

Perfluoroalkyl Derivatives of Nitrogen. Part XXVIII.¹ Reaction of Trifluoronitrosomethane with Trifluoroacryloyl Fluoride: A Route to Perfluoro-(3-azabut-2-enoyl) Fluoride and hence Trifluoromethyl Isocyanide

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Trifluoronitrosomethane combines with trifluoroacryloyl fluoride to yield a 1 : 1 alternating copolymer, mainly with structure $[-N(CF_3) \cdot O \cdot CF_2 \cdot CF(COF)-]_n$, and a small amount of material believed to be perfluoro-(4-fluorocarbonyl-2-methyl-1,2-oxazetidine), $CF_3 \cdot N \cdot O \cdot CF(COF) \cdot CF_2$. Pyrolysis of the copolymer gives, *inter alia*, perfluoro-(3-azabut-2-enoyl) fluoride, which is hydrolysed to oxalic acid by aqueous base. Pyrolysis of the butenoyl fluoride over potassium fluoride causes α -elimination of carbonyl fluoride, to give trifluoromethyl isocyanide. The isocyanide isomerises to trifluoromethyl cyanide when heated, reacts with mercuric oxide to yield trifluoromethyl isocyanate, and readily yields a polymer that possibly has the structure $[-C(N \cdot CF_3) \cdot C(N \cdot CF_3)-]_n$.

As part of a general study of the reaction of trifluoronitrosomethane with perfluorovinyl monomers, $CF_2 \cdot CFX$ ($X = F$,² Cl ,^{2,3} H ,⁴ CF_3 ,² or SO_2F ⁵), the nitroso-compound has been treated with trifluoroacryloyl fluoride. Like its sulphur analogue, trifluoroethylenesulphonyl fluoride,⁵ the alkenoyl fluoride combines reluctantly with trifluoronitrosomethane and even under forcing conditions only traces of an oxazetidine are formed.

Treatment of trifluoronitrosomethane with trifluoroacryloyl fluoride at 20°/ca. 6 atm. led, during 6 months, to 30% conversion of reactants into an elastomeric 1 : 1 copolymer; use of a higher temperature (80°/ca. 7 atm.) facilitated reaction, so that after 3 months the nitroso-compound and alkenoyl fluoride were recovered in 60 and 57% yield, respectively, together with a colourless, viscous, oily 1 : 1 copolymer (39% yield) and products arising from thermal decomposition of trifluoronitrosomethane.⁶ With an initial pressure of ca. 28 atm., 63% consumption of the reactants occurred during one week at 80°, to give an oily 1 : 1 copolymer, a product (3% yield) believed to be predominantly or exclusively perfluoro-(4-fluorocarbonyl-2-methyl-1,2-oxazetidine) (I), traces of a 2 : 1 adduct of trifluoroacryloyl fluoride with trifluoronitrosomethane, and small amounts of decomposition products arising from the nitroso-compound. The vapour of the oxazetidine showed strong i.r. absorptions at 5.31 and 7.30 μm characteristic, respectively, of a perfluoroacyl fluoride⁷ and a polyfluoro-oxazetidine,^{2,4} and its mass spectrum showed a top-mass peak at m/e 227, corresponding to a compound with molecular formula $C_4F_7NO_2$. Support for structure (I), which is consistent with a diradical mechanism for oxazetidine formation (see Scheme 1),² is provided by the appearance in the mass spectrum of peaks with m/e values of 94 ($C_2F_2O_2^+$) and 133 ($C_2F_5N^+$).

¹ Part XXVII, E. S. Alexander, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, *J. Chem. Soc. (C)*, 1968, 796.

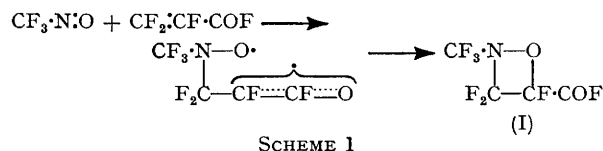
² D. A. Barr, R. N. Haszeldine, and C. J. Willis, *J. Chem. Soc.*, 1961, 1351.

³ R. E. Banks, F. Bennett, and R. N. Haszeldine, unpublished results.

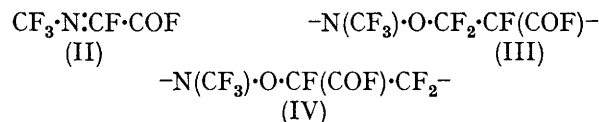
⁴ R. E. Banks, R. N. Haszeldine, H. Sutcliffe, and C. J. Willis, *J. Chem. Soc.*, 1965, 2506.

