

# Polyhalogeno-allenes and -acetylenes. Part 16.<sup>1</sup> Further 1,3-Dipolar Cycloadditions to Perfluoropropadiene

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The nitrones  $\text{PhCH}=\dot{\text{N}}(\text{R})\bar{\text{O}}$  ( $\text{R} = \text{Me, Et, PhCH}_2, \text{ and Ph}$ ) react rapidly with perfluoropropadiene to give the corresponding 2-R-4-difluoromethylene-5,5-difluoro-3-phenylisoxazolidines in good yield, although these isoxazolidines are unstable and decompose during catalytic hydrogenation. Perfluoropropadiene also reacts with diazophenylmethane and diazodiphenylmethane, giving 4-difluoromethylene-3,3-difluoro-5-phenyl- and 5,5-diphenyl- $\Delta^1$ -pyrazolines. The diphenylpyrazoline decomposes on distillation giving 3-difluoromethylene-2,2-difluorodiphenylcyclopropane. The regioselectivity of these dipolar cycloadditions is discussed in relation to frontier orbital theory. Benzoyldiazophenylmethane decomposes during a slow reaction with perfluoropropadiene and the only adduct isolated is 3-difluoromethylene-2,2-difluoro-4,5-diphenyldihydrofuran. Diazodiphenylmethane reacts with perfluoropropyne to give a 1:1 adduct believed to be 5-fluoro-3,3-diphenyl-4-trifluoromethyl-3*H*-pyrazole.

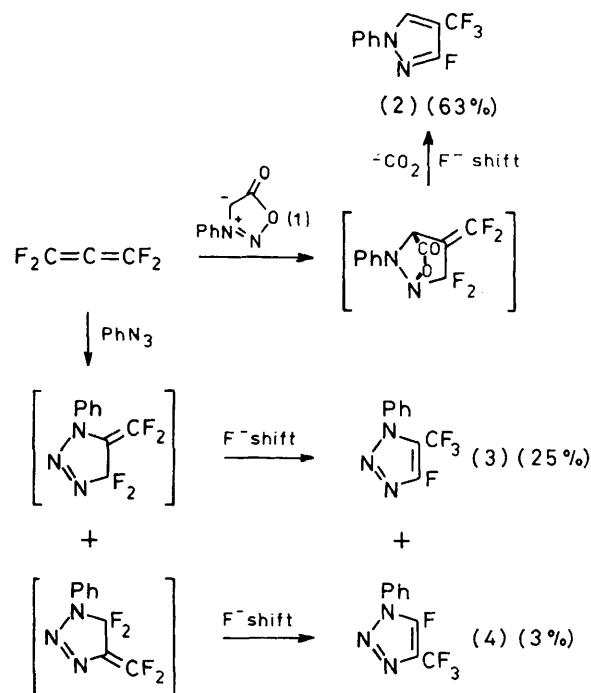
We recently reported that perfluoropropadiene undergoes facile 1,3-dipolar cycloadditions with *N*-phenylsydnone (1) and with aryl azides.<sup>1</sup> These reactions afford a new synthesis of fluorotrifluoromethylpyrazoles and 1,2,3-triazoles, since the cycloadditions are accompanied by aromatization through anionotropic rearrangement of the fluorocarbon moiety (Scheme 1).

The rearrangement step is believed to follow rather than precede the cycloaddition because the corresponding reactions of perfluoropropyne gave quite different product distributions. Thus, with compound (1) it gave mainly (42%) the 4-fluoro-3-trifluoromethylpyrazole (5) and only 21% of the 3-fluoro-4-trifluoromethylpyrazole (2), and with phenyl azide the only 1,2,3-triazole detected was (4) (32% isolated).

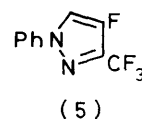
We now report two further types of 1,3-dipolar cycloaddition to this fluorinated allene, namely those involving nitrones and aryl-substituted diazoalkanes; neither of these additions is accompanied by fluoride migration.

**Reactions of Perfluoropropadiene with Nitrones.**—The first three *N*-alkyl-*C*-phenylnitrones † (6a–c) which were investigated all reacted rapidly with perfluoropropadiene at ambient temperature in benzene or in the absence of a solvent, the reactions being essentially complete within a few hours. There appeared to be only a single product (71–99%) in each case, analysing correctly for a 1:1 adduct; that from *N*-benzylidene (6c) crystallized readily but the others remained as oils even after distillation.

