

## PERFLUOROARALKYL ETHERS

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### SUMMARY

Some perfluorinated ethers have been prepared containing both alkyl and aryl groups and either one or two oxygen atoms.

Pentafluorophenylmagnesium bromide, with octafluoroadipoyl chloride, perfluoro-oxylacetyl chloride and perfluoro-oxylpropionyl chloride, gave the corresponding diketones which, upon treatment with sulphur tetrafluoride, afforded perfluoro-1,6-diphenylhexane, perfluoro-bis(2-phenylethyl)ether and perfluoro-bis(3-phenylpropyl)ether, respectively.

Pentafluorophenylmagnesium bromide with perfluoro-2-methyl-3-oxanonadiol fluoride (prepared from octafluoroadipoyl fluoride and hexafluoropropene oxide) gave a diketone which was treated with sulphur tetrafluoride to give perfluoro-2-methyl-1,9-diphenyl-3-oxanonane.

Reactions between octafluoroadipoyl chloride and pentafluorophenol, nonafluoro-4-hydroxybiphenyl and perfluoro-3-hydroxy-4,4'-dimethylbiphenyl gave the corresponding diesters which were then each treated with sulphur tetrafluoride and hydrogen fluoride. The first two diesters gave perfluoro-1,6-diphenoxyhexane and perfluoro-1,6-bis(4-phenylphenoxy)hexane, but the corresponding diether was not isolated from the third diester.

The effect of structure upon the liquid ranges of the ethers is discussed.

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### INTRODUCTION

This paper describes the preparation of some fully-fluorinated aralkyl ethers. Because of the known high thermal stability of hexafluorobenzene<sup>1</sup> and decafluorobiphenyl<sup>2</sup>, these ethers were prepared with one or more pentafluorophenyl or nonafluorobiphenyl groups incorporated into the molecule.

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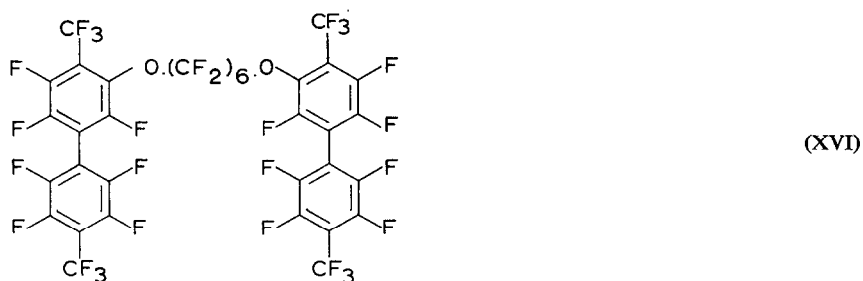


Fig. 1. Structural formulae of the compounds I-XVI.

#### DISCUSSION

The preparation of some  $\alpha,\omega$ -diphenylperfluoroalkanes has been described recently by two groups<sup>3,4,5</sup>, but neither was concerned with the preparation of the fully-fluorinated compounds.

We obtained reproducibly high yields (75–80%) of perfluoro-1,4-dibenzoylbutane (I) from the reaction between pentafluorophenylmagnesium bromide and octafluoroadipoyl chloride in ether solution, when a catalytic amount of cuprous chloride was present. In the absence of cuprous chloride, variable yields of (I) were obtained and higher boiling material was produced, sometimes in predominating yield. This material which showed—OH absorption in its infrared spectrum, appeared to be either the mono- or di-tertiary alcohol, or a mixture of both, formed by further reaction of the Grignard reagent with the carbonyl group. Cuprous chloride has been shown previously to favour ketone formation in certain reactions between Grignard reagents and acid chlorides<sup>6</sup>. It is possible that pentafluorophenyl copper<sup>7,8</sup> is an intermediate in the reaction.

In similar cuprous chloride catalysed reactions, pentafluorophenylmagnesium bromide gave, with perfluoro-oxydiacetyl chloride in ether solution, perfluoro-bis(benzoylmethyl)ether (II) in 73% yield, and with perfluoro-oxydipropionyl chloride in ether solution, perfluoro-bis(2-benzoylethyl)ether (III) in 75% yield.

The perfluoro-oxydiacyl chlorides were prepared by treating the corresponding acids with thionyl chloride containing a small quantity of dimethylformamide. Some of these acyl chlorides have been described previously<sup>9,10</sup> but were not always completely characterised. The perfluoro-oxydialkanoic acids were prepared either by electrochemical fluorination, or by other routes<sup>10–14</sup>. The oxidation of 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran<sup>11,13,14</sup> is the most practical route to perfluoro-oxydiacetic acid.

Fluorination of the carbonyl groups in these compounds was carried out by sulphur tetrafluoride<sup>15</sup> in the presence of aluminium fluoride<sup>16</sup>. Although optimum conditions were not determined, it was found that using temperatures in the range 160–175°, prolonged reaction times of 70–150 h were required before carbonyl absorptions were absent in the infrared spectra of the crude products. From the fluorination of (I), (II) and (III), perfluoro-1,6-diphenylhexane (V) (49% yield),

perfluoro-bis(2-phenylethyl)ether (VI) (53% yield) and perfluoro-bis(3-phenylpropyl)ether (VII) (93% yield) were obtained, respectively.

