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POLYFLUOROPHENYL ACETYLENES AND RELATED COMPOUNDS

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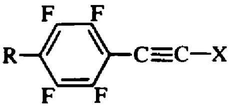
Abstract—From the reaction of pentafluoro- and 4-substituted-tetrafluoroiodobenzene (the substituent group R being CF_3–, H–, CH_3– or CH_3O–) with copper(I) 3-(2′-tetrahydropyranyloxy)prop-1-ynide has been obtained the corresponding 3-(polyfluorophenyl) prop-2-ynol derivative. Where R = $N(CH_3)_2$– and NH_2– the acetylenic alcohol was not obtained; these were synthesized by the reaction of dimethylamine and ammonia with 3-(pentafluorophenyl)prop-2-ynol itself. The acetylenic alcohols were converted to the corresponding polyfluorophenyl acetylenes by nickel peroxide in dioxan/aqueous NaOH. With benzene at 60° as solvent 3-(pentafluorophenyl)prop-2-ynol was oxidized to the aldehyde and acid and in refluxing benzene 1,4-bis(polyfluorophenyl)butadiynes and polyfluorophenyl acetylenes were obtained. The mechanism of some of the reactions has been discussed.

INTRODUCTION

No simple route exists for the synthesis of polyfluorophenyl - acetylenes and -acetylenic alcohols. Pentafluorophenylacetylene itself has been prepared by the reductive dehalogenation of 1,1,2 - trichloro - 2 - pentafluorophenyl ethylene,[1] reaction of lithium acetylide with hexafluorobenzene affording only polymeric products.[2] A procedure using copper acetylide and aryl iodides[3-5] has been devised for the synthesis of diphenyl acetylenes and some phenyl acetylenes have been obtained by reaction between bromo- or iodo-ethynyl (trimethyl)- or -(triethyl)-silanes and aryl copper reagents.[6,7] We now report a simple synthesis of a number of polyfluorophenyl acetylenic alcohols, aldehydes and acids, in addition to the phenyl acetylenes themselves, from readily available reagents.

DISCUSSION

As part of our research interest in the electrochemical reactions of polyfluorocompounds we wished to prepare some polyfluorophenyl - acetylenes and -acetylenic alcohols of the general formula



where X = –H or –CH_2OH, in order to study the effect of the substituent R on the half wave polarographic reduction potentials of the acetylenic group. The route employed was essentially the procedure of Castro and Stephens;[3] in our case copper(I) - 3 - (2′ - tetrahydropyranyloxy)prop - 1 - ynide (prepared from ammoniacal copper(I) iodide and aqueous 3 - (2′ - tetrahydropyranyloxy)prop - 1 - yne) reacted with a 4 - substituted - 2,3,5,6 - tetrafluoroiodobenzene to afford, after hydrolysis of the dihydropyran protecting group with $MeOH/H_2SO_4$, the corresponding polyfluoro aromatic prop-2-ynol. This was then oxidized with nickel peroxide.[8]

The iodopolyfluoro aromatic precursors were prepared by previously reported methods except 4 - iodo - heptafluorotoluene and 1 - iodo - 4 - methyltetrafluorobenzene. The first of these was obtained by the trans metallation of 4*H* - heptafluorotoluene[9] with ethyl magnesium bromide to afford heptafluorotolyl magnesium bromide, which was converted to the desired iodide with iodine. The product from this reaction was shown to be 4 - iodo - heptafluorotoluene by chemical analysis and the usual spectrographic methods. 1 - Iodo - 4 - methyltetrafluorobenzene was synthesised by treating 4 - methyl - tetrafluorophenylhydrazine with silver oxide and iodomethane, the product having a correct chemical analysis, IR and NMR spectra.

From the reaction between the copper acetylide and pentafluoroiodobenzene in pyridine at room temperature was obtained 3 - (pentafluorophenyl)prop - 2 - ynol and decafluorobiphenyl in approximately equal molar amount, and hexa - 2,4 - diyne - 1,6 - diol, a known compound.[10] Attempts were made to improve the yield of the propynol by the use of alternative solvents and addition of 2,2′ - bipyridyl, known[11] to catalyse copper assisted displacement reactions. However, although addition of bipyridyl considerably increased the rate of reaction in pyridine (possibly due to much more ready dissolution of the acetylide), the ratio of propynol: biphenyl remained essentially unaltered. With other solvents (hexamethylphosphoramide, DMF, DMSO) a higher temperature was necessary to obtain dissolution of the acetylide (and reaction with the aryl iodide), and the proportion of biphenyl increased, as occurred with pyridine at elevated temperatures.

Using pyridine at the lowest temperature consistent with a convenient rate of reaction 1 - iodo - 4 - methoxy - , 1 - iodo - 4 - trifluoromethyl - and 1 - iodo - 4 - methyl - tetrafluorobenzene were similarly converted to the corresponding prop - 2 - ynol and biphenyl derivatives by reaction with the copper acetylide, although the methoxy- and methyl - iodobenzenes were of lower reactivity. From the reaction with 2,3,5,6 - tetrafluoroiodobenzene was obtained only a poor yield of 4*H*, 4′*H* - octa - fluorobiphenyl and 3 - (2′,3′,5′,6′ - tetrafluorophenyl)prop - 2 - ynol, and a third product which was identified as 1,4 - *bis*(3′ - hydroxyprop - 1′ - ynol)tetrafluorobenzene.

The reaction of the copper acetylide with 1 - (N,N - dimethyl - amino) - 4 - iodotetrafluorobenzene and 1 - amino - 4 - iodotetrafluorobenzene in pyridine failed to give any of the desired propynols. From 1 - (N,N - dimethylamino)4 - iodo - tetrafluorobenzene was obtained only an indifferent yield of 4,4′ - *bis*(N,N - dimethylamino)octafluorobiphenyl and hexa - 2,4 - diyne - 1,6 - diol. No identifiable products could be isolated from the corresponding reaction using 1 - amino - 4 - iodotetrafluorobenzene. In each case addition of 2,2′-bipyridyl was without effect on the composition of the products. 4 - N,N - Dimethylamino - and 4 - amino - tetrafluorophenyl - propynol were eventually prepared by the nucleophilic substitution of 3 - (pentafluorophenyl)prop - 2 - ynol using dimethylamine and ammonia respectively in ether at room temperature. The observed substitution at the 4-position of the pentafluorophenyl ring and the ease of reaction is in accord with previous observations.[2]

