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PERFLUOROBIPHENYLS AND PERFLUOROBIPHENYL ETHERS

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SUMMARY

Nucleophilic attack by various polyfluoro- and perfluoro-phenoxides upon decafluorobiphenyl, perfluoro-4-methylbiphenyl and perfluoro-4,4′-dimethylbiphenyl in dimethylacetamide solution gave a number of high boiling aryl ethers by mono- and di-substitution. The disodium salt of octafluoro-4,4′-dihydroxybiphenyl with octafluoroanisole in dimethylacetamide gave another aryl ether containing four rings, but the dipotassium salt of hexafluoro-3,3′-dihydroxy-4,4′-bis(trifluoromethyl)biphenyl (prepared by the action of potassium hydroxide upon perfluoro-4,4′-dimethylbiphenyl) with octafluorotoluene gave a complex mixture of products. The syntheses of various new compounds used as intermediates are described.

INTRODUCTION

This paper describes the synthesis of some substituted perfluorobiphenyls and perfluorobiphenyl ethers for evaluation as thermally stable fluids of possibly greater oxidative stability than similar hydrocarbon compounds. Polyphenyl ethers have been considered for use as lubricants and hydraulic fluids[1,2] and when substituted with trifluoromethoxy groups have been shown to have good thermal stability[3,4]. Nevertheless, some recent work[5] suggests that perfluoroaryl and polyfluoroaryl ethers compare unfavourably with their hydrocarbon analogues in terms of thermal stability, fire resistance and viscosity characteristics.

The general methods of synthesis used in this work were as follows: (i) nucleophilic substitution by perfluorophenoxides from pentafluorophenol, trifluoro-

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methoxytetrafluorophenol and 2,4,5,6-tetrafluoro-3-methoxyphenol on decafluorobiphenyl, perfluoro-4-methylbiphenyl and perfluoro-4,4′-dimethylbiphenyl, (ii) attack by disodium or dipotassium salts of 3,3′- and 4,4′-dihydroxyperfluorobiphenyls upon octafluorotoluene and octafluoroanisole. DePasquale and Tamborski[6] first showed dimethylacetamide to be an effective solvent for reactions between pentafluorophenoxide ion and various polyfluoroaromatic compounds and we found this solvent suitable for our reactions.

Decafluorobiphenyl itself reacts with nucleophiles in the 4 and 4′ positions[6–8] but when these are blocked by trifluoromethyl groups we find that predominant attack occurs on the 3 and 3′ sites. For example, treatment of perfluoro-4,4′-dimethylbiphenyl with potassium hydroxide in t-butanol yields hexafluoro-3,3′-dihydroxy-4,4′-bis(trifluoromethyl)biphenyl in 55% yield. Again, treatment of the same substrate with potassium t-butoxide leads to a 3,3′-disubstituted product (28% yield). If only the 4 position is blocked, it is most likely that a nucleophile will attack the 4′ position, as in the formation of perfluoro(4-methyl-4′-phenoxybiphenyl) from perfluoro-4-methylbiphenyl and sodium pentafluorophenoxide; further attack may then occur on the 3 and 3′ positions.

Intermediates used in the syntheses were prepared as follows. Perfluoro-4-methylbiphenyl (I) was prepared by a published procedure[9] and perfluoro-4,4′-dimethylbiphenyl (II) was prepared by the Ullmann reaction from 4-bromoheptafluorotoluene[10] in 86% yield, or more conveniently from 4-chloroheptafluorotoluene[11] in 60% yield.

4-Bromoheptafluorotoluene[10] was made from 4-amino-2,3,5,6-tetrafluorobenzonitrile[10] by diazotisation in anhydrous hydrogen fluoride and reaction with cuprous bromide giving 4-bromo-2,3,5,6-tetrafluorobenzonitrile[10]. Hydrolysis of this to the bromo acid followed by treatment with sulphur tetrafluoride gave the required product.

4-Chloroheptafluorotoluene was prepared from octafluorotoluene and aluminium chloride according to the method of Wall[11].

