Polyfluoroarenes. Part XIX.[1] Pentafluorophenylation of Biphenyl and 2,3,4,5,6-Pentafluorobiphenyl

By **J. Michael Birchall, Leonard R. Evans,** and **Robert N. Haszeldine,*** Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Pentafluorophenylation of 2,3,4,5,6-pentafluorobiphenyl with radicals from the oxidation of pentafluorophenylhydrazine gives only low yields of terphenyls, but excellent yields of 2,2″,3,3″,4,4″,5,5″,6,6″-decafluoro-*o*-, *m*-, and *p*-terphenyl are obtained by photochemical pentafluorophenylation with radicals from pentafluoroiodobenzene. The photochemical reaction of pentafluoroiodobenzene with biphenyl itself also gives high yields of terphenyls. Unambiguous syntheses of the three 2,2″,3,3″,4,4″,5,5″,6,6″-decafluoroterphenyls and the three 2,3,4,5,6-pentafluoroterphenyls are described.

Both nucleophilic [1,2] and electrophilic [1,3] substitution reactions of 2,3,4,5,6-pentafluorobiphenyl have been described, but no free-radical reactions of this substrate have been investigated. Its reaction with pentafluorophenyl radicals is described here and compared with the reaction of biphenyl itself under identical conditions.

Pentafluorophenylation Reactions.—A number of methods for the generation of pentafluorophenyl radicals are now known,[4] and for the present purpose we have investigated the two processes developed in this Department. However, both of these, the oxidation of pentafluorophenylhydrazine [5] and the photolysis of pentafluoroiodobenzene,[6] have been used before only in the presence of liquid substrates, and the presence of an inert solvent was clearly desirable for the solid biphenyls.

The oxidation of pentafluorophenylhydrazine with a suspension of silver oxide in perfluoro-n-pentane was examined first in the absence of an aromatic substrate and gave pentafluorobenzene in very high yield (94%), thus suggesting that perfluoropentane is a suitable medium for oxidations of this type. However, repetition of this reaction in the presence of an excess of 2,3,4,5,6-pentafluorobiphenyl, which is sparingly soluble in perfluoropentane, led only to the formation of small amounts of an unidentified solid, most (90%) of the biphenyl being recovered. In fact, better results were obtained when molten 2,3,4,5,6-pentafluorobiphenyl (m.p. 112 °C) was used in the absence of a separate solvent at 115—120 °C; very low yields of pure 2,2″,3,3″,4,4″,5,5″,6,6″-decafluoro-*m*- and *p*-terphenyl [*m*-$C_6H_4(C_6F_5)_2$ and *p*-$C_6H_4(C_6F_5)_2$] were isolated, but this reaction was clearly unsuitable as a basis for the determination of isomer ratios.

Much better results were obtained when the pentafluorophenyl radical was generated by the photolysis of pentafluoroiodobenzene in the presence of an equimolar proportion of 2,3,4,5,6-pentafluorobiphenyl in carbon tetrachloride; carbon tetrachloride is a good solvent for both reactants and has been shown to undergo only a very slow photochemical reaction with pentafluoroiodobenzene.[6a] The pentafluorophenylation reaction was carried out in duplicate at 80 °C for a period (400 h) which left *ca.* 25% of the pentafluoroiodobenzene unchanged; under these conditions, the yields of terphenyls are extremely high and the overall results show excellent reproducibility (Table 1). Although it is known that free radicals will effect substitution in perfluoroaromatic rings, attack by the pentafluorophenyl radical on the pentafluorophenyl group in the biphenyl would be expected to be slow,[4,7] and virtually all the pentafluorophenylation occurs in the hydrocarbon ring to give the three symmetrical terphenyls, *o*-, *m*-, and *p*-$C_6H_4(C_6F_5)_2$. Samples of these major products have been isolated and identified by comparison with authentic specimens (see later), and quantitative analysis of the mixture by g.l.c. yields the isomer ratios shown in Table 2. Traces of unidentified compounds are formed, and these may arise by attack of the pentafluorophenyl radical at the fluorinated ring of the biphenyl; *ca.* 20% of the pentafluorophenyl radicals produced are not accounted for in the identified products, and degradation of only some of these at the wall of the reaction vessel would account for the small amounts of silicon tetrafluoride produced. No decafluorobiphenyl is detected, and mass spectrometry reveals that the quaterphenyl content of the product is negligible.

Table 1

Products of duplicate photochemical pentafluorophenylations in CCl_4 at 80 °C

	Recovered reactants (%)		Products (%)				
Substrate	C_6F_5I	ArPh	HCl [a]	I_2 [b]	C_6F_5Cl [b]	Terphenyls	
						a	*b*
$C_6F_5{\cdot}C_6H_5$	(i) 25	41	117	97	3	96	76
	(ii) 22	40	116	98	3	97	75
$C_6H_5{\cdot}C_6H_5$	(i) 25	24	113	97	3	91	92
	(ii) 27	24	112	97	3	90	93

[a] Yields based on substrate consumed. [b] Based on C_6F_5I consumed.