The <sup>19</sup>F n.m.r. spectra of the 1:1 adducts revealed (i) two strongly coupled ( $J_{\text{AB}}$  168–180 Hz) endocyclic fluorines at sufficiently low field ( $\delta_{\text{F}}$  9–10 p.p.m.) to suggest proximity to the nitron's oxygen terminus and (ii) an exocyclic difluoromethylene group ( $\text{C}=\text{C}$  stretch at  $1786\text{ cm}^{-1}$  in each case) with the coupling ( $^2J_{\text{FF}}$  26–27 Hz) expected for geminal fluorines on an  $\text{sp}^2$ -hybridised carbon.<sup>2</sup> The low-field exocyclic fluorine ( $\delta_{\text{F}}$  ca. 0 p.p.m.) is quite strongly coupled (9 Hz) to the endocyclic fluorines: this *cis*  $^4J_{\text{FF}}$  coupling is the same as that recently reported by Burger and Goth for 4-difluoromethylene-5,5-difluoro-2-oxazolines (7).<sup>3</sup> The high-field exocyclic fluorine ( $\delta_{\text{F}}$  –2.5 to –7.0 p.p.m.) revealed a



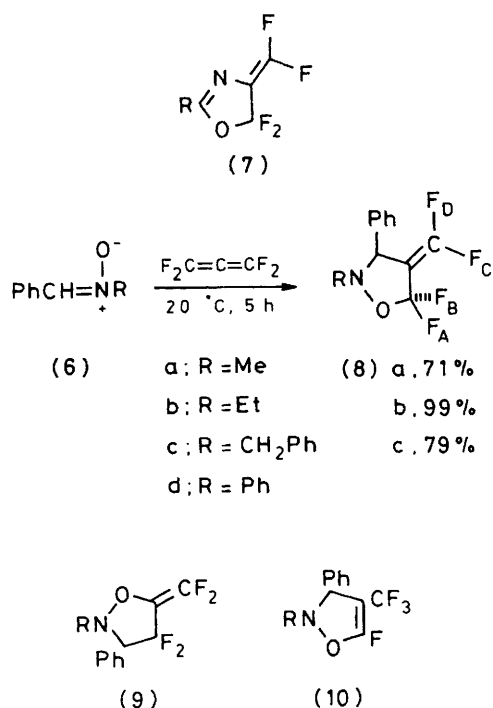
Scheme 1



4 Hz coupling to the nitron's methine proton, also evident in the <sup>1</sup>H spectra. The magnitude of this coupling indicates the proximity of this fluorine to the nitron's carbon terminus and confirms that these adducts are the 4-difluoromethylene-5,5-difluoro-isoxazolidines (8a–c).

No isomeric adducts with the alternative orientation (9) were detected, nor was there any evidence for the occurrence of trifluoromethylisoxazolidines (10), arising by a similar type

† For ease of reference to the literature, names based on nitron have been used throughout. The systematic I.U.P.A.C. names would be of the type *N*-benzylidene-alkylamine *N*-oxides.

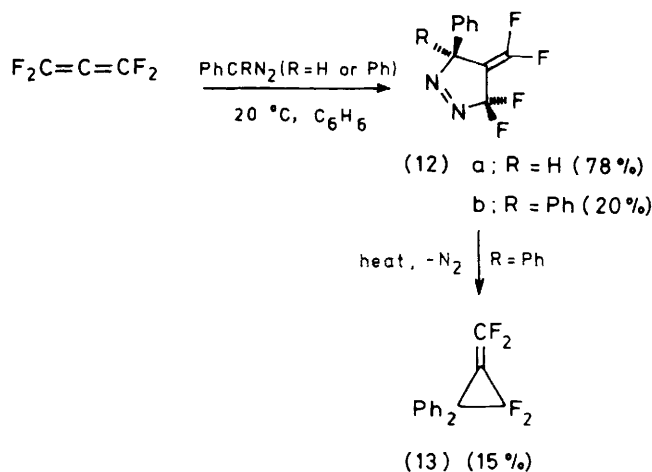
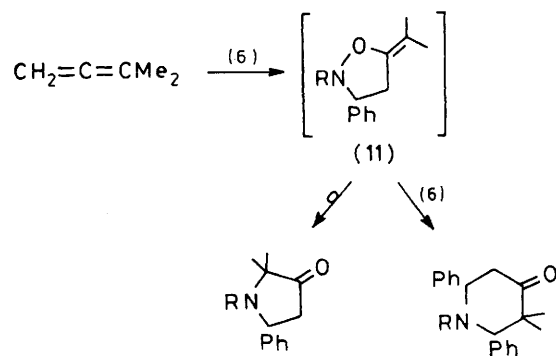


of fluoride migration as had been found to occur in the reactions of this allene with sydnone and azides.

An attempt was made to hydrogenate catalytically the adducts (8a) and (8c) but, after uptake of two moles/mole of hydrogen, decomposition ensued. From the methyl compound (8a) no identifiable products were obtained, and from the hydrogenation of the benzyl derivative (8c) only benzylamine hydrofluoride was isolated. These isoxazolidines are not very stable and both (8a) and (8b) decompose to dark viscous tars on standing at room temperature.