⁵ R. E. Banks, G. M. Haslam, R. N. Haszeldine, and A. Peppin, *J. Chem. Soc. (C)*, 1966, 1171.

Like most raw nitroso-rubbers,⁸ the 1 : 1 copolymer of trifluoronitrosomethane with trifluoroacryloyl fluoride begins to degrade when heated to ca. 200°. Complete



pyrolysis at 560° *in vacuo* gave carbonyl fluoride (93%), perfluoro-(3-azabut-2-enoyl) fluoride (II) (86%), carbon monoxide (8%), perfluoro(methylenemethylamine) (8%), and small amounts of trifluoromethyl isocyanate



and silicon tetrafluoride (from attack on the silica pyrolysis tube by the methylenemethylamine⁹). This result indicates that the copolymer has an alternating structure, like all other polymers derived from trifluoronitrosomethane and fluoro-olefins,^{2-5,8,10} and that the predominant repeating unit (at least 86%) is (III) (see Scheme 2). Although no oxalyl fluoride was detected in the products, the formation of perfluoro-(methylenemethylamine) in low yield indicates that unit (IV) makes a minor contribution to the structure of the copolymer (see Scheme 3); under the pyrolysis conditions oxalyl fluoride would decompose into carbonyl fluoride and carbon monoxide,¹¹ the yield of which did correspond to that of perfluoro(methylenemethylamine).

⁶ R. E. Banks, M. G. Barlow, R. N. Haszeldine, M. K. McCreath, and H. Sutcliffe, *J. Chem. Soc.*, 1965, 7209.

⁷ J. K. Brown and K. J. Morgan, in 'Advances in Fluorine Chemistry,' ed. M. Stacey, J. C. Tatlow, and A. G. Sharpe, Butterworths, London, 1965, vol. 4, p. 290.

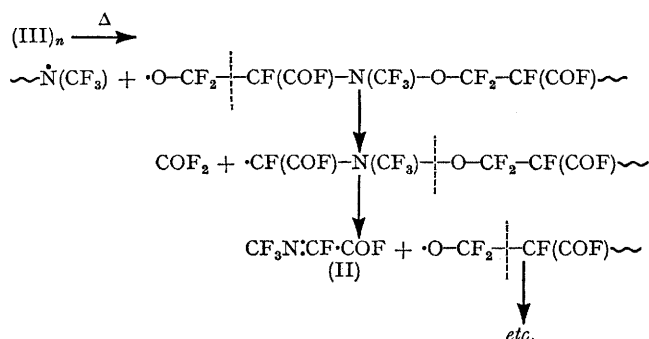
⁸ M. C. Henry, C. G. Griffis, and E. C. Stump, in 'Fluorine Chemistry Reviews,' ed. P. Tarrant, Edward Arnold, London, 1967, vol. 1, p. 1.

⁹ D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 1956, 3416.

¹⁰ R. E. Banks, M. G. Barlow, and R. N. Haszeldine, *J. Chem. Soc.*, 1965, 6149.

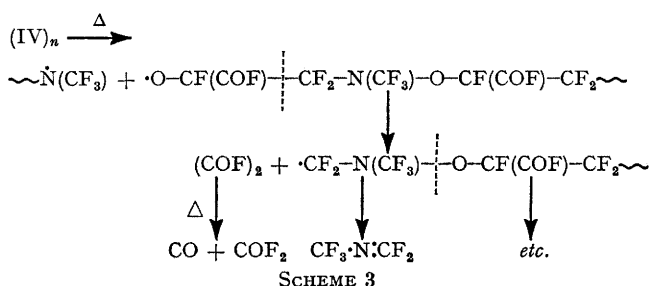
¹¹ See R. E. Banks, E. D. Burling, B. A. Dodd, and K. Mullen, *J. Chem. Soc. (C)*, 1969, 1706, and references cited.

Production of perfluoro(methylenemethylamine) and carbon monoxide *via* thermal decomposition of perfluoro-(3-azabut-2-enoyl) fluoride formed initially is not



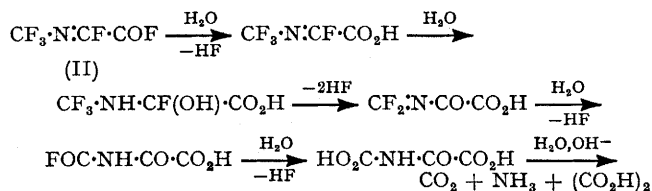
SCHEME 2

thought to be important, since the butenoyl fluoride was recovered in 98% yield after flow pyrolysis in platinum at 550°/ca. 2 mm. The occurrence of (III) as the predominant repeating unit is consistent with the free-radical copolymerisation mechanism for nitroso-rubber



SCHEME 3

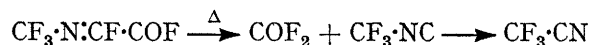
formation^{2,12} coupled with the expected preference for radical attack on the CF₂ group of trifluoroacryloyl fluoride, leading to a new radical with allylic stabilisation (*cf.* Scheme 1).



