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POLYFLUOROARYL ORGANOMETALLIC COMPOUNDS XIV. 5-PHENYL-OCTAFLUORODIBENZOPHOSPHOLE*

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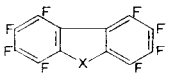
SUMMARY

The 5-phenyl-octafluorodiphenzophosphole (V) has been synthesised by reaction of octafluoro-2,2′-dilithiobiphenyl with phenyldichlorophosphine and was most effectively oxidised to the 5-oxide (VI) using t-butylhydroperoxide. It is shown, by synthesis, that nucleophilic substitution occurs at C_3 in the phosphole (V) and at C_2 in the phosphole oxide (VI). These orientations are discussed together with results from related dibenzo systems.

INTRODUCTION

The present paper extends our studies of the polyfluorinated derivatives of the dibenzo series[1], (I)-(IV), in that we have now synthesised 5-phenyl-octafluorodibenzophosphole (V) and the corresponding 5-oxide (VI);



(I) X = S
(II) X = O
(III) X = SO_2
(IV) X = CO
(V) X = P–C_6H_5
(VI) X = P(O)C_6H_5

these make a particularly interesting comparison with the dibenzothiophen derivatives (I) and (III), as discussed later.

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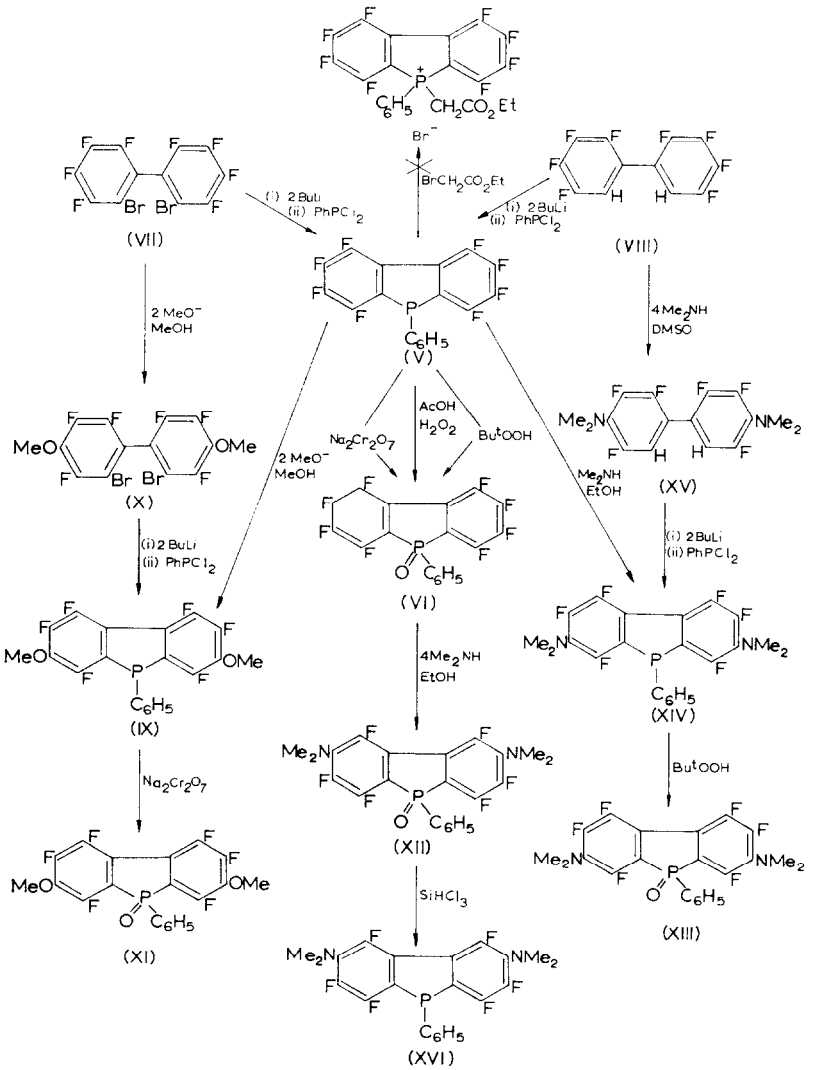
RESULTS AND DISCUSSION

Synthesis of (V) was achieved by reaction of octafluoro-2,2′-dilithiobiphenyl, made from (VII)[2] or (VIII)[3], with phenyldichlorophosphine (see Scheme 1).