The reaction between *C,N*-diphenylnitrone (6d) and perfluoropropadiene was also investigated. Rapid extraction of the crude involatile product gave a very unstable oil, believed to be the corresponding isoxazolidine (8d) on the basis of its i.r. (C=C stretch at 1786 cm<sup>-1</sup>) and <sup>19</sup>F n.m.r. spectra, although satisfactory elemental analytical data were not obtainable. Interestingly, the fine structure of the <sup>19</sup>F resonances of the endocyclic CF<sub>A</sub>CF<sub>B</sub> grouping was more clearly resolved for (8d) than for any of the previously isolated adducts (8a–c), presumably because the nitrogen atom's inversion is inhibited in this compound by mesomerism with the adjacent phenyl group.

The regioselectivity of the nitrone-perfluoropropadiene cycloadditions is in accord with the general pattern of orientations observed in reactions between nitrones and olefinic dipolarophiles;<sup>4,5</sup> such reactions are, in the terminology of frontier orbital theory,<sup>6</sup> normally controlled by nitrone-LUMO (orbital energy –0.4 eV)<sup>7,8</sup> olefin-HOMO (–11.2 eV for C<sub>3</sub>F<sub>4</sub>)<sup>9,10</sup> interactions unless strongly electron-withdrawing substituents on the dipolarophile bring the nitrone-HOMO (–8 eV)<sup>11</sup> and olefin-HOMO (thought to be 3–4 eV in C<sub>3</sub>F<sub>4</sub>)<sup>1</sup> closer in energy. Since the nitrone-LUMO has a much larger C-coefficient than O-coefficient and the propadiene-HOMO has a larger C-2 than C-1 coefficient,<sup>10</sup> the result observed concurs neatly with the theoretical predictions. It should be noted that the orientation observed for perfluoropropadiene is opposite to that reported for allenic hydrocarbons and nitrones,<sup>12</sup> which react to give, initially at least, 5-alkylideneisoxazolidines [e.g. (11) (Scheme 2)]. However, since the relative sizes of the C(1)- and C(2)-coefficients

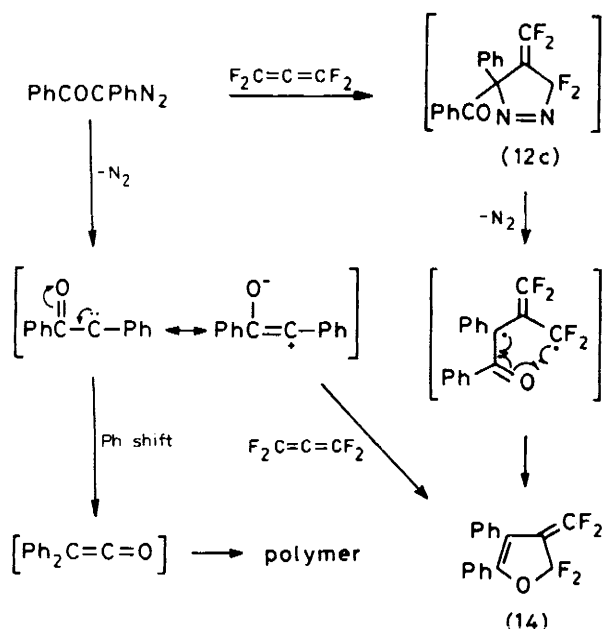


are reversed in the HOMO of an allenic hydrocarbon,<sup>13</sup> this changeover may also be rationalised.

**Reactions of Perfluoropropadiene with Diazoalkanes.**—When the fluorinated allene was placed in contact with a dilute solution of diazophenylmethane at room temperature, a rapid reaction occurred so that the colour of the diazo-compound was entirely discharged in about thirty minutes. In solution the product was relatively stable but after removal of the solvent under reduced pressure it evolved hydrogen fluoride rapidly. Identification of the adduct therefore rests wholly on spectroscopic data.

Its i.r. spectrum displays a strong C=C stretching absorption (1770 cm<sup>-1</sup>) compatible with an exocyclic =CF<sub>2</sub> group. The <sup>19</sup>F n.m.r. spectrum confirms this unit and shows in addition an AB system (*J*<sub>AB</sub> 255 Hz) attributable to an endocyclic CF<sub>2</sub> group, placed adjacent to the nitrogen terminus of the diazoalkane rather than the carbon terminus on the basis of its downfield shift (–0.5 p.p.m.). The various coupling constants are also compatible with a Δ<sup>1</sup>-pyrazoline (12a) (Scheme 3).