The same general route was used to prepare the unsymmetrical ether perfluoro-2-methyl-1,9-diphenyl-3-oxanonane (VIII), but in this case pentafluorophenylmagnesium bromide was reacted with the oxydiacid fluoride, namely perfluoro-2-methyl-3-oxanonanedioyl fluoride (IX) in ether solution to give perfluoro-1,7-dibenzoyl-1-methyl-2-oxaheptane (IV) in 71% yield. Prolonged fluorination with sulphur tetrafluoride then gave (VIII) in 35% yield. The oxydiacid fluoride (IX) was prepared by reaction between octafluoroadipoyl fluoride and hexafluoropropene oxide in the presence of caesium fluoride in acetonitrile solution. Reactions of this type where a caesium fluoride-perfluorocarboxylic acid fluoride complex adds to one or more hexafluoropropene oxide molecules are well known<sup>17-19</sup> but this particular oxydiacid fluoride does not seem to have been reported. Also octafluoroadipoyl fluoride, for which preparative details are given here, has not hitherto been well described. Both octafluoroadipoyl fluoride and the oxydiacid fluoride (IX) were characterised as diamides of the parent acids.

Perfluoro- $\alpha,\omega$ -bis(aryloxy)alkanes were next prepared by fluorination of the carbonyl groups of their diester precursors.

Perfluoro-3-hydroxy-4,4'-dimethylbiphenyl (XII) was prepared by treatment of perfluoro-4,4'-dimethylbiphenyl<sup>20</sup> with potassium hydroxide in tertiary butanol solution. Nonafluoro-4-hydroxybiphenyl has been described<sup>21</sup> but not its convenient isolation in the pure state by steam distillation<sup>22</sup>.

Pentafluorophenol, nonafluoro-4-hydroxybiphenyl and perfluoro-3-hydroxy-4,4'-dimethylbiphenyl gave with octafluoroadipoyl chloride and ion-exchange resin in boiling benzene solution dipentafluorophenyl octafluoroadipate (X), bis(nonafluoro-4-biphenyl)octafluoroadipate (XI) and perfluoro-1,6-bis[3-(4,4'-dimethylbiphenyl)]octafluoroadipate (XIII), respectively, all in high yield. Later, it was discovered that pentafluorophenol reacts with octafluoroadipoyl chloride in boiling benzene to give the diester (X) in very good yield, in the absence of ion-exchange resin. Thus, the presence of the resin is probably not essential in this type of reaction.

Fluorination of these diesters was carried out with sulphur tetrafluoride and anhydrous hydrogen fluoride following a published procedure for ester fluorination<sup>23</sup>. As with the diketones, lengthy periods of heating at 150-180° were required to effect complete fluorination. Under these conditions, compounds (X) and (XI) gave perfluoro-1,6-bis(phenoxy)hexane (XIV), (53% yield) and perfluoro-1,6-bis(4-phenylphenoxy)hexane (XV), (38% yield), respectively. Some overheating occurred during the fluorination of (XIII) and although the crude product appeared to be fully fluorinated (no  $>C=O$  absorption in the IR spectrum), none of the expected diether (XVI) was isolated. High vacuum distillation of the product gave a fraction with boiling range 120-130°/0.01 mmHg. Multiple recrystallisation of a part of this material afforded a small yield of white crystals, m.p. 128-130°. The infrared spectrum of this material did not contain the strong  $-(CF_2)_n$  absorptions

expected, but bore a marked similarity to that of perfluoro-4,4'-dimethylbiphenyl. It seems that some fission of the molecule occurred in the fluorination process.

### IR spectra

The infrared spectra of the diketones (I), (II), (III) and (IV) showed strong  $>C=O$  absorptions in the region 1745–1750  $\text{cm}^{-1}$  together with the characteristic pentafluorophenyl ring absorptions in the region 1500  $\text{cm}^{-1}$ . Strong absorption in the region 1100–1250  $\text{cm}^{-1}$ , characteristic of multiple  $-CF_2-$  units, occurred in each compound. The fully-fluorinated compounds (V), (VI), (VII) and (VIII) derived from the diketones showed the pentafluorophenyl ring absorption in the region of 1500  $\text{cm}^{-1}$  and the characteristic complex strong absorptions in the region of about 1100–1250  $\text{cm}^{-1}$  associated with multiple  $-CF_2-$  units.

The infrared spectra of the three diesters (X), (XI) and (XIII) all showed carbonyl absorption in the region 1820–1840  $\text{cm}^{-1}$ , the highly fluorinated aromatic ring absorption in the region 1490–1520  $\text{cm}^{-1}$  and complex  $\{-CF_2\}_n$  absorption in the region 1100–1250  $\text{cm}^{-1}$ . The derived ethers (XIV) and (XV) showed the highly-fluorinated ring and  $\{-CF_2\}_n$  bands in the same regions as their precursor diesters.

