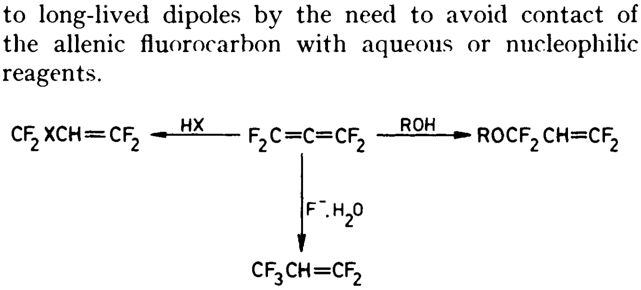
Polyhalogeno-allenes and -acetylenes. Part 15.[1] Dipolar Cycloadditions of *N*-Phenylsydnone and Aryl Azides to Perfluoropropadiene and Perfluoropropyne

By **Gordon B. Blackwell, Robert N. Haszeldine, and David R. Taylor,*** Department of Chemistry, The University of Manchester Institute of Science and Technology, Manchester M60 1QD

N-Phenylsydnone reacts with perfluoropropadiene to give 3-fluoro-1-phenyl-4-trifluoromethylpyrazole (2), anionotropic rearrangement following the dipolar cycloaddition; with perfluoropropyne, giving a 1 : 2 mixture of (2) and the isomeric 4-fluoro-1-phenyl-3-trifluoromethylpyrazole (3); and with perfluorobut-2-yne to give the homologue 1-phenyl-3,4-bis(trifluoromethyl)pyrazole (4). Phenyl azide and perfluoropropadiene react at 50 °C to give a 9 : 1 mixture of 4-fluoro-1-phenyl-5-trifluoromethyl-1,2,3-triazole (5) and 5-fluoro-1-phenyl-4-trifluoromethyl-1,2,3-triazole (6), also by consecutive cycloaddition and anionotropic rearrangement. The minor isomer, believed to be compound (6), was the only adduct isolated by similar treatment of perfluoropropyne. Perfluoropropadiene and pentafluorophenyl azide react slowly to give a low yield of an adduct believed to be 4(or 5)-fluoro-1-pentafluorophenyl-5(or 4)-trifluoromethyl-1,2,3-triazole. The orientations of these additions are discussed in terms of the frontier orbitals involved.

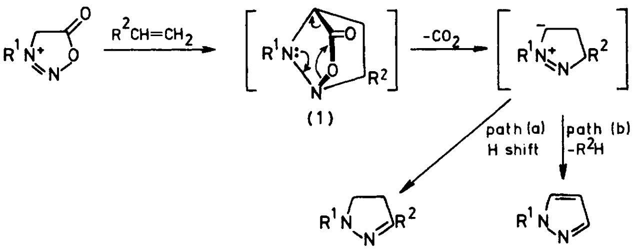
THERE have been relatively few reports of 1,3-dipolar cycloadditions to polyfluoro-alkenes or -alkynes,[2-13] and none have yet involved a perfluoroallene. We have shown [14,15] that perfluoropropadiene is readily attacked at C-1 by nucleophiles (H_2O, MeOH, MeSH) and that it is also highly reactive towards typical electrophiles such as halogens and hydrogen halides, undergoing protonation at C-2 in the latter case (Scheme 1). These observations prompted an investigation of the cycloadditions between perfluoropropadiene and a series of 1,3-dipolar reagents, the choice of which was restricted to long-lived dipoles by the need to avoid contact of the allenic fluorocarbon with aqueous or nucleophilic reagents.



SCHEME 1

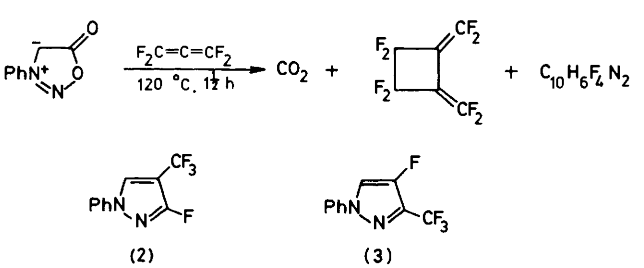
Here we report those cycloadditions of perfluoropropadiene which were found to be accompanied by anionotropic rearrangement of the fluorocarbon moiety, namely those with *N*-phenylsydnone and aryl azides. The investigation of these reactions was extended to include a study of the corresponding cycloadditions of perfluoropropyne [16] and, in one case, perfluorobut-2-yne.