In a similar, albeit slower, reaction between the allene and diazodiphenylmethane, the involatile product was found to contain benzophenone azine. Column chromatography on alumina removed this and another, unidentified, by-product leaving a residual oil which was sufficiently stable to permit elemental and m.s. analyses to be achieved. These showed that a 1 : 1 adduct, identified spectroscopically as the diphenyl-Δ<sup>1</sup>-pyrazoline (12b), had been formed. Its <sup>19</sup>F n.m.r. spectrum



Scheme 4

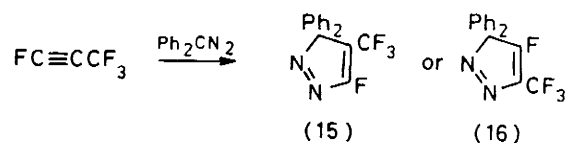
although simpler than that of compound (12a) since the centre of asymmetry is no longer longer present, is generally similar, and in particular confirms the orientation since the endocyclic  $\text{CF}_2$  group resonates at 0.8 p.p.m., *i.e.*, it is adjacent to a nitrogen atom.

The mass spectrum of compound (12b) displayed no parent ion, and the occurrence of an intense peak at  $m/z$  278, corresponding to loss of molecular nitrogen, suggested that thermal extrusion of nitrogen might occur readily. This proved to be the case: when the liquid pyrazoline was distilled a liquid, b.p.  $99^\circ\text{C}$  at 0.5 mmHg, was collected and identified spectroscopically as the cyclopropane (13).

The two diazoalkanes used in the above reactions are generally regarded as HOMO-controlled dipoles with large atomic orbital (a.o.) coefficients at the terminal carbon. The energy and shape of the perfluoropropadiene-LUMO has not been accurately calculated but is unlikely to be of sufficiently high energy to force a changeover to dipole-LUMO/dipolarophile-HOMO control. It should have the larger a.o. coefficient at C-2 on the basis of calculations reported for 1,1-difluoroallene<sup>14</sup> and allenic hydrocarbons.<sup>13</sup> The observed regioselectivity is therefore once again in accord with frontier orbital predictions.

When an attempt was made to extend this type of cycloaddition to benzyldiazophenylmethane, two products were isolated by chromatography on alumina. One was a white solid, also formed during an unsuccessful attempt to achieve a [2 + 2] cycloaddition of diphenylketene to perfluoropropadiene and during the synthesis of diphenylketene,<sup>15</sup> and therefore believed to be a polymer of diphenylketene. The other, an oil, was identified spectroscopically as the difluoromethylenedihydrofuran (14) (Scheme 4). No evidence for the expected 1 : 1 adduct (12;  $\text{R} = \text{PhCO}$ ) was obtained.

The i.r. spectrum of compound (14) suggested the presence of either a carbonyl group or an exocyclic  $=\text{CF}_2$  group, the latter being confirmed by the  $^{19}\text{F}$  n.m.r. spectrum which, unlike that of the pyrazolidine (12a), showed no AB system for the endocyclic  $\text{CF}_2$  group. Structures such as (12;  $\text{R} = \text{PhCO}$ ) are therefore excluded. Moreover the mass spectrum showed no ions above  $m/z$  306 ( $\text{C}_{11}\text{H}_{10}\text{F}_4\text{O}$ ), and an intense ion signal occurred at  $m/z$  240, corresponding to loss of  $\text{CF}_2\text{O}$ .



The furan (14) would be expected to arise if the diazo-compound decomposed prior to cycloaddition, since an incipient ketocarbene ( $\text{PhCO}\cdot\dot{\text{C}}\text{Ph}$ ) would then be formed which could also function as a 1,3-dipole and be trapped by perfluoropropadiene. Equally possible is the decomposition of an initially formed cycloadduct such as (12;  $\text{R} = \text{PhCO}$ ), followed by rearrangement (Scheme 4). The low reactivity of this diazoalkane towards perfluoropropadiene (nearly one-third of the allene was recovered after four weeks in contact with the diazoalkane at room temperature) necessitated gentle heat ( $65^\circ\text{C}$ ); this and the formation of poly(diphenylketene) as a by-product favours the former mechanism for the formation of the furan. Similar furans have been reported to arise in cycloadditions of ethyl diazoacetate.<sup>16</sup>

#### Reaction of Perfluoropropyne with Diazodiphenylmethane.—

For comparison with the behaviour of perfluoropropadiene, its isomer perfluoropropyne was also treated with diazodiphenylmethane at room temperature. An oily 1 : 1 adduct was isolated in 35% yield, the spectroscopic properties of which are compatible with either of the isomeric 1,3-dipolar cycloadducts (15) and (16). The  $^{19}\text{F}$  n.m.r. chemical shifts of the vinylic fluorine (a quartet at 42 p.p.m. upfield of  $\text{CF}_3\text{-CO}_2\text{H}$ ) suggests proximity to nitrogen rather than carbon,<sup>1,17</sup> and thus favours (15) over (16). The heterocycle is, of course, non-aromatic.

