

## Reactions of Tetrafluoroethene Oligomers. Part 7.<sup>1</sup> Some Reactions of 4-Diazo-1,1,1,2,2-pentafluoro-3-pentafluoroethyl-3-trifluoromethylbutane

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The title diazo compound (1) alone or in the presence of  $\text{Cu}^{2+}$  ions reacted with trifluoroacetic acid to give  $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{CCH}_2\text{O}_2\text{CCF}_3$  (2). Careful hydrolysis of (2) with dilute alkali afforded  $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{CCH}_2\text{OH}$  (3) which on oxidation gave the corresponding aldehyde (4). Treatment of (3) with stronger base yielded  $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{CH}$  (5) and  $\text{CF}_3\text{C}_2\text{F}_5\text{C}=\text{CF}_3$  (6). Reaction of (1) with acetic acid in the presence of  $\text{Cu}^{2+}$  ions produced the unexpected compound  $\text{CF}_3\text{C}_2\text{F}_5\text{C}=\text{CHOCCH}_3$  (7) and a trace of  $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{CCH}=\text{CF}_3$  (13). In a similar reaction chloroacetic acid gave  $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{CCH}_2\text{OCOCH}_2\text{Cl}$  (8) and  $\text{CF}_3\text{C}_2\text{F}_5\text{C}=\text{CHOCCH}_2\text{Cl}$  (9) in the ratio 4:1. Treatment of (1) with concentrated sulphuric acid gave the dialkyl sulphate  $[\text{CF}_3(\text{C}_2\text{F}_5)_2\text{CCH}_2]_2\text{SO}_4$  (12). Reaction of (1) with methanol/ $\text{Cu}^{2+}$  or ethanol/ $\text{Cu}^{2+}$  gave mainly  $\text{CF}_3\text{C}_2\text{F}_5\text{C}=\text{CHOMe}$  (10) and  $\text{CF}_3\text{C}_2\text{F}_5\text{C}=\text{CHOEt}$  (11) respectively. Reflux of (1) in acetone/ $\text{Cu}^{2+}$  gave only the olefin (13). No reaction occurred in ether or hexane at their reflux temperatures.

In earlier papers in this series we briefly reported the preparation of the diazobutane (1)<sup>2</sup> and more recently<sup>3</sup> we described an improved preparation of compound (1) and some studies of its thermal and photochemical stability. We now describe some reactions of compound (1) with protic materials of varying acid strength and in the presence of  $\text{Cu}^{\text{II}}$  salts.

The alkylation of acids, phenols, and certain alcohols by diazoalkanes under a variety of conditions is well known and has been extensively reviewed.<sup>4</sup> The known reactions of the relatively few fluorodiazoalkanes have received rather less attention but have, nevertheless, been subject to a review.<sup>5</sup> More recently additions of these reagents to alkenes and alkynes have been reported<sup>6</sup> and some reactions with carbonyl compounds,<sup>7</sup> metal derivatives<sup>8</sup> and, after this work had been started, with phenols, thiols, and carboxylic acids<sup>9</sup> are described in the literature. We are interested in the electronic and steric effects of bulky fluorocarbon groups on the reactivity of functional groups. Thus, the chemistry of the diazoalkane (1) was of interest. When we began this study, the work of Koller and Dorn<sup>9</sup> using  $\text{CF}_3\text{CHN}_2/\text{HBF}_4$  and hydroxy and mercapto compounds had not appeared, and the only reaction described with a carboxylic acid was that by Dyatkin<sup>7</sup> who reported the formation of  $\text{CHCl}_2\text{CO}_2\text{CH}_2\text{CF}_3$ . Thus, we have studied reactions of acids and alcohols with compound (1) under a variety of conditions.

Reaction of compound (1) with trifluoroacetic acid alone was found to be relatively slow compared, for example, with the corresponding reaction with diazomethane and a period of 12 h under reflux in Freon 113 was necessary for complete reaction. Subsequently, it was found that the reaction of (1) with the acid in the presence of a crystal of copper(II) perchlorate at room temperature was extremely rapid. Examination of the product mixture from either reaction showed the presence of one component. Distillation afforded a clear liquid, the i.r. spectrum of which showed the disappearance of characteristic absorption at  $2150\text{ cm}^{-1}$  and the appearance of a strong band at  $1805\text{ cm}^{-1}$ , typical of an ester carbonyl group. The  $^{19}\text{F}$  n.m.r. spectrum showed the presence of the  $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{C}$  group and an additional  $\text{CF}_3$  group. The mass spectrum showed  $m/z$  427 corresponding to the compound being  $\text{C}_9\text{H}_2\text{F}_{16}\text{O}_2$ . These data indicate that (2) is  $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{CCH}_2\text{O}_2\text{CCF}_3$ , i.e. the

expected ester from the reaction of a diazoalkane with an acid.