### Liquid range of the perfluoro ethers

The melting and boiling points of the perfluoro ethers prepared are given in Table 1. The effect of the position of the ether link upon the liquid range of the compounds can be explained in terms of the permitted degree of rotation about the ether link. Courtauld's molecular models show that when an oxygen atom is bonded to a perfluoro aromatic ring and to a difluoromethylene chain, steric interaction between the ring *ortho*-fluorine atoms and the fluorine atoms of the difluoromethylene group bonded to oxygen is such that little rotation can occur. Thus, the liquid ranges of compounds (V) and (XIV) are about the same although the latter contains two ether links. Again, molecular models show that the oxygen atom must be at least two difluoromethylene units distant from the point of attachment

TABLE 1

MELTING POINTS AND BOILING POINTS OF SOME PERFLUOROARALKYL ETHERS AND PERFLUORO-1,6-DIPHENYLHEXANE

Compound	M.p. ( $^{\circ}\text{C}$ )	B.p. ( $^{\circ}\text{C}/\text{mmHg}$ )
(V)	59–60	284–6/755
(VI)	*	ca. 270/760
(VII)	ca. –20	288/770
(VIII)	45–46	319/765
(XIV)	75–76	296/765
(XV)	122–123	375/765

\* Mobile liquid at 20°. M.p. not determined.

of the difluoromethylene chain to the pentafluorophenyl ring before unrestricted rotation can occur. This condition is met in compound (VII) where, although no definite melting point was observed (the ether setting to a glass in the region  $-20^{\circ}$  to  $-30^{\circ}$ ), the liquid range is obviously much greater than that of compounds (V) and (XIV). A similar situation occurs with compound (VI). In compound (VIII), which is the only unsymmetrical ether described here, although the oxygen atom is six difluoromethylene units from one aromatic ring, it is also bonded to a carbon bearing both a fluorine atom and a trifluoromethyl group. Again, a model suggests complete (or almost complete) hindrance to free rotation and the melting point is higher than would be expected in the analogous compound in which a fluorine atom replaces the trifluoromethyl group. A possible contribution to a reduction in melting point by the chain branch and the non-symmetry does not appear to be enough to counteract the steric effect of the  $\text{CF}_3$  group. In compound (XV), the increase in boiling point with increased molecular weight has been accompanied by an increase in melting point which has not been much offset by the presence of the two greatly hindered ether links. It is therefore concluded that the perfluoro aromatic "dumb-bell" molecule for a compound of the desired liquid range, requires about 40 carbon atoms and a non-branched perfluoroalkylene chain interrupted by at least one ether link. The oxygen atom should be separated from the perfluoro aromatic rings by at least two perfluoromethylene groups.

#### *Thermo-oxidative stability*

The boiling points of all of the ethers prepared are too low for standard thermo-oxidative stability tests (*e.g.* the Dornte test<sup>24</sup>) or for the isoteniscope thermal stability test to be applied<sup>25</sup>. However, perfluoro-1,6-diphenylhexane has been examined in a micro thermo-oxidative stability test<sup>26</sup> and showed a similar order of stability to a five-ring hydrocarbon phenyl ether,  $\text{C}_6\text{H}_5(\text{OC}_6\text{H}_4)_3\text{O}\cdot\text{C}_6\text{H}_5$ .

#### EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer Infracord Model 337 spectrophotometer. Molecular weights were determined by mass spectrometry using an A.E.I. MS 702 instrument with photoplate detection. Melting points are uncorrected.

Bromopentafluorobenzene (I.S.C. Chemicals Limited) used in Grignard reactions was of +99% purity and was dried with magnesium sulphate. Thionyl chloride (B.D.H.) was boiled with iron filings for several hours before being fractionally distilled prior to use. Aluminium fluoride (B.D.H.) was dried at  $150\text{--}200^{\circ}/0.1$  mmHg for 3–6 h prior to use. Sulphur tetrafluoride (E.I. du Pont de Nemours or Air Products) was used without further purification. Potassium fluoride (B.D.H.) was dried at  $200^{\circ}/0.1$  mmHg for 8 h before use in halogen-exchange reactions. Caesium fluoride (American Potash and Chemical Corporation) was dried at  $200\text{--}250^{\circ}/0.1$  mmHg before use. Hexafluoropropene oxide (Peninsular Chem-

Research Inc.) was used without further purification. Anhydrous hydrogen fluoride (I.S.C. Chemicals Limited) contained about 200 ppm water and was used without further purification.

*Perfluoro-1,4-dibenzoylbutane (I) (nc)*

Pentafluorophenylmagnesium bromide was prepared from bromopentafluorobenzene (12.35 g, 0.05 mole) and magnesium turnings (1.27 g, 0.052 g atom) in diethyl ether (25 ml). Anhydrous cuprous chloride (0.22 g, purified according to the method of Keller and Wycoff<sup>27</sup>) was added and the stirred solution was cooled to +10° (internal temperature) by an ice/water mixture.