#### Experimental

The spectroscopic techniques (i.r., n.m.r., m.s.) were described in the previous Part.<sup>1</sup> *C*-Phenyl-*N*-methyl-, -*N*-ethyl-, and -*N*-benzyl-nitrones,<sup>18</sup> *C,N*-diphenylnitron,<sup>19</sup> diphenylketene,<sup>15</sup> diazodiphenylmethane,<sup>20</sup> and benzyldiazophenylmethane<sup>21</sup> were prepared by published procedures. Perfluoropropadiene and perfluoropropyne were prepared as described earlier in this series.<sup>22</sup> Diazophenylmethane was prepared by oxidation of hydrazine-free benzaldehyde hydrazone using yellow mercuric oxide in light petroleum (b.p.  $30\text{--}40^\circ\text{C}$ ) at  $20^\circ\text{C}$  and was purified by cautious vacuum transfer immediately prior to use.<sup>23</sup>

**Reactions of Perfluoropropadiene.**—(a) *With N-methyl-C-phenylnitron.* The nitron (0.75 g, 5.6 mmol), perfluoropropadiene (0.78 g, 7.0 mmol), and anhydrous benzene (25  $\text{cm}^3$ ) were shaken for 5 h in a sealed 90- $\text{cm}^3$  Pyrex tube at  $20^\circ\text{C}$ . Perfluoropropadiene (0.6 mmol, 71% recovery) and the solvent were removed and the residual oil (1.05 g) was distilled through a short Vigreux column to give a colourless liquid, b.p.  $60\text{--}62^\circ\text{C}$  at 0.4 mmHg, identified spectroscopically as 4-difluoromethylene-5,5-difluoro-2-methyl-3-phenylisoxazolidine (8a) (1.0 g, 4.0 mmol, 71% from nitron) (Found: C, 52.9; H, 4.0; F, 29.0; N, 5.6%;  $M^+$ , 247.  $\text{C}_{11}\text{H}_9\text{F}_4\text{NO}$  requires C, 53.4; H, 3.6; F, 30.8; N, 5.7%;  $M$ , 247);  $\nu_{\text{max}}$  (cap. film)  $1786\text{ s}^{-1}$  ( $\text{C}=\text{C}$  str.);  $\delta_{\text{H}}$  (50%  $\text{CCl}_4$ ; w.r.t. external  $\text{C}_6\text{H}_6$ ) — 4.0 (s, MeN), —2.2 (apparent t,  $^4J_{\text{HF}}$  4 Hz, CHPh), and 0.7 (m, Ph);  $\delta(^{19}\text{F})$  (w.r.t. external  $\text{CF}_3\text{CO}_2\text{H}$ ) — 4.0 (dq,  $^2J_{\text{FF}}$  27 Hz,  $J_{\text{CF}}$  4 Hz,  $=\text{CF}$  *syn.* to CHPh), 0.1 (dtd,  $J_{\text{AB}}$  4 and 27 Hz,  $J_{\text{CF}}$  9 Hz,  $=\text{CF}$  *syn.* to  $\text{CF}_2$ ), and 9.0 p.p.m. (AB dd,  $J_{\text{AB}}$  168 Hz, endocyclic  $\text{CF}_2$ );  $m/z$  (identified ions only) 247 (75%, P), 202 (73, P — MeNO), 170 (84,  $\text{C}_9\text{H}_5\text{F}_3$ ), and 151 (57,  $\text{C}_9\text{H}_5\text{F}_2$ ).



(b) *With N-ethyl-C-phenylnitrone.* The *N*-ethylnitrone (1.48 g, 9.9 mmol) and perfluoropropadiene (2.28 g, 20.4 mmol), kept in a sealed 90-cm<sup>3</sup> Pyrex tube at 20 °C for 5 h, gave, after removal of excess of perfluoropropadiene (7.3 mmol, 36% recovery), a pale-yellow oil which was identified without further purification (crystallization did not occur readily) as 4-difluoromethylene-2-ethyl-5,5-difluoro-3-phenylisoxazolidine (8b) (2.56 g, 9.8 mmol, 99% from nitrone) (Found: C, 56.2; H, 5.1; F, 27.8; N, 4.7%;  $M^+$ , 261.  $C_{12}H_{11}F_4NO$  requires C, 55.2; H, 4.2; F, 29.1; N, 5.4%;  $M$ , 261);  $\nu_{\max}$  (cap. film) 1786s cm<sup>-1</sup> (C=C str.);  $\delta_H$ (50%  $CCl_4$ ; w.r.t. internal  $Me_4Si$ ) 7.4 (m, Ph), 4.64 (t,  $^4J_{HF}$  4 Hz, CHPh), 2.90 (q,  $^3J_{HH}$  7 Hz,  $CH_2Me$ ), and 1.15 (t,  $CH_2Me$ );  $\delta(^{19}F)$  (ext.  $CF_3CO_2H$ ) -7.0 (dq,  $^2J_{FF}$  27 Hz,  $J_q$  4 Hz, =CF *syn* to CHPh), -0.5 (dtd,  $J_d$  27 and 4 Hz,  $J_t$  9 Hz, =CF *syn* to  $CF_2$ ), and 10.0 p.p.m. (AB dd,  $J_{AB}$  180 Hz, endocyclic  $CF_2$ );  $m/z$  261 (100%,  $P$ ), 246 (49,  $P - Me$ ), 226 (11,  $P - Me - HF$ ), 202 (74,  $C_{10}H_6F_4$ ), 201 (49,  $C_{10}H_5F_4$ ), 199 (24,  $C_{10}H_6F_3O$ ), 184 (70,  $C_{10}H_7F_3$ ), 182 (20,  $C_{10}H_5F_3$ ), 181 (14,  $C_6H_3F_4NO$ ), 151 (53,  $C_6H_4F_2$ ), 133 (81,  $C_6H_5F_2N$ ), 131 (31,  $C_6H_4F_2N$ ), 119 (43,  $C_7H_5NO$ ), 113 (19,  $C_6H_8FN$ ), and 109 (75,  $C_7H_6F$ ).