SCHEME 4

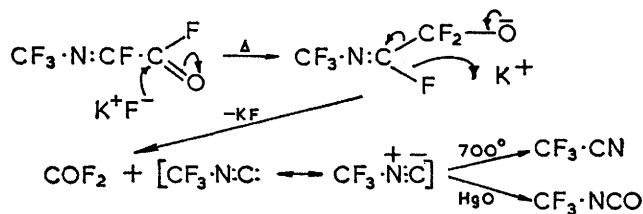
Perfluoro-(3-azabut-2-enoyl) fluoride was isolated as a volatile (b.p. 27.7°) liquid that was rapidly hydrolysed to oxalic acid by aqueous base; this reaction and the presence of strong absorptions at 5.36 (COF str.) and 5.71 μm (C:N str.) (*cf.*¹³ CF₂:CF·COF, 5.40 and 5.72 μm) in the i.r. spectrum of the compound clearly clinch the

structure as (II) (see Scheme 4). Pyrolysis of perfluoro-(3-azabut-2-enoyl) fluoride in platinum at 720°/ca. 2 mm. gave mainly (80%) the decarbonylation product perfluoro(methylenemethylamine), but the formation of carbonyl fluoride (14%) and trifluoromethyl cyanide (13%) indicated the occurrence of an α-elimination reaction followed by thermal isomerisation of trifluoromethyl isocyanide thus liberated:



Flow pyrolysis of perfluoro-(3-azabut-2-enoyl) fluoride at 550°/ca. 2 mm. in platinum left it essentially unchanged (*vide ut supra*), but passage over anhydrous potassium fluoride at 450°/ca. 2 mm. converted it cleanly into a mixture of trifluoromethyl isocyanide (100% yield based on 57% consumption of butenoyl fluoride) and carbonyl fluoride (83%) that could not be separated by fractional condensation *in vacuo* (this is consistent with the report that trifluoromethyl isocyanide boils at -84 to -83°;¹⁴ carbonyl fluoride boils¹⁵ at -83.1 ± 0.5°). The presence of trifluoromethyl isocyanide was indicated by the occurrence of a strong absorption in the i.r. spectrum

of the mixture at 4.70 μm [CF₃·N≡C str.; *cf.* alkyl isocyanides, 4.60–4.72 μm,¹⁶ and C₆F₅·NC (the only other fluorocarbon isocyanide) 4.68 μm¹⁷] and confirmed by mass spectrometry [major peaks at *m/e* 95 (C₂F₃N⁺, 32% rel. abundance), 76 (C₂F₂N⁺, 47%), and 69 (CF₃⁺, 100%)] and by conversion of the isocyanide into the corresponding cyanide and isocyanate in conventional fashion^{18,19} (see Scheme 5).



SCHEME 5

When a *ca.* 55:45 molar mixture of trifluoromethyl isocyanide and carbonyl fluoride was stored in Pyrex at room temperature for 48 hr., a pale-yellow solid deposited on the glass and the carbonyl fluoride was recovered. The elemental composition of the solid was close to that expected for poly(trifluoromethyl isocyanide), and its mass spectrum was consistent with that for a polymer made up of repeating units with composition C₂F₃N [peaks were detected with *m/e* values corresponding to the fragments (C₂F₃N)_{*n*}⁺, where *n* = 2–6]. The i.r. spectrum of the solid was broad and

¹² G. H. Crawford, B. F. Landrum, and D. E. Rice, *J. Polymer Sci.*, 1963, **A1**, 565; J. D. Crabtree, R. N. Haszeldine, K. Ridings, R. F. Simmons, and S. Smith, publication in preparation.

¹³ P. Tarrant and J. Savory, *J. Org. Chem.*, 1963, **28**, 1728.

¹⁴ S. P. Makarov, M. A. Englin, A. F. Videiko, and T. V. Nikolaeva, *J. Gen. Chem. U.S.S.R.*, 1967, **37**, 2667.

¹⁵ R. D. W. Kemmitt and D. W. A. Sharp, in 'Advances in Fluorine Chemistry,' ed. M. Stacey, J. C. Tatlow, and A. G. Sharpe, Butterworths, London, 1965, vol. 4, p. 160.