Scheme 1.

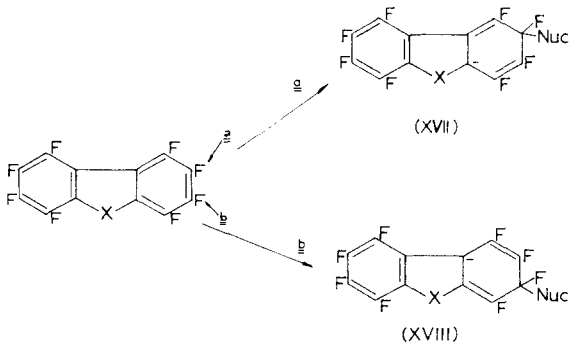
Expansion of the covalency of phosphorus in (V) is apparently more difficult than in triphenylphosphine, since quaternisation with ethylbromoacetate, which occurs readily with the latter[4], did not occur with (V). Nevertheless, oxidation to 5-

phenyl-octafluorodibenzophosphole-5-oxide (VI) occurred readily with the reagents[5] shown in the scheme, although the mildest reagent, t-butylhydroperoxide, in stoichiometric amounts, proved to be the most effective. Peroxytrifluoroacetic acid was also tried but appeared to be too vigorous, giving only an intractable tar.

The orientation of nucleophilic substitution in (V) by methoxide was established as shown since the same dimethoxy derivative (IX) was obtained both by direct reaction of (V) with two equivalents of methoxide and by cyclisation of the known[1] dimethoxy biphenyl (X). This dimethoxydibenzophosphole (IX) was then oxidised to the phosphole oxide (XI) in order to relate the orientation of substitution in (VI) to that of (V), but, unfortunately, reaction of the dibenzophosphole oxide (VI) with methoxide gave a complex mixture of products. These apparently arise from ring cleavage at phosphorus as well as nucleophilic displacement of fluorine, and therefore the orientation of attack in (VI) could not be determined by this route.

However reaction of the dibenzophosphole oxide (VI) with dimethylamine gave exclusive displacement of fluorine to yield the di-*N*,*N*-dimethylamino derivative (XII), and this parallels the observations of other workers on related systems [5b]. This dibenzophosphole oxide derivative (XII) must, from a consideration of ^{19}F NMR shifts (see Table 1), have the dimethylamino groups at either C_2 or C_3 since the very low field resonance in this compound (XII) is incompatible with substitution at C_1 or C_4. Substitution must therefore have occurred at C_2 since (XII) was different from the 3,7-di-*N*,*N*-dimethylamino derivative (XIII). The structure of this compound is unambiguously assigned since it was obtained by oxidation of the corresponding di-*N*,*N*-dimethylaminodibenzophosphole (XIV), which itself was synthesised by direct reaction of (V) with dimethylamine. Furthermore, the structure of (XIV) was unambiguously determined by cyclisation of the biphenyl derivative (XV) as shown in Scheme 1. These structural determinations were confirmed by the reduction of (XII) with trichlorosilane [6] to give a di(*N*,*N*-dimethylamino)dibenzophosphole (XVI) which was different from the isomer (XIV) prepared by direct reaction and cyclisation. This sequence of reactions clearly establishes that nucleophilic substitution occurs at C_3 in the phosphole (V) and at C_2 in the phosphole oxide (VI).

Early attempts at determining the orientation of nucleophilic substitution in (I)–(IV) were confused by the inadequacies of arguments based on the use of model compounds for NMR assignment[1]. Final proof of orientation was provided by unambiguous synthesis of dibenzothiophens[1] and has been confirmed by work on related compounds [7]. It is now clear that substitution occurs at *a* for (IV) and at *b* for (I)–(III). These results as well as relative rate measurements for (I), (II) and (IV) can be accommodated by assuming Wheland intermediates (XVII) and (XVIII) and considering the relative effects of the group X and a polyfluoro aromatic ring on the stability of an adjacent carbanionic centre[1].