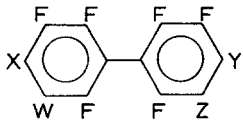
2,4,5,6-Tetrafluoro-3-methoxyphenol (X) was prepared in 60% yield by the reaction between pentafluorophenol and potassium methoxide in methanol solution. Attempts to convert the hydroxyl group in this compound to trifluoromethoxyl by treatment with carbonyl fluoride followed by sulphur tetrafluoride[4] were unsuccessful. This reaction which involves formation of the fluoroformate followed by the hydrogen-fluoride-catalysed fluorination of the carbonyl group by sulphur tetrafluoride has been successfully used with hydrocarbon phenyl ethers bearing hydroxyl groups[4].

Trifluoromethoxytetrafluorophenol (VIII) was, however, prepared in 70% yield as an isomeric mixture (containing predominately the *para* isomer) by reaction between octafluoroanisole[4,12] and potassium hydroxide in tertiary butanol solution.

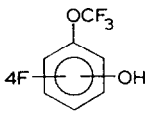
Octafluoroanisole was prepared from 2,3,4,5,6-pentafluoroanisole by chlorination and subsequent fluorination (a new chlorodifluoromethoxypenta-

fluorobenzene was isolated as well), and from pentafluorophenol by reaction with carbonyl fluoride followed by sulphur tetrafluoride.

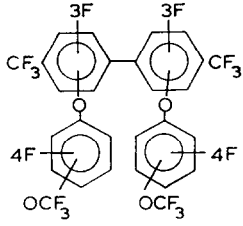
RESULTS AND DISCUSSION



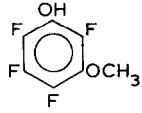
(I) $X = CF_3$; $W = Y = Z = F$
(II) $X = Y = CF_3$; $W = Z = F$
(III) $X = CF_3$; $W = Z = F$; $Y = C_6F_5O-$
(IV) $X = Y = CF_3$; $W = Z = OH$
(V) $X = Y = CF_3$; $W = Z = -OC(CH_3)_3$
(VI) $X = Y = 4\text{-}CF_3OC_6F_4O-$; $W = Z = F$
(VII) $X = Y = 3\text{-}CH_3OC_6F_4O-$; $W = Z = F$



(VIII)



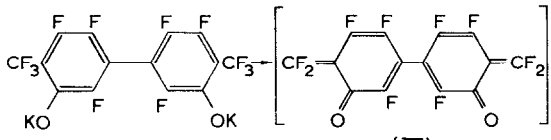
(IX)



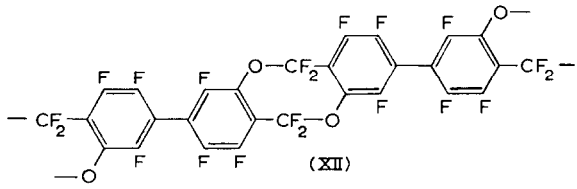
(X)

The reaction between sodium pentafluorophenoxide and perfluoro-4-methylbiphenyl (I) in dimethylacetamide gave a small yield of perfluoro(4-methyl-4′-phenoxybiphenyl) (III) as a syrupy liquid. When a similar reaction was carried out with perfluoro-4,4′-dimethylbiphenyl (II), a complex mixture of high boiling products was obtained which contained no starting materials. It was suspected that, after initial pentafluorophenoxy substitution, further attack had occurred on the substituent group or groups *via* the fluorine atom *para* to the ether link. When compound (II) was treated with the sodium salt of an isomeric mixture of trifluoromethoxytetrafluorophenols[12] (VIII) (containing 61% of the *para*, 27% of the *ortho* and 12% of the *meta* isomers) in dimethylacetamide solution, perfluoro-[4,4′-dimethyl-bis(methoxyphenoxy)biphenyl] (IX) (mixed isomers) was obtained in 14% yield as a viscous high boiling oil (boiling range 120–135°/10^{-4} mmHg). The action of potassium hydroxide in t-butanol upon (II) gave hexafluoro-3,3′-dihydroxy-4,4′-bis(trifluoromethyl)biphenyl (IV) in 55% yield. The same compound was also prepared by acid fission of 3,3′-bis(t-butoxy)-4,4′-bis(trifluoromethyl)-hexafluorobiphenyl (V) formed in 28% yield by treatment of (II) with potassium