Reactions of N-*Phenylsydnone*.—(a) *With perfluoropropadiene*. The mesoionic sydnones are well-known [17] to react with dipolarophiles when moderately heated, yielding heterocyclic products which arise by extrusion of carbon dioxide from the initially formed cycloadducts (1). When the dipolarophile is an alkene the loss of CO_2 regenerates the azomethine-imine dipolar unit, which then commonly undergoes either prototropic isomerization to give a Δ^2-pyrazoline [path (a)] or elimination to give a pyrazole [path (b)] (Scheme 2).



SCHEME 2

The reaction between *N*-phenylsydnone and an excess of perfluoropropadiene, conducted in anhydrous xylene at 120 °C, was completed within 2 h. Volatile products comprised carbon dioxide and the dimer of the propadiene, perfluoro(1,2-dimethylenecyclobutane).[18] A white solid was isolated from the involatile residue in 63% yield by sublimation and column chromatography, and shown to be an adduct of the expected formula $C_{10}H_6F_4N_2$ by elemental analysis and mass spectrometry (*m*/*z* 230, 100%) (Scheme 3).



SCHEME 3

The ^{19}F n.m.r. spectrum of the adduct displays two multiplets of relative intensity 3 : 1, with mutual coupling ($^4J_{FF}$ 6 Hz) compatible with a *cis*-FC=CCF$_3$ unit. This observation demonstrates that the propadiene residue has undergone isomerization at some stage during the addition elimination sequence, leading to one of the isomeric pyrazoles (2) or (3). Of these, (2) is indicated because the ^1H and ^{19}F n.m.r. spectra of the adduct show negligible (less than 2 Hz) HF coupling, which is not compatible with the presence of a HC=CF unit as found in (3), and because the ^{19}F chemical shifts are close to those reported for related heterocycles containing the N=CF group.[19]

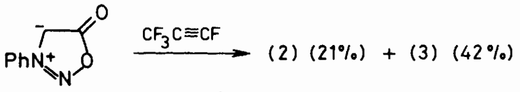
The isomerization of the fluorocarbon moiety must be anionotropic, and may be catalysed by traces of fluoride ion produced by decomposition of fluorocarbons on the glass reactor's surfaces. Furthermore, rearrangement cannot have occurred prior to the cycloaddition, since we have separately shown (below) that the isomeric perfluoropropyne reacts with *N*-phenylsydnone to give a quite different product distribution arising from a non-regiospecific process. None of the isomeric pyrazole (3) was detected in this reaction, although even quite low concentrations would have been observable.

A high degree of regioselectivity is quite normal in sydnone cyclizations, even though the C-acyl group tends to equalise the terminal coefficients in the LUMO of the sydnone's azomethine-imine dipole, the interaction of which with the HOMO of the dipolarophile is considered normally to control the orientation in such processes.[20,21] The use of perfluoropropadiene as the dipolarophile should not, in our opinion, lead to a changeover to dipole-HOMO (orbital energy for a sydnone,[21] *ca.* -9 eV), dipolarophile-LUMO (orbital energy for perfluoropropadiene,* $>$*ca.* $+3$ eV) as the controlling interaction, since the dipole-LUMO (*ca.* -1 eV)[21] and dipolarophile-HOMO (-11.2 eV)† are much closer in energy. This reaction therefore provides another example of regioselectivity arising from secondary orbital interactions.[22-24]

Although photochemical reactions between sydnones and dipolarophiles often proceed differently to thermal reactions,[25] photolysis of a mixture of *N*-phenylsydnone and perfluoropropadiene in benzene through Pyrex gave only (2), albeit in lower yield than obtained in the thermal reaction.

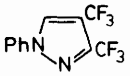
(b) *With perfluoropropyne.* To test the possibility that the allene was rearranging prior to the cycloaddition, the corresponding reaction between the sydnone and the isomeric alkyne, $CF_3C{\equiv}CF$, was investigated. Under identical conditions to those used for the propadiene, an inseparable 1 : 2 mixture of the previously isolated adduct (2) and the isomeric pyrazole (3) was obtained. The ^1H and ^{19}F n.m.r. spectra of the mixture clearly show that the major isomer contains a HC=CF unit ($^3J_{HF}$ 6 Hz), an observation which strengthens the evidence already advanced for the structure of (2) (Scheme 4).