Octafluoroadipoyl chloride (8.15 g, 0.025 mole) in ether (12.5 ml) was added in 1 min to the rapidly stirred solution causing the internal temperature to rise to +30° with simultaneous formation of a white precipitate. The suspension was stirred at ambient temperature for 8.5 h, then sulphuric acid (20 ml, 9 N) was added and the organic phase was separated off and combined with ether extracts of the aqueous phase. The dried extracts were distilled to yield perfluoro-1,4-dibenzoylbutane (I), (11.9 g, 79%), b.p. 117–118°/ca. 0.2 mmHg, 97.7% by GLC analysis.

In a second experiment on twice the scale, the product (I) was obtained in 72% yield.

Further fractional distillation yielded an analytical sample, b.p. 110°/0.2 mmHg, m.p. 34.5°, +99% pure by GLC analysis. (Found: C, 36.2; F, 58.0%. C<sub>18</sub>F<sub>18</sub>O<sub>2</sub> requires: C, 36.6; F, 57.9%.)

*Perfluoro-1,6-diphenylhexane (V) (nc)*

Perfluoro-1,4-dibenzoylbutane (24.8 g, 0.042 mole) and anhydrous aluminium fluoride (2 g) were sealed in a 950 ml capacity stainless-steel autoclave which was then cooled in liquid nitrogen. Sulphur tetrafluoride (56 g, 0.52 mole) was added by vacuum transfer and the vessel was then shaken and heated at 175° for 70 h. The cold autoclave was vented through 3 N sodium hydroxide solution. The brown solid residue in the autoclave was taken up in diethyl ether (150 ml) and the ether solution was washed with 2.5% sodium bicarbonate solution, water and dried. After evaporation of the ether, there remained a brown crystalline solid (19.2 g), m.p. 45–56°, which was recrystallised twice from absolute ethanol and gave white crystals of perfluoro-1,6-diphenylhexane (V), (13.1 g, 49%), m.p. 59–60°, b.p. 284–286°/755 mmHg. (Found: C, 34.2; F, 65.7%. C<sub>18</sub>F<sub>22</sub> requires: C, 34.1; F, 65.9%.) The mass spectrum showed a band at 634 attributable to the parent ion and the IR spectrum was in accord with the structure proposed, which was further confirmed by <sup>19</sup>F NMR spectroscopy.

Subsequent reactions have given yields up to 75%.

*Perfluoro-oxydiacetyl chloride*

Perfluoro-oxydiacetic acid (5.4 g, 0.026 mole), re-distilled thionyl chloride (6.59 g, 0.055 mole) and dimethylformamide (0.2 ml) were stirred together and

heated at 80° for 12.5 h, then distilled through a 10 cm indented column to give perfluoro-oxydiacetyl chloride (3.71 g, 59%), b.p. 96–98°/753 mmHg. (Found: C, 19.4; Cl, 28.6%.  $C_4Cl_2F_4O_3$  requires: C, 19.8; Cl, 29.2%.)  $\nu_{max}$ . (liquid film) 1785  $cm^{-1}$  ( $>C=O$ ). Longer periods of heating (24 h) increased the yield to 70–75%.

*Perfluoro-bis(benzoylmethyl)ether (II) (nc)*

Pentafluorophenylmagnesium bromide was prepared from bromopentafluorobenzene (51.8 g, 0.21 mole) and magnesium turnings (5.61 g, 0.23 g atom) in diethyl ether (110 ml). The stirred solution was cooled to –10° and anhydrous cuprous chloride (0.95 g) was added followed by a solution of perfluoro-oxydiacetyl chloride (25.3 g, 0.104 mole) in ether (10 ml) over 3 min. A vigorous reaction ensued with deposition of solid. The mixture was stirred at ambient temperature for 8 h, then sulphuric acid (100 ml, 9 N) was added. The ether phase was separated off and combined with the ether extracts of the aqueous phase. The ether solution was water-washed, dried and distilled to leave a residue (53 g).

A second reaction on the same scale gave a residue (55 g) which was combined with the first residue and distilled through a 15 cm glass helices-packed column to give a main fraction (78.3 g, 73%), b.p. 98–105°/1 mmHg, 97.5% pure by GLC analysis. Preparative GLC was used to give +99% pure perfluoro-bis(benzoylmethyl)ether (II). (Found: C, 37.5; F, 52.8%.  $C_{16}F_{14}O_3$  requires: C, 37.9; F, 52.5%.) The IR spectrum was in accord with the expected structure.

A little decafluorobiphenyl (4.5 g), identified by its IR spectrum, was also isolated from these combined reaction products.

*Perfluoro-bis(2-phenylethyl)ether (VI) (nc)*

Perfluoro-bis(benzoylmethyl)ether (77.7 g, 0.15 mole), anhydrous aluminium fluoride (10 g) and sulphur tetrafluoride (73 g, 0.68 mole) were shaken and heated together in a 200 ml capacity stainless-steel autoclave at 165–170° for 141 h. After venting the volatile components at 20°, the residue was taken up in 100 ml petroleum fraction (boiling range 40–60°). The suspension was filtered and the filtrate was washed with saturated sodium bicarbonate solution, then with water and dried. After evaporation of the solvent, distillation gave a main fraction (45.5 g, 53%), b.p. 145–146°/23 mmHg, 96.7% pure by GLC. An analytical sample of perfluoro-bis(2-phenylethyl)ether (VI) (98.7% by GLC) was obtained by further distillation. (Found: C, 33.9; F, 62.7%.  $C_{16}F_{18}O$  requires: C, 34.9; F, 62.1%.) The mass spectrum showed a band at 550 attributable to the parent ion and the IR spectrum was in accord with the structure.