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[1] Part XVIII, J. M. Birchall, R. N. Haszeldine, and H. Woodfine, *J.C.S. Perkin I*, 1973, 1121.

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[5] J. M. Birchall, R. N. Haszeldine, and A. R. Parkinson, *J. Chem. Soc.*, 1962, 4966.

[6] (*a*) J. M. Birchall, R. Hazard, R. N. Haszeldine, and A. W. Wakalski, *J. Chem. Soc.* (*C*), 1966, 47; (*b*) J. M. Birchall, R. N. Haszeldine, and J. G. Speight, *ibid.*, 1970, 2187.

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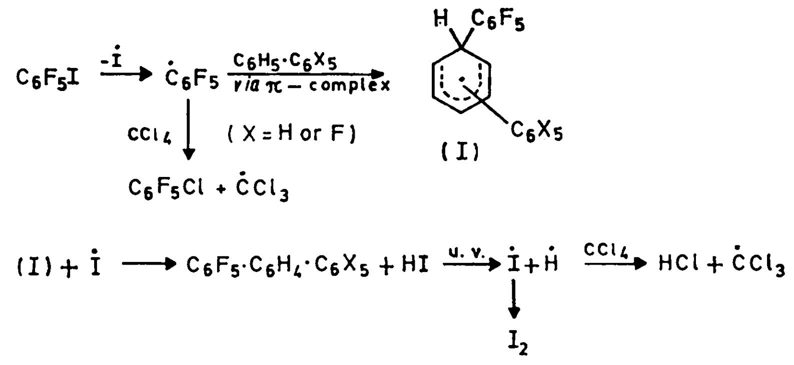
Similar photolysis of pentafluoroiodobenzene in the presence of biphenyl itself in carbon tetrachloride gives high yields of the expected 2,3,4,5,6-pentafluoroterphenyls (*o*-, *m*-, and *p*-$C_6F_5{\cdot}C_6H_4{\cdot}C_6H_5$), again identified by comparison with authentic specimens and quantitatively analysed by g.l.c. (Tables 1 and 2). Consumption of the hydrocarbon biphenyl is slightly faster than that of the pentafluoro-compound, and a little more tar is produced, but the two reactions follow essentially the same course.

The mechanism proposed earlier for pentafluorophenylation by pentafluoroiodobenzene[6] needs little modification to accommodate the results of the work described here (Scheme). Removal of the hydrogen atom from the σ-complex (I) by an iodine atom would lead to hydrogen iodide, photolysis of which gives iodine (accounted for almost quantitatively) and, by abstraction from the solvent, hydrogen chloride [the reactions produce more than the theoretical amount of hydrogen chloride (Table 1), suggesting that the small amounts of tar are also formed by reactions involving the solvent]. The chloropentafluorobenzene produced also arises by radical abstraction from the solvent,[6a] although the fate of the residual trichloromethyl radical is unknown.



SCHEME

TABLE 2

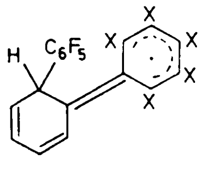
Isomer ratios in arylations at 80 °C

Substrate	Radical		Terphenyls (%)			Reactivity
			ortho	*meta*	*para*	*meta*/*para*[a]
$C_6F_5{\cdot}C_6H_5$	$\dot{C}_6F_5$	1.	14·0	49·7	36·3	0·68
		2.	14·0	49·5	36·5	
$C_6H_5{\cdot}C_6H_5$	$\dot{C}_6H_5$	1.	24·4	36·7	38·9	0·47
		2.	25·0	36·1	38·9	
$C_6H_5{\cdot}C_6H_5$	$\dot{C}_6H_5$[b]		48·5	23·0	28·5	0·41

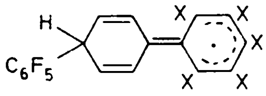
[a] Mean values, statistically corrected to allow for the presence of two *meta*-positions. [b] J. I. G. Cadogan, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 1954, 794. The phenylation of biphenyl has also been studied at 100 °C (H. Stangl and G. Juppe, *Chem. Ber.*, 1969, **102**, 2419) and at 255 °C (P. J. Bain, E. J. Blackman, W. Cummings, S. A. Hughes, E. R. Lynch, E. B. McCall, and R. J. Roberts, *Proc. Chem. Soc.*, 1962, 186).