¹⁶ R. T. Conley, 'Infrared Spectroscopy,' Allyn and Bacon, Boston, 1966, p. 112.

¹⁷ R. E. Banks, R. N. Haszeldine, and B. G. Willoughby, unpublished results.

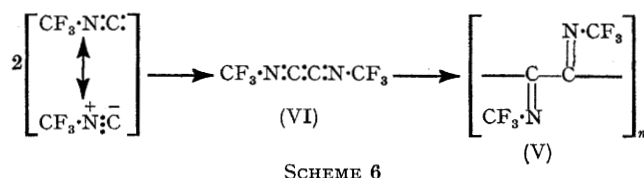
¹⁸ See J. Casanova, N. D. Werner, and R. E. Schuster, *J. Org. Chem.*, 1966, **31**, 3473, and references cited therein.

¹⁹ P. A. S. Smith, 'The Chemistry of Open-Chain Organic Nitrogen Compounds,' Benjamin, New York, 1965, vol. 1, p. 227.

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diffuse, the main features being absorption covering the range 5.5–6.2 μm , indicative of the presence of C:N and/or C:C linkages, and C-F absorption in the region 7.0–9.5 μm ; weak absorptions compatible with the presence of N-H and C-H bonds were present, and this is consistent with the results of combustion analysis, which revealed that the solid contained 1.0% of hydrogen. Apparently the solid is essentially poly(trifluoromethyl isocyanide), which, from the above evidence, the destruction of the polymer by aqueous sodium hydroxide with release of fluoride ions, and the assignment of polyaldimine structures to homopolymers of phenyl and cyclohexyl isocyanide,²⁰ is tentatively suggested to possess structure (V); obviously further work is required to establish the structure. A plausible precursor of the polymer (V) would be the cumulene (VI) (see Scheme 6); in connection with this, perfluorobuta-1,2,3-triene ($\text{CF}_2\text{:C:C:CF}_2$) is known to yield a pale-yellow solid when stored in glass at room temperature.²¹

The presence of N-H bonds in the polymer could plausibly arise through reaction of the polymer with traces of hydrogen fluoride generated by reaction of trifluoromethyl isocyanide and/or carbonyl fluoride with adventitious moisture during storage (addition of H-F across C:N bonds in perfluorinated compounds is a well-known reaction,²² e.g., $\text{CF}_3\text{:N:CF}_2 + \text{HF} \xrightarrow{25^\circ} \text{CF}_3\text{:NH}\cdot\text{CF}_3$), and the C-H bonds may have been caused by residual ether, which was used to extract the polymer from the reaction vessel and to cast the film for i.r. measurements.



Since the above work was completed, it has been reported¹⁴ that treatment of the amine $\text{CF}_3\text{:NH}\cdot\text{CF}_2\text{Br}$ with magnesium gives trifluoromethyl isocyanide, which 'readily polymerises and explodes when heated above 200°', is hydrolysed to carbonate and formate when treated with 40% aqueous potash, and combines with bromine to yield dibromomethylenetrifluoromethylamine; neither spectroscopic data nor details of the polymer were given.

EXPERIMENTAL

I.r. spectra were measured with a Perkin-Elmer spectrophotometer model 21, ^{19}F n.m.r. spectra with a Perkin-Elmer R10 instrument operating at 56.46 MHz and 35°, and mass spectra with an A.E.I. MS/2H spectrometer. Molecular weights were determined by Regnault's method unless stated otherwise.

²⁰ Y. Yamamoto, N. Hagihara, and T. Takizawa, *J. Chem. Soc. Japan*, 1966, **87**, 1355.

²¹ E. L. Martin and W. H. Sharkey, *J. Amer. Chem. Soc.*, 1959, **81**, 5256.

²² R. E. Banks, 'Fluorocarbons and their Derivatives,' Oldbourne, London, 1964.

Trifluoronitrosomethane was prepared by photolysis of trifluoriodomethane in the presence of nitric oxide²³ and by pyrolysis of trifluoroacetyl nitrite.²⁴ Trifluoroacryloyl fluoride was obtained by pyrolysis of tetrafluorosuccinic anhydride in the presence of anhydrous potassium fluoride.²⁵