*Perfluoro-oxydipropionyl chloride*

Perfluoro-oxydipropionic acid (3.12 g, 0.01 mole), re-distilled thionyl chloride (3.75 g, 0.03 mole) and dimethylformamide (0.1 ml) were heated and



stirred together at gentle reflux for 13 h. Distillation gave perfluoro-oxydipropionyl chloride (2.76 g, 80%), b.p. 76–78°/150 mmHg.

An analytical sample was obtained from material produced in lower yield from a preliminary experiment where potassium chloride and thionyl chloride were used as the reagent. (Found: C, 20.8; Cl, 20.8; F, 44.5%.  $C_6Cl_2F_8O_3$  requires: C, 21.0; Cl, 20.7; F, 44.3%.) The IR spectrum was consistent with the proposed structure,  $\nu_{max}$ . (liquid film) 1810  $cm^{-1}$  ( $>C=O$ ).

*Perfluoro-bis(2-benzoyl ethyl) ether (III) (nc)*

Pentafluorophenylmagnesium bromide (0.02 mole) in diethyl ether (12 ml) was prepared from bromopentafluorobenzene (4.96 g, 0.02 mole) and magnesium turnings (0.54 g, 0.022 g atom). Anhydrous cuprous chloride (0.1 g) was added and the solution was cooled to 0°. A solution of perfluoro-oxydipropionyl chloride (3.48 g, 0.01 mole) in diethyl ether (5 ml) was rapidly added to the stirred solution causing a vigorous reaction with ether reflux and deposition of solid. The mixture was stirred at ambient temperature for 10 h and was then acidified with sulphuric acid (10 ml, 9 N). The ether layer was separated off, combined with the ether extracts (4 × 10 ml) of the aqueous phase and dried. Distillation then gave a main fraction (4.69 g, 75%) b.p. 99–102°/0.15 mmHg, 97% pure by GLC. Preparative GLC was used to isolate a +99% pure sample of perfluoro-bis(2-benzoyl ethyl)-ether (III). (Found: C, 35.4; F, 56.2%.  $C_{18}F_{18}O_3$  requires: C, 35.7; F, 56.4%.) The IR spectrum supported the expected structure.

*Perfluoro-bis(3-phenylpropyl) ether (VII) (nc)*

Perfluoro-bis(2-benzoyl ethyl) ether (7.46 g, 0.012 mole), sulphur tetrafluoride (13 g, 0.12 mole) and anhydrous aluminium fluoride (1 g) were shaken and heated in a 200 ml capacity stainless-steel autoclave at 160° for 43 h and at 175° for 72 h. When cool, the volatile components were vented off, and the residue was taken up in 100 ml petroleum fraction (boiling range 40–60°), washed with saturated sodium bicarbonate solution, water and then dried. Evaporation of the solvent gave crude product (7.5 g, 93%), 97% pure by GLC analysis. Preparative GLC was used to isolate a +99% pure (GLC) sample of perfluoro-bis(3-phenylpropyl) ether (VII). (Found: C, 33.1; F, 63.4%.  $C_{18}F_{22}O$  requires: C, 33.3; F, 64.3%), b.p. 288°/771 mmHg (Siwoloboff). The mass spectrum showed a band at 650 attributed to the parent ion and the IR spectrum was consistent with the expected structure.  $^{19}F$  NMR spectroscopy confirmed the structure absolutely.

*Octafluoroadipoyl fluoride (nc)*

*(a) Preparation in sulpholane*

Octafluoroadipoyl chloride<sup>28</sup> (33.5 g, 0.10 mole) and dry potassium fluoride (45 g, 0.78 mole) were stirred together in sulpholane (200 ml) at 100° for 1.5 h and at 120–130° for 3 h. Volatile product (25 g) passed through a short indented column

and was collected in a receiver cooled in a solid carbon dioxide–acetone bath. Fractional distillation of the crude product through a  $15 \times 1.2$  cm glass helices-packed column gave octafluoroadipoyl fluoride (15.2 g, 49%) b.p.  $70\text{--}74^\circ$ , 94% by GLC, with an IR spectrum consistent with its structure,  $\nu_{\text{max}}$ . (liquid film)  $1885\text{ cm}^{-1}$  ( $>\text{C} = \text{O}$ ). Treatment of a sample of the acid fluoride (3.9 g) with methanol gave dimethyl octafluoroadipate (3.88 g) which with ammonia gave octafluoroadipic acid diamide (3.17 g)<sup>29</sup>. Recrystallisation (aqueous ethanol) gave pure material (1.94 g), m.p.  $244\text{--}245^\circ$ . (Found: C, 25.0; H, 1.5; F, 52.7; N, 9.4%.  $\text{C}_6\text{H}_4\text{F}_8\text{N}_2\text{O}_2$  requires: C, 25.0; H, 1.4; F, 52.7; N, 9.7%.)  $\nu_{\text{max}}$ . (KBr) 3390, 3180 ( $>\text{NH}$ ), 1710 ( $>\text{C} = \text{O}$ ),  $1620\text{ cm}^{-1}$  ( $>\text{NH}$ ).