This qualitative picture now becomes more acceptable since it is found to accommodate the results for the dibenzophosphole (V) and the phosphole oxide (VI). Available substituent constants[7,8] suggest that carbanion stabilising influences decrease in the series

$$Ph_2\overset{\overset{O}{\|}}{P}- > \quad C_6F_5- > \quad Ph_2-P-$$

and consequently it is reasonable to anticipate that for X = P–C_6H_5 intermediate (XVIII) is of lower energy while for X = P(O)C_6H_5 intermediate (XVII) is preferred. In accord with this rationalisation, qualitative observations (see experimental details) indicate that (VI) is very much more reactive than (V) towards dimethylamine.

Therefore this picture of substitution in these compounds accommodates the results from (I) to (VI) with the exception of (III). This compound remains completely anomalous, on this basis, in that it is of comparable reactivity with (IV) yet gives the orientation pattern (*b*). Clearly, the sulphone group has a rigid conformation in (III), with respect to the aromatic rings, and it has been suggested that this type of conformation is least effective in stabilising carbanions[10]. Perhaps this is at the root of the anomalous behaviour of (III) and it could account for the observed orientation pattern although not the high reactivity[1].

EXPERIMENTAL

All reactions involving organo lithium compounds were carried out in apparatus which had been baked overnight in an oven and then purged with dry nitrogen.

2,2'-Dibromo-octafluorobiphenyl[11] *and octafluoro-2,2'-dihydrobiphenyl*[12]

These compounds ((VII) and (VIII)) were prepared by the titanium tetrachloride coupling of 2-bromotetrafluorophenyl-lithium and 2,3,4,5-tetrafluorophenyl-lithium respectively in yields of 77% and 89%.

5-Phenyl-octafluorodibenzophosphole (V)

From 2,2'-dibromo-octafluorobiphenyl (VII)

n-Butyl-lithium (16 ml of a hexane solution, 32 mmole) in dry hexane (15 ml) was added drop-wise to a stirred solution of (VII) (7.0 g, 15.4 mmoles) in dry ether (150 ml) at −75°. After 3 h a solution of phenyldichlorophosphine (2.75 g, 15.4 mmole) in dry ether (15 ml) was added drop-wise and the resulting mixture allowed to warm to room temperature over 1 h. Dilute sulphuric acid was added and the orange coloured organic layer was separed and dried ($CaCl_2$). Removal of the solvent on a rotary evaporator left a brown oil which solidified after pumping under vacuum. Sublimation (130°/10^{-2} mm Hg) yielded a sticky yellow solid (4.5 g) which from analytical scale VPC appeared to consist of one major component (~85%) and several minor components. Recrystallisation from ethanol yielded 5-phenyl-octafluorodibenzophosphole (V) (nc) (Found: C, 53.2; H, 1.1. $C_{18}H_5F_8P$ requires C, 53.5; H, 1.3%) as white needles, m.p. 123–124° (Yield, 3.3 g, 53%). (Note that the corresponding hydrocarbon compound has a melting point of 94.5–95°[13].) The ^1H NMR spectrum showed a broad resonance centred at 2.5 τ which is assigned to the phenyl group.

From octafluoro-2,2'-dihydrobiphenyl (VIII)

n-Butyl-lithium (45 ml of a hexane solution, 90 mmole) in dry hexane (25 ml) was added drop-wise to a stirred solution of (VIII) (13.3 g, 44.6 mmole) in THF (150 ml, freshly distilled from lithium aluminium hydride (LAH) at −75°. After 3 h a solution of phenyldichlorophosphine (8.0 g, 44.7 mmole) in THF (15 ml) was added drop-wise and the mixture allowed to warm to room temperature over 2 h. Dilute sulphuric acid was added and the yellow organic layer separated and dried ($CaCl_2$). Removal of the solvent on a rotatory evaporator left a yellow oil. This was transferred to an alumina column and then eluted with petrol (40/60°); a yellow band moved down the column. Removal of the solvent from the eluant and sublimation (~130°/10^{-2} mm Hg) of the residue yielded a white solid (11.2 g, 62%) and a black intractable tar. The solid was shown to be 5-phenyl-octafluorodibenzophosphole by comparison of its IR spectrum with that of a previously-prepared sample.