Treatment of compound (2) with dilute aqueous sodium hydrogen carbonate at room temperature afforded a single compound which was readily identified by i.r. and n.m.r. spectroscopy and mass spectrometry as the alcohol  $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{CCH}_2\text{OH}$  (3). This reaction, was, however, rather slow. In an attempt to speed up the reaction it was carried out at  $50^\circ\text{C}$  with the same base concentration and at room temperature with sodium hydroxide. In both cases rapid decomposition occurred to give very volatile materials. This result was readily explained when it was shown that the alcohol (3) was decomposed to the same materials, which were trapped out, by heating under reflux in DMSO. The products were shown, by comparison with authentic samples, to be perfluoro-3-methylpent-2-ene (6) and 3H-3-trifluoromethyldecafluoropentane (5). This result is paralleled in turn by the decomposition to the same products of  $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{CCH}_2\text{NH}_3^+\text{HSO}_4^-$  and is a measure of the stability of the  $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{C}^-$  ion as a leaving group. Thus, it is clear that hydrolysis of the ester (2) with strong base gives first the alcohol (3) which decomposes to the olefin (5), and this then reacts further with hydroxide ion leading to total decomposition. As part of another study on the electrochemistry of fluorocarbon acids<sup>10</sup> we needed the acid  $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{CCO}_2\text{H}$ , and oxidation of (3) under acidic conditions was thought to be a potential route. Thus, the alcohol (3) was smoothly oxidised with chromium(VI) oxide in sulphuric acid to give a single product in good yield. The i.r. spectrum of this showed strong carbonyl absorption ( $1760\text{ cm}^{-1}$ ) whilst the  $^1\text{H}$  n.m.r. spectrum showed a single sharp peak at  $\delta$  9.7 characteristic of the CHO group; shaking the sample with  $\text{D}_2\text{O}$  caused no change in the spectrum. Since the  $^{19}\text{F}$  n.m.r. spectrum showed the presence of the  $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{C}$  group, the product is clearly the aldehyde  $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{CCHO}$  (4). Use of a wide variety of oxidation conditions failed to oxidise the aldehyde (4) to the corresponding acid.

We next investigated the reaction of the diazoalkane (1) with acetic acid. Although little or no reaction occurred at room temperature even in the presence of  $\text{Cu}^{2+}$  ions, warming the mixture at  $50^\circ\text{C}$  with  $\text{Cu}^{2+}$  ions present gave a vigorous reaction with evolution of nitrogen and a rapid disappearance

of the yellow colour of the diazoalkane. The product mixture was shown, by analytical g.l.c., to contain three components two of which were barely resolved on several columns. The mixture was separated into two fractions by preparative g.l.c. the larger fraction being the two barely separable components. The first fraction was identified as 3*H*-perfluoro-4-ethyl-4-methylhex-2-ene (13) (see below). The  $^{19}\text{F}$  and  $^1\text{H}$  n.m.r. spectra of the mixture indicated two similar compounds to be present almost certainly as an *E:Z* mixture in the ratio 1:3. The  $^{19}\text{F}$  spectra surprisingly did not show the characteristic pattern for the  $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{C}$  group instead, two sets of signals for a  $\text{CF}_3$  and a  $\text{C}_2\text{F}_5$  group were present and from the chemical shifts of the signals it was clear the groups were attached to a  $\text{C}=\text{C}$  double bond. The proton spectrum showed two sets of signals for a  $\text{CH}_3\text{CO}$  group and a coupled olefinic proton. From the coupling constants of the H to  $\text{CF}_3$  of 2 Hz for the minor isomer and 0.5 Hz for the major<sup>11</sup> we assigned the *E:Z* ratio as 1:3. Thus, the product (7) is an *E:Z* mixture of 3,3,4,4,4-pentafluoro-2-trifluoromethylbut-2-enyl acetate. This was further confirmed by i.r. spectroscopy which showed  $\text{C}=\text{C}$  and  $\text{C}=\text{O}$  absorptions and by mass spectrometry which gave a breakdown pattern entirely consistent with the proposed structure.

