticable on a small scale. It was detected by infrared-spectroscopic examination of a sample exposed to ultraviolet light to destroy the trifluorodiazaoethane.

2,2,2-Trifluorodiazaoethane vapour decomposes slowly in a blackened bulb at room temperature (60% in 3 months), but it can be kept indefinitely at -196° . It can be manipulated satisfactorily in a conventional vacuum system provided that exposure to light is kept to a minimum. Precautions must be taken against explosion.

Photolysis of 2,2,2-Trifluorodiazaoethane.—(a) *In the presence of liquid diazoethane.* 2,2,2-Trifluorodiazaoethane (6.78 g., 61.6 mmoles), sealed *in vacuo* in a silica tube (250 ml.; ca. 2.5 atm.), was irradiated with the liquid phase unshielded (20 hr.). The volatile products, separated by fractional condensation and gas chromatography, were identified by molecular-weight determination, microanalysis, and infrared and gas-chromatographic analysis as nitrogen (1.27 g., 74%) (Found: *M*, 28.0. Calc. for N_2 : *M*, 28.0), trifluoroethylene (0.51 g., 10%) (Found: C, 29.2; H, 1.3%; *M*, 82.0. Calc. for C_2HF_3 : C, 29.3; H, 1.2%; *M*, 82.0), *trans*-1,1,1,4,4,4-hexafluorobut-2-ene (0.64 g., 13%) (Found: C, 29.1; H, 1.2%; *M*, 163. Calc. for $C_4H_2F_6$: C, 29.3; H, 1.2%; *M*, 164), *cis*-1,1,1,4,4,4-hexafluorobut-2-ene (0.30 g., 6%) (Found: C, 29.5; H, 1.1%; *M*, 165), b. p. (isoteniscope) $31.9 \pm 0.5^\circ$ (lit.,¹⁴ 33.2°). A small fraction (0.07 g., 1.5%) (Found: *M*, 157) isolated by gas chromatography (4 m. dinonylphthalate) was later shown to be mainly 1,1,2-trifluoro-3-trifluoromethylcyclopropane, with some olefinic impurity. The liquid product (b. p. $117-137^\circ$) was shown by gas chromatography (2 m. silicone oil at 100°) to contain at least five components. The major component, isolated by gas chromatography (6 m. \times 38 mm. i.d. glass columns, packed with 40% w/w silicone oil on Celite, at 80°) was 1,3,5-tris(trifluoromethyl)-2-pyrazoline (2.24 g., 40%) (Found: C, 26.3; H, 1.3; N, 10.1. $C_6H_3F_9N_2$ requires C, 26.3; H, 1.1; N, 10.2%), b. p. $20^\circ/4$ mm. The involatile residue, washed from the tube with ether, gave a viscous brown oil (0.42 g.) (Found: C, 27.7; H, 1.6; N, 6.7%), and polytrifluoromethylcarbene (0.35 g., 7%) (Found: C, 29.2; H, 1.25; N, 0.0. $[C_2HF_3]_n$ requires C, 29.3; H, 1.2; N, 0.0%), as an ether-insoluble solid, m. p. $220-235^\circ$ (decomp.), which was scraped from the tube.

A series of irradiations under these conditions gave essentially the same product ratios. In some experiments carbon dioxide (ca. 0.3 mmole) was identified. Irradiation with the liquid phase shielded gave the same product ratios, but the reaction period was longer (30-40 hr.). On one occasion the diazo-alkane exploded violently after it had reached room temperature.

(b) *At 0.47 atm.* 2,2,2-Trifluorodiazaoethane (4.70 g., 42.7 mmoles) in a silica flask (2.26 l.) was irradiated (19 hr.), to give nitrogen (0.99 g., 83%) (Found: *M*, 28.1), carbon dioxide (0.04 g., 1%), trifluoroethylene (0.79 g., 22%), *trans*-1,1,1,4,4,4-hexafluorobut-2-ene (1.45 g., 41%), and *cis*-1,1,1,4,4,4-hexafluorobut-2-ene (0.71 g., 20%), identified by molecular-weight determination and by infrared and gas-chromatographic analysis. The liquid product (0.03 g.) had an infrared spectrum similar to that of the crude liquid product obtained in (a). An involatile liquid (0.07 g.) was removed from the flask with ether, but a thin polymeric film could not be removed.

(c) *At 0.11 atm.* 2,2,2-Trifluorodiazaoethane (1.12 g., 10.2 mmoles) in a silica flask (2.26 l.) was irradiated (6 hr.), to give nitrogen (0.25 g., 88%), trifluoroethylene (0.27 g., 32%), *trans*-1,1,1,4,4,4-hexafluorobut-2-ene (0.22 g., 26%), and *cis*-1,1,1,4,4,4-hexafluorobut-2-ene (0.18 g., 22%). The liquid product (0.04 g.) and involatile material (0.05 g.) were similar to those obtained in (a) and (b).

