

Reactions of Perfluoroalkylcopper Compounds. Part V.¹ The Preparation of Some Polyfluoroalkyl-substituted Acids and Alcohols

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Reaction of perfluoroheptylcopper(I) with (*E*)-1,2-di-iodoethylene gave (*E*)-1*H*,2*H*-1-iodopentadecafluoronon-1-ene (I) which with copper(I) cyanide in dimethylformamide yielded (*E*)-1*H*,2*H*-1-cyanopentadecafluoronon-1-ene (II). Hydrolysis of (II) with sulphuric acid under vigorous conditions afforded (*E*)-2*H*,3*H*-pentadecafluorodec-2-enoic acid (III) which was readily hydrogenated to 2*H*,2*H*,3*H*,3*H*-pentadecafluorodecanoic acid (IV). Reduction of (IV) with lithium aluminium hydride afforded 1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-pentadecafluorodecanol (V). Mild hydrolysis of the nitrile (II) gave (*E*)-2*H*,3*H*-pentadecafluorodec-2-enamide (VI). Reaction of 1,3-di-iodohexafluoropropane with copper bronze and an excess of (*E*)-1,2-di-iodoethylene similarly afforded (1*E*,6*E*)-3,3,4,4,5,5-hexafluoro-1,7-di-iodohepta-1,6-diene (VII) and (1*E*,6*E*,11*E*)-3,3,4,4,5,5,8,8,9,9,10,10-dodecafluoro-1,12-di-iodododeca-1,6,11-triene (VIII). Treatment of (VII) with copper(I) cyanide and hydrolysis of the resulting dinitrile gave (2*E*,7*E*)-4,4,5,5,6,6-hexafluoronona-2,7-diene-1,9-dioic acid (IX). Hydrogenation of (IX) gave 4,4,5,5,6,6-hexafluorononane-1,9-dioic acid (X). Reaction of (*E*)-1,2-di-iodoethylene with copper(I) cyanide gave (*E*)-2-iodoacrylonitrile.

In previous Parts we have described the reactions of perfluoroalkylcopper compounds with halogeno-olefins,² olefins,³ aromatic compounds,⁴ acetylenes,¹ and halogeno-acetylenes,¹ illustrating the scope of the reactions of various copper species. We now report the use of polyfluoroalkylcopper compounds in the synthesis of some compounds of current practical interest as surfactants and which have not yet been made by classical procedures.

The preparation of polyfluoroalkyl derivatives of acids and esters has been extensively studied by Brace⁵ who used the free radical addition of perfluoroalkyl iodides to olefinic acids followed by the reductive dehalogenation of the resulting iodopolyfluoroalkyl derivatives. These reactions were satisfactory for the preparation of many polyfluoroalkyl acids and esters with the notable exception of compounds derived from acrylic acid and its esters. It was found that polymerisation of these derivatives occurred and only small amounts of the 1 : 1 adducts were obtained. We have now devised a route to these compounds based on reactions of halogeno-olefins with polyfluoroalkyl compounds.

Previously² we have shown that (*E*)-1,2-di-iodoethylene reacted with polyfluoroalkylcopper compound to give bis(polyfluoroalkyl)ethylenes and it was felt that by careful control of the reaction conditions it should be possible to prepare the monosubstituted compound. It was found that use of a large excess of the iodo-olefin and generation of the copper compound *in situ* resulted in a smooth reaction giving a mixture of the desired olefin and unchanged di-iodoethylene. This latter could be readily removed by cooling an ether solution of the mixture since the di-iodo-compound is only sparingly soluble in cold ether. Distillation of the residue afforded the desired compound.

Thus, by this method, (*E*)-1*H*,2*H*-1-iodopentadecafluoronon-1-ene (I) was prepared from perfluoroheptyl iodide. The structure of (I) was confirmed by mass

spectrometry and elemental analysis and the stereochemistry about the double bond confirmed by ¹H n.m.r. spectroscopy showing the expected H-H coupling across the double bond. Reaction of (I) with copper(I) cyanide in dimethylformamide gave the olefinic nitrile (II) in good yield. Although there are some reports of this type of reaction in the literature⁶ they are rather sparse, and until a brief report by Newman⁷ of the preparation of cinnamonitrile using *N*-methyl-2-pyrrolidone, they have been carried out without solvents and the yields were low. We have found that the reactions under the conditions described gave good yields. On the basis of the ¹H n.m.r. spectra as stated above the stereochemistry of the products is the same as that of the starting olefin, *i.e.* *E*. This is in keeping with the idea of the reaction proceeding through co-ordination of the halogen with the copper as previously suggested² and seems to exclude an addition-elimination type reaction when a non-stereospecific product mixture would have been expected.