Isomer Ratios.—In view of the high yields of terphenyls produced in these reactions and the excellent reproducibility of the results, it seems likely that the isomer ratios obtained accurately reflect the position of attack of the pentafluorophenyl radical on the substrate concerned.

The proportion of attack at the *ortho*-position in both the reactions described is substantially less than that observed in the *phenylation* of biphenyl with radicals from the thermal decomposition of benzoyl peroxide at 80 °C (Table 2), and at least some of the reduced relative reactivity at this position may be caused by steric effects. Simple hindrance to attack by the larger pentafluorophenyl radical may be involved, coupled with effects arising from the relative orientations of the reactants in the preliminary complex[4,6a] and steric hindrance to coplanarity of the two nuclei from the original biphenyl molecule in the σ-complex [(I) or (Ia)]. Steric hindrance to coplanarity in pentafluorobiphenyl itself is revealed by u.v. spectroscopy [$C_6H_5{\cdot}C_6H_5$, $\lambda_{max.}$ 247 nm (log ε 4·21); $C_6F_5{\cdot}C_6H_5$, $\lambda_{max.}$ 236 nm (log ε 4·10) (in hexane)],[8] and stabilisation by resonance of the σ-complex, which must involve the C_6X_5 group when radical attack is *ortho* or *para* to it [(Ia) or (Ib)], will hence be less for pentafluorobiphenyl than for biphenyl.



(Ia)



(Ib)

Although attack at the more crowded *ortho*-position would be expected to be most subject to retardation brought about by steric inhibition of resonance, the fact that canonical forms contributing to (Ib) are less significant for X = F than for X = H must also influence the isomer ratios. The higher *meta* : *para* ratio observed for pentafluorophenylation of pentafluorobiphenyl than for the corresponding reaction of biphenyl (Table 2) is consistent with this expectation. The electrophilic character of the pentafluorophenyl radical, observed previously in pentafluorophenylations of

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[8] *Cf.* D. E. Fenton, *Chem. and Ind.*, 1969, 695

monocyclic arenes,[4,6a] would also lead to a higher proportion of *meta* attack in pentafluorobiphenyl than in biphenyl itself (*cf.* ref. 1). However, this last factor should result in a lower *meta* : *para* ratio for pentafluorophenylation than for phenylation of biphenyl; the fact that this trend is not observed in the results shown in Table 2 may indicate that polar effects do not play a major role in determining the isomer ratios in this series.

Reference Compounds.—None of the terphenyls required for characterisation of the products of the pentafluorophenylation reactions has been prepared previously. The three 2,2″,3,3″,4,4″,5,5″,6,6″-decafluoroterphenyls were obtained unambiguously by mixed Ullmann reactions between *o*-, *m*-, or *p*-dibromobenzene and an excess of bromopentafluorobenzene in the presence of copper bronze at 200 °C (35, 55, and 63% yields, respectively); 2′-bromo-2,3,4,5,6-pentafluorobiphenyl was obtained in 20% yield as a by-product during the preparation of the *o*-terphenyl. The 2,3,4,5,6-pentafluoroterphenyls were obtained, again unambiguously (22—41% yield), by the reaction of biphenyl-2-, 3-, or 4-yl-lithium with an excess of hexafluorobenzene in ether; 2,3,4,5,6-pentafluoro-*o*-terphenyl may also be prepared (25% yield) by an Ullmann reaction between bromopentafluorobenzene and 2-bromobiphenyl. The i.r., n.m.r., u.v., and mass spectroscopic properties of these compounds are in full agreement with the proposed structures.

EXPERIMENTAL

Oxidation of Pentafluorophenylhydrazine.—(a) *In perfluoropentane.* The hydrazine (4·0 g, 20 mmol) [5] was added in small amounts to a stirred suspension of silver oxide (12·0 g, 51 mmol) in dry perfluoropentane (60 ml) during 5 h. Nitrogen (total 20 mmol, 100%) was evolved slowly after a short induction period, and the heat of reaction was sufficient to maintain a steady reflux. When the addition was complete, the mixture was heated under reflux for a further 45 min, and the solvent, b.p. 28·5—29 °C, was then removed by distillation through a packed column (16 cm × 15 mm i.d.). Pentafluorobenzene (3·2 g, 94%), identified by i.r. spectroscopy and shown to be pure by g.l.c., was isolated from the remaining volatile material by repeated fractional condensation *in vacuo*. Extraction of the solid products with ether gave a red oily solid, which was recrystallised twice from ethanol to give unidentified pale yellow needles (0·030 g), m.p. 229—231 °C.