*(b) Preparation without solvent*

Octafluoroadipoyl chloride (9.4 g, 0.03 mole) and anhydrous potassium fluoride (65 g, 1.1 mole) were sealed under vacuum in a 100 ml capacity Pyrex ampoule and heated at  $150^\circ$  for 24 h and at  $170^\circ$  for 24 h. When cool, the ampoule was opened and the volatile product (8.48 g, 98%) was collected in receivers cooled in liquid nitrogen. The octafluoroadipoyl fluoride was of 98% purity by GLC analysis.

*Perfluoro-2-methyl-3-oxanonanedioyl fluoride (IX) (nc)*

Anhydrous caesium fluoride (3 g) and a solution of octafluoroadipoyl fluoride (17.17 g, 0.058 mole) in dry acetonitrile (35 ml) were contained in a flask, fitted to a mechanical shaker and connected to a manometer, vacuum pump, and *via* a drying tube to a cylinder of hexafluoropropene epoxide. The flask was cooled in an acetone–solid carbon dioxide bath and evacuated. Hexafluoropropene epoxide was admitted as the flask was shaken and heated to  $40^\circ$ . After 4 h at this temperature, 12 g (0.072 mole) of the epoxide had been taken up and no further uptake was occurring. The volatile materials were distilled from the flask *in vacuo* and the lower fluorocarbon layer in the distillate was separated off and distilled through a 10 cm glass helices-packed column. The title compound (IX) was obtained as a colourless liquid (9.08 g, 34%) b.p.  $122\text{--}128^\circ$ .  $\nu_{\text{max}}$ . (liquid film)  $1880\text{ cm}^{-1}$  ( $>\text{C} = \text{O}$ ) and characterised by conversion of a sample (2.02 g) into perfluoro-2-methyl-3-oxanonanedioic acid diamide (nc) (1.74 g, 87% yield). Recrystallisation (aqueous ethanol) gave an analytical sample, m.p.  $161\text{--}162.5^\circ$ , (Found: C, 24.1; H, 0.7; F, 58.4; N, 5.8%.  $\text{C}_9\text{H}_4\text{F}_{14}\text{N}_2\text{O}_3$  requires: C, 23.8; H, 0.9; F, 58.6; N, 6.2%.)  $\nu_{\text{max}}$ . (KBr) 3400, 3200 ( $>\text{NH}$ ), 1710 ( $>\text{C} = \text{O}$ ),  $1620$  ( $>\text{NH}$ ),  $1043\text{ cm}^{-1}$  (C–O–C?).

*Perfluoro-1,7-dibenzoyl-1-methyl-2-oxaheptane (IV) (nc)*

A stirred solution of pentafluorophenylmagnesium bromide prepared from bromopentafluorobenzene (8.90 g, 0.036 mole) and magnesium turnings (0.96 g, 0.039 g atom) in diethyl ether (25 ml) was cooled in a nitrogen atmosphere to

–15°. Anhydrous cuprous chloride (0.35 g) was added, followed by 95% (GLC purity) perfluoro-2-methyl-3-oxanonediol fluoride (8.83 g, 0.018 mole) in ether (5 ml) over 5 min. Vigorous reaction occurred with immediate deposition of a precipitate. The resulting mixture was stirred at room temperature for 10.5 h and was then acidified with sulphuric acid (15 ml, 9 *N*). The precipitate slowly dissolved on continued stirring. The ethereal layer was separated, combined with the ether extracts of the aqueous phase and dried. Removal of the ether and two fractional distillations (10 × 0.6 cm glass helices-packed column) gave the suspected title compound (IV) (5.56 g, 41%) b.p. 118–120°/0.15 mmHg, 96% by GLC, with an IR spectrum supporting the assigned structure.

*Perfluoro-2-methyl-1,9-diphenyl-3-oxanonane (VIII) (nc)*

The suspected perfluoro-1,7-dibenzoyl-1-methyl-2-oxaheptane (5.34 g, 0.007 mole), prepared as above, anhydrous aluminium fluoride (1 g) and sulphur tetrafluoride (12 g, 0.11 mole) were shaken and heated together in a 200 ml capacity stainless-steel autoclave at 175° for 157 h. After venting the volatile materials, there remained a viscous liquid which was taken up in ether (25 ml). The ethereal solution was washed with saturated sodium bicarbonate solution, water and dried. Removal of the ether left a viscous residue which crystallised on cooling. Recrystallisation (acetone–ethanol–water) yielded white crystals (1.93 g, 35%) of perfluoro-2-methyl-1,9-diphenyl-3-oxanonane (VIII) m.p. 45–46°. (Found: C, 31.1; F, 66.4%.  $C_{21}F_{28}O$  requires: C, 31.5; F, 66.5%.) The mass spectrum showed a band at 800 attributable to the parent ion and the IR spectrum was consistent with the proposed structure which was confirmed by  $^{19}F$  NMR spectroscopy.