The nitrile (II) was readily hydrolysed to the corresponding acid (III) by 60% sulphuric acid at 130° and to the amide (VI) by more gentle conditions, 60–70° for 10 min. Hydrogenation of (III) over palladium on carbon at atmospheric pressure afforded the saturated acid (IV) which in turn was readily reduced to the alcohol (V) by lithium aluminium hydride.

The formation of difunctional compounds by the free radical route is much more difficult and there are few reports of successful reactions of this kind. However, using our procedure, we have found that the dicopper derivatives from 1,3-di-iodohexafluoropropane reacted with (*E*)-1,2-di-iodoethylene to yield mainly (1*E*,6*E*)-3,3,4,4,5,5-hexafluoro-1,7-di-iodohepta-1,6-diene (VII) and some (1*E*,6*E*,11*E*)-3,3,4,4,5,5,8,8,9,9,10,10-dodecafluoro-1,12-di-iodododeca-1,6,11-triene (VIII) identified by spectroscopic and analytical means, the stereo-

¹ Part IV, P. L. Coe and N. E. Milner, *J. Organometallic Chem.*, in the press.

² J. Burdon, P. L. Coe, C. R. Marsh, and J. C. Tatlow, *J.C.S. Perkin I*, 1972, 639.

³ P. L. Coe and N. E. Milner, *J. Organometallic Chem.*, 1972, 39, 395.

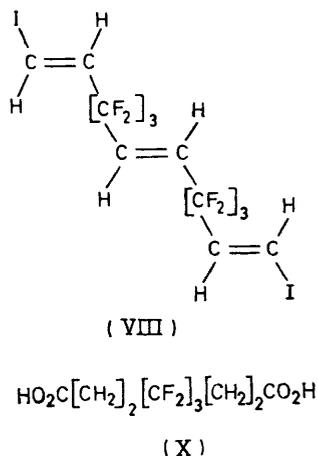
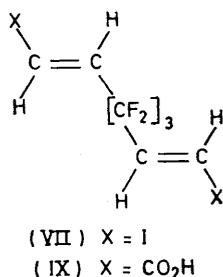
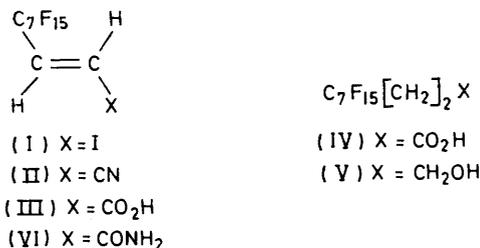
⁴ P. L. Coe and N. E. Milner, *J. Fluorine Chem.*, 1972–1973, 2, 167.

⁵ N. O. Brace, *J. Amer. Chem. Soc.*, 1962, 84, 3020.

⁶ (a) C. F. Koelsch, *J. Amer. Chem. Soc.*, 1936, 58, 1328; (b) W. Gaade, *Rec. Trav. chim.*, 1946, 65, 823; (c) J. Jenners, *Bull. Classe Sci. Acad. Roy. belge*, 1936, 22, 1169.

⁷ H. Boden and M. S. Newman, *J. Org. Chem.*, 1969, 26, 2525.

chemistry of the double bonds being assigned as *E* in view of the coupling between the olefinic hydrogens in the ^1H n.m.r. spectrum. Reaction of (VII) with copper(I) cyanide followed by hydrolysis of the resulting nitrile yielded (2*E*,7*E*)-4,4,5,5,6,6-hexafluoronona-2,7-diene-1,9-dioic acid (IX) as a monohydrate. It was found difficult



to remove completely the last traces of water from this compound, in common with many other fluorinated acids. Hydrogenation of (IX) gave 4,4,5,5,6,6-hexafluoronona-1,9-dioic acid (X).

In an attempt to improve the process, (*E*)-2-iodoacrylonitrile was prepared by reaction of (*E*)-1,2-diiodoethylene with one mol. equiv. of copper(I) cyanide. Previously reaction of this ethylene has been shown to give maleonitrile.^{6c} Reaction of the iodoacrylonitrile with perfluoroalkylcopper compounds however, gave only muconitrile in good yield.