5-Phenyl-hexafluoro-3,7-dimethoxydibenzophosphole (IX)

From 5-phenyl-octafluorodibenzophosphole (V)

A solution of sodium (0.051 g, 2.2 mmole) in dry methanol (15 ml) was added drop-wise to a refluxing solution of (V) (0.407 g, 1.0 mmole) in dry methanol (30 ml). Reflux was continued for 20 h and the mixture then poured into dilute sulphuric acid and extracted with ether. The extracts were combined, dried ($CaCl_2$), the solvent removed on a rotary evaporator, and the residue sublimed (140°/10^{-2} mm Hg) to yield a white solid (0.4 g). Recrystallisation from ethanol yielded 5-phenyl-hexafluoro-3,7-dimethoxydibenzophosphole (IX) (nc) (Found: C, 56.0; H, 2.5. $C_{20}H_{11}F_6O_2P$ requires C, 56.1; H, 2.6%) as white needles,

m.p. 141–143°. The ^{1}H NMR spectrum shows two resonances, one at 2.5 τ (5 protons), corresponding to the phenyl protons, and the other, a triplet, $J = 1.4$ Hz, at 5.8 τ (6 protons) corresponding to the methoxyl protons.

From 2,2′-dibromohexafluoro-4,4′-dimethoxybiphenyl (X)

n-Butyl-lithium (5.6 ml of a hexane solution, 11.2 mmole) in dry hexane (15 ml) was added drop-wise to a stirred solution of 2,2′-dibromohexafluoro-4,4′-dimethoxybiphenyl[1] (2.7 g 5.6 mmole) in dry ether (130 ml) at −75°. After 4 h phenyldichlorophosphine (1.0 g. 5.6 mmole) in dry ether (10 ml) was added drop-wise and the resulting mixture allowed to warm slowly (2 h) to room temperature. Dilute sulphuric acid was added and the clear yellow organic layer separated and dried ($CaCl_2$). The solvent was removed on a rotary evaporator and the residue sublimed to yield a white solid (1.5 g). Analytical scale VPC indicated it to be a mixture of two components; the major component (~70%) had the same retention time as the 5-phenyl-hexafluoro-3,7-dimethoxydibenzophosphole prepared previously, and the minor component (~30%) appeared to be hexafluoro-2,2′-dihydro-4,4′-dimethoxybiphenyl[1]; the ^{19}F NMR spectrum confirmed these identifications. Recrystallisation from hexane and then ethanol yielded 5-phenyl-hexafluoro-3,7-dimethoxydibenzophosphole, m.p. 143–144° (mixed m.p. 141–143°) whose spectroscopic properties were identical with those of the sample obtained previously.

*5-Phenyl-hexafluoro-3,7-di(*N,N*-dimethylamino)dibenzophosphole (XIV)*

From 5-phenyl-octafluorodibenzophosphole (V)

Dimethylamine (6 ml of a 4 *M* solution in ethanol, 24 mmole) was added to a refluxing solution of (V) (0.6 g, 1.5 mmole) in dry ethanol (50 ml). Reflux was continued for 5 d. (Reflux for shorter periods of time, *e.g.* 3 d, gave mixtures containing starting material and a mono-dimethylamino derivative.)

The ethanol was removed on a rotary evaporator and water added to the residue which was then extracted with ether. The extracts were dried ($CaCl_2$). Removal of the ether and sublimation (150°/10^{-2} mm Hg) of the residue yielded a yellow solid (0.6 g). This was recrystallised from ethanol to yield 5-phenyl-hexafluoro-3,7-di(*N*,*N*-dimethylamino)dibenzophosphole (XIV) (nc) (Found: C, 58.3; H, 3.5; N, 6.0. $C_{22}H_{17}F_6N_2P$ requires C, 58.2; H, 3.8; N, 6.2%) as pale yellow needles m.p. 149–150°. The ^{1}H NMR spectrum shows two resonances; a broad one at ~ 2.6 τ (5 protons) is assigned to the phenyl group and the other, a triplet ($J = 2.2$ Hz) at 7.0 τ (12 protons), is assigned to the dimethylamino groups.