Reaction of Trifluoronitrosomethane with Trifluoroacryloyl Fluoride.—(a) *At 20°.* An equimolar mixture of trifluoronitrosomethane (1.44 g., 14.5 mmoles) and trifluoroacryloyl fluoride (1.86 g., 14.5 mmoles) was kept in a 52-ml. Dreadnought glass tube (calculated initial pressure ca. 6 atm.) at 20° in the dark for 6 months. Fractionation of the volatile product gave trifluoronitrosomethane (1.01 g., 10.2 mmoles; 70% recovery) (Found: *M*, 99. Calc. for CF_3NO : 99) and trifluoroacryloyl fluoride (1.28 g., 10.0 mmoles; 69% recovery) (Found: *M*, 128. Calc. for $\text{C}_3\text{F}_4\text{O}$: 128), both with correct i.r. spectra. A colourless, involatile, elastomeric 1:1 copolymer (0.92 g., 28% yield) [Found: C, 21.2; N, 6.2. ($\text{C}_4\text{F}_7\text{NO}$)_n requires C, 21.2; N, 6.2%], λ_{max} (film deposited from a solution in $n\text{-C}_6\text{F}_{14}$) 5.32 (COF carbonyl str.), 7.45–10.20 μm (broad, diffuse; C-F str.), remained in the reaction vessel.

(b) *At 80°/ca. 7 atm.* Trifluoronitrosomethane (3.54 g., 35.8 mmoles) and trifluoroacryloyl fluoride (4.58 g., 35.8 mmoles), heated at 80° for 3 months in the dark in a 230-ml. Dreadnought glass tube (calculated initial pressure ca. 7 atm.), gave a volatile product that was shown by a combination of fractionation, i.r., and g.l.c. techniques to comprise trifluoronitrosomethane (2.11 g., 21.3 mmoles; 60% recovery), trifluoroacryloyl fluoride (2.61 g., 20.4 mmoles; 57% recovery) (Found: *M*, 128. Calc. for $\text{C}_3\text{F}_4\text{O}$: *M*, 128), and traces of perfluoro(methylenemethylamine), trifluoromethyl isocyanate, carbonyl fluoride, carbon dioxide, and silicon tetrafluoride. By using dry-box techniques (nitrogen atmosphere), a colourless, involatile, viscous copolymer oil (3.2 g., 39%) [Found: C, 21.4; N, 6.3. ($\text{C}_4\text{F}_7\text{NO}$)_n requires C, 21.2; N, 6.2%] with an i.r. spectrum identical to that of the copolymer obtained in (a) above was recovered from the reaction vessel.

(c) *At 80°/ca. 28 atm.* A mixture of trifluoronitrosomethane (1.54 g., 15.6 mmoles) and trifluoroacryloyl fluoride (2.00 g., 15.6 mmoles) was heated at 80° for 7 days in a 16-ml. stainless-steel autoclave (calculated initial pressure ca. 28 atm.). Fractionation of the volatile product, *in vacuo*, gave: (–196° trap) trifluoronitrosomethane (0.57 g., 5.8 mmoles; 37% recovery) contaminated (by i.r. spectroscopy) with small amounts of trifluoronitromethane, perfluoro(methylenemethylamine), and trifluoromethyl isocyanate; (–96° trap) a mixture (0.798 g.; Found: *M*, 132) of trifluoroacryloyl fluoride (0.730 g., 5.70 mmoles; 37% recovery, calculated from *M* value for mixture) and material believed to be perfluoro-(4-fluorocarbonyl-2-methyl-1,2-oxazetidine) (0.068 g., 0.300 mmoles, 3%); and (–45° trap) a trace of material that may have been a 2:1 adduct of trifluoroacryloyl fluoride and trifluoronitrosomethane [Found: *M* (mass spec.), 355. Calc. for $\text{C}_7\text{F}_{11}\text{NO}_3$: *M*, 355], λ_{max} (vapour) 5.31 μm (COF carbonyl str.). The –96° fraction was shaken with an excess of bromine at room temperature and the product, after removal of uncombined bromine with mercury, was fractionated to give

²³ A. H. Dinwoodie and R. N. Haszeldine, *J. Chem. Soc.*, 1965, 1675.

²⁴ R. E. Banks, M. G. Barlow, R. N. Haszeldine, and M. K. McCreath, *J. Chem. Soc. (C)*, 1966, 1350.

²⁵ R. E. Banks, J. M. Birchall, T. Clarke, R. N. Haszeldine, M. J. Stevenson, and H. Iserson, *J. Chem. Soc. (C)*, 1968, 266.