The reactions of Cu(I) compounds with aryl iodides and bromides have been extensively investigated,[12-14] most authors concluding that the reaction proceeeds via coordination of the aryl halide with the Cu atom, (which is also further coordinated to solvent) according to

$$ArI + CuL_3X \rightleftharpoons [ArICuL_2X] \rightarrow ArX + CuL_3I.$$

A

Replacement of the iodine atom by the group X takes place via a four centred transition state.[3,14,15] During these reactions, depending on the compounds involved and the solvent and ligands present, the formation of polyfluorobiphenyls,[13a] reduction products[13b] and diynes[3,5] has been observed. Their presence has been ascribed to the presence of Cu metal, other Cu salts or traces of oxygen, depending on the reaction conditions. We also envisage the formation of the arylpropynol occurring via a coordination complex similar to **A** above. The value of pyridine as a solvent and catalytic effect of bipyridyl may then be due to their greater ability to coordinate to copper with a consequent lower temperature required for solution of the acetylide. In addition the increasing strength of the Cu-solvent coordination may result in increased polarization of the Cu–C bond in the acetylide with a more ready exchange of ligands with the aryl halide.

In contrast with some other work on the reaction of aryl halides we observe the formation of biphenyls in large amounts. We envisage these arising by an intermolecular rearrangement of complex **A** in an equilibrium reaction to form a polyfluorophenyl Cu(I) complex and iodoacetylene according to

$$XCuL_3 + ArI \rightleftharpoons [L_2CuXArI] \rightleftharpoons L_3CuAr + IX$$

in which the formation of the aryl copper is aided by the relatively high stability of polyfluorophenyl Cu(I) compounds. This may also permit the formation of free iodoacetylene(XI), without reaction within the complex. The subsequent reactions of the polyfluorophenylcopper and iodoacetylene products from the equilibrium with the copper acetylide complex and the aryl iodide then affords the biphenyl and diacetylene. Ligand exchange of this type has previously been postulated[3b] to account for the formation of thianaphthalene from o-bromothiophenol and copper phenylacetylene, and this may explain the formation of biphenyl from pentafluoroiodobenzene and phenylcopper[14] and decafluorobiphenyl from bromopentafluorobenzene and perfluoroheptyl copper.[13a]

A major product product from the reaction of 2,3,5,6 - tetrafluorobenzene with the copper acetylide was 1,4 - *bis*(3′ - hydroxyprop - 1′ - ynyl)tetrafluorobenzene. This we believe arises from exchange reactions of the type outlined above together with a trans-metallation reaction involving the *para* H atom in the fluoro-aromatic ring leading eventually to the disubstituted product.

The propynols were then oxidized with nickel peroxide in both benzene and aqueous organic solvents as previously described.[8,16] Oxidation of 3 - (pentafluorophenyl)prop - 2 - ynol in benzene at 60° afforded three products. The first was identified as 3 - (pentafluorophenyl)prop - 2 - ynal (confirmed by conversion to the 2,4 - dinitrophenylhydrazone) and the second as pentafluorophenylacetylene. Finally, by acidification of the nickel peroxide residue was isolated 3 - (pentafluorophenyl)prop - 2 - ynoic acid. From the oxidation in refluxing benzene no aldehyde or acid was obtained, the principal product being 1,4 - *bis*((pentafluorophenyl) - butadiyne together with pentafluorophenylacetylene. In both of these systems the yield was approximately 30%. The butadiyne was also obtained from pentafluorophenylacetylene itself with nickel peroxide in refluxing benzene. Under similar conditions 3 - (4′ - trifluoromethyltetrafluorophenyl)prop - 2 - ynol afforded 1,4 - *bis*(4′ - trifluoromethyltetrafluorophenyl)butadiyne as the sole product in 20% yield. These observations are consistent with complete deformylation of the aldehyde to afford the acetylene (see below) in refluxing benzene before further oxidation to the acid is possible. Oxidation of the acetylene then takes place at the surface of the nickel peroxide to polyfluorophenylethynyl radicals (*cf* oxidation of chloroform with nickel peroxide[8]), which dimerize to the butadiyne.

Oxidation of the pentafluorophenylpropynol using aqueous methanolic alkali gave pentafluorophenylacetylene and a second compound, subsequently identified as 4 - methoxytetrafluorophenylacetylene, the latter presumably arising from nucleophilic attack of methoxide ion on the pentafluorophenyl ring. Finally in alkaline aqueous dioxan at 50° 3 - (pentafluorophenyl)prop - 2 - ynol was converted to pentafluorophenylacetylene only in 70% yield. Similarly, 4 - trifluoromethyl - , 4 - methoxy - , 4 - methyl - , 4 - amino - and 4 - N,N - dimethylaminotetrafluorophenylacetylene could be obtained from the corresponding 3 - (4′ - polyfluorophenyl)prop - 2 - ynol precursors in good yield. All these were identified by chemical analysis and the usual spectrographic methods, and additionally for 4 - trifluoromethyl - and 4 - methoxy - tetrafluorophenylacetylene, by the formation of the corresponding copper acetylides.

The conversion of the alcohol directly to the acetylene proceeds, as in previously reported examples[16] via deformylation of the aldehyde rather than decarboxylation of the acid, since in aqueous sodium hydroxide/dioxan 3 - (pentafluorophenyl)prop - 2 - ynal afforded pentafluorophenylacetylene, whereas under identical conditions the corresponding acid remained unchanged.

EXPERIMENTAL

Spectroscopy. Mass spectra were measured on an AEI MS9 mass spectrometer and IR spectra on a Perkin-Elmer 257 Spectrophotometer. NMR Spectra were determined with a Perkin-Elmer R10 or R12B spectrometer at 38.5°; proton chemical shifts (at 60 MHz) are quoted in δ values (ppm from TMS internal standard) and ^{19}F chemical shifts (at 56.4 MHz) in ϕ values (ppm from CCl_3F internal standard). UV Spectra were recorded on a Unicam SP 800A Spectrophotometer in EtOH.

Gas-liquid chromatography. The separation of volatile mixtures was done using a column 900 cm × 8 mm i.d., silicone gum.

S.E.30: chromosorb P = 9:1, and a Pye 104 gas–liquid chromatograph, flame ionization detector.