EXPERIMENTAL

(*E*)-1*H*,2*H*-1-Iodopentadecafluoronon-1-ene.— Perfluoroheptyl iodide (50 g), activated copper (15.0 g), and (*E*)-1,2-

di-iodoethylene (56 g) in dimethylformamide (80 cm³) were heated together at 120° for 56 h. The cooled mixture was poured into ether (500 cm³), and the ether decanted from the precipitated solid and combined with the ethereal washings of the solid residue. The combined ether layers were washed with water (3 × 200 cm³), dried (MgSO₄), and distilled to yield a semi-solid (44.3 g). The mixture was cooled in a refrigerator when the excess of di-iodoethylene crystallised out, and filtration under suction yielded after distillation *in vacuo* (*E*)-1*H*,2*H*-1-iodopentadecafluoronon-1-ene (16.7 g), b.p. 182–183° (Found: C, 20.6; H, 0.6; F, 54.4. C₉H₂F₁₅I requires C, 20.7; H, 0.4; F, 54.7%).

(*E*)-1*H*,2*H*-1-Cyanopentadecafluoronon-1-ene.— (*E*)-1*H*,2*H*-1-iodopentadecafluoronon-1-ene (52 g) and copper(I) cyanide (10 g) in dimethylformamide (80 cm³) were stirred at 110° under nitrogen for 15 h. The cooled mixture was added to ether (500 cm³), the ether decanted, and the residue washed with more ether (2 × 100 cm³). The combined ether layers were washed with water (3 × 200 cm³) and dried (MgSO₄), and the ether was distilled off to yield, after distillation *in vacuo*, (*E*)-1*H*,2*H*-1-cyanopentadecafluoronon-1-ene (38 g), b.p. 192° (Found: C, 28.9; H, 0.7; F, 67.2; N, 3.7. C₈H₂F₁₅N requires C, 28.5; H, 0.5; F, 67.7; N, 3.3%).

(*E*)-2*H*,3*H*-Pentadecafluorodec-2-enoic Acid.—(*E*)-1*H*,2*H*-1-Cyanopentadecafluoronon-1-ene (42 g) was slowly added to 60% (v/v) sulphuric acid (400 cm³). The mixture was heated at 120° for 15 h, cooled, and poured into water (500 cm³). The dark brown aqueous layer was extracted with ether (3 × 100 cm³) and the combined ether layers were dried (MgSO₄), decolourised with charcoal, and distilled to yield (*E*)-2*H*,3*H*-pentadecafluorodec-2-enoic acid (39 g), m.p. 94–95° [from light petroleum (b.p. 60–80°)] (Found: C, 27.0; H, 1.0; F, 65.0. C₈H₃F₁₅O₂ requires C, 27.3; H, 0.7; F, 64.8%).

2*H*,2*H*,3*H*,3*H*-Pentadecafluorodecanoic Acid.—(*E*)-2*H*,3*H*-Pentadecafluorodec-2-enoic acid (22 g) in ethanol (100 cm³) and 10% palladium on carbon (0.5 g) were shaken together under hydrogen for 15 h; the required amount of hydrogen had then been absorbed. Ether (500 cm³) was added, the catalyst filtered off, and the ether layer washed with water (3 × 200 cm³), dried (MgSO₄), and distilled to yield 2*H*,2*H*,3*H*,3*H*-pentadecafluorodecanoic acid (21 g), m.p. 85° [from light petroleum (b.p. 80–100°)] (Found: C, 27.5; H, 1.2; F, 64.2. C₈H₃F₁₅O₂ requires C, 27.2; H, 1.1; F, 64.5%).

(*E*)-2*H*,3*H*-Pentadecafluorodec-2-enamide.—(*E*)-1*H*,2*H*-1-Cyanopentadecafluoronon-1-ene (25 g) was heated and stirred at 60–70° for 10 min with concentrated sulphuric acid (100 cm³). The mixture was poured into ice-water (500 cm³) and the aqueous layer extracted with ether (3 × 100 cm³). The combined, dried (MgSO₄) ether layers were distilled to give (*E*)-2*H*,3*H*-pentadecafluorodec-2-enamide (24 g), m.p. 114–115° (from ethanol) (Found: C, 27.3; H, 1.3; F, 65.3; N, 3.1. C₈H₄F₁₅NO requires C, 27.4; H, 0.9; F, 64.9; N, 3.2%).

1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-Pentadecafluorodecanol.— 2*H*,2*H*,3*H*,3*H*-Pentadecafluorodecanoic acid (22 g) in dry ether (50 cm³) was slowly added to a stirred suspension of lithium aluminium hydride (1.9 g) in dry ether (50 cm³) at 18°. When the addition was complete (1 h) the mixture was stirred for 15 h at 18°. Ethanol (20 cm³) was carefully added and then the mixture was poured into 25% v/v sulphuric acid (500 cm³). The ether layer and the combined,

dried (MgSO_4) extracts of the aqueous layer were distilled to leave a low melting solid (20 g). Purification by sublimation at 110° and 11 mmHg gave 1H,1H,2H,2H,3H,3H-pentadecafluorodecanol (183 g), m.p. 19° , b.p. $211\text{--}212^\circ$ (Found: C, 27.8; H, 1.9; F, 66.2. $\text{C}_8\text{H}_5\text{F}_{15}\text{O}$ requires C, 28.0; H, 1.6; F, 66.5%).