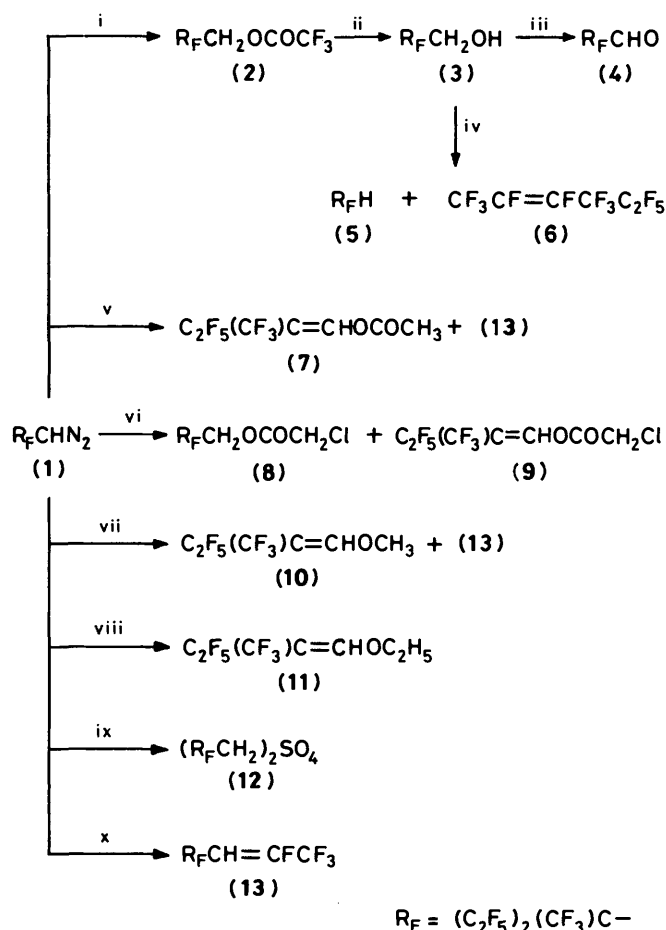
In a similar reaction to the above, but with chloroethanoic acid, an inseparable mixture of three components was obtained which was shown by  $^{19}\text{F}$  and  $^1\text{H}$  n.m.r. spectroscopy to be a 4:1 mixture of 2-pentafluoroethyl-3,3,4,4,4-pentafluoro-2-trifluoromethylbutyl chloroacetate (8) and *E:Z* 3,3,4,4,4-pentafluoro-2-trifluoromethylbut-2-enyl chloroacetate (9), *i.e.* some product corresponding to the trifluoroacetic acid route and some from the acetic acid route with the former as the predominant product.

We next investigated a mineral acid reaction; treatment of the diazoalkane (1) in  $\text{CF}_2\text{ClCFCl}_2$  with 75% (v/v) sulphuric acid gave a vigorous reaction with gas evolution (mass spectrometry indicated only nitrogen to have been evolved). Isolation of the single product by distillation yielded a clear oil.  $^{19}\text{F}$  N.m.r. spectroscopy showed the presence of the familiar  $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{C}$  pattern and the  $^1\text{H}$  spectrum showed a single sharp peak at  $\delta$  4.88. The mass spectrum showed a peak at  $m/z$  443 corresponding to  $M - \text{C}_6\text{F}_{13}$  with satellite peaks for the sulphur isotopes. Elemental analysis confirmed the compound as bis(2-pentafluoroethyl-3,3,4,4,4-pentafluoro-2-trifluoromethylbutyl) sulphate (12). We were unable to hydrolyse this material to the corresponding alcohol (3), probably due to its seemingly total immiscibility with aqueous media. This would have been followed by decomposition of any alcohol (3) so formed under strongly basic conditions, *e.g.* NaOMe in methanol, to the mixture of compounds (5) and (6) previously obtained.

Reactions of the diazoalkane (1) with ethanol and methanol in the presence of  $\text{Cu}^{2+}$  ions followed a very similar pathway. In the methanol reaction three products were formed which could be separated by preparative g.l.c. The first component isolated was shown by  $^{19}\text{F}$  n.m.r. spectroscopy to contain the  $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{C}$  group, a  $\text{CF}_3$  group, and a single olefinic fluorine atom. The  $^1\text{H}$  n.m.r. spectrum showed a single resonance in the olefinic region split to a doublet ( $J$  33 Hz). The mass spectrum gave a breakdown pattern characteristic of a  $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{C}$  containing compound. The i.r. spectrum showed a strong band at  $1730\text{ cm}^{-1}$  from a  $\text{C}=\text{C}$  system.