(c) *With N-benzyl-C-phenylnitrone.* The *N*-benzylnitrone (2.15 g, 10.2 mmol), perfluoropropadiene (1.4 g, 12.5 mmol), and anhydrous benzene (25 cm<sup>3</sup>) were shaken for 20 h at 20 °C in a sealed Pyrex tube. After perfluoropropadiene (3.8 mmol, 30% recovery) and the solvent had been removed under reduced pressure, a buff-coloured solid was obtained which was identified spectroscopically as 2-benzyl-4-difluoromethylene-5,5-difluoro-3-phenylisoxazolidine (8c) (2.63 g, 8.1 mmol, 79% from nitrone) (Found: C, 63.1; H, 4.5; F, 22.0; N, 4.3%;  $M^+$ , 323.  $C_{17}H_{13}F_4NO$  requires C, 63.2; H, 4.0; F, 23.5; N, 4.3%;  $M$ , 323), m.p. 52–53 °C [from light petroleum (b.p. 30–40 °C)];  $\nu_{\max}$  (mulls) 1786s cm<sup>-1</sup> (C=C str.);  $\delta_H$ (20%  $CCl_4$ , w.r.t. int.  $Me_4Si$ ) 7.3 (m, Ph), 4.77 (apparent t,  $^4J_{HF}$  4 Hz, CHPh), and 4.1 (s,  $CH_2$ );  $\delta(^{19}F)$  (ext.  $CF_3CO_2H$ ) -2.5 (dq,  $^2J_{FF}$  26 Hz, =CF *syn* to CHPh), 0.0 (dtd,  $^4J_{FF}$  11 Hz, =CF *syn* to  $CF_2$ ), and 10.0 p.p.m. (AB dd,  $J_{AB}$  168 Hz, endocyclic  $CF_2$ );  $m/z$  323 (25%  $P$ ), 91 (100,  $C_7H_7$ ), 77 (12,  $C_6H_5$ ), and 51 (11,  $C_4H_3$ ).

(d) *With C,N-diphenylnitrone.* Diphenylnitrone (1.9 g, 9.6 mmol), perfluoropropadiene (1.5 g, 13.4 mmol), and anhydrous benzene (40 cm<sup>3</sup>) were shaken at 20 °C for 3 days in a sealed 90-cm<sup>3</sup> Pyrex tube. After the removal of perfluoropropadiene (4.3 mmol, 32% recovery) and the solvent, the yellow oily residue containing traces of a dark suspended solid was extracted with light petroleum (b.p. 30–40 °C). The residue (ca. 2 g) was a black solid; evaporation of the extract gave a yellow oil (ca. 50 mg) which rapidly decomposed to a black solid. The solids could not be chromatographically purified. In a further experiment the nitrone (1.0 g, 5.1 mmol) and perfluoropropadiene (0.48 g, 4.3 mmol) in benzene (30 cm<sup>3</sup>) were shaken at 20 °C for 3 h, the solvent and propadiene (28% recovery) were removed and the residual oil was rapidly extracted with light petroleum. Evaporation of the extract under reduced pressure gave an unstable viscous oil, believed to be 4-difluoromethylene-5,5-difluoro-2,3-diphenylisoxazolidine (8d) on the basis of its i.r., and  $^1H$  and  $^{19}F$  n.m.r. spectra;  $\nu_{\max}$  (cap. film) 1786s cm<sup>-1</sup> (C=C str.);  $\delta_H$ (50%  $CCl_4$ , w.r.t. ext.  $C_6H_6$ ) 0.3 (m, Ph), 0.5 (m, Ph), and -1.55 (t,  $^4J_{HF}$  4 Hz, CHPh);  $\delta(^{19}F)$  (ext.  $CF_3CO_2H$ ) -1.0 (dq,  $^2J_{FF}$  27 Hz, =CF *syn* to CHPh), 0.0 (dddd,  $J_d$  4, 27, 11.5, and 7.5 Hz, =CF *syn* to  $CF_2$ ), and 9.0 p.p.m. (AB dddd,  $J_{AB}$  162 Hz, endocyclic  $CF_2$ ).