*From 4,4′-di(*N,N*-dimethylamino)-hexafluoro-2,2′-dihydrobiphenyl (XV)*

n-Butyl-lithium (27 ml of a hexane solution, 60 mmole) was added drop-wise to a mixture of THF (150 ml, freshly distilled) and dry hexane (15 ml) at −78°. A solution of (XV) (10.4 g, 29.9 mmole) in THF (50 ml) was then added drop-wise and the dark coloured solution stirred at −78° for 4 h. Phenyldichlorophosphine

(5.3 g, 29.6 mmole) in THF (20 ml) was then added and, after 0.5 h at −78°, the mixture allowed to warm slowly to room temperature. Dilute sulphuric acid was added and the yellow organic layer was separated and dried ($CaCl_2$). Removal of the solvent left a red oil which was run on to an alumina column and eluted with petrol–benzene. This yielded a brown oil which on sublimation (120°/10^{-2} mm Hg) gave a yellow solid (4 g), identified by NMR spectroscopy as starting material. The residue from the sublimation was dissolved in a little benzene and run on to a silica gel (cc. 4) column and eluted with petrol–benzene (1:1). The middle fractions (2.2 g) proved to contain material of the same R_f value as the compound (XIV) prepared as described above. Analytical scale GLC indicated that it consisted of starting material (XV), (XIV), and another unidentified component in the approximate ratios 1:2:1. The starting material was removed by fractional sublimation and the residue was recrystallised from hexane/chloroform and then from ethanol to yield 5-phenyl-hexafluoro-3,7-di(*N*,*N*-dimethylamino)dibenzophosphole (XIV) which was identified by comparison of its m.p. and IR spectrum with that of (XIV) prepared above.

Oxidation of 5-phenyl-octafluorodibenzophosphole (V)

With $Na_2Cr_2O_7$ [5a]

A mixture of 5-phenyl-octafluorodibenzophosphole (1.0 g, 2.5 mmole), $Na_2Cr_2O_7$ (6.6 g, 25.2 mmole), glacial acetic acid (16.5 ml), water (16.5 ml) and conc. H_2SO_4 (6.6 ml) was heated under reflux for 5 h, then poured into cold water and extracted with methylene dichloride. The extracts were dried ($CaCl_2$), the solvent removed on a rotary evaporator, and the residue sublimed (130°/10^{-2} mm Hg) to yield a white solid (0.5 g, 48%). The ^{19}F NMR spectrum showed only four resonances which were not those of the starting material. The product was recrystallised from hexane/$CHCl_3$ to yield 5-phenyl-octafluorodibenzophosphole-5-oxide (VI) (nc) (Found: C, 51.7; H, 1.1. $C_{18}H_5F_8OP$ requires C, 51.4; H, 1.2%) as colourless needles m.p. 189–190°. (Note that the corresponding hydrocarbon compound has a melting point of 167–168°[13].) The IR spectrum shows a P=O stretching absorption at 1222 cm^{-1}. The ^1H NMR spectrum shows a broad, complex absorption centred around 2.2 τ due to the phenyl protons.

With H_2O_2/CH_3COOH [5b]

A mixture of 5-phenyl-octafluorodibenzophosphole (0.9 g, 2.2 mmole), glacial acetic acid (40 ml) and hydrogen peroxide (100 vol., 7 ml) was heated under reflux for 2 h and then poured into cold water. Ferrous sulphate was added to destroy the excess peroxide and the mixture was extracted three times with ether. The combined extracts were dried ($CaCl_2$), the solvent removed, and the residue sublimed to yield a white solid (0.6 g, 67%) which was identified as 5-phenyl-octafluorodibenzophosphole-5-oxide by comparison of its spectroscopic properties with those of the sample prepared previously.