Preparation of copper(I) 3 - (2′ - *tetrahydropyranyloxy*) - *prop* - 1 - *ynide*. 3 - (2′ - tetrahydropyranyloxy)prop - 1 - yne (14.0 g) was dissolved in EtOH (500 ml) and water (1 l) under N_2. Copper(I) iodide (30.0 g) in NH_3 (d. 0.880, 500 ml) was added, and the mixture stirred for 30 min, when the product was filtered off, washed with water, EtOH and ether and dried *in vacuo* (0.01 mm. Hg, P_2O_5) to give the acetylide (17.2 g) (Found: C, 47.3; H, 5.2. $C_8H_{11}CuO_2$ requires: C, 47.4; H, 5.4%).

General procedure for the acetylide reactions. The acetylide reactions were done in a reaction flask fitted with a stirrer, reflux condenser, tap funnel for admitting reagents and solvent, and mercury manometer. The outlet from the apparatus was connected to a vacuum pump and source of O_2 free N_2. The acetylide was placed in the flask and the system evacuated and refilled with N_2 3 times. Dry solvent was placed in the funnel and deoxygenated with N_2 from the apparatus through the tap of the funnel (*ca.* 15 min) when it was then added to the acetylide through a stream of N_2. The aromatic fluorocarbon dissolved in a small volume of deoxygenated solvent was then added, with no N_2 flow. Finally, the whole system was purged with N_2 and the pressure adjusted to slightly (*ca.* 20 mm Hg) above atmospheric, the manometer acting as a mercury seal.

Preparation of the acetylenic alcohols

(i) 3 - (*Pentafluorophenyl*)*prop* - 2 - *ynol*. The copper acetylide (25.0 g), dry pyridine (600 ml) and pentafluoroiodobenzene (30.0 g) were stirred at room temp. for 15 hr; the acetylide dissolved after 3 hr. The brown soln was then poured into conc. HCl (600 ml) and ice (*ca.* 700 g) and the mixture filtered and ether extracted (3 × 300 ml). The ether extracts were filtered, dried ($MgSO_4$) and evaporated to leave a residue (33.7 g) which was hydrolysed with MeOH (200 ml) and conc. H_2SO_4 (20 ml) under reflux for 12 hr. Water was added and the mixture steam distilled. The distillate was ether extracted (3 × 300 ml), the extracts washed with water (3 × 100 ml) and dried and evaporated. The residue (26.4 g) was distilled under reduced pressure (15 mm Hg) to afford (i) a mixture (10.4 g) shown by ^{19}F NMR spectroscopy to be essentially free of fluorocarbon; (ii) a residue (15.8 g) which, after two recrystallizations from petroleum (b.p. 40–50°), gave 3 - (*pentafluorophenyl*)*prop* - 2 - *ynol* (6.5 g), m.p. 68–69° (Found: C, 49.0; H, 1.5; F, 42.6. $C_9H_3F_5O$ requires: C, 48.7 H, 1.4; F, 42.8%). M^+ 222 (required); ν_{max} (Nujol) 3200–3340 (–OH), 2240 (–C≡C–) and 1490–1520 cm^{-1}·(fluoroaromatic ring); δ (CCl_4), 3.16 (1H, s, –OH) and 4.51 (2H, s, >CH_2); ϕ 136.1 (2F, m, F-2,6), 163.2 (2F, m, F-3,5) and 153.5 (1F, tr J 25 Hz, F-4).

The mother liquors from the recrystallizations were combined, evaporated and the residue sublimed under reduced pressure (15 mm Hg) to afford decafluorobiphenyl (9.3 g), m.p. 67–68° (lit.[17] 67–69°), m.m.p. 67–68.5°, identified by IR spectroscopy. The aqueous residue from the steam distillation was extracted with ether (3 × 300 ml) and the extracts dried and evaporated to a solid (4.0 g) which was recrystallized from CCl_4 four times to give hexa - 2,4 - diyn - 1,6 - diol (1.0 g). (Found: C, 65.6; H, 5.6. Calc. for $C_6H_6O_2$ C, 65.4; H, 5.5%); M^+ 110 ($C_6H_6O_2^+$ requires: 110). The UV,[10] IR and NMR spectra were consistent with the proposed structure.

(ii) *Optimization of the yield of* 3 - (*pentafluorophenyl*)*prop* - 2 - *ynol*. A series of reactions was carried out using various solvents at the minimum temp. required for reaction. In each case the acetylide (4.2 g) was reacted with pentafluoroiodobenzene (5.0 g) in the selected solvent (75 ml). Since earlier experiments had shown some variation in the reactivity of the acetylide, all the reactions were carried out with an aliquot of a single sample. For water miscible solvents the product was poured into water (200 ml), extracted with ether (3 × 130 ml), and the extracts washed with water (3 × 300 ml) and dried ($MgSO_4$). For basic solvents, the mixture was poured into a mixture of ice and conc. HCl, and treated as previously described for pyridine. The dried ethereal extracts were then evaporated and the residue hydrolysed, steam distilled and separated as described above to afford 3 - (pentafluorophenyl) - prop - 2 - ynol and decafluorobiphenyl. The following solvents were used: (A) pyridine, (B) pyridine + 2,2′ - bipyridyl (1.3 g), (C) N,N - dimethylformamide, (D) Hexamethylphosphoramide and (E) Dimethylsulphoxide (the last three distilled from CAH_2 at 15 mm Hg). The yields of products together with the reaction time and temperature are given in Table 1.

An attempted preparation using bromopentafluorobenzene (4.3 g) and the acetylide (4.2 g) in pyridine (65 ml) at 75° for 24 hr afforded, after the usual work up and separation procedures, bromopentafluorobenzene (1.66 g) only.

Purification of the steam distillation residue from all of these reaction systems yielded varying quantities of hexa - 2,4 - diyn - 1,6 - diol, identified by IR spectroscopy.