The formation of a mixture of adducts, in which the major isomer has the electron-withdrawing group of the acetylenic reagent adjacent to the 2-nitrogen atom of the pyrazole, has previously been observed in reactions between sydnones and, for example, cyanoacetylene[26] and methyl propiolate.[27] The formation of isomers corresponding to compound (2) has, in such cases, been interpreted as being due to increased dipole-HOMO control, since acetylenic dipolarophiles usually have lower HOMO energies than correspondingly substituted alkenes.



SCHEME 4

(c) *With perfluorobut-2-yne.* For comparison of ^{19}F n.m.r. shift values with those of the adducts (2) and (3), the reaction between *N*-phenylsydnone and perfluorobut-2-yne was also carried out. A rapid cycloaddition was observed, the sole product isolated (70%) being identified spectroscopically as the bis(trifluoromethyl)pyrazole (4), formed by a similar addition-elimination pathway.



(4)

The ^{19}F n.m.r. shifts of the trifluoromethyl groups in these three pyrazoles (2)—(4) are not only internally consistent [3-CF_3 groups in (4) (δ_F 17.0 p.p.m.) and (3) (δ_F 16.5 p.p.m.); 4-CF_3 groups in (4) (δ_F 21.7 p.p.m.) and (2) (δ_F 21.0 p.p.m.)] but they also agree well with the shifts quoted for the few known trifluoromethylpyrazoles already reported.[28]

Reactions of Azides with Perfluoropropadiene.—(a) *Phenyl azide.* When a mixture of phenyl azide and perfluoropropadiene was gently heated in the absence of a solvent a slow reaction occurred. Although almost half of the allene consumed was converted into its dimer (43%), a small quantity of a 9 : 1 mixture of two isomeric adducts was isolated by extraction of the involatile residue, followed by column chromatography. The mixture of $C_9H_5F_4N_3$ isomers proved to be inseparable by either vacuum sublimation or chromatography (h.p.l.c. was not available when this work was carried out) and it was therefore analysed directly.

The ^{19}F n.m.r. spectrum of the mixture of isomers showed that both were 1,2,3-triazoles containing the $CF_3C{=}CF$ grouping: *i.e.* as in the sydnone cycloaddition, an anionotropic rearrangement had occurred. Unfortunately, the ^{19}F chemical shifts of the CF groups in the major isomer (δ_F $-$ 65.5 p.p.m.) and in the minor isomer (δ_F -67.5 p.p.m.) are not sufficiently different to provide a reliable basis for deciding whether (5) or (6) is the major product. Mass spectrometry is also of little value, since the predominant fragmentation is by loss of nitrogen.

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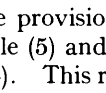
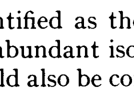
* The value calculated by *ab initio* procedures for the LUMO of 1,1-difluoropropadiene (3.28 eV) (see L. N. Domelsmith, K. N. Houk, C. Piedrahita, and W. J. Dolbier, *J. Am. Chem. Soc.*, 1978, **100**, 6908) is affected by strong stabilisation of the $C_2C_3\pi^*$ orbital by interaction with the remote CF_2 group, but this effect will be opposed in $F_2C{=}C{=}CF_2$ by the adjacent lone pairs of the fluorines. The value calculated for the LUMO of C_3H_4 is 5.01 eV (D. J. Pasto, *J. Am. Chem. Soc.*, 1979, **101**, 37).

† The negative of the vertical ionization energy, determined by photoelectron spectroscopy, see R. K Thomas and H. Thompson, *Proc. R. Soc. London, Ser. A*, 1974, **339**, 29.

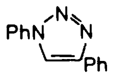
On theoretical grounds, *viz* the expectation that the orientation will be controlled by dipole-HOMO/C_3F_4-LUMO interaction, the more abundant isomer (25% yield) can be provisionally identified as the 5-trifluoromethyltriazole (5) and the less abundant isomer (3%) as compound (6). This result would also be consistent with orientations we have observed to occur in cycloadditions of azides to other perfluoroallenes.[29]





A separate experiment showed that perfluoropropyne reacts with the azide to give mainly (32% yield) the minor isomer (6) obtained from perfluoropropadiene. This shows that little, if any, of the anionotropic rearrangement occurring during the cyclization of the propadiene can have preceded the cyclization, as was also found for the sydnone reaction.