t-butoxide in t-butanol. It was hoped that the dipotassium salt of (IV) would react with octafluorotoluene to give perfluoro[4,4′-dimethyl-3,3′-bis(methylphenoxy)-biphenyl] which, having a trifluoromethyl group in the 4 position on each phenoxy substituent, was thought to be less susceptible to further nucleophilic attack. However a complex mixture of products was obtained and this was ascribed to the decomposition of the dipotassium salt *via* an *ortho*-quinonoid intermediate (XI) analogous to that postulated by McLoughlin and Thrower[13] to account for the polymerisation of the potassium salt of heptafluoro-*p*-cresol.



(XI)



(XII)

Some support for this idea was given by the fact that when (IV) was neutralized with aqueous sodium hydroxide and the solution was evaporated to dryness an acetone-soluble resin was obtained. It is tentatively suggested that this may have the structure (XII).

The disodium salt of octafluoro-4,4′-dihydroxybiphenyl[7], however, gave with octafluoroanisole[4,12] in dimethylacetamide solution, perfluoro[4,4′-bis(4-methoxy-phenoxy)biphenyl] (VI) as a white solid m.p. 68-9°, b.p. $130/10^{-3}$ mmHg. The structure of the product was confirmed by mass spectroscopy and the ^{19}F NMR spectrum was quite consistent with the material having an all-*para*-linked structure with no appreciable amounts of other isomers being present. Since, however, the action of potassium hydroxide upon octafluoroanisole gives an isomeric mixture of trifluoromethoxytetrafluorophenols, it is quite possible that isomers of perfluoro-[bis(methoxyphenoxy)biphenyl] were formed in the reaction. The yield of product (8%) was low and other isomers could well have been lost during the work-up. The thermal decomposition temperature (T_D) of this compound, determined in a glass isoteniscope under nitrogen as described by Blake[14], was 363° * and it was felt that the compound had an encouragingly low melting point for an entirely *para*-linked structure.

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* We thank Mr. E. R. Lynch, Monsanto Chemicals Ltd., Ruabon for this result.

Trifluoromethoxy groups attached in positions *meta* to the ether links in hydrocarbon polyphenyl ethers have been shown to lower the melting point[3,4]. In an attempt to prepare an isomer of (VI) in which these groups were in *meta* positions with respect to the ether links, the sodium salt of 2,4,5,6-tetrafluoro-3-methoxyphenol (X) and decafluorobiphenyl were heated together in dimethylacetamide solution. Octafluoro-4,4′-bis(2,4,5,6-tetrafluoro-3-methoxyphenoxy)-biphenyl (VII) was obtained in 47% yield as a viscous liquid, boiling range 170–210°/2 × 10^{-3} mmHg. The pure material had m.p. 88–90°. It was intended to convert the methoxy groups to trifluoromethoxy groups by one of two ways (i) acidic fission of the methoxyl group and reaction of the resultant hydroxyl group with carbonyl fluoride and sulphur tetrafluoride[4], (ii) by exhaustive chlorination to form trichloromethoxy groups which would be subsequently fluorinated. However, even under the vigorous conditions used, hydriodic acid did not cleave the methoxyl groups and chlorination was incomplete.

EXPERIMENTAL

Infrared spectra were measured on a Perkin–Elmer 337 grating spectrophotometer. NMR spectra were measured on Perkin–Elmer R10 and Varian HA-100 spectrometers and molecular weights were determined by mass spectrometry using an A.E.I. MS 9 instrument or an A.E.I. MS 702 with photoplate detection. Dimethylformamide (B.D.H.) was dried over phosphoric oxide and distilled collecting the fraction b.p. 44–5°/20 mmHg. Dimethylacetamide (B.D.H.) was distilled under N_2 from phosphoric oxide, collecting the fraction of b.p. 113°/146 mmHg. t-Butanol (B. P. Chemicals) and sulphur tetrafluoride (E. I. du Pont de Nemours and Co.) were used without further purification. Melting points are uncorrected.

Decafluorobiphenyl was available as a product of I.S.C. Chemicals Ltd.