With t-BuOOH[5c]

5-Phenyl-octafluorodibenzophosphole (2.3 g, 5.7 mmole), t-butylhydroperoxide (0.6 g, 6.7 mmole) were heated together in dry ethanol (50 ml) for 1.5 h. The solvent was then removed on a rotary evaporator and the solid residue sublimed (130°/10^{-2} mm Hg) to yield a white solid (2.3 g, 96%) which was identified as 5-phenyl-octafluorodibenzophosphole-5-oxide by comparison of its spectroscopic properties with those of an authentic sample.

With CF_3COOH

This reagent, with (V) in refluxing CH_2Cl_2/CF_3COOH, gave, on work-up, only an intractable tar.

Oxidation of 5-phenyl-hexafluoro-3,7-dimethoxydibenzophosphole (IX)

A mixture of (IX) (1.0 g, 2.34 mmole), glacial acetic acid (16 ml), $Na_2Cr_2O_7$ (1.7 g, 6.5 mmole), conc. H_2SO_4 (7 ml) and water (15 ml) was heated under reflux for 4 h, poured into cold water (800 ml) and extracted with methylene dichloride. The extracts were combined, dried ($CaCl_2$), the solvent removed, and the residue sublimed to yield a pale yellow solid (0.5 g) and a black intractable residue. Analytical scale VPC of the yellow solid indicated the presence of one major component (~90%) and recrystallisation from hexane/chloroform yielded 5-phenyl-hexafluoro-3,7-dimethoxydibenzophosphole-5-oxide (XI) (nc) (Found: C, 53.8; H, 2.6. $C_{20}H_{11}F_6O_3P$ requires C, 54.1; H, 2.5%) as white crystals m.p. 154–155°. The IR spectrum shows a P=O stretching frequency at 1211 cm^{-1}. The ^1H NMR spectrum shows two resonances; a broad resonance at 2.3 τ (5 protons) and a triplet ($J = 1.5$ Hz) at 5.8 τ (6 protons) which are assigned to the phenyl and methoxyl groups respectively.

Oxidation of 5-phenyl-hexafluoro-3,7-di(N,N-dimethylamino)dibenzophosphole (XIV)

With t-BuOOH

A mixture of 5-phenyl-hexafluoro-3,7-di(*N*,*N*-dimethylamino)dibenzophosphole (XIV) (0.73 g, 1.6 mmole), t-butylhydroperoxide (0.18 g, 2.0 mmole) and dry ethanol (70 ml) was heated under reflux for 4 h. The solvent was removed on a rotary evaporator and the yellow solid residue (0.8 g) was recrystallised from hexane/chloroform to yield 5-phenyl-hexafluoro-3,7-di(*N*,*N*-dimethylamino)dibenzophosphole-5-oxide (XIII) (nc) (Found: C, 55.9; H, 3.4; N, 5.9. $C_{22}H_{17}F_6N_2OP$ requires C, 56.2; H, 3.6; N, 6.0%) as yellow plates m.p. 198–200°. The ^1H NMR spectrum shows two resonances; a broad one around 2.3 τ (5 protons) is assigned to the phenyl group and the other, a triplet ($J = 2.3$ Hz) at 7.1 τ (12 protons), is assigned to the dimethylamino groups.

With $Na_2Cr_2O_7$ and with $H_2O_2/AcOH$

The same procedure was used with each of those two reagents as with the

oxidation of (V), given above. In both cases complex mixtures of products were obtained, which were not investigated further.