These data suggest the product is (*Z*)-3*H*-perfluoro-4-ethyl-4-methylhex-2-ene (13) the same product obtained on reaction with acetic acid. The *Z*-stereochemistry was assigned on the basis of the H-F coupling constant,  $J_{\text{H,F}}$  33 Hz.<sup>11</sup> The second component isolated was shown by  $^{19}\text{F}$  n.m.r. spectroscopy to contain a  $\text{C}_2\text{F}_5$  and a  $\text{CF}_3$  group both attached to a double bond. The  $^1\text{H}$  n.m.r. spectrum indicated an olefinic proton coupled to a  $\text{CF}_3$  group ( $J_{\text{H,CF}}$  *ca.* 0.5 Hz) and peaks characteristic of an  $\text{OCH}_3$  group. The mass spectrum and elemental

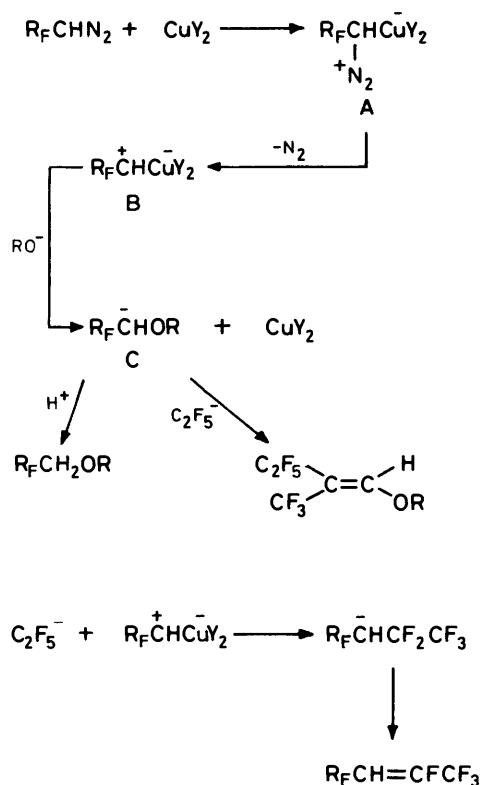
analysis suggested an empirical formula  $\text{C}_6\text{H}_4\text{F}_8\text{O}$ . Thus, the product is (*Z*)-methyl-3,3,4,4,4-pentafluoro-2-trifluoromethyl butenyl ether (10a). We assign the *Z*-stereochemistry on the basis of the H- $\text{CF}_3$  coupling constant of 2 Hz. In a similar experiment but using ethanol we obtained the corresponding *E* and *Z* ethyl esters (11a) and (11b) in the ratio *E:Z* 1:2 but none of the olefin (13) was isolated. These results are summarised in Scheme 1. Previous studies<sup>7</sup> have shown that  $\text{CF}_3\text{CHN}_2$



Scheme 1. Reagents: i,  $\text{CF}_3\text{CO}_2\text{H}$ ; ii,  $\text{NaHCO}_3$ ; iii,  $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$ ; iv,  $\text{Me}_2\text{SO}$  or  $\text{KOH}$ ; v,  $\text{CH}_3\text{CO}_2\text{H}$ ; vi,  $\text{CH}_2\text{ClCO}_2\text{H}$ ; vii,  $\text{CH}_3\text{OH}/\text{Cu}^{2+}$ ; viii,  $\text{C}_2\text{H}_5\text{OH}/\text{Cu}^{2+}$ ; ix,  $\text{H}_2\text{SO}_4$ ; x,  $\text{CH}_3\text{COCH}_3$

forms oxiranes on reaction with carbonyl compounds. We thus attempted a reaction with acetone and the diazoalkane (1) at room temperature in the presence of  $\text{Cu}^{2+}$  ions. No reaction occurred, but on heating the mixture to reflux, nitrogen was evolved to give a clear colourless solution. However, the only isolable product was the olefin (13) with no incorporation of acetone. In a series of reactions of the diazoalkane (1) using inert solvents, hexane, diethyl ether, and acetonitrile no observable decomposition took place in the presence or absence of  $\text{Cu}^{2+}$  ions below  $60^\circ\text{C}$ . These results clearly present some mechanistic problems. In the light of the much increased rate of reaction in the presence of  $\text{Cu}^{2+}$  ions, it seems likely that copper is involved in the decomposition; further, the lack of decomposition in inert (non-protic) solvents suggests attack by the solvent, its conjugate base, or by protons. Further, the acidity of the solvent seems to play a part in determining the nature of the products.