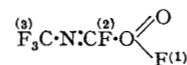
1,2-dibromo-1,2,2-trifluoropropionyl fluoride (1.64 g., 5.69 mmoles), with correct i.r. spectrum,²⁵ and a trace of a sub-

stance believed to be the oxazetidine $\text{CF}_3\cdot\text{N}\cdot\text{O}\cdot\text{CF}(\text{COF})\cdot\text{CF}_2$, λ_{max} (vapour) 5.31 (COF carbonyl str.), 7.30 μm (oxazetidine ring), the mass spectrum of which contained the following main peaks (a peak corresponding to the parent ion, $\text{C}_4\text{F}_7\text{NO}_2^+$, had a relative abundance of <1%): m/e 133 ($\text{C}_2\text{F}_5\text{N}^+$, 5%), 119 (C_2F_5^+ , 9%), 114 ($\text{C}_2\text{F}_4\text{N}^+$, 8%), 101 (19%), 100 (C_2F_4^+ , 5%), 97 ($\text{C}_2\text{F}_3\text{O}^+$, 6%), 94 ($\text{C}_2\text{F}_2\text{O}_2^+$, 4%), 85 (CF_3O^+ , 5%), 83 (CF_3N^+ , 4%), 82 (7%), 81 (C_2F_3^+ , 16%), 69 (CF_3^+ , 100%), 64 (CF_2N^+ , 11%), 51 (25%), 50 (CF_2^+ , 6%), 47 (COF^+ , 38%), 44 (CO_2^+ , 8%), 31 (CF^+ , 11%), 28 (CO^+ , 25%). A viscous, involatile, amber oil (ca. 2 g.) with an i.r. spectrum almost identical to that of the copolymer described in (b) above was recovered from the autoclave by extraction with 1,1,2-trichlorotrifluoroethane.

Preparation of Perfluoro-(3-azabut-2-enoyl) Fluoride.—A platinum boat containing a sample (0.96 g.) of the copolymer of trifluoronitrosomethane with trifluoroacryloyl fluoride [prepared as described in (b) above] was placed near the sealed end of a 81 \times 0.9 cm. i.d. silica tube, the central portion of which was housed in a 56-cm. horizontal electric furnace (ca. 15 cm. of the sealed end of the silica tube protruded from the furnace); the outlet of the silica tube was connected to a vacuum system *via* a train comprising two Pyrex traps cooled to -196° and a cold (-196°) trap packed with activated charcoal. The apparatus was evacuated continuously to 10^{-3} mm. Hg while the temperature of the main furnace was raised to 560° and then isolated from the vacuum system; a small cold electric furnace (18 cm.) was then slipped over that section of the tube containing the platinum boat, switched on, and brought quickly (ca. 4 min.) to 560° . After 3 hr. (almost certainly an excessive period), the charcoal-filled trap was found to contain carbon monoxide (0.36 mmoles), identified by i.r. analysis, and the condensates in the -196° traps were combined and subjected to trap-to-trap fractional condensation, *in vacuo*, to yield: (i) (-196° trap) a mixture (0.285 g., 4.170 mmoles. Found: M , 68) of carbonyl fluoride (3.92 mmoles, 93% yield) and silicon tetrafluoride (0.25 mmole) containing a trace of trifluoromethyl isocyanate (analysed by i.r. spectroscopy; composition estimated from M value); (ii) (-140° trap) a mixture (0.085 g., 0.587 mmole. Found: M , 145) of perfluoro(methylenemethylamine) (0.335 mmole, 8% yield) and perfluoro-(3-azabut-2-enoyl) fluoride (0.252 mmole) [analysed in the same way as fraction (i)] containing a trace of trifluoromethyl isocyanate; and (iii) (-96° trap) perfluoro-(3-azabut-2-enoyl) fluoride (0.548 g., 3.400 mmoles; total yield 3.652 mmoles, 86%) (Found: C, 22.6; N, 8.7%; M , 161. $\text{C}_3\text{F}_5\text{NO}$ requires C, 22.4; N, 8.7%; M , 161), b.p. 27.7° (isoteniscope), λ_{max} (vapour) 5.36s (COF carbonyl str.), 5.71s (C : N str.), 7.25w, 7.62s, 7.94vs, 8.27vs, 8.96s (C-F str.), 9.73w, 10.13w, 11.23m, 11.80m-w, 13.57, 13.65, 13.73m μm (triplet; CF_3 def.).

The principal peaks (relative abundance >10%) in the mass spectrum of perfluoro-(3-azabut-2-enoyl) fluoride occur at m/e values of 114 ($\text{C}_2\text{F}_4\text{N}^+$, 53%), 69 (CF_3^+ , 100%), 47 (CFO^+ , 12%), and 28 (CO^+ , 70%); a weak (<2%) parent ion ($\text{C}_3\text{F}_5\text{NO}^+$) occurs at m/e 161. The ^{19}F n.m.r. spectrum (ref.: $\text{CF}_3\cdot\text{CO}_2\text{H}$ interchange) of the butenoyl fluoride (VII) consisted of three absorption band systems of relative intensities 1:1:3 centred at -97.2 (sharp doublet; $|J_{1,3}|$ ca. 0, $|J_{1,2}|$ 21.2 c./sec.), -53.4 (broadened

doublet of quartets), and -18.4 p.p.m. (broad doublet, width at half-height 4.5 c./sec.; $|J_{2,3}|$ 14.3 c./sec.).