(e) *With diazophenylmethane.* Diazophenylmethane (0.76 g, 6.4 mmol), perfluoropropadiene (1.55 g, 13.8 mmol), and anhydrous benzene (15 cm<sup>3</sup>) were kept in a sealed 90-cm<sup>3</sup> Pyrex tube at 20 °C for 15 h, by which time the colour of the diazo-compound had discharged. After removal of perfluoro-

propadiene (10.8 mmol, 78% recovery) and the solvent under reduced pressure an involatile colourless oil was obtained, believed to be 4-difluoromethylene-3,3-difluoro-5-phenyl- $\Delta^1$ -pyrazoline (12a) (0.54 g, 2.35 mmol, 78% on  $C_3F_4$  consumed) on the basis of its i.r., and  $^1H$  and  $^{19}F$  n.m.r. spectra;  $\nu_{\max}$  (cap. film) 1770s cm<sup>-1</sup> (C=C str.);  $\delta_H$ (40%  $CCl_4$  w.r.t. ext.  $C_6H_6$ ) -0.6 (poorly resolved m, CHPh) and 0.5–0.7 p.p.m. (m, Ph);  $\delta(^{19}F)$  (ext.  $CF_3CO_2H$ ) 11.0 (ddt,  $^2J_{FF}$  10 Hz,  $^4J_{HF}$  3 Hz,  $^4J_{FF}$  3–4 Hz, =CF, *syn* to CHPh), 4.0 (qd,  $^4J_{FF}$  10 Hz, =CF *syn* to  $CF_2$ ), and -0.5 p.p.m. (AB dddd,  $J_{AB}$  255 Hz, endocyclic  $CF_2$ ); however it was too unstable for an analytically pure sample to be isolated.

(f) *With diazodiphenylmethane.* Perfluoropropadiene (0.91 g, 8.1 mmol), diazodiphenylmethane (1.94 g, 10.0 mmol), and anhydrous benzene (30 cm<sup>3</sup>) were kept at 20 °C in a sealed 300-cm<sup>3</sup> Pyrex tube for 2 days. Volatile materials, including nitrogen and perfluoropropadiene (3.1 mmol, 38% recovery) were removed, and the residue was chromatographed on alumina to give benzophenone azine (0.29 g, 0.8 mmol), m.p. 160–163 °C (lit.<sup>24</sup> m.p. 164 °C), an unidentified colourless solid, m.p. 103–104 °C (20 mg), and a colourless oil identified spectroscopically as 4-difluoromethylene-3,3-difluoro-5,5-diphenyl- $\Delta^1$ -pyrazoline (12b) (0.30 g, 0.98 mmol, 20% on  $C_3F_4$  consumed) (Found: C, 63.4; H, 3.6; F, 23.7; N, 8.3%.  $C_{16}H_{10}F_4N_2$  requires C, 62.7; H, 3.3; F, 24.8; N, 9.2%);  $\nu_{\max}$  (cap. film) 1757s cm<sup>-1</sup> (C=C str.);  $\delta_H$ (50%  $CCl_4$ , int.  $Me_4Si$ ) 7.3–7.4 (m);  $\delta(^{19}F)$  (ext.  $CF_3CO_2H$ ) 12.0 (td,  $^4J_{FF}$  10 Hz, =CF *syn* to  $CF_2$ ), 5.0 (dt,  $^2J_{FF}$  9 Hz,  $^4J_{FF}$  4 Hz, =CF *syn* to  $CPh_2$ ), and -0.8 p.p.m. (dd, endocyclic  $CF_2$ );  $m/z$  278 (100%,  $P - N_2$ ) 258 (17,  $C_{16}H_9F_3$ ), 257 (31,  $C_{16}H_8F_3$ ), 256 (21,  $C_{16}H_7F_3$ ), 228 (13,  $C_{16}H_{10}F_2$ ), 201 (29,  $P - Ph$ ), 77 (41, Ph) and 28 (87%,  $N_2$ ). On storage at room temperature decomposition with loss of nitrogen occurred; the i.r. band at 1757 cm<sup>-1</sup> was simultaneously replaced by one at 1818 cm<sup>-1</sup>, attributed to the cyclopropane (13) (below).