Of the possible mechanistic schemes proposed for  $\text{Cu}^{2+}$ -catalysed decomposition of diazoalkanes summarised in Patai's



review,<sup>4</sup> we favour that of Yates<sup>12</sup> involving the intermediacy of copper carbenoid species. We suggest the reaction follows the pathway outlined in Scheme 2. Firstly, the diazoalkane coordinates *via* the  $\alpha$ -carbon atom to the copper to give complex A which, by loss of nitrogen, affords the carbenoid B. Attack of B by the nucleophile ( $RO^-$ ;  $R = CH_3CO, CF_3CO, CH_2ClCO, HSO_3, Me, Et$ ) yields the anionic species C and the copper(II) salt. The anion C may now react in two ways depending on the acidity of the medium. In strongly acidic media protonation is fast compared to the alternative pathway, loss of  $C_2F_5^-$  (either directly or by loss of  $F^-$  and  $C_2F_4$ ). Thus trifluoroacetic acid and sulphuric acid follow the former route, chloroacetic acid, a mixture of both routes, whilst acetic acid, ethanol, and methanol follow the latter pathway. In acetone and to a small extent in other solvents, the carbenoid B seemingly can be captured by  $C_2F_5^-$  to give the observed product, although we cannot at this stage discount an alternative pathway involving rearrangement processes.

Thus, the diazobutane shows some remarkable and unexpected reactions and further work is continuing on the chemistry of this fascinating compound.

**Experimental**

**3,3,4,4,4-Pentafluoro-2-pentafluoroethyl-2-trifluoromethyl-butyl Trifluoroacetate (2).**—Method (a). Trifluoroacetic acid (22.3 g) was slowly added to a diazobutane (1) (36 g) in 1,2,2-trichlorotrifluoroethane (Freon 113) (20 cm<sup>3</sup>). The mixture was heated under reflux for 24 h, when the yellow colour had disappeared. The mixture was washed with water (5 × 20 cm<sup>3</sup>), dried ( $MgSO_4$ ), and evaporated to afford, on distillation, the *title compound* (2) (22.7 g), b.p. 137 °C (Found: C, 23.7; H, 0.5; F, 68.5.  $C_9H_2F_{16}O_2$  requires C, 24.2; H, 0.5; F, 68.2%);  $\nu_{max}$  1 805 cm<sup>-1</sup> (C=O);  $\delta_H$  5.01 (s,  $CH_2$ );  $m/z$  427 ( $M - F^+$ ), 377 ( $M - CF_3^+$ ), and 333 ( $M - CO_2CF_3^+$ ).

*Method (b).* Although there was no reaction on addition of trifluoroacetic acid (2.0 cm<sup>3</sup>) to the diazobutane (1) (5.0 g) at 18 °C, addition of a crystal of copper(II) perchlorate induced a vigorous reaction. After 5 min when the yellow colour of the diazoalkane had been discharged and gas evolution had ceased, the reaction mixture was washed with water (2 × 10 cm<sup>3</sup>), dried ( $MgSO_4$ ), and distilled to yield the ester (6) (3.6 g, 88%).

**3,3,4,4,4-Pentafluoro-2-pentafluoroethyl-2-trifluoromethylbutanol.**—A mixture of the ester (2) (22.3 g), sodium hydrogen carbonate (8.4 g), and water (50 cm<sup>3</sup>) was stirred at 18 °C for 48 h. The fluorocarbon layer and the ether extracts (5 × 10 cm<sup>3</sup>) of the aqueous layer were combined, dried ( $MgSO_4$ ), and distilled to yield the *title compound* (3) (8.8 g), b.p. 135 °C (Found: C, 23.9; H, 0.9; F, 70.9.  $C_7H_3F_{13}O$  requires C, 24.0; H, 0.9; F, 70.6%);  $m/z$  281 ( $M - CF_3^+$ ) and 231 ( $M - C_2F_5^+$ ).

**3,3,4,4,4-Pentafluoro-2-pentafluoroethyl-2-trifluoromethylbutanal (4).**—The alcohol (3) (7.5 g) in Freon 113 was added to a stirred mixture of chromium(VI) oxide (15 g) in water (24 cm<sup>3</sup>) and 98% sulphuric acid (14 cm<sup>3</sup>). The mixture was heated at reflux for 5 h and then cooled and poured into water (50 cm<sup>3</sup>). The lower fluorocarbon layer was separated, the solvent removed, and the residue distilled to give the *title compound* (4) (5.3 g), b.p. 83 °C (Found: C, 24.0; H, 0.5; F, 70.9.  $C_7HF_{13}O$  requires C, 24.1; H, 0.3; F, 71.0%);  $\nu_{max}$  1 760 cm<sup>-1</sup> (C=O);  $\delta_H$  9.7 (s, CH);  $m/z$  347 ( $M - H^+$ ), 329 ( $M - F^+$ ), and 281 ( $M - CHO^+$ ).