(d) *At 0.35 atm. with radiation of wavelength $> 3000 \text{ \AA}$.* 2,2,2-Trifluorodiazaoethane (0.59 g.,

¹⁴ Henne and Finnegan, *J. Amer. Chem. Soc.*, 1949, **71**, 298.

5.35 mmoles) in a Pyrex flask (370 ml.) was irradiated (*ca.* 15 hr.), to give nitrogen (0.145 g., 97%), trifluoroethylene (0.90 g., 21%), carbon dioxide (0.01 g., 0.3%), *trans*-1,1,1,4,4,4-hexafluorobut-2-ene (0.16 g., 36%), *cis*-1,1,1,4,4,4-hexafluorobut-2-ene (0.12 g., 27%). The higher-boiling materials (0.04 g.) were similar to those obtained in other experiments, and were not examined further.

(e) *In the presence of an excess of trifluoroethylene.* 2,2,2-Trifluorodiazaoethane (1.20 g., 10.9 mmoles) and trifluoroethylene (3.49 g., 42.6 mmoles) were sealed *in vacuo* in a silica tube (240 ml.). There was no reaction in the dark (3 days); the vapour phase was then irradiated (3 hr.), to give nitrogen (0.27 g., 88%), trifluoroethylene (3.46 g., 99%), *trans*-1,1,1,4,4,4-hexafluorobut-2-ene (0.24 g., 27%), *cis*-1,1,1,4,4,4-hexafluorobut-2-ene (0.22 g., 25%), and 1,1,2-trifluoro-3-trifluoromethylcyclopropane (0.17 g., 9%) (Found: C, 29.4; H, 1.3%; *M*, 163. $C_4H_2F_6$ requires C, 29.3; H, 1.2%; *M*, 164), b. p. (isoteniscope) $22.7 \pm 0.5^\circ$, isolated from the isomeric hexafluorobut-2-enes by gas chromatography (4 m. dinonyl phthalate). The higher-boiling material consisted of a colourless liquid (0.05 g.) similar to that obtained from previous irradiations, and a brown viscous oil (0.13 g.), neither of which was examined further. The vapour pressure of the cyclopropane is given by $\log_{10} p$ (mm.) = $8.129 - 1553/T$, whence $L_v = 7.10$ kcal. mole⁻¹ and Trouton's constant = 24.0 cal. mole⁻¹ deg.⁻¹.

(f) *In the presence of an excess of ethylene.* 2,2,2-Trifluorodiazaoethane (1.25 g., 11.3 mmoles) and ethylene (1.26 g., 45.0 mmoles) were sealed *in vacuo* in a silica tube (250 ml.). There was no reaction in the dark (3 days), and the vapour was then irradiated (6 hr.) to give: (i) nitrogen (0.187 g., 59%); (ii) a mixture of ethylene and trifluoroethylene (1.21 g., 39.2 mmoles) (Found: *M*, 30.9); (iii) *trans*-1,1,1,4,4,4-hexafluorobut-2-ene (0.03 g., 4%); (iv) trifluoromethylcyclopropane (0.32 g., 26%) (Found: C, 43.4; H, 4.7%; *M*, 111. Calc. for $C_4H_5F_3$: C, 43.6; H, 4.6%; *M*, 110), b. p. (isoteniscope) $19.0^\circ \pm 0.5^\circ$ (lit.,⁸ 21.6° for a sample prepared by pyrolysis of the pyrazoline obtained from diazomethane and 3,3,3-trifluoropropene), isolated from the hexafluorobutene by gas chromatography, and distinguished from the isomeric trifluorobutenes by its b. p. and infrared spectrum; its vapour pressure is given by the equation $\log_{10} p$ (mm.) = $7.747 - 1422/T$, whence $L_v = 6.51$ kcal. mole⁻¹ and Trouton's constant = 22.3 cal. mole⁻¹ deg.⁻¹; (v) a fraction (0.59 g.) probably consisting mainly of 3-trifluoromethylpyrazoline (Found: C, 34.4; H, 3.6; N, 18.3. Calc. for $C_4H_5F_3N_2$: C, 34.8; H, 3.6; N, 10.3%); and (vi) a small amount (0.136 g.) of an involatile liquid.