(iii) 3 - (4′ - *Methoxytetrafluorophenyl*)*prop* - 2 - *ynol*. The acetylide (25.0 g), dry pyridine (600 ml) and 1 - iodo - 4 - methoxytetrafluorobenzene (30.6 g), prepared as previously described,[18] were stirred at 50° for 16 hr; the acetylide dissolved after 4 hr. The mixture was worked up as described in (i) above to afford a mixture (42.1 g), which was hydrolysed with $MeOH/H_2SO_4$ for 12 hr. The products were steam distilled, and the distillate ether extracted. The extracts were evaporated to afford a residue (35.0 g). Distillation of this under reduced pressure (15 mm Hg) gave (i) a mixture A (13.7 g), containing no fluorine (^{19}F NMR) and (ii) a residue (20.8 g). This residue was sublimed (15 mm Hg, 120°) to afford (i) an oil (1.3 g), shown by GLC to be similar to mixture A, (ii) a solid (19.0 g) and (iii) a residue (0.3 g), not further investigated. The solid was recrystallized from n-hexane twice to give 3 - (4′ - *methoxytetrafluorophenyl*)*prop* - 2 - *ynol* (6.4 g) m.p. 76–77° (Found: C, 51.6; H, 2.9; F, 32.1. $C_{10}H_6F_4O_2$ requires: C, 51.3; H, 2.6; F, 32.5%). M^+ 234 (required); ν_{max} (Nujol) 3200–3260 (-OH) and 1480–1490 cm^{-1} (fluoro aromatic ring); δ (CCl_4) 2.15 (1H, s, -OH), 4.56 (2H, s, >CH_2) and 4.13 (3H, s, –OCH_3); ϕ 138.8 (2F, m, F-2,6) and 158.9 (2F, m, F-3,5).

Evaporation of the mother liquors from the crystallization of the propynol afforded a residue (11.7 g) which was sublimed (15 mm Hg, 150°) to give 4,4′ - dimethoxyoctafluorobiphenyl (10.4 g) m.p. 88–89° (lit. 90–91.2°[18]), identified by a comparison of the IR spectrum with that of an authentic sample.

(iv) 4 - *Iodoheptafluorotoluene* (with G. E. Ditchfield). To Mg (10 g) in Na^2 dried ether (130 ml) was added EtBr (45 g). When reaction was complete the soln of EtMgBr was added slowly to a cooled (0°) mixture of 4*H* - heptafluorotoluene[9] (43.8 g), ether (30 ml) and THF (100 ml). When evolution of ethane had ceased (4.2 l) the mixture was warmed to room temp. and I_2 (93 g) in THF (200 ml) added. The mixture was refluxed for 2 hr and 2M H_2SO_4 (200 ml) and water (300 ml) added. The aqueous phase was extracted with ether (300 ml) and the ether soln washed with water (3 × 300 ml), $Na_2S_2O_3$ soln, water (300 ml) and dried ($MgSO_4$). The ethereal soln was then evaporated to a residue (86.6 g) which was distilled under reduced pressure (15 mm Hg) to a liquid (57.3 g), which was redistilled to afford 4 - *iodoheptafluorotoluene* b.p. 64–68°/15 mm Hg (49.9 g), b.p. 183° (Found: C, 24.6; F, 38.7. C_7F_7I requires: C, 24.4; F, 38.7%); λ_{max} 242 nm (ϵ 3.18 × 10^3); υ_{max} (liquid film) 1645 and 1580 cm^{-1} (aromatic ring); ϕ (CCl_4) 57,2 (3F, tr, –CF_3), 118.0 (2F, m, F-2,6) and 139.2 (2F, m, F-3,5).

(v) 3 - (4′ - *Trifluoromethyltetrafluorophenyl*)*prop* - 2 - *ynol*. The acetylide (25.0 g) dry pyridine (600 ml) and 4 - iodo - heptafluorotoluene (34.4 g) were stirred at room temp. for 13 hr; the acetylide dissolved after 1 hr. The mixture was worked up as described above to give a residue (37.9 g) which was hydrolysed with $MeOH/H_2SO_4$ and steam distilled. Evaporation of the ethereal extracts of the steam distillate gave a product (30.9 g) which was distilled under reduced pressure (15 mm Hg) to yield a

Table 1.

Solvent	Temp. (°C)	Time (h)	Propynol (g)	Biphenyl (g)
(A)	25	15	1.02	1.12
(B)	25	2	0.91	1.16
(C)	110	16	0.23	0.72
(D)	70	16	0.27	0.91
(E)	130	16	0.56	1.55

residue (26.7 g). This was separated by column chromatography (silica gel, petroleum b.p. 40–50°) to give Fraction 1, (9.3 g), and further elution with a mixture of petroleum b.p. 40–50°/ether = 4 : 1 afforded, Fraction 2 (14.6 g). Fraction 1 was re-separated by column chromatography (silica gel, petroleum b.p. 40–50°) to give a solid which was sublimed to yield 4,4′ - *bis*(trifluoromethyl)octafluorobiphenyl (8.3 g) m.p. 100–101° (lit.[19] 101.5–102°), with a correct IR spectrum.[20]

Fraction 2 was purified by column chromatography (silica gel, petroleum b.p. 40–50°) and recrystallized from the same solvent to give 3 - (4 - *trifluoromethyltetrafluorophenyl*)*prop* - 2 - *ynol* (11.2 g) m.p. 41–42° (Found: C, 44.0; H, 1.3; F, 49.0. $C_{10}H_3F_7O$ requires: C, 44.1; H, 1.1; F, 48.9%). M^+ 272 (required); ν_{max} (Nujol) 3220–3260 (–OH), 2240 (–C≡C–) and 1470–1495 cm^{-1} (aromatic ring); δ (CCl_4) 3.21 (1H, s, –OH) and 4.60 (2H, s, >CH_2); ϕ 136.3 (2F, m, F-2,6), 141.9 (2F, m, F-3,5) and 57.6 (3F, tr J22.2 Hz, CF_3–).

(vi) 1 - *Iodo* - 4 - *methyltetrafluorobenzene.* 4 - Methyltetrafluorophenylhydrazine (47.0 g), prepared as previously described,[21] was added in small portions (*ca.* 0.5 g) to a stirred suspension of Ag_2O (95.0 g) in iodomethane (250 ml) at 0°.[22] The mixture was refluxed for 2 hr, cooled, dried ($MgSO_4$) and the iodomethane removed under reduced pressure. The residue was extracted with ether and the extracts filtered, dried ($MgSO_4$) and evaporated to a liquid residue (63.7 g) which was distilled under reduced pressure to afford 1 - *iodo* - 4 - *methyltetrafluorobenzene* (51.7 g), b.p. 94–96° (15 mm Hg) (Found: C, 28.9; H, 1.0; F, 25.9; I, 44.1. $C_7H_3F_4I$ requires: C, 29.0; H, 1.0; F, 26.2; I, 43.8%). The mass spectrum gave an accurate top mass of 289.9197 ($C_7H_3F_4I^+$ requires: 289.9215); ν_{max} 2930 (aliphatic C–H) and 1465 cm^{-1} (fluoroaromatic ring); δ (CCl_4) 2.26 (tr J 2.1 Hz, –CH_3); ϕ 142.0 (2F, m, F-2,6) and 122.0 (2F, m, F-3,5).