Perfluoro-4,4′-dimethylbiphenyl

(a) From 4-bromoheptafluorotoluene

4-Bromoheptafluorotoluene[10] (124.3 g, 0.42 mole) and copper bronze (29.4 g, 0.46 g atom) were stirred together in boiling dimethylformamide (420 ml) for 6 h. The product was isolated by steam distillation as white crystals (85.2 g) which were recrystallised (ethanol) giving perfluoro-4,4′-dimethylbiphenyl[10] (78.2 g, 86% yield) m.p. 102–102.5°, purity +99% by GLC. (Found: C, 38.4; F, 61.3%. $C_{14}F_{14}$ requires C, 38.7; F, 61.3%.) The infrared spectrum was consistent with the expected structure.

(b) From 4-chloroheptafluorotoluene

4-Chloroheptafluorotoluene[11] (23.7 g, 0.094 mole) and copper bronze (6.57 g, 0.1 g atom) were stirred in boiling dimethylformamide (75 ml) for 12.5 h. The product (14.0 g) isolated by steam distillation was recrystallised (ethanol) to

yield perfluoro-4,4′-dimethylbiphenyl (12.28 g, 60% yield); m.p. and mixed m.p. with material prepared in the previous experiment 101.5–102°.

2,4,5,6-Tetrafluoro-3-methoxyphenol (X) (nc)

A mixture of potassium methoxide (2 mole) and pentafluorophenol (184 g, 1 mole) in methanol (500 ml) was maintained at 175° for 20 h in an 800 ml capacity stainless-steel autoclave. The resultant mixture was acidified with hydrochloric acid and ether-extracted. The dried extracts were distilled to give pentafluorophenol (87.4 g) and 2,4,5,6-tetrafluoro-3-methoxyphenol (61.4 g, 31% yield).

In a small-scale initial preparation, the compound was obtained pure by distillation and had b.p. 99–100°/15 mmHg, n_D^{27} 1.4822 (Found: C, 42.2; H, 2.0; F, 38.8%. $C_7H_4F_4O_2$ requires C, 42.9; H, 2.1; F, 38.8%). The IR spectrum was consistent with the proposed structure: $\nu_{max.}$ (liq.) *ca.* 3580, 3400 (–OH), 2960 (C–H), *ca.* 1500 cm^{-1} (fluorinated aromatic ring). The mass spectrum showed a peak at 196 attributed to the parent ion. The ^{19}F NMR spectrum showed four signals of equal intensity consistent only with *meta* orientation. Each signal showed further multiplicity, but no evidence of the presence of *ortho* and *para* isomers was seen.

Octafluoroanisole

(a) Via *2,3,4,5,6-pentafluoroanisole*

A mixture of 88% trichloromethoxypentafluorobenzene[12] (205 g, 0.6 mole: prepared by the chlorination of 2,3,4,5,6-pentafluoroanisole[15]), antimony trifluoride (210 g, 1.2 mole) and antimony pentachloride (10 g) was stirred and boiled until all volatile product (boiling range 50–150°) had distilled out. The distillate was washed with 12 *N* hydrochloric acid (2 × 50 ml) and then with water. The product was distilled (30 cm column packed with 2 mm × 2 mm Dixon gauzes) to give (i) octafluoroanisole (69 g, 45% yield) b.p. 104–105° with IR spectrum in accord with published data[4,12] and (ii) chlorodifluoromethoxypentafluorobenzene (nc) (18.8 g, 12% yield), b.p. 135–137° (Found: C, 31.5; Cl, 13.3; F, 49.8%. C_7ClF_7O requires C, 31.3; Cl, 13.2; F, 49.5%) having an IR spectrum consistent with the proposed structure: $\nu_{max.}$ (liq.) 1510 (fluorinated aromatic ring), 760 cm^{-1} (C–Cl ?). The mass spectrum showed peaks at 268 ($C_7{}^{35}ClF_7O$) and 270 ($C_7{}^{37}ClF_7O$) attributed to the parent ions.