*Reaction of the Alcohol (7) with Me<sub>2</sub>SO.*—The alcohol (7) (10 g) was heated at 140 °C for 1 h in dry  $Me_2SO$  (40 cm<sup>3</sup>) using a solid  $CO_2$ -acetone condenser. The condenser was then removed and any volatile material was distilled from the reaction mixture into a liquid-air cooled trap. The distillate (5.02 g) was separated by preparative-scale gas chromatography to give perfluoro-3-methylpent-2-ene (5) (1.6 g), b.p. 53 °C identical to an authentic sample<sup>2</sup> and 3*H*-3-trifluoromethyl-decafluoropentane (6) (3.0 g), b.p. 52 °C identical to an authentic sample.<sup>2</sup>

*Reaction of Diazobutane (1) with Acetic Acid.*—The diazobutane (1) (5 g) and acetic acid (2.0 g) were mixed at 18 °C and a crystal of copper(II) perchlorate was added. The mixture was slowly warmed to 50 °C when a vigorous reaction occurred with evolution of nitrogen to give, after 5 min, a clear colourless solution (4.5 g). Analytical g.l.c. showed the presence of three major components two of which were barely separated on several g.l.c. columns. Separation of a portion (3 g) of the product afforded (i) 3*H*-perfluoro-4-ethyl-4-methylhex-2-ene (13) (0.2 g) (see below); (ii) an *E:Z* mixture of 3,3,4,4,4-pentafluoro-2-trifluoromethylbut-2-enyl acetate (17) (0.95 g), b.p. 159—160 °C (isomer ratio 1:3) (Found: C, 30.1; H, 1.5.  $C_7H_4F_8O_2$  requires C, 30.8; H, 1.5%);  $\nu_{max}$  1 800 cm<sup>-1</sup> (C=O) and 1 670 cm<sup>-1</sup> (C=C);  $\delta$  1.9 (3 H, s,  $CH_3CO$ ) and 7.80 (1 H, c, CH=C);  $\delta_F$  (rel.  $CCl_3F$ ) 60.4 (3 F, cq,  $J_{CF,H}$  2 Hz,  $CF_3C=$ ), 87.4 (3 F, c,  $CF_3CF_2$ ), and 113.5 (2 F, q,  $J_{FF}$  10 Hz,  $CF_3CF_2$ ); for the *Z* isomer  $\delta_H$  1.90 (3 H, s,  $CH_3CO$ ) and 7.95 (q,  $J_{HCF}$  2 Hz,  $H=C$ ). <sup>19</sup>F N.m.r. 63.5 (3 F, c,  $CF_3C=$ ), 87.4 (3 F, c,  $CF_3CF_2$ ), and 115.3 (2 F, q,  $J_{AB}$  11 Hz,  $CF_3CF_2$ ); for the *E* isomer  $m/z$  272, 253 ( $M - F^+$ ), 203 ( $M - CF_3^+$ ), and 194 ( $M - F - CH_3CO_2$ ).

*Reaction of Diazobutane (1) with Chloroacetic Acid.*—In a similar experiment to the above, the diazobutane (4.3 g) and chloroacetic acid (1.1 g) in ether (20 cm<sup>3</sup>) were treated with a crystal of copper(II) perchlorate to give slow evolution of nitrogen and, after 15 min, a colourless solution. The mixture was washed with 10% aqueous sodium hydrogen carbonate and water, dried ( $MgSO_4$ ), and evaporated to leave a colourless oil,

which on distillation afforded a fraction (2.0 g), b.p. 62–64 °C (15 mmHg). Analytical g.l.c. showed a broad unresolved peak;  $\nu_{\max}$ . 1785 (C=O) and 1680  $\text{cm}^{-1}$  (C=C);  $^1\text{H}$  and  $^{19}\text{F}$  n.m.r. spectroscopy showed the product to be a mixture of 3,3,4,4,4-pentafluoro-2-pentafluoroethyl-2-trifluoromethylbutyl chloroacetate (**8**) and 2,3,4,4,4-pentafluoro-2-trifluoromethylbutenyl chloroacetate (**9**);  $\delta_{\text{H}}$  for (**9**) 4.02 (2 H, s,  $\text{ClCH}_2\text{C}$ ) and 4.82 [2 H, s,  $(\text{C}_2\text{F}_5)_2\text{CF}_3\text{CCH}_2$ ] and for (**8**) 4.05 (2 H, s,  $\text{ClCH}_2\text{C}$ ) and 7.4–7.8 (1 H, br s, HC=);  $\delta_{\text{F}}$ (rel.,  $\text{CCl}_3\text{F}$ ) for (**8**) 61.6 (3 F, c,  $\text{CF}_3\text{C}$ ), 78.9 [6 F, c,  $(\text{CF}_3\text{CF}_2) \times 2$ ], 109.4 [F, c,  $(\text{CF}_3\text{CF}_2) \times 2$ ] and for (**9**) 60.2 (3 F, s,  $\text{CF}_3\text{C}=\text{C}$ ), 79.7 (3 F, c,  $\text{CF}_3\text{CF}_2$ ), and 109.3 (2 F, c,  $\text{CF}_3\text{CF}_2$ ).