(vii) 3 - (4′ - *Methyltetrafluorophenyl*)*prop* - 2 - *ynol.* Dry pyridine (260 ml), the acetylide (13.5 g) and 1 - iodo - 4 - methyltetrafluorobenzene (15.0 g) were stirred together for 14 hr at 60°. The soln was cooled, poured onto a mixture of ice (*ca.* 400 g) and conc. HCl (350 ml), filtered and ether extracted (3 × 300 ml). The ether extracts were dried ($MgSO_4$) and the ether distilled off to leave a residue (19.8 g). This was hydrolysed in methanol (100 ml) and conc. H_2SO_4 (10 ml) under reflux for 12 hr. Water was then added and the mixture steam distilled. The distillate was ether extracted (3 × 300 ml), the extracts washed with water (3 × 100 ml), dried ($MgSO_4$) and evaporated to leave a residue (16.7 g) which was distilled under reduced pressure (15 mm Hg). The residue (12.4 g) was separated by column chromatography (silica gel, 200 g); elution with petroleum b.p. 40–50° afforded Fraction 1 (8.0 g). Further elution with a mixture of petroleum b.p. 40–50°: ether = 7 : 3 gave Fraction 2 (3.7 g).

Fraction 1 was a mixture of two components: on standing crystals appeared which were identified as 4,4′ - dimethyloctafluorobiphenyl[22] (2.3 g) m.p. 148–149° (Found: C, 51.3; H, 2.1; F, 46.9. Calc. for $C_{14}H_6F_8$: C, 51.6; H, 1.8; F, 46.6%). M^+ 326 (required); with an IR spectrum identical with that of an authentic sample.

Distillation of the mother liquors afforded 1 - iodo - 4 - methyltetrafluorobenzene (4.8 g), identified by IR spectroscopy.

Fraction 2 (3.7 g) was recrystallized from petroleum b.p. 40–50° to give 3 - (4′ - *methyltetrafluorophenyl*)*prop* - 2 - *ynol* (3.4 g), m.p. 83–84° (Found: C, 55.5, H, 3.0; F, 34.6. $C_{10}H_6F_4O$ requires: C, 55.1; H, 2.8; F, 34.8%). M^+ 218 (required); ν_{max} (Nujol) 3140–3280 (–OH), 2230 (–C≡C–) and 1460–1480 cm^{-1} (fluoroaromatic ring); δ (CCl_4) 2.05 (1H, s, –OH), 4.53 (2H, s, >CH_2) and 2.31 (3H, s, –CH_3); ϕ 139.3 (2F, m, F-2,6) and 145.2 (2F, m, F-3,5).

(viii) 3 - (2′,3′,5′,6′ - *Tetrafluorophenyl*)*prop* - 2 - *ynol.* A mixture of the acetylide (25.0 g), dry pyridine (600 ml) and 1*H* - 4 - iodotetrafluorobenzene[24] (26.4 g) were reacted for 15 hr at 50°. The usual work-up and extraction procedure gave a mixture (26.8 g) which was hydrolysed in MeOH (200 ml) and conc. H_2SO_4 (20 ml) under reflux for 12 hr. Water was then added and the mixture ether extracted (3 × 200 ml), the extracts washed with water, dried ($MgSO_4$) and evaporated to a residue (21.6 g), which was further evaporated under reduced pressure (15 mm Hg). The involatile residue (14.0 g) was separated by column chromatography (silica gel, 200 g); elution with petroleum b.p. 40–50° gave Fraction 1, (3.1 g); further elution with a mixture of petroleum b.p. 40–50°: ether = 9 : 1 afforded Fraction 2 (3.1 g) and elution with ether gave Fraction 3 (6.4 g). Fraction 1 was sublimed under reduced pressure (15 mm Hg) to give 4*H*,4′*H* - octafluorobiphenyl (2.1 g) m.p. 80–81° (lit.[25,26] 81°–83.5°) (Found: C, 48.6; H, 0.9; F, 50.7. Calc. for $C_{12}H_2F_8$: C, 48.3; H, 0.7; F, 51.0%). The IR spectrum was identical with that of an authentic sample.[27] Fraction 2 was distilled under reduced pressure (15 mm Hg) to give an oil (2.7 g), b.p. 132° which slowly crystallized to afford 3 - (2′,3′,5′,6′ - *tetrafluorophenyl*)*prop* - 2 - *ynol* (2.2 g), m.p. 60–60.5°. (Found: C, 52.8; H, 1.8; F, 36.9. $C_9H_4F_4O$ requires: C, 53.0; H, 2.0; F, 37.2%). M^+ 204 (required); ν_{max} (Nujol) 3200–3300 (–OH), 2240 (–C≡C–) and 1480–1500 cm^{-1} (fluoroaromatic ring); δ (CCl_4) 3.22 (1H, s, –OH), 4.61 (2H, s, >CH_2) and 7.05 (1H, m, aryl H); ϕ 137.2 (2F, m, F-2,6) and 139.4 (2F, m, F-3,5).

A portion (1.0 g) of Fraction 3 was sublimed under reduced pressure to yield a solid (0.7 g) which was recrystallized from aqueous acetone to give 1,4 - *bis*(3′ - *hydroxyprop* - 1′ - *ynyl*)*tetrafluorobenzene* (0.5 g) m.p. 164–165°. (Found: C, 56.5; H, 2.7. $C_{12}H_6F_4O_2$ requires: C, 55.8; H, 2.3%). M^- 258 (required); ν_{max} (KBr disc) 3360 (–OH), 2860 and 2900 (C–H), 2220 (–C≡C–) and 1470–1490 cm^{-1} (fluoroaromatic ring); δ [$(CD_3)_2CO$] 2.80 (1H, s, –OH), 4.55 (2H, s >CH_2); ϕ 139.3 (s).