(b) Via *pentafluorophenol*

A mixture of pentafluorophenol (37 g, 0.2 mole) and carbonyl fluoride (18 g, 0.37 mole) was heated and shaken in a 200 ml capacity stainless-steel autoclave at 100° for 1 h and 200° for 2 h. The autoclave was cooled in ice/water and vented (to remove excess of carbonyl fluoride while retaining hydrogen fluoride) then cooled in liquid nitrogen while sulphur tetrafluoride (26 g, 0.24 mole) was added by vacuum transfer. The autoclave was then heated for 2 h at 100°, 2 h at

150° and for 2 h at 175°. Distillation of the crude product gave octafluoroanisole (6.71 g, 13% yield) b.p. 104°.

Hydroxylation of octafluoroanisole

A mixture of octafluoroanisole (25.2 g, 0.1 mole), tertiary butanol (100 ml) and potassium hydroxide (90%, 13.75 g, 0.22 mole) was boiled under reflux for 1 h then diluted with water (250 ml). t-Butoxyheptafluoroanisole was removed from the mixture by steam distillation, dried and the t-butyl ether link cleaved by saturation with dry hydrogen chloride gas. The resulting trifluoromethoxytetrafluorophenol was combined with that obtained by acidification of the residue from the steam distillation, and distilled giving trifluoromethoxytetrafluorophenol[16] (19.3 g, 77% yield) b.p. 150–155°. Part of this material was purified by preparative GLC giving an analytical sample, b.p. 155–156°. (Found: C, 33.5; H, 0.7; F, 52.9%. $C_7HF_7O_2$ requires C, 33.6; H, 0.4; F, 53.2%.) The IR spectrum was consistent with the expected structure: $\nu_{max.}$ (liq.) *ca.* 3500 (–OH), 1500 (fluorinated aromatic ring), *ca.* 1270, *ca.* 1200 cm^{-1} (–OCF_3 on ring).

The ^{19}F NMR spectrum showed three groups of separate trifluoromethoxy signals. The major and minor ones were present as 1:2:1 triplets and were therefore assigned to either the *meta*- or *para*-substituted compound. The signal of intermediate intensity was a 1:1 doublet and therefore arose from the *ortho*-substituted compound. The remainder of the spectrum upfield of the trifluoromethoxy signals contained two major signals of equal intensity assigned to two pairs of chemically equivalent fluorine atoms in the *para* isomer. Since these were the major signals, the largest trifluoromethoxy signal was therefore also ascribed to the *para* isomer. The isomeric composition of the mixture could then be determined by integration of the trifluoromethoxy signals, and was 27% *ortho*, 12% *meta* and 61% *para*. This result compared well with the values determined by gas chromatography (28% *ortho*, 12% *meta* and 60% *para*) eluting in this order from a 6 m Apiezon grease/Celite-packed column at 175°.

Perfluoro(4-methyl-4'-phenoxybiphenyl) (III) (nc)

A mixture of sodium pentafluorophenoxide (8.2 g, 0.04 mole) and perfluoro-4-methylbiphenyl[9] (7.7 g, 0.02 mole) in dry dimethylacetamide (70 ml) was heated at 140° for 2 h. The mixture was poured into water and extracted with ether. The aqueous phase contained 0.606 g ions of fluoride (required for elimination of two fluorine atoms per biphenyl molecule, 0.76 g ions of fluoride). Distillation of the extracts gave crude product (7.8 g) which was distilled to give perfluoro(4-methyl-4'-phenoxybiphenyl) as a syrupy liquid (0.85 g, 8% yield) b.p. 158–163°/7 mmHg. (Found: C, 41.3; F, 55.5%. $C_{19}F_{16}O$ requires C, 41.6; F, 55.5%.)

The ^{19}F NMR spectrum confirms the fully *para*-linked structure having eight signals in intensity ratio 3:2:2:2:4(2:2):1:2. Six pairs of chemically equivalent fluorine atoms are present and fall into two groups of three, the fluorine atoms of

one group having *ortho*-fluorine and -carbon atoms, the other having *ortho*-fluorine and either *ortho*-fluorine or *ortho*-oxygen atoms. Overlap occurs between a pair of signals from the latter group. The trifluoromethyl signal is split into a 1:2:1 triplet showing that the group has two equivalent fluorine atoms *ortho* to it. IR spectrum (liq.): *ca.* 1480 (fluorinated aromatic ring), 1305, 1195, 1160 ($-CF_3$ on aromatic ring), 1025 cm^{-1} (ether link?). In a second experiment, equimolar quantities of reagents were heated at 120° for 6 h and the product was isolated in 22% yield.