**Reaction of Diazobutane (1) with Sulphuric Acid.**—Sulphuric acid (75%, v/v; 3  $\text{cm}^3$ ) was added dropwise to a stirred solution of the diazobutane (**1**) (5 g) in Freon 113 (5  $\text{cm}^3$ ) at 18 °C to give slow evolution of nitrogen. The mixture was stirred for 1 h after the addition was complete by which time it had become colourless. Water (10  $\text{cm}^3$ ) was added and the lower fluorocarbon layer separated, washed with water (10  $\text{cm}^3$ ) and 10% aqueous sodium hydrogen carbonate (2  $\times$  10  $\text{cm}^3$ ), dried, and distilled to leave an oily residue. Distillation under reduced pressure afforded 3,3,4,4,4-pentafluoro-bis(2-pentafluoroethyl-2-trifluoromethylbutyl) sulphate (**12**) (2.4 g), b.p. 78–80 °C/0.5 mmHg (Found: C, 22.2; H, 0.5; F, 65.2.  $\text{C}_{17}\text{H}_4\text{F}_{26}\text{O}_4\text{S}$  requires C, 22.0; H, 0.5; F, 64.8%);  $m/z$  443 ( $M - \text{C}_6\text{F}_{13}$ )<sup>+</sup>, 413 ( $M - \text{C}_7\text{F}_{13}\text{H}_2\text{O}$ ), and 349 ( $\text{C}_7\text{H}_2\text{F}_{13}\text{O}$ );  $\delta_{\text{H}}$  4.85 (sh s,  $\text{CH}_2$ ). The  $^{19}\text{F}$  n.m.r. was characteristic of the  $(\text{C}_2\text{F}_5)_2\text{CF}_3\text{C}$  group.

**Reaction of Diazobutane (1) with Methanol/Cu<sup>2+</sup>.**—The diazobutane (**1**) (5 g) was added dropwise to methanol (5  $\text{cm}^3$ ) containing a crystal of copper(II) perchlorate to give a vigorous reaction with evolution of nitrogen. After 5 min the solution was colourless but it was left for a further 30 min after which it was washed with water (2  $\times$  15  $\text{cm}^3$ ) and dried ( $\text{MgSO}_4$ ) to yield a clear liquid (4.8 g). Separation of a sample by g.l.c. afforded the following compounds. (i) (Z)-3H-Perfluoro-4-ethyl-4-methylhex-2-ene (**13**) (0.53 g), b.p. 138–140 °C (Found: C, 25; H, 0.2.  $\text{C}_9\text{HF}_{17}$  requires C, 25.0; H, 0.2%);  $\nu_{\max}$ . 1730  $\text{cm}^{-1}$  (C=C);  $\delta_{\text{H}}$  5.35 (d,  $J_{\text{HF}}$  33 Hz);  $\delta_{\text{F}}$ (rel.  $\text{CCl}_3\text{F}$ ) 63.4 (3 F, c,  $\text{CF}_3$ ), 77.3 (3 F, c,  $\text{CF}_3\text{-C}=\text{C}$ ), 82.8 [6 F, c,  $(\text{CF}_3\text{CF}_2)_2$ ], and 113.6 [5 F, c,  $\text{CF}(\text{CF}_2\text{-Cl}_3)_2$ ];  $m/z$  432 ( $M$ )<sup>+</sup>, 413 ( $M - \text{F}$ )<sup>+</sup>, and 363 ( $M - \text{CF}_3$ )<sup>+</sup>.