Reaction of 5-phenyl-octafluorodibenzophosphole-5-oxide (VI) with nucleophiles

With dimethylamine in ethanol

Dimethylamine (3 ml of a 4 *M* solution in ethanol, 12 mmole) was added to a stirred solution of (VI) (1.1 g, 2.62 mmole) in dry ethanol (50 ml) at room temperature. After 19 h the solvent was removed on a rotary evaporator, water added to the residue which was then extracted with ether. The extracts were dried ($CaCl_2$), and the solvent removed to leave a yellow solid (1.2 g) which was recrystallised from hexane/chloroform to yield 5-phenyl-hexafluoro-2,8-di(*N*,*N*-dimethylamino)dibenzophosphole-5-oxide (XII) (nc) (Found: C, 56.3; H, 3.3; N, 6.3. $C_{22}H_{17}F_6N_2OP$ requires C, 56.2; H, 3.6; N, 6.0%) as cream coloured crystals m.p. 208–210°. The IR spectrum shows a P=O stretching absorption at 1210 cm^{-1}. The ^1H NMR spectrum shows two resonances, one ~2.3 τ (5 protons) and the other ~6.9 τ (12 protons) which were assigned to the phenyl protons and to the dimethylamino protons respectively. The latter appeared as a doublet ($J = 2.6$ Hz) of triplets ($J = 1.3$ Hz) at both 56.4 MHz and 90 MHz. Also raising the temperature to +140° had no effect on the splitting of this peak.

With sodium methoxide/methanol

A solution of sodium (0.069 g, 3.0 mmole) in dry methanol (15 ml) was added drop-wise to a refluxing solution of (VI) (0.6 g, 1.43 mmole) in dry methanol (30 ml). After 18 h the mixture was poured into dilute sulphuric acid and extracted with ether. The extracts were dried ($CaCl_2$) and the solvent removed to yield a yellow oil (0.6 g). TLC and ^{19}F NMR analyses indicated it to be a complex mixture with several major components.

*Reduction of 5-phenyl-hexafluoro-2,8-di(*N,N*-dimethylamino)dibenzophosphole-5-oxide (XII)*

With trichlorosilane[6]

A mixture of (XII) (0.7 g), trichlorosilane (10 ml) and dry benzene (70 ml) was heated to reflux, under an atmosphere of dry nitrogen, for 18 h. The solvent was removed by distillation, water added to the residue, which was then extracted with ether. The ether extracts were separated and dried ($CaCl_2$). Removal of the ether on a rotary evaporator and sublimation of the residue gave a cream coloured solid (0.7 g). Recrystallisation from ethanol yielded 5-phenyl-hexafluoro-2,8-di-(*N*,*N*-dimethylamino)dibenzophosphole (XVI) (nc) (Found: C, 57.9; H, 3.8; N, 6.4. $C_{22}H_{17}F_6N_2P$ requires C, 58.2; H, 3.8; N, 6.2) as colourless crystals m.p. 136–137°. The ^1H NMR spectrum shows two resonances; a broad one at ~2.6 τ (5 protons) is assigned to the phenyl group and the other, a doublet ($J \sim 2$ Hz) of triplets ($J \sim 1$ Hz) at 7.0 τ (12 protons), is assigned to the dimethylamino groups.

Other reagents

Reduction of (XII) was also attempted with $NaBH_4$ and $LiAlH_4$; with the former, starting material was recovered and with the latter a complex mixture of products was obtained.

*4,4'-Di(*N,N*-dimethylamino)-hexafluoro-2,2'-dihydrobiphenyl (XV)*

Octafluoro-2,2'-dihydrobiphenyl (VIII) (8.2 g, 27.5 mmole) was dissolved in dry DMSO (150 ml) and heated to 100°. A solution of dimethylamine in ethanol (30 ml of a 4 *M* solution, 120 mmole) was added and the resulting yellow solution stirred, at this temperature, for 3 d. The mixture was poured into 2 l of cold water, and the cream coloured precipitate filtered off, washed with more water, dissolved in ether and dried ($CaCl_2$). Removal of the ether on a rotary evaporator and sublimation (120°/10^{-2} mm Hg) of the residue yielded a white solid (8.8 g, 92%) which was recrystallised from ethanol to yield 4,4'-di(*N,N*-dimethylamino)-hexafluoro-2,2'-dihydrobiphenyl (XV) (nc) (Found: C, 54.9; H, 3.8; N, 7.9. $C_{16}H_{14}F_6N_2$ requires C, 55.2; H, 3.9; N, 8.0%) as white needles m.p. 121–122°. The ^1H NMR spectrum shows two resonances; a broad and complex peak $\sim$ 2.9 τ (2 protons), which is assigned to the ring protons, and a triplet (J = 2.1 Hz) at 6.9 τ, which is assigned to the dimethylamino groups.