The apparent regiospecificity of the addition of the propyne is unusual for phenyl azide: with phenylacetylene, for example, it yields a nearly equimolar proportion of the isomeric triazoles (7) and (8).[30]



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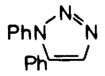
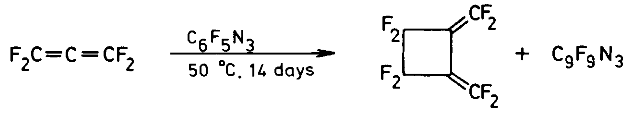


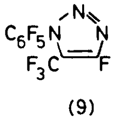
(8)

An attempt to hydrogenate catalytically the mixture of adducts (5) and (6) was unsuccessful, even in acidified ethanol at 50 °C. Recovery of the unchanged adducts showed that there was no rapid decomposition to aziridines, however.

(b) *Pentafluorophenyl azide*. In an attempt to provide further evidence for the structure of the triazoles (5) and (6), the corresponding reaction between perfluoropropadiene and pentafluorophenyl azide[31] was investigated. At 50 °C a very slow reaction occurred, most (75%) of the allene consumed (52%) being converted into dimer. An unstable oil was obtained by extraction of the residue and although available in very small amount it was provisionally identified as a 1 : 1 adduct $C_9F_9N_3$.

Disappointingly, the ^{19}F n.m.r. spectrum showed no coupling between the fluorines of the pentafluorophenyl group and either the CF_3-group (a doublet, $^3J_{FF}$ *ca*. 8 Hz, δ_F 15 p.p.m.) or the CF (δ_F −68 p.p.m., a quartet). Thus, which of the two isomers (9) or (10) is present cannot be decided.





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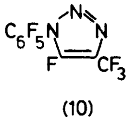

(10)

EXPERIMENTAL

New compounds were characterised by i.r. (Perkin-Elmer Models 137 and 257, with NaCl and grating optics, respectively), n.m.r. [Perkin Elmer R10 or Hitachi Perkin-Elmer R20A, operated at 56.46 MHz for ^{19}F and 60 MHz for ^1H, and Varian HA100 operated at 94.1 MHz for ^{19}F and 100 MHz for ^1H; δ values are positive downfield of TMS (^1H) or external CF_3CO_2H(for ^{19}F), in CCl_4], and mass (AEI MS9) spectroscopy.

Perfluoropropadiene was prepared by Mg–THF debromination of 2,3-dibromo-1,1,3,3-tetrafluoropropene,[16] and perfluoropropyne by Zn–dioxan debromination of 1,2-dibromo-1,3,3,3-tetrafluoropropene, obtained by $AlBr_3$-catalyzed rearrangement of 2,3-dibromo-1,1-3,3-tetrafluoropropene.[16] Perfluorobut-2-yne was obtained by Zn-dechlorination of 2,2,3,3-tetrachlorohexafluorobutane.[32]

Column chromatography was carried out using 60 cm × 3.4 cm i.d. and 55 cm × 2 cm i.d. glass tubes fitted with No.2 glass sinters, and packed with Laporte H alumina or 60—120 mesh BDH silica gel. Paper chromatography was performed on Whatman SG81 paper and t.l.c. on pre-coated aluminium sheets (Woelm F254/366 silica gel).

Reactions of N-*Phenylsydnone*.—(a) *With perfluoropropadiene*. *N*-Phenylsydnone[33] (1.0 g, 6.2 mmol), perfluoropropadiene (1.58 g, 14.1 mmol), sodium-dried xylene (technical, 50 cm³), and mixed terpenes (50 : 50 terpinolene and dipentene) inhibitor (0.1 g), kept at 120 °C for 1.5 h in a 300 cm³ Pyrex tube, gave (i) a mixture (7 mmol) of carbon dioxide and perfluoropropadiene, (ii) perfluoro-1,2-dimethylenecyclobutane (0.76 g, 3.4 mmol, 48% on C_3F_4 taken), and (iii) an involatile residue (1.32 g) which was sublimed at 0.2 mmHg. At 50—60 °C a yellow sublimate (0.99 g) was collected; this was purified by elution (benzene) from a column of silica gel to give a white solid identified spectroscopically as 3-*fluoro*-1-*phenyl*-4-*trifluoromethylpyrazole* (2) (0.90 g, 3.9 mmol, 63% yield on sydnone) (Found: C, 52.2; H, 2.9; F, 33.1; N, 11.9%; M^+, 230. $C_{10}H_6F_4N_2$ requires C, 52.2; H, 2.6; F, 33.0; N, 12.2%; *M*, 230), m.p. 52.5—54.5 °C; $\nu_{max.}$ (mulls) 1 587m, 1 515m, 1 449w, 1 290m, 1 205w, 1 163m, 1 143s, 1 117s, 1 058m, 837w, 763m, 708w, and 690w cm^{-1}; ^1H n.m.r. δ 7.4 (m,Ph) and 7.8 (s, NC*H*=); ^{19}F n.m.r. δ 21.0 (d, $^4J_{FF}$ 6 Hz, CF_3) and −51.0 p.p.m. (q, CF); *m/z* 230 (100%, *P*), 229 (8%), 211 (33%, *P*–F), 204 (27%, *P*-CN), 191 (7%), 184 (6%), 183 (8%), 161 (10%), 160 (6%), 135 (8%), 134 (19%), 133 (20%), 115 (8%), 108 (12%), 104 (23%), 78 (12%), 77 (68%, Ph), 76 (10%), 75 (15%), 74 (8%), 69 (8%, CF_3), 64 (9%), 63 (13%), 52 (8%), 51 (48%), 50 (22%), 39 (15%), and 38 (6%).