(ix) 3 - (4′ - N,N - *Dimethylaminotetrafluorophenyl*)*prop* - 2 - *ynol.* (a) The acetylide (6.25 g), 2,2′ - bipyridyl (2.5 g), pyridine (120 ml) and 1 - (N,N - dimethylamino) - 4 - iodotetrafluorobenzene[24] (8.0 g) were stirred for 17 hr at 50°. The mixture was added to conc. HCl (150 cm^3) and ice (*ca.* 250 g), filtered and continuously ether extracted for 2 days. The ether extract was dried, evaporated and the residue (10.7 g) hydrolysed with MeOH (30 ml) and conc. H_2SO_4 (3.76 ml) under reflux for 12 hr. The soln was neutralized ($NaHCO_3$), ether extracted (3 × 200 cm^3) and the ethereal extracts washed with water (3 × 100 cm^3), dried ($MgSO_4$) and evaporated to give a residue (5.1 g) which was sublimed under reduced pressure to give a solid (2.9 g). The solid was recrystallized from CCl_4 to yield hexa - 2,4 - diyn - 1,6 - diol (0.7 g), identified by IR spectroscopy.

The mother liquors from the recrystallization were evaporated and the residue recrystallized twice from aqueous EtOH to afford 4,4′ - *bis*(N,N - dimethylamino)octafluorobiphenyl (0.9 g) m.p. 107–108° (lit.[26] 107–108°). The ^1H and ^{19}F NMR spectra were consistent with the structure.

(b) Dimethylamine soln (33% w/w in EtOH, 11.1 g) and 3 - (pentafluorophenyl)prop - 2 - ynol (9.0 g) in EtOH (2 ml) were shaken for 2 days in a sealed tube at room temp. The contents were then dissolved in ether (400 ml), the ethereal soln washed with water (3 × 100 ml), dried ($MgSO_4$) and evaporated to a solid (12.0 g). Recrystallization from petroleum b.p. 40–50° gave 3 - (4′ - N,N - *dimethylaminotetrafluorophenyl*)*prop* - 2 - *ynol* (7.9 g) m.p. 67–68°. (Found: C, 53.4; H, 3.5; F, 30.9; N, 5.4. $C_{11}H_9F_4NO$ requires: C, 53.5; H, 3.6; F, 30.8; N, 5.7%). M^+ 247 (required); ν_{max} (Nujol) 3180–3220 (–OH), 2230 (–C≡C–) and 1490 cm^{-1} (fluoroaromatic ring); δ (CCl_4) 2.43 (1H, s, –OH), 3.01 (6H, tr J2.4 Hz, –$N(CH_3)_2$) and 4.53 (2H, s, >CH_2); ϕ 139.9 (2F, m, F-2.6) and 153.3 (2F, m, F-3,5).

(x) 3 - (4′ - *Aminotetrafluorophenyl*)*prop* - 2 - *ynol.* A mixture of anhydrous ammonia (*ca.* 15 ml), ether (40 ml) and 3 - (pentafluorophenyl)prop - 2 - ynol (9.0 g), in sealed tubes, were shaken for 2 days at room temp. The contents of the tubes were then filtered, dried ($MgSO_4$) and distilled. The residue (11.6 g) was extracted with boiling petroleum b.p. 80–90° and recrystallized from the same solvent to afford 3 - (4′ - *aminotetrafluorophenyl*)*prop* - 2 - *ynol* (6.8 g) m.p. 104–105° (Found: C, 49.0; H, 2.4; F, 34.9; N, 6.1. $C_9H_5F_4NO$ requires: C, 49.3; H, 2.3; F, 34.7; N, 6.4%). M^+ 219 (required); ν_{max} 3500–3200 (–OH, –NH_2), 2220 (–C≡C–) and 1490–1520 cm^{-1} (fluoroaromatic ring); δ (C_6D_6) 3.98 (2H, s, >CH_2), 3.15 (2H, s, –NH_2) and 1.26 (1H, s, –OH); ϕ 140.2 (2F, m, F-2,6) and 162.9 (2F, m, F-3,5).

Reactions with nickel peroxide

3 - (*Pentafluorophenyl*)*prop* - 2 - *ynol.* (a) The alcohol (5.0 g), nickel peroxide[8] (10.5 g) and benzene (70 ml) were stirred together for 24 hr at 60° when the mixture was filtered, the residue washed with ether and the mixed organic solutions evaporated to leave a

residue (5.0 g). A portion (4.5 g) of the residue was separated by GLC (170°) to give (i) mixture (C) (1.9 g), (ii) 3 - (pentafluorophenyl)prop - 2 - ynol (0.3 g), identified by IR spectroscopy and (iii) 3 - *(pentafluorophenyl)prop - 2 - ynal* (1.2 g). (Found: C, 49.2; H, 0.8; F, 43.5. C_9HF_5O requires: C, 49.1; H, 0.5; F, 43.2%). M^+ 220 (required); ν_{max} (liquid film) 2860 (C–H), 2190 and 2220 (–C≡C–), 1665 (>C=O), and 1480–1520 cm^{-1} (fluoroaromatic ring); δ (CCl_4) 9.48 (s); ϕ 133.5 (2F, m, F-2,6), 161.0 (2F, m, F-3,5) and 147.5 (1F, m, F-4). The mixture C was separated by GLC (130°) to afford:

(i) benzene (1.2 g) and (ii) pentafluorophenylacetylene (0.5 g) identified by IR spectroscopy.[1]

The nickel oxide residue from the reaction was dissolved in 4*M* HCl (400 ml) and the solution extracted with ether (3 × 200 ml). The ethereal extracts were dried ($MgSO_4$) and evaporated to a solid (2.2 g) which was sublimed under reduced pressure. The sublimate (1.1 g) was recrystallized from n-hexane to yield 3 - *(pentafluorophenyl)prop - 2 - ynoic acid* (1.0 g) m.p. 105–106° (Found: C, 45.6; H, 0.6; F, 40.7. $C_9HF_5O_2$ requires: C, 45.8; H, 0.4; F, 40.2%). M^- 236 (required); ν_{max} (Nujol) 2240 (–C≡C–), 1680 (>C=O) and 1580 cm^{-1} (fluoroaromatic ring); in hexachlorobutadiene the spectrum showed a broad peak at 2820–2960 cm^{-1} (–OH); δ [$(CD_3)_2CO$] 8.70 (s); ϕ 135.1 (2F, m, F-2,6), 161.8 (2F, m, F-3,5) and 149.6 (1F, tr of tr J 20.4 and 7.6 Hz, F-4).