*Octafluoro-4,4'-di(*N,N*-dimethylamino)biphenyl (XIX)*

Dimethylamine (8 ml of a 4 *M* solution in ethanol, 32 mmole) was added to a solution of decafluorobiphenyl (2.2 g, 6.6 mmole) in dry ethanol (50 ml) and the mixture was refluxed for 44 h. The ethanol was removed on a rotary evaporator, water added to the residue which was then extracted with ether. The extracts were dried ($CaCl_2$), and the solvent removed to yield a cream coloured solid (2.4 g). This was recrystallised from ethanol to yield octafluoro-4,4'-di(*N,N*-dimethylamino)biphenyl (XIX) (nc) (Found: C, 50.0; H, 3.1; N, 7.4. $C_{16}H_{12}F_8N_2$ requires C, 50.0; H, 3.2; N, 7.3%) as white needles. The ^1H NMR spectrum showed just a single triplet (J = 2.3 Hz) at 7.0 τ.

NMR spectra

The ^{19}F NMR shifts (relative to C_6F_6) are given in Table 1 together with the assignments. The data for (V) and (VI) are consistent with that for other members of the dibenzo series in that the resonances due to F_1 and F_4 are to much lower fields than those due to F_2 and F_3. Comparisons of the observed shifts for (IX) with those for (V), and those of (XI) with those of (VI) are consistent with accepted values of methoxyl substituent shifts[14]. The assignments for (XII)–(XVI) were made with the help of 4,4'-di(*N,N*-dimethylamino)-octafluorobiphenyl (XIX) for determining the substituent chemical shifts for the dimethylamino group.

The ^1H NMR spectra of these compounds present no unusual features, *e.g.* the expected coupling[15] between the methyl groups and adjacent *ortho*

fluorines is observed. However (XIV) did show what is probably a long-range H–P coupling, between the protons of the dimethylamino groups and the phosphorus, of 2.6 Hz. A similar coupling (1.8 Hz) was shown by (XVI). Long-range H–P couplings in conjugated systems have been observed in other systems[16].

TABLE 1

^{19}F NMR SPECTRAL DATA

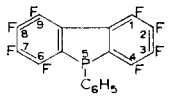
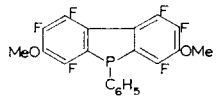
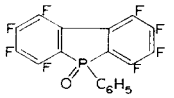
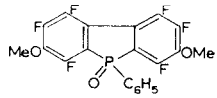
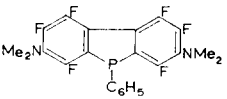
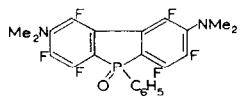
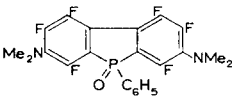
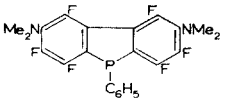
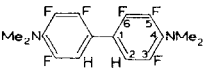
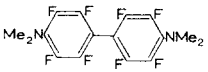
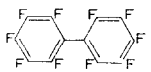
Compound	Solvent	Shifts	
 (V)	acetone	—33.5 —31.4 —11.4 —9.1	F_1 F_4 F_2 F_3
 (IX)	acetone	—37.7 —30.8 —15.8	F_4 F_1 F_2
 (VI)	acetone	—34.9 —30.7 —18.1 —12.4	F_1 F_4 F_2 F_3
 (XI)	acetone	—37.0 —31.6 —22.0	F_4 F_1 F_2
 (XIV)	chloroform	44.4 —27.7 —20.9	F_4 F_1 F_2
 (XII)	chloroform	—48.0 —27.9 —19.5	F_1 F_4 F_3
 (XIII)	chloroform	—44.1 —28.6 —27.1	F_4 F_1 F_2

Table 1 cont.

 (XVI)	chloroform	—47.6 —27.8 —18.7	F_1 F_4 F_3
 (XV)	acetone	—38.1 —20.4 —18.7	F_3 F_6 F_5
 (XIX)	acetone	—21.7 —11.6	F_2, F_6 F_3, F_5
	acetone	—25.4 —12.1 —1.7	F_2, F_6 F_4 F_3, F_5

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