The pyrazole was stable to air and water at 25 °C. It was also the only identified product (27%) of the photochemical reaction, (sealed 300 cm³ Pyrex tube, 500-W Hanovia Hg-vapour lamp at 20 cm for 24 h) of *N*-phenylsydnone (6.8 mmol) with perfluoropropadiene (16.1 mmol) in benzene.

(b) *With perfluoropropyne*. *N*-Phenylsydnone (1.0 g, 6.2 mmol), xylene (50 cm³), and perfluoropropyne (1.78 g, 15.9 mmol) kept in a Pyrex tube (300 cm³) for 3 h at 120 °C, gave a mixture (8 mmol) of CO_2 and perfluoropropyne and an involatile residue (2.42 g) from which an orange solid (1.29 g) was sublimed *in vacuo*. Chromatographic purification on silica gel (benzene and light petroleum–benzene, 1 : 1) gave a solid (0.91 g) shown by n.m.r. to consist of a 1 : 2 mixture of the previously isolated pyrazole (2) (*ca.* 0.3 g, 1.30 mmol, 21% on sydnone and 4-fluoro-1-phenyl-3-trifluoromethylpyrazole (3) (*ca.* 0.6 g, 2.61 mmol, 42% on sydnone); ^{1}H n.m.r. δ 7.35 (Ph) and 7.65 (NC*H*=); ^{19}F n.m.r. δ 16.5 (d, $^{4}J_{FF}$ 7 Hz, CF_3) and −95.0 p.p.m. (q, CF). The mixture of isomers could not readily be separated.

(c) *With perfluorobut-2-yne. N*-Phenylsydnone (1.0 g, 6.2 mmol), xylene (50 cm^3), and perfluorobutyne (1.97 g, 12.2 mmol) kept in a Pyrex tube (300 cm^3) at 120 °C for 3 h, gave a mixture (9.6 mmol) of CO_2 and perfluorobutyne and an involatile solid. The solid was eluted (CH_2Cl_2–light petroleum, 1 : 5) through silica gel and isolated as colourless needles identified spectroscopically as 1-*phenyl*-3,4-*bis*(*trifluoromethyl*)*pyrazole* (4) (1.22 g, 4.36 mmol, 70% on sydnone) (Found: C, 47.5; H, 2.3; F, 40.6; N, 10.1%; M^+, 280. $C_{11}H_6F_6N_2$ requires C, 47.5; H, 2.1; F, 40.7; N, 10.0%; *M*, 280), m.p. 50—51 °C; $\nu_{max.}$ (mulls) 1 600m, 1 575m, 1 493m, 1 460s, 1 408m, 1 370m, 1 316s, 1 235s, 1 176s, 1 149bs, 1 064s, 1 010s, 966m, 763m, 738m, and 687m cm^{-1}; ^{1}H n.m.r. δ 7.5 (m, Ph) and 8.2 (s, CH); ^{19}F n.m.r. δ 17.0 (q, $^{5}J_{FF}$ 6 Hz, N=CCF_3) and 21.7 p.p.m. (q, CH=CCF_3); *m/z* 280(100%, *P*), 261 (22%, *P*-F), 260 (9%), 254 (7% *P*-CH), 233 (5%), 211 (15%, *P*-CHF_3), 191 (9%), 184 (12%), 183 (13%), 165 (11%), 142 (8%), 140 (6%), 133 (6%), 104 (16%), 96 (6%), 90 (8%), 78 (10%), 77 (42%, Ph), 76, (13%), 75 (9%), 69 (11%, CF_3), 65 (6%), 64 (6%), 63 (8%), 52 (5%), 51 (19%), 50 (13%), 39 (10%), and 32 (8%).