*Dipentafluorophenyl octafluoroadipate (X) (nc)*

Pentafluorophenol (18.4 g, 0.1 mole) and Amberlite IRA 401 (OH) ion-exchange resin (10 g) were stirred together in boiling benzene (140 ml) and the residual water was removed by azeotropic distillation. Octafluoroadipoyl chloride (16.4 g, 0.05 mole) in benzene (20 ml) was then added over 0.25 h and the mixture was boiled and stirred for 16 h. The resin was filtered from the hot mixture and the filtrate was distilled down to about 30 ml volume. The title compound crystallised from the cooled solution as white crystals (28.7 g, 92%), m.p. 82–83°. Recrystallisation of a sample from benzene gave white crystals of dipentafluorophenyl octafluoroadipate (X) m.p. 82–83°. (Found: C, 34.5; F, 54.9%.  $C_{18}F_{18}O_4$  requires: C, 34.8; F, 55.0%.) The IR spectrum was in accord with the expected structure.

*Perfluoro-1,6-bis(phenoxy)hexane (XIV) (nc)*

Dipentafluorophenyl octafluoroadipate (31.1 g, 0.05 mole), anhydrous hydrogen fluoride (25 ml) and sulphur tetrafluoride (19 g, 0.18 mole) were shaken and heated together in a 200 ml capacity stainless-steel autoclave at 150° for 9 h. The volatile products were vented from the cold autoclave and IR examination of

the crude product showed that some ketonic material remained. The residue was therefore shaken and heated for a further 22 h at 175°\* with additional anhydrous hydrogen fluoride (25 ml) and sulphur tetrafluoride (14.5 g, 0.13 mole). After venting the autoclave, the residue was dissolved in diethyl ether (500 ml) containing suspended sodium fluoride. Filtration and evaporation of the ethereal solution then gave brown plates (23.8 g) which after two recrystallisations (ethanol) gave perfluoro-1,6-bis(phenoxy)hexane (XIV) as white plates (17.5 g, 53%) m.p. 75–76°, b.p. 296°/764 mmHg. (Found: C, 32.2; F, 63.0%.  $C_{18}F_{22}O_2$  requires: C, 32.4; F, 62.8%.) The mass spectrum showed a band at 666 attributed to the parent ion and the IR spectrum was consistent with the expected structure which was confirmed by  $^{19}F$  NMR spectroscopy.

#### *Nonafluoro-4-hydroxybiphenyl*

Decafluorobiphenyl (100 g, 0.3 mole) and crushed potassium hydroxide (34 g, 0.52 mole) were stirred together in boiling t-butanol (600 ml) for 2 h and the mixture was evaporated to dryness *in vacuo*. Water (500 ml) was added and the suspension was steam distilled to remove decafluorobiphenyl (20.5 g). Hydrochloric acid (200 ml, 6 N) was added to the residue which was steam distilled to give nonafluoro-4-hydroxybiphenyl (41.2 g, 41%) m.p. 119–120° (sealed tube). The residue (46.5 g) was octafluoro-4,4'-dihydroxybiphenyl, m.p. 212–215°.

#### *Bis(nonafluoro-4-biphenyl)octafluoroadipate (XI) (nc)*

Nonafluoro-4-hydroxybiphenyl (36.5 g, 0.11 mole), Amberlite IRA 401 (OH) ion-exchange resin (20 g) and octafluoroadipoyl chloride (20.3 g, 0.06 mole) were stirred in boiling benzene (260 ml) for 48 h. Removal of resin and solvent yielded a solid (45 g) which was heated at 120–130°/0.05 mmHg for 6 h to sublime off nonafluoro-4-hydroxybiphenyl (2 g) leaving (XI) as white crystals (42 g, 83%) m.p. 164–168°. Recrystallisation of a portion from methylcyclohexane gave white needles of bis(nonafluoro-4-biphenyl)octafluoroadipate (XI) m.p. 168.5–169.5°. (Found: C, 39.3; F, 53.8%.  $C_{30}F_{26}O_4$  requires: C, 39.2; F, 53.8%), with an IR spectrum in accord with the structure.

#### *Perfluoro-1,6-bis(4-phenylphenoxy)hexane (XV) (nc)*

Bis(nonafluoro-4-biphenyl)octafluoroadipate (18.4 g, 0.02 mole), sulphur tetrafluoride (17 g, 0.16 mole) and anhydrous hydrogen fluoride (40 ml) were shaken and heated together in a 200 ml capacity stainless-steel autoclave at 170° for 23 h and at 180° for 49 h. Volatile materials were vented off and a part (0.9 g) of the residue (20.4 g) was dissolved in ether (200 ml). This solution was washed with 2.5% sodium hydroxide solution, then water and dried. Evaporation of the

\* Since the critical temperature of hydrogen fluoride is 188°, careful temperature control is essential.

ether gave a residue (0.63 g) which after two recrystallisations (4:1 v/v ethanol: toluene) yielded white crystalline perfluoro-1,6-bis(4-phenylphenoxy)hexane (XV) (0.18 g) m.p. 119–122°. (Found: C, 37.6; F, 59.5%.  $C_{30}F_{30}O_2$  requires: C, 37.4; F, 59.2%.)