(b) The alcohol (2.0 g), nickel peroxide (5.7 g) and benzene (60 ml) were refluxed for 36 hr. The products were worked up as above and the residue (1.9 g) distilled in vacuum at 25°. The distillate (0.74 g) was separated by GLC (120°) into (i) benzene (0.42 g) and (ii) pentafluorophenylacetylene (0.21 g), (IR spectroscopy). The residue (0.9 g) from the distillation was sublimed *in vacuo* to give 1,4 - *bis*(pentafluorophenyl)butadiyne (0.6 g) m.p. 113–114° (lit.[4,7] 104–105° and 113–114°), identified by IR and UV spectroscopy, with consistent chemical analysis, and ^1H and ^{19}F NMR spectra.

(c) Nickel peroxide (1.8 g), N NaOH (50 ml), MeOH (4 ml) and 3 - (pentafluorophenyl)prop - 2 - ynol (1.0 g) were stirred together for 35 min at 55° and the mixture acidified (4M HCl), ether extracted (3 × 100 ml) and the ether extracts dried ($MgSO_4$) and evaporated to a residue (1.04 g). Distillation *in vacuo* afforded a mixture (0.52 g) which was separated by GLC (160°) into (i) ether (0.1 g), (ii) pentafluorophenylacetylene (0.23 g) and (iii) 4 - methoxytetrafluorophenylacetylene (0.11 g) (see later), all identified by IR spectroscopy.

(d) Nickel peroxide (3.6 g), M NaOH (120 ml), dioxan (10 ml) and 3 - (pentafluorophenyl)prop - 2 - ynol (2.0 g) were stirred together at 50° for 30 min, when all the nickel peroxide had reacted. The mixture was acidified (4M HCl), ether extracted (3 × 100 ml), and the ether extracts washed with water (3 × 50 ml). The ethereal solution was dried ($MgSO_4$) and evaporated to a residue (2.3 g), a portion (0.93 g) of which was separated by GLC (120°) to afford (i) ether (0.2 g) and (ii) pentafluorophenylacetylene (0.5 g), both identified by IR spectroscopy.

(ii) *Pentafluorophenylacetylene.* The title compound (0.18 g), nickel peroxide (0.5 g) and benzene (1.5 ml) were refluxed for 36 hr under nitrogen. The products were treated as in (a) above to afford, after sublimation of the solid products (0.12 g), 1,4 - *bis*(pentafluorophenyl)butadiyne (0.08 g), identified by IR and UV spectroscopy.

(iii) 3 - (4' - *Trifluoromethyltetrafluorophenyl)prop - 2 - ynol.* (a) The alcohol (1.5 g), nickel peroxide (5.1 g) and benzene (20 ml) were refluxed for 36 hr. The suspension was filtered and the nickel oxide washed with ether and the washings combined with the filtrate. The organic soln was dried ($MgSO_4$) and the ether distilled off to leave a benzene soln from which crystals (0.5 g) precipitated on cooling. The solid was dried *in vacuo* and recrystallized from $MeOH/CHCl_3$ mixture to afford 1,4 - *bis*(4' - *trifluoromethyltetrafluorophenyl)butadiyne* (0.32 g) m.p. 120–121° (Found: C, 44.5; F, 55.2. $C_{18}F_{14}$ requires C, 44.8; F, 55.2%) M^- 482 (required); ν_{max} (Nujol) 2170 (–C≡C–) and 1490–1500 cm^{-1} (fluoroaromatic ring); ϕ [$(CD_3)_2CO$] 56.3 (3F, tr J 22.6 Hz, $-CF_3$), 1339 (2F, m, F-2,6) and 140.9 (2F, m, F-3,5).

(b) Nickel peroxide (1.7 g), *M* NaOH (60 ml), dioxan (10 ml) and 3 - (4' - trifluoromethyltetrafluorophenyl)prop - 2 - ynol (1.0 g) were stirred at 50° for 40 min. The mixture was cooled, acidified with 4M HCl (30 cm^3) and ether extracted (3 × 100 ml). The extracts were washed with water (3 × 50 ml), dried ($MgSO_4$) and evaporated to a residue (1.23 g), a portion (1.07 g) of which was separated by GLC (150°) to give (i) ether (0.18 g) and (ii) 4 - *trifluoromethyltetrafluorophenylacetylene* (0.4 g), b.p. 145–146° with dec. (Found: C, 44.7; H, 0.6; F, 55.1. C_9HF_7 requires: C, 44.6; H, 0.4; F, 54.9%). M^+ 242 (required); ν_{max} (liquid film) 3300 (C≡C–H), 2120 (–C≡C–) and 1470–1510 cm^{-1} (fluoroaromatic ring); δ (CCl_4) 3.70 (s); ϕ 57.9 (3F, tr J 22.6 Hz, $-CF_3$), 135.3 (2F, m, F-2,6) and 141.6 (2F, m, F-3,5).

(iv) 3 - (4' - *Methoxytetrafluorophenyl)prop - 2 - ynol.* The title compound (1.8 g), nickel peroxide (3.6 g), M NaOH (130 ml) and dioxan (20 ml) were stirred at 50° for 30 min. The mixture was cooled, acidified and ether extracted as in (iii) above to afford a product (2.18 g) which was separated by column chromatography (silica gel). Elution with n-hexane gave a solid (1.1 g) which was sublimed (15 mm Hg, 50°) to yield 4 - *methoxytetrafluorophenylacetylene* (0.93 g) m.p. 58–59° (Found: C, 52.6; H, 2.0; F, 37.2. $C_9H_4F_4O$ requires: C, 53.0; H, 2.0; F, 37.2%); ν_{max} (CCl_4) 3300 (–C≡C–H), 3000 and 2950 (–C–H) and 1480–1500 cm^{-1} (fluoroaromatic ring); M^+ 204 (required); δ (C_6D_6) 2.96 (1H, s, –C≡C–H) and 3.39 (3H, tr J 1.7 Hz, $-OCH_3$); ϕ 139.1 (2F, m, F-2,6) and 158.1 (2F, m, F-3,5). Further elution of the column with n-hexane: ether = 9:1 gave starting material (0.34 g), identified by IR spectroscopy.