Reactions of Phenyl Azide.—(a) *With perfluoropropadiene.* Phenyl azide [34] (1.12 g, 9.4 mmol), perfluoropropadiene (1.29 g, 11.5 mmol), and mixed terpene inhibitor (0.1 g), kept in a sealed Pyrex tube (300 cm^3) for 14 days at 50 °C, gave perfluoropropadiene (4.0 mmol, 35% recovery), perfluoro-1,2-dimethylenecyclobutane (0.36 g, 1.6 mmol, 43% on C_3F_4 consumed), a liquid (90 mg) shown to contain phenyl azide and a fluorocarbon, and a yellow involatile residue (730 mg). The residue was extracted with a little light petroleum (b.p. 40—60 °C) and the extract evaporated to give an oil (490 mg) shown spectroscopically to consist of a 9 : 1 mixture of two 1 : 1 adducts believed to be (see Discussion) 4-fluoro-1-phenyl-5-trifluoromethyl-1,2,3-triazole (5) (25% based on C_3F_4 consumed) and 5-fluoro-1-phenyl-4-trifluoromethyl-1,2,3-triazole (6) (3%) on the basis of the ^{19}F n.m.r. spectrum (neat, 56.46 MHz); δ_F 17.0 (d 90% of 3F, $^{4}J_{FF}$ 8.5 Hz), 15.5 (d, 10% of 3F, $^{4}J_{FF}$ 8 Hz), −66.5 (q, 90% of 1F), and −67.5 p.p.m. (q, 10% of 1 F).

(b) *With perfluoropropyne.* Phenyl azide (0.38 g, 3.2 mmol) and perfluoropropyne (0.64 g, 5.7 mmol) kept at 50 °C for 14 days in a Pyrex tube (300 cm^3), gave perfluoropropyne (12% recovery) and an involatile residue (900 mg) from which was obtained [by 2 × 3 cm^3 extractions with light petroleum (b.p. 30—40 °C) and evaporation of the extracts] a yellow oil (360 mg), provisionally identified (see Discussion) as 5-fluoro-1-phenyl-4-trifluoromethyl-1,2,3-triazole (6) (1.6 mmol, 32% on C_3F_4 consumed); $\nu_{max.}$ (liq) 1 639s, 1 515m, 1 389m, 1 266m, 1 220s, 1 175—1 135br,s, 1 070s, 980s, 769m, 755s, and 670s cm^{-1}; ^{1}H n.m.r. (60 MHz, neat, C_6H_6 reference) δ 0.85; ^{19}F n.m.r. (94 MHz, neat) δ 15.5 (d, CF_3, $^{4}J_{FF}$ 8 Hz) and −67.6 p.p.m. (q, =CF); *m/z* 203 (8%, *P*–N_2), 183 (100%, $C_9H_4F_3N$), 163 (5%), 133 (7%), 93 (26%), 83 (10%), and 77 (Ph, 9%).

Reaction of Perfluoropropadiene with Pentafluorophenyl Azide.—Pentafluorophenyl azide [31] (0.19 g, 0.9 mmol) perfluoropropadiene (0.51 g, 4.6 mmol), and mixed terpene inhibitor (0.1 cm^3) kept in a Pyrex tube (90 cm^3) at 50 °C for 14 days gave perfluoropropadiene (48% recovery), perfluoro-1,2-dimethylenecyclobutane (200 mg, 75% on C_3F_4 consumed), and an involatile residue (250 mg) which was extracted with a little light petroleum (b.p. 60—80 °C), and the extract evaporated to give an unstable yellow oil (100 mg), provisonally identified (see Discussion) as 4 (or 5)-fluoro-1-pentafluorophenyl-5(or 4)-trifluoromethyl-1,2,3-triazole (0.3 mmol, 13% on C_3F_4 consumed); $\nu_{max.}$ 2 198w, 1 709b,w, 1 639m, 1 538s, 1 515b,s, 1 449s, 1 379m, 1 255m, 1 192m, 1156b,s, 1 091s, 1 070m, 1 000s, and 858s cm^{-1}; ^{19}F n.m.r. δ −84 to −88 (C_6F_5), −68.0 (q, =CF), and 15.0 p.p.m. (d, $^{4}J_{FF}$ 8.5 Hz, CF_3).

[2/124 *Received, 22nd January,* 1982]

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