In a similar reaction between perfluoropropadiene (4.0 g, 35.7 mmol) and diazodiphenylmethane (5.45 g, 28.0 mmol), from which, after 6 days, perfluoropropadiene (11.4 mmol) was recovered, low-pressure distillation of the involatile product (ca. 6 g) gave a colourless liquid, b.p. 99 °C at 0.5 mmHg, identified spectroscopically as 3-difluoromethylene-2,2-difluorodiphenylcyclopropane (13) (1.0 g, 3.6 mmol, 15% on  $C_3F_4$  consumed) (Found: C, 70.0; H, 4.1%;  $M^+$ , 278.  $C_{16}H_{10}F_4$  requires C, 69.1; H, 3.6%;  $M$ , 278);  $\nu_{\max}$  (cap. film) 1818s cm<sup>-1</sup> (C=C str.);  $\delta_H$ (50%  $CCl_4$ , int.  $Me_4Si$ ) 7.3 (m, Ph);  $\delta(^{19}F)$  (ext.  $CF_3CO_2H$ ) 11.5 (dt,  $^2J_{FF}$  30 Hz,  $^4J_{FF}$  8 Hz, =CF *syn* to  $CPh_2$ ), 0.0 (dt,  $^4J_{FF}$  10 Hz, =CF *syn* to  $CF_2$ ), and -49.0 p.p.m. (dd, endocyclic  $CF_2$ ).

(g) *With benzoyldiazophenylmethane.* Perfluoropropadiene (0.93 g, 8.3 mmol), benzoyldiazophenylmethane (1.07 g, 4.8 mmol), anhydrous benzene (20 cm<sup>3</sup>), and polymerization inhibitor (ca. 0.1 cm<sup>3</sup> mixed terpinolene and dipentene), kept at 65 °C in a sealed 90-cm<sup>3</sup> Pyrex tube for 18 days, gave nitrogen (ca. 2.6 mmol), perfluoropropadiene (4 mmol), and an involatile residue (1.3 g) which was chromatographed on alumina to give a white solid (0.48 g) believed to be a polymer of diketene, and a colourless oil identified spectroscopically as 3-difluoromethylene-2,2-difluoro-4,5-diphenyl-2,3-dihydrofuran (14) (120 mg, 0.4 mmol, 9% on  $C_3F_4$  consumed);  $\nu_{\max}$  (cap. film) 1742s cm<sup>-1</sup> (C=C str.);  $\delta_H$ (20%  $CCl_4$  int.  $Me_4Si$ ) 7.3–7.4 (Ph);  $\delta(^{19}F)$  (ext.  $CF_3CO_2H$ ) -2.0 (dt,  $^2J_{FF}$  18 Hz,  $^4J_{FF}$  9 Hz, =CF *syn* to =CPh), -1.0 (dt,  $^4J_{FF}$  12 Hz, =CF *syn* to  $CF_2$ ), and 14.0 p.p.m. (dd, endocyclic  $CF_2$ );  $m/z$  306 (31%,  $P$ ), 240 (21,  $P - COF_2$ ), 167 (100,  $P - COF_2 - Ph$ ), and 77 (49, Ph).

In a similar reaction at room temperature, perfluoropropadiene (28%) was still recoverable after 28 days. The involatile material (2.5 g) was sublimed and yielded, at 50–

100 °C/1 mmHg, a white solid (1.3 g) believed to be a polymer of diphenylketen, on the basis of i.r. comparison with material formed during the preparation of diphenylketen.

(h) *With diphenylketen.* When perfluoropropadiene (12 mmol) and diphenylketen (6 mmol) were kept in a sealed tube for 8 days at 20–25 °C, the only identifiable products were perfluoropropadiene (75% recovery) and a white polymeric solid, also isolated during the preparation of diphenylketen.<sup>15,21</sup>

*Reaction of Perfluoropropyne with Diazodiphenylmethane.*—Diazodiphenylmethane (1.94 g, 10.0 mmol), perfluoropropyne (1.1 g, 9.8 mmol), and anhydrous benzene (25 cm<sup>3</sup>) were kept at 20 °C in a sealed 90-cm<sup>3</sup> Pyrex tube for 14 days. Volatile materials (nitrogen and benzene) were removed, the yellow oily residue (2.5 g) was triturated with light petroleum (b.p. 30–40 °C), and benzophenone azine (0.7 g, 1.9 mmol) was filtered off. Evaporation of the filtrate yielded an oil which was purified by chromatography on silica gel (20% Et<sub>2</sub>O in light petroleum as eluant), and identified spectroscopically as either 5(or 4)-fluoro-3,3-diphenyl-4(or 5)-trifluoromethyl-3H-pyrazole (1.06 g, 3.5 mmol, 35%);  $\nu_{\text{max}}$  (cap. film) 3 030w, 2 941w, 1 695m, 1 667m, 1 399s, 1 274m, 1 205s, 1 149s, 775w, 746w, and 699br, s cm<sup>-1</sup>;  $\delta_{\text{H}}$ (50% CCl<sub>4</sub>, int. Me<sub>4</sub>Si) 7.3–7.4;  $\delta(^{19}\text{F})$  (ext. CF<sub>3</sub>CO<sub>2</sub>H) –42 (q,  $^4J_{\text{FF}}$  12 Hz, =CF), and 15 p.p.m. (d, CF<sub>3</sub>).

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