Reaction of 1,3-Di-iodohexafluoropropane with a Large Excess of (E)-1,2-Di-iodoethane and Activated Copper Bronze.—1,3-Di-iodohexafluoropropane (6 g), (E)-1,2-di-iodoethylene (10 g), activated copper bronze (6 g), and dry dimethylformamide (20 cm^3) were stirred together for 18 h under nitrogen at 110° . The mixture was allowed to cool and then added to ether (250 cm^3). The suspension was filtered and the precipitate washed with ether ($2 \times 50 \text{ cm}^3$). The combined ether extracts were washed with water ($3 \times 100 \text{ cm}^3$) and dried (MgSO_4), and the ether was removed under reduced pressure to give a pale brown solid (4.4 g). Separation of a small amount (2.0 g) of this material (dissolved in ether) by g.l.c. [Silicone gum (SE 30)–Univ B (1:9); N_2 , 4.51 h^{-1} ; 130°] gave (a) ether, identified by i.r. spectroscopy; (b) (E)-1,2-di-iodoethylene (0.4 g), identified by i.r. spectroscopy; and (c) (1E,6E)-1,7-di-iodo-3,3,4,4,5,5-hexafluorohepta-1,6-diene (1.3 g), m.p. $42\text{--}43^\circ$ (Found: C, 18.6; H, 0.8; F, 25.1; I, 55.9. $\text{C}_7\text{H}_4\text{F}_6\text{I}_2$ requires C, 18.5; H, 0.88; F, 25.1; I, 55.7%), m/e 202 ($M - \text{I}_2$)⁺, ν_{max} 3070 (=C–H stretch) and 1610 cm^{-1} (C=C stretch), ^1H n.m.r. τ 2.7 and 3.5 (AB, J_{AB} 15 Hz), ^{19}F n.m.r. (CCl_3F) 111.5 (2F, t, J 4 Hz) and 125.5 p.p.m. (1F, s); (d) (1E,6E,11E)-1,12-di-iodo-3,3,4,4,5,5,8,8,9,9,10,10-dodecafluorododeca-1,6-11-triene (0.3 g), m.p. 79° (Found: C, 23.1; H, 0.95; F, 36.1; I, 39.9. $\text{C}_{12}\text{H}_6\text{F}_{12}\text{I}_2$ requires C, 22.8; H, 1.0; F, 36.0; I, 40.2%), ^1H n.m.r. τ [(CD_3)₂CO] 2.65 and 3.5 (4H, AB, J_{AB} 15 Hz, $2 \times \text{--CH=CHI}$) and 3.25 (2H, t, J_{HF} 11 Hz, CCH=CHC), ^{19}F n.m.r. 111.3 (q, J_{HF} 11.5 Hz), 113.4 (m), and 125.9 p.p.m. (s), ν_{max} 3090 and 3060 (=C–H stretch) and 1620 and 1605 cm^{-1} (C=C stretch).

Reaction of (1E,6E)-1,7-Di-iodo-3,3,4,4,5,5-hexafluorohepta-1,6-diene with Copper(I) Cyanide.—(1E,6E)-1,7-Di-iodo-3,3,4,4,5,5-hexafluorohepta-1,6-diene (2 g), copper(I) cyanide (2 g) and dry dimethylformamide (15 cm^3) were stirred together under nitrogen at 100° for 17 h. The mixture was allowed to cool and then poured into ether (200 cm^3) and filtered. The precipitate was washed with ether ($2 \times 50 \text{ cm}^3$), the combined ether extracts were washed with water ($3 \times 100 \text{ cm}^3$) and dried (MgSO_4), and the ether was removed under reduced pressure to give a pale yellow solid (1.0 g), ν_{max} 3080 (=C–H stretch), 2220 (C=N stretch), and 1645 cm^{-1} (C=C stretch). This material was not further purified.