The remaining crude product was sublimed and a tan solid (12.3 g) was obtained at 150–170°/0.05 mmHg. Two recrystallisations from n-butanol and a further sublimation at 160°/0.05 mmHg gave pure material (8.9 g, 46%) m.p. 122–123°, b.p. *ca.* 375°/765 mmHg (determined by distillation in air using a thermocouple to record temperature). A band at 962 in the mass spectrum was attributed to the parent ion and the IR spectrum was consistent with the expected structure which was confirmed by  $^{19}F$  NMR spectroscopy.

*Perfluoro-3-hydroxy-4,4'-dimethylbiphenyl (XII) (nc)*

Perfluoro-4,4'-dimethylbiphenyl (8.68 g, 0.02 mole) was stirred in boiling t-butanol (50 ml) and crushed potassium hydroxide (2.64 g, 0.04 mole) was added in 0.75 h. The mixture was boiled for 3 h, then taken to dryness *in vacuo*. Hydrochloric acid (62 ml, 2.3 *N*) was added to the tacky residue and the solution was steam distilled. Ether extraction of the distillate and evaporation of the dried extracts gave a tan solid (7.75 g). Two recrystallisations (methylcyclohexane) and sublimation (80°/0.05 mmHg) gave white crystals of perfluoro-3-hydroxy-4,4'-dimethylbiphenyl (XII) (5.42 g, 63%) m.p. 83–84.5°. (Found: C, 38.9; H, 0.2; F, 57.6%; equiv. 445.  $C_{14}HF_{13}O$  requires: C, 38.9; H, 0.2; F, 57.2%; equiv. 432.) The infrared spectrum was consistent with the proposed structure,  $\nu_{max}$ . ( $CCl_4$ ) 3580 (–OH) *ca.* 1500 (highly-fluorinated ring) 1160, 1330  $cm^{-1}$  (–CF<sub>3</sub> on aromatic ring), which was confirmed by  $^{19}F$  NMR spectroscopy.

*Perfluoro-1,6-bis [3-(4,4'-dimethylbiphenyl)]octafluoroadipate (XIII) (nc)*

Perfluoro-3-hydroxy-4,4'-dimethylbiphenyl (8.64 g, 0.02 mole) and Amberlite IRA 401 (OH) ion-exchange resin (5 g) were stirred in boiling benzene (75 ml) while residual water was removed by azeotropic distillation. Octafluoroadipoyl chloride (3.27 g, 0.01 mole) in dry benzene (10 ml) was added and the mixture was stirred and boiled for 27.5 h. The resin was filtered off and the filtrate was evaporated to low volume and heated at 90°/0.1 mmHg for several hours. The cooled material solidified over several days to a tan solid (11.26 g, 100%) which could not be recrystallised successfully (oil formation). Part of this solid was distilled in a short-path still (bath temperature 160–180°) at 0.05 mmHg and gave a viscous distillate which slowly solidified to give perfluoro-1,6-bis[3-(4,4'-dimethylbiphenyl)]octafluoroadipate (XIII), a white solid, m.p. 101–105°. (Found: C, 36.4; F, 57.7%.  $C_{34}F_{34}O_4$  requires: C, 36.5; F, 57.8%.) The IR spectrum supported the ester structure which was confirmed by  $^{19}F$  NMR spectroscopy.

The IR spectrum of the analytically pure material was only marginally different from that of the crude product which was used in the following reaction.

*Perfluoro-1,6-bis[3-(4,4'-dimethylbiphenyloxy)]hexane (XVI) (attempted preparation)*

Perfluoro-1,6-bis[3-(4,4'-dimethylbiphenyl)]octafluoroadipate (41 g, 0.037 mole), anhydrous hydrogen fluoride (35 ml) and sulphur tetrafluoride (20 g, 0.18 mole) were shaken and heated together at 175° for 48 h in a 200 ml stainless-steel autoclave when failure of the heating control caused the temperature to rise to 210° with attendant rupture of the bursting disc. Some loss of material occurred. Crude product (17.5 g) was isolated and distilled giving a fraction (8.24 g) b.p. 120–130°/0.01 mmHg. Part (1.44 g) was repeatedly recrystallised (ethanol and cyclohexane) and gave white crystals (0.17 g) m.p. 128–130°. (Found: C, 38.0; F, 58.4%. C<sub>34</sub>F<sub>38</sub>O<sub>2</sub> requires: C, 35.1; F, 62.1%.)

The IR spectrum of this material did not show absorptions attributable to  $(-CF_2)_n$  in the 1200 cm<sup>-1</sup> region but had peaks at 1165 cm<sup>-1</sup>, 1310 cm<sup>-1</sup> ( $-CF_3$ ) and at ca. 1500 cm<sup>-1</sup> (highly-fluorinated aromatic ring). The spectrum was very similar to that of perfluoro-4,4'-dimethylbiphenyl.

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