(v) 3 - (4' - *Methyltetrafluorophenyl)prop - 2 - ynol.* Dioxan (10 ml), nickel peroxide (2.2 g), M NaOH (65 ml) and the title compound (1.0 g) were stirred at 50° for 40 min. The usual extraction procedure afforded a residue (1.43 g), a portion (1.19 g) of which was separated by GLC (150°) to give (i) ether (0.27 g), (ii) 3 - (4' - methyltetrafluorophenyl)prop - 2 - ynol (0.24 g), both identified by IR spectroscopy and (iii) 4 - *methyltetrafluorophenylacetylene* (0.34 g), m.p. 45–46° (Found: C, 57.6; H, 2.3; F, 40.4. $C_9H_4F_4$ requires: C, 57.5; H, 2.1; F, 40.4%); ν_{max} (Nujol) 3310 (–C≡C–H), 2120 (–C≡C–) and 1480–1490 cm^{-1} (fluoroaromatic ring); M^+ 188 (required); δ (C_6D_6) 3.01 (1H, s, –C≡CH) and 1.66 (3H, tr J 2.2 Hz, $-CH_3$); ϕ 139.5 (2F, m, F-2,6) and 144.6 (2F, m, F-3,5).

(vi) 3 - (4' - *Aminotetrafluorophenyl)prop - 2 - ynol.* The title compound (1.0 g), nickel peroxide (2.1 g), dioxan (10 ml) and M NaOH (70 ml) were stirred at 50° for 30 min. The mixture was then treated in the way described above to afford a residue (1.71 g) which was separated by column chromatography (silica gel, 50 g). Elution with n-hexane : ether = 9:1 gave a solid (0.67 g) which was sublimed (15 mm Hg, 50°) to 4 - *aminotetrafluorophenylacetylene* (0.6 g), m.p. 56–57° (Found: C, 50.7; H, 1.8; F, 40.1; N, 7.6. $C_8H_3F_4N$ requires: C, 50.8; H, 1.6; F, 40.2; N, 7.4%); ν_{max} (Nujol) 3480–3410 –(NH_2), 3300 (–C≡C–H), 2120 (–C≡C–) and 1500 cm^{-1} (fluoroaromatic ring); M^+ 189 (required); δ ($CDCl_3$) 3.42 (1H, s, –C≡CH) and 4.15 (2H, broad s, $-NH_2$); ϕ (C_6D_6) 140.9 (2F, m, F-2,6) and 163.9 (2F, m, F-3,5).

Further elution of the column with ether gave 3 - (4'-aminotetrafluorophenyl)prop - 2 - ynol (0.17 g), identified by IR spectroscopy.

(vii) 3 - (4' - N,N - *Dimethylaminotetrafluorophenyl)prop - 2 - ynol.* Dioxan (20 cm^3), M NaOH (30 cm^3), nickel peroxide (5.0 g) and the title compound (2.0 g) were stirred together at 50° for 50 min. The products were treated as described above to yield a mixture (2.4 g) which was separated by column chromatography (silica gel, 50 g). Elution with n-hexane : ether 9:1 gave a liquid (1.8 g), which was separated by GLC (150°) to give (i) n-hexane (0.6 g), identified by IR spectroscopy and (ii) 4 - (N,N - *dimethylamino)tetrafluorophenylacetylene* (0.9 g) (Found: C, 54.9; H, 3.2; F, 34.6; N, 6.2. $C_{10}H_7F_4N$ requires: C, 55.3; H, 3.2; F, 35.0; N, 6.5%). M^+ 217 (required); ν_{max} (Nujol) 3300 (–C≡C–H), 2120 (–C≡C–) and 1420–1530 cm^{-1} (fluoroaromatic ring); δ (C_6D_6) 2.53 (6H, tr J 2.2 Hz, $-N(CH_3)_2$) and 3.08 (1H, s, –C≡CH); ϕ 140.2 (2F, m, F-2,6) and 153.5 (2F, m, F-3,5).

Reactions of the acetylenes

(i) 3 - *(Pentafluorophenyl)prop - 2 - ynal.* (*a*) The aldehyde (0.2 g) in methanol (2 ml) was treated with 2,4 - dinitrophenylhydrazine in the usual way to afford, after recrystallization from MeOH 3 - *(pentafluorophenylprop - 2 - ynal - 2,4 - dinitrophenylhydrazone* (0.24 g), m.p. 180–181° (Found: C, 45.1; H, 1.4; F, 23.5;

N, 13.8. $C_{15}H_6F_5N_4O_4$ requires: (44.9; H, 1.5; F, 23.7; N, 14.0%); ν_{max} (KBr disc) 3260, 3080 (aromatic C-H), 2190 (-C≡C-) and 1490–1510 cm^{-1} (fluoroaromatic ring). The ^{1}H and ^{19}F NMR spectra were consistent with the proposed structure.

(b) Dioxan (10 ml), M NaOH (30 ml) and the aldehyde (0.2 g) were stirred together at 50° for 30 min. The mixture was acidified (4M HCl), ether extracted (3 × 50 ml) and the extracts washed with water, dried ($MgSO_4$) and evaporated to leave a residue (0.5 g). This was separated by GLC (130°) to afford (i) ether (0.2 g) and (ii) pentafluorophenylacetylene (0.1 g), identified by IR spectroscopy.

(ii) 4 - *Methoxytetrafluorophenylacetylene.* To the acetylene (0.1 g), dissolved in EtOH (5 ml) was added copper(I) iodide (0.5 g) in NH_4OH aq (28%, 15 cm^3) under N_2. Water (30 cm^3) was added, the ppt filtered off, washed with water, ethanol and ether and dried in vacuum over P_2O_5 to afford *Copper*(I) *4 - methoxytetrafluorophenylacetylide* (0.1 g) (Found: C, 40.6; H, 1.4. $C_9H_3CuF_4O$ requires: C, 40.7; H, 1.1%).

(iii) 4 - *Trifluoromethyltetrafluorophenylacetylene.* The acetylene (0.15 g) in EtOH was treated with copper(I) iodide as above to give *Copper*(I) *4 - trifluoromethyltetrafluorophenylacetylide* (0.15 g) (Found: C, 35.4; F, 44.0. C_9CuF_7 requires: C, 35.7; F, 43.5%).

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