Hydrolysis of Crude Cyanide.—The crude cyanide obtained above (0.8 g) and 60% v/v sulphuric acid (50 cm^3) were stirred together for 20 h at 130° . The mixture was allowed to cool and poured onto crushed ice and the volume made up to 250 cm^3 with distilled water. This solution was extracted with ether ($3 \times 100 \text{ cm}^3$), the ethereal solution dried (MgSO_4), and the ether removed under reduced pressure to give crude yellow solid (0.9 g). This was taken up in ether and the solution decolourized with charcoal, filtered, and evaporated to give a white solid (0.85 g). This was recrystallised from n-hexane–benzene to give white crystals

of (1E,6E)-3,3,4,4,5,5-hexafluoronona-1,6-diene-1,9-dioic acid monohydrate (0.8 g), m.p. $172\text{--}173^\circ$ (Found: C, 34.8; H, 2.6; F, 36.7. $\text{C}_9\text{H}_8\text{F}_6\text{O}_5$ requires C, 34.9; H, 2.6; F, 36.8%), ν_{max} 1720–1710 cm^{-1} (C=O stretch), ^1H n.m.r. τ 5.5br and 2.0br, ^{19}F n.m.r. 126.6 and 148.5 (AB, J_{AB} 271 Hz $\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}$) and 132.2 (s, $\text{CHCF}_2\text{CF}_2\text{CF}_2\text{CH}$).

Hydrogenation of (1E,6E)-3,3,4,4,5,5-Hexafluoronona-1,6-diene-1,9-dioic Acid Monohydrate.—(1E,6E)-3,3,4,4,5,5-Hexafluoronona-1,6-diene-1,9-dioic acid monohydrate (1 g) was dissolved in ethanol (5 cm^3) and 10% palladium–charcoal catalyst (ca. 100 mg) was added. The flask was then shaken under hydrogen for 3 days; the required amount of hydrogen had then been absorbed. The solution was filtered, the residue was washed with ether (10 cm^3), and the solutions were combined. Solvent was removed under reduced pressure to leave a white solid (1 g). This was recrystallised from cyclohexane to give white crystals of 4,4,5,5,6,6-hexafluoronona-1,9-dioic acid monohydrate (0.9 g), m.p. $158\text{--}159^\circ$ (Found: C, 34.4; H, 3.8; F, 36.0. $\text{C}_9\text{H}_8\text{F}_{12}\text{O}_5$ requires C, 34.4; H, 3.85; F, 36.4%).

Reaction of 1,2-Di-iodoethylene with Copper(I) Cyanide.—(E)-1,2-Di-iodoethylene (10 g), copper(I) cyanide (3 g), and dry dimethylformamide (40 cm^3) were placed in a flask and stirred magnetically while the apparatus was flushed with nitrogen. The flask was then heated to 100° and maintained at this temperature for 24 h. The mixture was allowed to cool and added to ether (200 cm^3), the solution was filtered, and the precipitate was washed with ether ($2 \times 50 \text{ cm}^3$). The ether solution was then washed with water ($3 \times 100 \text{ cm}^3$) and dried (MgSO_4). The ether was removed by distillation through a 10 cm Vigreux column leaving a dark yellow crystalline mass (3 g). These crystals were recrystallised twice from n-hexane to give needles of (E)-2-iodoacrylonitrile (1.0 g), m.p. $60\text{--}61^\circ$ (Found: C, 20.3; H, 1.05; I, 70.7; N, 7.9. $\text{C}_3\text{H}_2\text{IN}$ requires C, 20.2; H, 1.1; I, 70.9; N, 7.8%), ν_{max} (C=N stretch), 3050 (=C–H stretch), and 1565 cm^{-1} (C=C stretch), τ [(CD_3)₂CO] 2.6 and 4.0 (AB, J_{AB} 16.25 Hz).

Reaction between 2-Iodoacrylonitrile, 1,3-Di-iodohexafluoropropane, and Copper Bronze.—1,3-Di-iodohexafluoropropane (5 g), activated copper bronze (4 g), and dry dimethyl sulphoxide (10 cm^3) were stirred together under nitrogen at 115° . The copper was seen to turn a rusty colour and a white precipitate formed. The mixture was stirred for a further hour and then allowed to cool to room temperature. (E)-2-Iodoacrylonitrile (4.44 g) dissolved in a small amount of dimethyl sulphoxide was added and the mixture heated to 115° again. It was maintained at this temperature overnight and then allowed to cool. The black solution was then added to ether (200 cm^3), the suspension filtered, and the precipitate washed with ether ($2 \times 50 \text{ cm}^3$). This solution was washed with water ($3 \times 100 \text{ cm}^3$) and then dried (MgSO_4). The ether was removed by distillation through a 10 cm Vigreux column to give a yellow solid. This was sublimed at 100° using a water-pump and the yellow solid produced was crystallised from n-hexane–benzene to give white needles of (1E,3E)-1,4-dicyanobuta-1,3-diene (0.25 g), m.p. $159\text{--}160^\circ$, identified by i.r. and u.v. spectroscopy.

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