(g) *In the presence of an excess of cyclohexene.* 2,2,2-Trifluorodiazaoethane (5.65 g., 51.4 mmoles) and cyclohexene (15.4 g., 188 mmoles) were sealed *in vacuo* in a silica tube (300 ml.). There was no reaction in the dark (3 days), and the liquid phase alone was then irradiated (7 days), to give nitrogen (1.01 g., 70%), a mixture of trifluoroethylene, 1,1,1-trifluoroethane, and *trans*-1,1,1,4,4,4-hexafluorobut-2-ene (0.19 g.), cyclohexene (11.45 g.), some unidentified high-boiling material (1.23 g.) and 7-trifluoromethylnorcarane (3.9 g., 46%) (Found: C, 58.9; H, 6.9. $C_9H_{11}F_3$ requires C, 58.5; H, 6.7%), b. p. $132-135^\circ$. The infrared spectrum showed the absence of olefinic material. Gas chromatography showed the presence of two components, probably the *endo*- and *exo*-isomers.

Isomerisation of cis- and trans-1,1,1,4,4,4-Hexafluorobut-2-ene.—Pure *trans*-1,1,1,4,4,4-hexafluorobut-2-ene (0.26 g., 1.6 mmoles), prepared by the reaction of trifluoriodomethane with 2,2,2-trifluoropropene,¹⁵ followed by dehydroiodination with dry, powdered potassium hydroxide, was sealed *in vacuo* in a silica tube (10 ml.) and irradiated (3 days). Examination of the volatile material showed only a trace of the *cis*-isomer. After further irradiation (3 weeks) the product contained 7% of *cis*-1,1,1,4,4,4-hexafluorobut-2-ene and 93% of the *trans*-isomer. Irradiation of the pure *cis*-isomer (0.06 g., 0.37 mmole) under similar conditions (24 hr.) gave *trans*-1,1,1,4,4,4-hexafluorobut-2-ene (14%) and unchanged *cis*-isomer (86%).

Irradiation of 3,4,5-Tristrifluoromethylpyrazoline.—3,4,5-Tristrifluoromethylpyrazoline (0.262 g., 0.96 mmole), sealed *in vacuo* in a silica tube (12 ml.), was irradiated (4 days), to give nitrogen (0.04 mmole) and a mixture of at least 3 unidentified components. No pyrazoline was recovered.

Thermal Decomposition of 3,4,5-Tristrifluoromethylpyrazoline.—3,4,5-Tristrifluoromethylpyrazoline (0.110 g., 0.40 mmole), sealed in a silica tube (10 ml.), was unchanged after 2 days at 250° . It was heated at 340° (11 days), to give nitrogen (0.2 mmole), unknown material, and unchanged pyrazoline (0.010 g., 9%).

Pyrolysis of Polytrifluoromethylcarbene.—(a) *In a vacuum.* Polytrifluoromethylcarbene

¹⁵ Haszeldine, *J.*, 1952, 2504.

(0.0750 g.) was pyrolysed *in vacuo* in a silica tube at 800° connected to two traps in series at -196°. The volatile products were *trans*-1,1,1,4,4,4-hexafluorobut-2-ene (0.057 g., 76%), shown by infrared spectroscopy to be slightly contaminated with some other unidentified olefins, hexafluoroethane (0.010 g.), and a small amount of silicon tetrafluoride. No carbonisation occurred.

(b) *In air.* The polymer (0.039 g.) showed no change in weight when heated on a Stanton thermal balance until the temperature reached 290°. At this temperature, it was totally decomposed in 50 min.

Thermal Decomposition of 2,2,2-Trifluorodiazooethane.—2,2,2-Trifluorodiazooethane (0.98 g., 8.9 mmoles), sealed *in vacuo* in a Dreadnought tube (50 ml.), and heated at 115° (3 days), gave nitrogen (0.18 g., 72%), a liquid mixture (0.23 g.) shown by infrared spectroscopy and gas chromatography to be mainly 3,4,5-tris(trifluoromethyl)-2-pyrazoline, and a solid polymer (0.43 g., 59%) (Found: C, 29.1; H, 1.0; N, 0.0. Calc. for $[C_2HF_3]_n$: C, 29.3; H, 1.2; N, 0.0%), m. p. 184–190° (decomp.). The polymer was insoluble in water and in common organic solvents, and was unaffected by aqueous acid or alkali at room temperature.

The polymer (0.0819 g.), pyrolysed *in vacuo* at 785° in a silica tube connected to traps at -196°, gave *trans*-1,1,1,4,4,4-hexafluorobut-2-ene (0.068 g., 82%) and unidentified material (0.011 g.). Silicon tetrafluoride, trifluoromethane, and hexafluoroethane were absent.