Reaction between sodium pentafluorophenoxide and perfluoro-4,4′-dimethylbiphenyl

A solution of sodium pentafluorophenoxide (0.02 mole) and perfluoro-4,4′-dimethylbiphenyl (4.34 g, 0.01 mole) in dimethylacetamide (45 ml) was stirred at 140° for 1.5 h with formation of a precipitate, then poured into water (200 ml). The resultant suspension was ether-extracted, and the extracts were combined and dried. Evaporation of the ether left a residue (6.4 g) which was distilled at 0.025 mmHg pressure into several fractions with collective boiling range 110–190°. High-temperature GLC analyses (silicone oil and Apiezon grease stationary phases at 225°, 250° and 350°) showed these distillates to be complex mixtures containing five or more components, none of which was present in major proportions. The IR spectrum showed the absence of starting materials and in the 1000–1040 cm^{-1} region showed some resemblance to that of perfluorobiphenyl ether suggesting the presence of aryl ethers.

Reaction between sodium trifluoromethoxytetrafluorophenate and perfluoro-4,4′-dimethylbiphenyl

A solution of trifluoromethoxytetrafluorophenol (15 g, 0.06 mole) in 1 *N* sodium hydroxide (60 ml, 0.06 mole) was evaporated down and the residue dried by azeotropic distillation with toluene. Removal of the toluene *in vacuo* left the sodium salt of the phenol (16.13 g, 99% yield). To this salt was added a solution of perfluoro-4,4′-dimethylbiphenyl (13.02 g, 0.03 mole) in dimethylacetamide (100 ml) and the stirred mixture was heated at 110° for 2 h and at 150° for 19 h under a nitrogen atmosphere. The mixture was poured into 1.2 *N* hydrochloric acid (100 ml), the solution extracted with chloroform (100 ml) and the extract was water-washed and dried ($MgSO_4$).

The remaining aqueous acid layer was analysed for fluoride ion. (Found: 1.1 g, required for the elimination of two fluorine atoms per biphenyl molecule 1.14 g.) The chloroform solution was evaporated and the residue was distilled under high vacuum using a short-path distillation unit giving, as a viscous oil, perfluoro[4,4′-dimethyl-bis(methoxyphenoxy)biphenyl] (IX) (3.75 g, 14% yield), b.p. 120–135°/10^{-4} mmHg, as a mixture of isomers. (Found: C, 38.5; F, 53.9%. $C_{28}F_{26}O_4$ requires C, 37.6; F, 55.3%.) The IR spectrum was consistent with the proposed structure: $\nu_{max.}$ (CCl_4) 1500 (fluorinated aromatic ring), 1285, 1200

($-OCF_3$), 1310, 1160 cm^{-1} ($-CF_3$ on fluorinated aromatic ring). The mass spectrum showed a peak at 894 attributed to the parent ion.

Hexafluoro-3,3′-dihydroxy-4,4′-bis(trifluoromethyl)biphenyl (IV) (nc)

(a) From potassium hydroxide

A mixture of perfluoro-4,4′-dimethylbiphenyl (4.34 g, 0.01 mole) and powdered potassium hydroxide (2.54 g, 85%, 0.04 mole) in t-butanol (25 ml) was boiled for 1.25 h. Hydrochloric acid (20 ml, 6 *N*) was added and the t-butanol was distilled off. The aqueous solution remaining was ether-extracted and the dried extracts were evaporated to dryness. The solid residue (3.82 g) was recrystallised three times from petroleum fraction (boiling range 80–100°) to give white crystals of hexafluoro-3,3′-dihydroxy-4,4′-bis(trifluoromethyl)biphenyl (1.17 g, 27% yield) m.p. 89–91° (sealed tube). (Found: C, 39.4; H, 0.5; F, 53.3% equiv. 223. $C_{14}H_2F_{12}O_2$ requires C, 39.1; H, 0.5; F, 53.0% equiv. 215.) The IR spectrum of this material was consistent with the expected structure: $\nu_{max.}$ (CCl_3CN) 3400 (–OH), 1480 (fluorinated aromatic ring), 1150, 1320 cm^{-1} ($-CF_3$ substituent on aromatic ring). The ^{19}F NMR spectrum showed four signals of relative intensity 3:1:1:1. The trifluoromethyl signal was split into a 1:1 doublet showing the presence of only one *ortho*-fluorine atom, confirming 3,3′-substitution of the hydroxyl groups.