(ii) (Z)-Methyl 3,3,4,4,4-pentafluoro-2-trifluoromethylbutenyl Ether (**10a**) (0.7 g), b.p. 142 °C (Found: C, 29.6; H, 1.4.  $\text{C}_6\text{H}_4\text{F}_8\text{O}$  requires C, 29.5; H, 1.6%);  $\nu_{\max}$ . 1670  $\text{cm}^{-1}$  (C=C);  $\delta_{\text{H}}$  3.6 (3 H, s,  $\text{CH}_3\text{O}$ ) and 6.78 (1 H, c, C=CH);  $\delta_{\text{F}}$ (rel.  $\text{CCl}_3\text{F}$ ) 59.4 ( $\text{CF}_3\text{C}=\text{C}$ ), 87.4 (3 F, c,  $\text{CF}_3\text{CF}_2$ ), and 112.5 (q,  $J_{\text{CF}}$  11 Hz,  $\text{CF}_3\text{CF}_2$ );  $m/z$  244 ( $M$ )<sup>+</sup>, 223 ( $M - \text{F}$ )<sup>+</sup>, and 175 ( $M - \text{CF}_3$ )<sup>+</sup>.

(iii) (E)-Methyl 3,3,4,4,4-pentafluoro-2-trifluoromethylbutenyl Ether (**10b**) (0.4 g), b.p. 142 °C;  $\delta_{\text{H}}$  3.68 (3 H, s,  $\text{CH}_3\text{O}$ ) and 6.9 (1 H, c, CH=);  $\delta_{\text{F}}$ (rel.  $\text{CCl}_3\text{F}$ ) 62.9 (3 F, c,  $\text{CF}_3\text{C}=\text{C}$ ), 87.2 (3 F, c,  $\text{CF}_3\text{CF}_2$ ), and 114.4 (2 F, q,  $J$  10 Hz,  $\text{CF}_3\text{CF}_2$ ).

**Reaction of the Diazobutane (1) with Ethanol/Cu<sup>2+</sup>.**—In a similar experiment to the above, the diazobutane (**1**) with

ethanol and copper(II) perchlorate afforded a mixture (4.6 g) of two products. G.l.c. separation of a sample (2.5 g) of this afforded (i) (Z)-ethyl 3,3,4,4,4-pentafluoro-2-trifluoromethylbutenyl ether (**11a**) (0.8 g) and a mixture of (**11a**) and (**11b**) b.p. 136–138 °C (Found: C, 32.3; H, 2.2.  $\text{C}_7\text{H}_6\text{F}_8\text{O}$  requires C, 32.6; H, 2.3%);  $\nu_{\max}$ . 1670  $\text{cm}^{-1}$  (C=C);  $\delta_{\text{H}}$  1.08 (3 H, t,  $\text{CH}_3\text{CH}_2$ ), 3.8 (2 H, q,  $\text{CH}_3\text{CH}_2$ ), and 6.75 (1 H, c, HC=);  $\delta_{\text{F}}$ (rel.  $\text{CCl}_3\text{F}$ ) 59.4 (3 F, c,  $\text{CF}_3\text{C}=\text{C}$ ), 87.5 (3 F, c,  $\text{CF}_3\text{CF}_2$ ), and 112.5 (q,  $J$  11 Hz,  $\text{CF}_3\text{CF}_2$ ); (ii) (E)-ethyl 3,3,4,4,4-pentafluoro-2-trifluoro-2-methylbutenyl ether (**11b**) (0.4 g), b.p. 138 °C;  $\delta_{\text{H}}$  1.08 (3 H, t,  $\text{CH}_3\text{CH}_2$ ), 3.8 (2 H, q,  $\text{CH}_3\text{CH}_2$ ), and 6.75 (1 H, complex quartet, HC=C);  $\delta_{\text{F}}$ (rel.  $\text{CCl}_3\text{F}$ ) 62.9 (3 F, c,  $\text{CF}_3\text{C}=\text{C}$ ), 87.2 (3 F, c,  $\text{CF}_3\text{CF}_2$ ), and 114.4 (2 F, q,  $J$  11 Hz,  $\text{CF}_3\text{CF}_2$ ).

**Decomposition of the Diazobutane (1) in Acetone.**—The diazobutane (**1**) (2.5 g) in acetone (10  $\text{cm}^3$ ) and a crystal of copper(II) perchlorate was slowly heated to 60 °C to give evolution of nitrogen. After 2 h at 60 °C the solution had become colourless. Analytical g.l.c. showed the presence of a major component with a small amount of impurity. Separation of a portion (2 g) of the final product afforded (i) a mixture of very volatile material which could not be identified (0.28 g) and (ii) (Z)-3H-perfluoro-4-ethyl-4-methylhex-2-ene (**13**) (0.9 g) identical with a sample obtained from the reaction of compound (**1**) with methanol.

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