The polymer (0.058 g.) showed an initial loss of weight (0.007 g., 12%) when heated in air at 140° on a Stanton thermal balance, but there was no further loss of weight until 250°. Decomposition at this temperature was slow (65% in 3 hr.) but was more rapid (complete in 70 min.) at 290°.

Polytrifluoromethylcarbene.—(a) 2,2,2-Trifluorodiazooethane (1.23 g., 11.2 mmoles), sealed *in vacuo* in a 50 ml. Dreadnought tube, and kept in the dark at room temperature for 2.5 yr., gave unchanged trifluorodiazooethane (32%), nitrogen (44%), a colourless liquid (0.413 g.), and the polymer (0.234 g., 38%) (Found: C, 29.2; H, 1.1. $[C_2HF_3]_n$ requires C, 29.3; H, 1.2%), characterised by absorption bands at 3.29w, 3.42w, 7.32s, 7.70m, 7.90m, 8.07m, 8.48s, 8.75s, 9.14m, 9.90w, 10.90w, 12.42w, 13.10w, 13.82w μ . The polymer was not melted when heated to 310°. When heated in air on a Stanton thermal balance it lost no weight below 295°. Above 295° it slowly depolymerised. Pyrolysis of the polymer (0.0478 g.) *in vacuo* in a sealed tube at 360° during 2 hr. gave *trans*-1,1,1,4,4,4-hexafluorobut-2-ene (0.029 g., 61%) with negligible carbonisation.

(b) 2,2,2-Trifluorodiazooethane (0.460 g., 4.2 mmole) and $\alpha\alpha'$ -azodi-isobutyrate (0.01 g.) were sealed in a 20 ml. Pyrex tube in the dark at room temperature, and exposed to ultraviolet radiation for 1.5 hr. The white, ether-insoluble polymer (0.062 g., 18%) had m. p. 220–270°.

(c) Freshly prepared cuprous iodide (0.15 g.) was shaken with ether (10 ml.) saturated with methylamine. The solid was filtered off, and 2 ml. of the filtrate was added to a solution of the trifluorodiazooethane (0.3 g.) in di-*n*-butyl ether (10 ml.). Nitrogen was evolved, the yellow colour was discharged, and a white solid deposited (3 hr.). A further 10 ml. of the diazooethane solution was added and was decomposed overnight. The solid was washed with diethyl ether and dried at 80° (0.176 g., 29%) (Found: C, 29.3; H, 1.4%), m. p. 132–145°.

*2,2,3,3,4,4,4-Heptafluorodiazoo-*n*-butane.*—2,2,3,3,4,4,4-Heptafluoro-*n*-butylamine was prepared by reduction of heptafluorobutyramide with lithium aluminium hydride,¹⁶ the same precautions being observed as in the reduction of trifluoroacetamide. Since the butylamine hydrogen sulphate is insoluble in water, dilute sulphuric acid was added to the ethereal slurry of lithium and aluminium hydroxides, and the butylamine hydrogen sulphate was treated with concentrated sodium hydroxide. Concentrated hydrochloric acid (5 ml.) and water (5 ml.) were added slowly to a cold (0°) aqueous solution of 2,2,3,3,4,4,4-heptafluorobutylamine (10.0 g., 50 mmoles). Di-(2-chloroethyl) ether (10 ml.) was added, then sodium nitrite (4.0 g., 58 mmoles) in water (10 ml.) was slowly added (40 min.) to the cooled, stirred mixture, and stirring was continued for 1.5 hr.¹⁷ The yellow ethereal layer was decanted, the aqueous layer was washed with di(chloroethyl) ether (2 \times 5 ml.), and the combined extracts were washed with 5% aqueous sodium carbonate solution (5 ml.) and dried (MgSO₄). The volatile material was distilled from the ether *in vacuo* at room temperature and purified by fractional condensation *in vacuo* to give 2,2,3,3,4,4,4-heptafluorodiazobutane (7.12 g., 68%) (Found: C, 23.0; H, 0.6; N, 13.4%; *M*, 209. C₄HF₇N₂ requires C, 22.9; H, 0.5; N, 13.3%; *M*, 210), b. p. (isoteniscope) 54.7 \pm 0.5°. Its

¹⁶ Minnesota Mining and Manufacturing Company, B.P. 717,232/1954 (*Chem. Abs.*, 1955, **49**, 12,531).

¹⁷ Krogh, Reid, and Brown, *J. Org. Chem.*, 1954, **19**, 1124.

vapour pressure is given by the equation $\log_{10} p$ (mm.) = $8.006 - 1680/T$, whence $L_v = 7.69$ kcal. mole⁻¹, and Trouton's constant = 23.4 cal. mole⁻¹ deg.⁻¹. The vapour of the diazo-compound had λ_{\max} 399 m μ (ϵ 8.7), λ_{\min} 290 m μ (ϵ 0.4).