(VII)

Reactions of Perfluoro-(3-azabut-2-enoyl) Fluoride.—(a) **Hydrolysis.** The fluoride (0.15 g.) was shaken with 2M-sodium hydroxide (3 ml.), and oxalic acid was isolated from the product as its di-(*S*-benzylthiouronium) salt (0.25 g., 36%), m.p. and mixed m.p. 199° (lit.,²⁶ 198°) by using standard techniques.

(b) **Pyrolysis.** (i) In platinum. A sample (0.116 g., 0.721 mmole) of the butenoyl fluoride was passed at ca. 2 mm. pressure through a 100 \times 0.9 cm. i.d. platinum tube heated to 720° over 56 cm. of its length and connected to two traps at -196° and a charcoal-filled trap cooled to -196° . The last trap was found to contain carbon monoxide (0.683 mmole, 95%) (identified by i.r. spectroscopy); the condensable material was shown by a combination of fractionation, i.r. analysis, molecular weight determination, and mass spectrometric techniques to contain perfluoro-(methylenemethylamine) (0.580 mmole, 80%), carbonyl fluoride (0.099 mmole, 14%), trifluoromethyl cyanide (0.093 mmole, 13%), and traces of trifluoromethyl isocyanate, bis(trifluoromethyl)amine, and tetrafluoroethylene.

A sample (0.158 g.) of the butenoyl fluoride was recovered almost quantitatively (0.155 g., 98%) after similar pyrolysis at 550° .

(ii) In the presence of potassium fluoride. The vapour of perfluoro-(3-azabut-2-enoyl) fluoride (0.142 g., 0.882 mmole) was passed, at ca. 2 mm. pressure, through a 62 \times 0.9 cm. i.d. silica tube, the central portion of which contained a bed of anhydrous potassium fluoride (ca. 5 g.) and was heated to 450° by a 56-cm. electric furnace. The product, condensed in two traps cooled to -196° , was separated by trap-to-trap fractional condensation, *in vacuo*, to yield: (i) (-96° trap) perfluoro-(3-azabut-2-enoyl) fluoride (0.061 g., 0.379 mmole; 43% recovery) (Found: M , 161. Calc. for $\text{C}_3\text{F}_5\text{NO}$: M , 161) with correct i.r. spectrum; (ii) (-140° trap) traces of perfluoro(methylenemethylamine) and trifluoromethyl isocyanate (by i.r. analysis); and (iii) (-196° trap) a ca. 45:55 molar mixture (0.076 g., 0.927 mmole) (Found: M , 82) of carbonyl fluoride (0.416 mmole; 83% yield based on the butenoyl fluoride consumed), trifluoromethyl isocyanide (0.510 mmole; 100%) containing traces of silicon tetrafluoride, perfluoro(methylenemethylamine), and trifluoromethyl isocyanate [analysed by i.r. spectroscopy {major features: λ_{max} 4.33, 4.34 ($\text{CF}_3\cdot\text{N}\cdot\text{C}\cdot\text{O}$ str.), 4.70 ($\text{CF}_3\cdot\text{N}\equiv\text{C}$ str.), 5.11, 5.19 ($\text{F}_2\text{C}\cdot\text{O}$ str.), 5.55 μm ($\text{CF}_3\cdot\text{N}\cdot\text{CF}_2$ str.)}; composition estimated from M value by neglecting the three minor products]. The mass spectrum of fraction (iii) showed peaks with m/e values of 95 ($\text{C}_2\text{F}_5\text{N}^+$, 32%), 76 ($\text{C}_2\text{F}_4\text{N}^+$, 47%), 69 (CF_3^+ , 100%), 66 (CF_2O^+ , 8%), 64 (CF_2N^+ , 1%), 57 (C_2FN^+ , 2%), 50 (CF_2^+ , 23%), 47 (CFO^+ , 15%), 38 (C_2N^+ , 5%), 31 (CF^+ , 17%), 28 (CO^+ , 25%), and 26 (CN^+ , 6%).

Reactions of Trifluoromethyl Isocyanide.—(a) **Polymerisation.** A ca. 55:45 molar mixture (0.164 g.) of trifluoromethyl isocyanide (ca. 0.10 g.) and carbonyl fluoride [pre-

²⁶ A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, 3rd edn., 1956, p. 366.