(b) From potassium t-butoxide

Perfluoro-4,4′-dimethylbiphenyl (4.34 g, 0.01 mole) in dry t-butanol (25 ml) was added rapidly to a stirred solution of potassium t-butoxide prepared by dissolving potassium metal (0.78 g, 0.02 g atom) in boiling t-butanol (30 ml). The reaction mixture was boiled and stirred for 1 h, then evaporated to dryness. The residue (6.05 g) was taken up in ether and the potassium fluoride was filtered off. Evaporation of the dried ether solution gave a solid which after three recrystallisations from ethanol gave white crystals of 3,3′-di(t-butoxy)-4,4′-bis(trifluoromethyl)hexafluorobiphenyl (V) (nc) (1.53 g, 28% yield) m.p. 120.5–121.5°. (Found: C, 49.0; H, 3.4; F, 42.3%. $C_{22}H_{18}F_{12}O_2$ requires C, 48.7; H, 3.3; F, 42.0%.)

Part of this product (0.91 g) was dissolved in dry benzene (30 ml) and dry hydrogen chloride was passed through the stirred solution for 4 h. There was obtained, after evaporation of the benzene, hexafluoro-3,3′-dihydroxy-4,4′-bis-(trifluoromethyl)biphenyl (0.7 g, 97% yield) m.p. 91–93° (sealed tube) with an IR spectrum identical to that of authentic material produced in (a) above.

Attempted preparation of perfluoro[4,4′-dimethyl-3,3′-bis(4-methylphenoxy)-biphenyl]

Hexafluoro-3,3′-dihydroxy-4,4′-bis(trifluoromethyl)biphenyl (4.30 g, 0.01 mole) in dry methanol (10 ml) was added to a pre-cooled (−10°) solution of potassium methoxide (0.02 mole) in methanol (20 ml). The mixture was stirred at ambient temperature for 0.75 h, then evaporated to dryness *in vacuo* to leave

the pale yellow dipotassium salt of (IV), (5.07 g, 100% yield). The dipotassium salt (5.0 g, 0.01 mole) in dimethylacetamide (20 ml) was added to a stirred solution of octafluorotoluene (7.11 g, 0.03 mole) in dimethylacetamide (20 ml) at 120° over 1 h while under a nitrogen atmosphere. The mixture was stirred at 110–120° for 17 h, a heavy white precipitate appearing.

The suspension was poured into water (200 ml), the resultant emulsion ether-extracted and the dried extracts evaporated to leave a residue (7.45 g). The aqueous layer contained 0.285 g of fluoride ion. (Required for elimination of two fluorine atoms per biphenyl molecule, 0.380 g fluoride ion.)

The residue was distilled into three fractions collectively having boiling ranges 100–144°/0.05 mmHg but high-temperature GLC analysis (lithium chloride on Chromosorb P) showed each to be a mixture of about five major components.

Treatment of compound (IV) (7.26 g, 0.017 mole) with aqueous sodium hydroxide (1 *N*, 33.8 ml) afforded a brown resin (8.54 g) instead of the expected disodium salt. The aqueous phase contained 0.5 g of fluoride ion. The resin was soluble in acetone and had a melting point below 100°.

Perfluoro[4,4'-bis(4-methoxyphenoxy)biphenyl] (VI) (nc)

A solution of octafluoro-4,4'-dihydroxybiphenyl[7] (16.5 g, 0.05 mole) in normal sodium hydroxide (100 ml, 0.10 mole) was evaporated to dryness. The residue was further dried by azeotropic distillation with toluene. Evaporation of the toluene *in vacuo* gave the anhydrous disodium salt (18.8 g, 100% yield).