A sample of the heptafluorodiazobutane being used for analysis exploded violently.

Irradiation of 2,2,3,3,4,4,4-Heptafluorodiazobutane.—(a) *In the vapour phase* ($\lambda > 3000$ Å). 2,2,3,3,4,4,4-Heptafluorodiazobutane (0.87 g., 4.15 mmoles) in a Pyrex flask (250 ml.) was irradiated (24 hr.) to give nitrogen (0.11 g., 95%), 1,1,3,3,4,4,4-heptafluorobutene (0.23 g., 31%) (Found: C, 26.6; H, 0.7%; M , 183. C_4HF_7 requires C, 26.4; H, 0.6%; M , 182), uncontaminated by any isomeric olefin, and 1,1,1,2,2,3,3,6,6,7,7,8,8,8-tetradecafluoro-oct-4-ene (0.36 g., 47%) (Found: C, 26.6; H, 0.8%; M , 362. $C_8H_2F_{14}$ requires C, 26.4; H, 0.6%; M , 364), b. p. (isoteniscope) $104.7 \pm 0.5^\circ$, shown to be pure by gas chromatography, and an involatile liquid (0.10 g., 11% by weight of starting material). The vapour pressure of the octene is given by the equation $\log_{10} p$ (mm.) = $7.990 - 1930/T$, whence $L_v = 8.84$ kcal. mole⁻¹ and Trouton's constant = 23.4 cal. mole⁻¹ deg.⁻¹.

(b) *In the liquid and vapour phases* ($\lambda > 2000$ Å). 2,2,3,3,4,4,4-Heptafluorodiazobutane (0.44 g., 2.1 mmoles), sealed *in vacuo* in a silica tube (10 ml.), and irradiated (28 hr.), gave (i) nitrogen (0.055 g., 93%), (ii) a fraction (0.070 g.) (Found: C, 26.6; H, 0.7%; M , 182. Calc. for C_4HF_7 : C, 26.4; H, 0.6%; M , 182) containing 1,1,3,3,4,4,4-heptafluorobutene (0.058 g., 0.32 mmole, 15%), and an unidentified compound (0.005 g., 0.03 mmole, 2%) not formed in (a) above but readily distinguished by gas chromatography, (iii) 1,1,1,2,2,3,3,6,6,7,7,8,8,8-tetradecafluoro-oct-4-ene (0.18 g., 48%), and (iv) an involatile liquid (0.10 g., 23% by weight of starting material). A thin polymeric film remained in the tube.

1,1,3,3,4,4,4-Heptafluorobutene.—Pentafluoroiodoethane (6.64 g., 27.0 mmoles) and 1,1-difluoroethylene (1.73 g., 27.0 mmoles), sealed *in vacuo* in a silica tube, and irradiated (5 days; S.250 lamp), with the liquid phase shielded, gave (i) 1,1,3,3,4,4,4-heptafluoroiodobutane (5.51 g., 66%) (Found: M , 305. Calc. for $C_4H_2F_7I$: M , 310, λ_{\max} (hexane) 271 m μ (ϵ 265), λ_{\min} (hexane) 212 m μ (ϵ 30), λ_{\max} (ethanol) 263 m μ (ϵ 275), λ_{\min} (ethanol) 217 m μ (ϵ 60), (ii) pentafluoroiodoethane (0.66 g., 10%), (iii) 1,1-difluoroethylene (0.13 g., 9%), (iv) 1,1,3,3,4,4,4-heptafluorobutene (0.33 g., 7%), (v) a liquid (b. p. $82-108^\circ$), and (vi) iodine. 1,1,3,3,4,4,4-Heptafluoroiodobutane (0.40 g., 1.3 mmole) was condensed *in vacuo* into a flask (100 ml.) containing dry, powdered potassium hydroxide (*ca.* 20 g.) and kept at room temperature for 16 hr. Fractionation gave 1,1,3,3,4,4,4-heptafluorobutene (0.22 g., 93%) (Found: C, 26.6; H, 0.7%; M , 183. Calc. for C_4HF_7 : C, 26.4; H, 0.6%; M , 182), b. p. (isoteniscope) $4.5 \pm 0.2^\circ$; its vapour pressure is given by the equation $\log_{10} p$ (mm.) = $8.100 - 1450/T$, whence $L_v = 6.63$ kcal. mole⁻¹, and Trouton's constant = 23.8 cal. mole⁻¹ deg.⁻¹.

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