Org.

pared as described in (b) above] was left in a 30-ml. Pyrex ampoule at room temperature for 48 hr. The inner surface of the ampoule became coated with a film of pale-yellow solid polymer, and the residual gas was shown by i.r. spectroscopy to be mainly carbonyl fluoride together with traces of silicon tetrafluoride, trifluoromethyl isocyanide, and carbon dioxide. The yellow polymer (0.08 g., 80%) [Found: C, 25.1; H, 1.0; N, 12.6. Calc. for $(C_2F_3N)_n$: C, 25.3; H, 0.0; N, 14.7%] was recovered from the ampoule by solvent extraction, by using dry ether. The i.r. spectrum of a film of the polymer, cast from ether solution, was broad and diffuse, with λ_{\max} 3.0–3.1 μ (bonded N–H str.), 3.35 μ , 3.4 μ (C–H str.), 5.7 μ s (sh), 5.8 μ s, 5.95 μ s (sh.) (C–N and/or C–C str.), 6.5 μ (bonded N–H def.), 8.0–8.7 μ s (C–F str.), 13.3–14.0 μ (CF_3 def.). The mass spectrum of the polymer showed a top mass peak of 570 ($C_{12}F_{18}N_6^+$, 0.2%), and contained peaks with m/e values of 475 ($C_{10}F_{15}N_5^+$, 0.2%), 380 ($C_8F_{12}N_4^+$, 0.6%), 285 ($C_6F_9N_3^+$, 0.6%), 190 ($C_4F_6N_2^+$, 0.9%), 83 (CF_3N^+ , 9.9%), 76 ($C_2F_2N^+$, 4.0%), 69 (CF_3^+ , 100.0%), 64 (CF_2N^+ , 0.7%), 57 (C_2FN^+ , 9.9%), 50 (CF_2^+ , 4.5%), and 31 (CF^+ , 1.4). When heated in air (Stanton Thermobalance, heating rate 4.5°/min.), the yellow polymer started to lose weight at 210°. Pyrolysis of a small sample (0.009 g.) of the polymer at 700°, by using the technique described above for pyrolysis of the trifluoronitrosomethane-trifluoroacryloyl fluoride copolymer, gave (by i.r. spectroscopy) a mixture of trifluoromethyl cyanide, perfluoro(methylenemethylamine), trifluoromethyl isocyanate, carbonyl fluoride, carbon dioxide, and silicon tetrafluoride. The polymer dissolved in 0.1M-sodium hydroxide at 20° with formation of fluoride ions, but appeared to be unchanged (by i.r. analysis) after exposure to the atmosphere for 48 hr.

When a mixture of trifluoromethyl isocyanide (2.2 mmoles) and carbonyl fluoride (4.2 mmoles), condensed into an acid-washed (tube rinsed with concentrated hydro-

chloric acid, drained, oven dried, and flamed-out) Pyrex tube at -196° , *in vacuo*, was allowed to warm to room temperature in the dark, the isocyanide polymerized rapidly to a viscous yellow oil, leaving the carbonyl fluoride unchanged. The oil, which was soluble in ether and in chloroform, was heated *in vacuo* to 120° in a simple still, but no distillate was obtained during a period of 1 hr. and the material began to darken in colour; when cooled to room temperature, the distillate solidified to a yellow material, m.p. 128°, which had an i.r. spectrum very similar to that of the yellow solid polymer described above.

(b) *Pyrolysis.* A ca. 55:45 molar mixture (0.99 mmole) of trifluoromethyl isocyanide and carbonyl fluoride [containing traces of trifluoromethyl isocyanate, perfluoro(methylenemethylamine), carbon dioxide, and silicon tetrafluoride] was passed at ca. 2 mm., pressure through a 100 \times 0.9 cm. platinum tube heated to 700° over 56 cm. of its length. The product (0.97 mmole) trapped at -196° , was shown by i.r. spectroscopy to contain carbonyl fluoride and trifluoromethyl cyanide and small amounts of trifluoromethyl isocyanate, perfluoro(methylenemethylamine), trifluoromethyl isocyanide, carbon dioxide, and silicon tetrafluoride.

(c) *With mercuric oxide.* A ca. 55:45 mixture (0.5 mmole) of trifluoromethyl isocyanide and carbonyl fluoride containing the usual impurities (see above) was condensed, *in vacuo*, onto dry mercuric oxide (5 g.) at -196° in a 30-ml. Pyrex tube. The tube was sealed, warmed to 20°, and stored at this temperature for 3 hr. The volatile product was shown by i.r. spectroscopy to contain much trifluoromethyl isocyanate, carbonyl fluoride, and silicon tetrafluoride, but no trifluoromethyl isocyanide.

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