To the dry disodium salt was added a solution of octafluoroanisole[4,12] (30.24 g, 0.12 mole) in dimethylacetamide (150 ml). The mixture was stirred at 100–110° for 3 h and at 150° for 21 h under nitrogen in which time a white precipitate formed. The mixture was poured into dilute hydrochloric acid and the solution was extracted with methylene chloride. Evaporation of the water-washed and dried extract gave a residue (33.9 g). The aqueous acid solution remaining was analysed for fluoride ion. (Found: 1.5 g, required for the elimination of one fluorine atom per molecule of octafluoroanisole, 1.9 g.)

The residue, after an alkaline wash to remove phenolic material, was distilled in a short-path distillation unit to give perfluoro[4,4'-bis(4-methoxyphenoxy)-biphenyl] (3.10 g) b.p. 130°/10^{-3} mmHg, m.p. 68–69°. (Found: C, 39.1; F, 52.5%. $C_{26}F_{22}O_4$ requires C, 39.3; F, 52.6%.) The IR spectrum of this material was consistent with the proposed structure: $\nu_{max.}$ (CCl_4) 1480 (fluorinated aromatic ring), *ca.* 1290, *ca.* 1200 (–OCF_3 on ring), 1025 cm^{-1} (ether link ?). The ^{19}F NMR spectrum showed the presence of four sets of four chemically equivalent fluorine atoms, two of the sets overlapping slightly, and six other chemically equivalent fluorine atoms. These latter showed as a single peak to low field of the others and arose from the two equivalent trifluoromethoxy groups. These results are consistent only with a symmetrical *para*-linked structure and from the spectrum it seemed that no appreciable amounts of other isomers were present. The mass spectrum

showed a peak at 794 attributed to the parent ion. High-temperature GLC using a LiCl stationary phase showed the presence of two minor components suspected to be isomers. The T_D value[14], determined under N_2, was 363°.

Octafluoro-4,4′-bis(2,4,5,6-tetrafluoro-3-methoxyphenoxy)biphenyl (VII) (nc)

A mixture of decafluorobiphenyl (16.7 g, 0.05 mole), sodium 2,4,5,6-tetrafluoro-3-methoxyphenoxide (21.8 g, 0.1 mole) and dimethylacetamide (180 ml) was stirred at 150° for 5 h under nitrogen. After working up by pouring into water and ether-extracting the suspension of product, there was obtained by distillation octafluoro-4,4′-bis(2,4,5,6-tetrafluoro-3-methoxyphenoxy)biphenyl (16.1 g, 47%), boiling range 170–210°/2 × 10^{-3} mmHg, as a viscous liquid which crystallised on standing. Three recrystallisations (60–80° petroleum fraction) gave pure material m.p. 88–90° (Found: C, 45.5; H, 0.8; F, 44.5%. $C_{26}H_6F_{16}O_4$ requires C, 45.5; H, 0.9; F, 44.3%).

The IR spectrum was consistent with the proposed structure: $\nu_{max.}$ (CCl_4) 2960 (C–H), *ca.* 1480 cm^{-1} (fluorinated aromatic ring), which was confirmed by mass spectroscopy (parent ion peak at 686). The ^{19}F NMR spectrum consisted of signals of relative intensity 4:2:2:4:2:2 as the field increased. The two groups of four chemically equivalent fluorine atoms are associated with the central 4,4′-substituted octafluorobiphenyl unit and confirm the 4,4′ substitution. The remaining fluorine atoms show up as four pairs of chemically equivalent fluorine atoms as expected from a 3-methoxytetrafluorophenoxy unit. Since it is known that the starting 3-methoxytetrafluorophenol is isomerically pure, the only possible isomers in the product are those resulting from 2 or 3 substitution in decafluorobiphenyl. No evidence for the presence of these was detected in the NMR spectrum.

When this compound (4 g) was stirred with hydriodic acid (d 1.27, 20 ml) at 120° for 55 h, it was recovered quantitatively.

Attempts to chlorinate the two methoxy groups in the above compound by using chlorine gas and UV irradiation in carbon tetrachloride and nitrobenzene solvents gave only incompletely chlorinated material.

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