(b) *In perfluoropentane containing* 2,3,4,5,6-*pentafluorobiphenyl.* The hydrazine (2·5 g, 12·5 mmol) was added in small amounts during 3 h to a stirred suspension of the biphenyl (12·0 g, 50 mmol) and silver oxide (7·0 g, 30 mmol) in perfluoropentane (300 ml), and the mixture was then heated under reflux for 1 h. Nitrogen was evolved, but distillation, solvent extraction, and liquid-phase chromatography led only to the recovery of pure pentafluorobiphenyl (10·8 g, 90%) and an unidentified brown solid (0·30 g), m.p. 70—140 °C.

(c) *In molten* 2,3,4,5,6-*pentafluorobiphenyl.* The hydrazine (3·0 g, 16 mmol) was added in small amounts during 1 h to a stirred suspension of silver oxide (7·0 g, 30 mmol) in the hot (115 °C) biphenyl. The mixture was stirred at 120 °C for a further 45 min and then extracted with hot benzene (250 ml); the extract was filtered and the benzene was removed by careful distillation, leaving a pale brown solid (11·5 g). Sublimation of this at 105—110 °C *in vacuo* and resublimation at 80 °C *in vacuo* gave a mixture, which was fractionally crystallised from ethanol to give pentafluorobiphenyl (8·0 g) and impure 2,2″,3,3″,4,4″,5,5″,6,6″-*decafluoro*-m-*terphenyl* (0·56 g), m.p. 92—99 °C, which yielded a pure specimen (Found: C, 53·0; H, 1·2. $C_{18}H_4F_{10}$ requires C, 52·7; H, 1·0%), m.p. 99—100 °C, on recrystallisation. A white solid (0·20 g), obtained by distillation *in vacuo* of the residue from the first sublimation, was combined with the residue from the second sublimation, and fractional crystallisation from ethanol gave the decafluoro-*m*-terphenyl (0·10 g, total yield *ca.* 10%), m.p. 99—100 °C, and the more insoluble 2,2″,3,3″,4,4″,5,5″,6,6″-*decafluoro*-p-*terphenyl* (0·15 g, 2%) (Found: C, 53·0; H, 1·2%), m.p. 207·5—208 °C. The identities of the terphenyls were confirmed by spectroscopic comparison with authentic specimens (see later), and their purity was established by g.l.c. (4 m Apiezon L on Celite; 250 °C).

Arylations with Pentafluoroiodobenzene.—(a) 2,3,4,5,6-*Pentafluorobiphenyl.* Pentafluoroiodobenzene (5·0 g, 17 mmol), 2,3,4,5,6-pentafluorobiphenyl (4·2 g, 17 mmol), and carbon tetrachloride (50 ml), sealed *in vacuo* in a silica tube (300 ml), were heated to 80 ± 2 °C and irradiated with light from a 500 W Hanovia mercury-discharge lamp for 400 h with continuous shaking. The volatile products [12·5 mmol (*M*, 41·7); 12·5 mmol (*M*, 41·9); results of duplicate experiments shown throughout], which distilled *in vacuo* through a trap at −78 °C, were identified by i.r. spectroscopy as hydrogen chloride (95% of the mixture in each case) containing traces of silicon tetrafluoride and some unidentified component(s). The remaining products were diluted with carbon tetrachloride (200 ml) and washed with standard aqueous sodium thiosulphate (50 ml; 0·4035N) and then water (3 × 25 ml); the aqueous phases were combined, washed with carbon tetrachloride (3 × 25 ml), and back-titrated with standard iodine solution to determine the amount of iodine formed in the reaction (6·20 mmol; 6·45 mmol). The combined organic phases were dried ($CaCl_2$) and the carbon tetrachloride and volatile liquid products were slowly distilled *in vacuo* from a vessel maintained at 30 °C (bath) into a trap cooled at −78 °C. Careful fractional distillation of the contents of the trap gave pure (g.l.c.) carbon tetrachloride and a residue (2·80 g; 2·35 g), shown by g.l.c. (4 m Apiezon L and 4 m Silicone MS550; 155 °C), to consist of carbon tetrachloride (1·47 g; 1·15 g), chloropentafluorobenzene (0·08 g; 0·08 g), and pentafluoroiodobenzene (1·25 g; 1·12 g); chloroform was not detected. The residue from the distillation at 30 °C *in vacuo* was dissolved in ether (500 ml) and the solution was divided into two portions. The ether was evaporated from one to ascertain the weight of the solute (3·37 g; 3·40 g), and the residue from the second portion was sublimed *in vacuo* until no further sublimation occurred at 180 °C (bath), leaving a small residue (0·35 g; 0·30 g). The sublimate (3·00 g; 3·10 g) was analysed by g.l.c. (4 m Apiezon L; 250°) by means of a Griffin and George D6 instrument, fitted with a gas-density balance detector; careful calibration showed that *ca.* 94% of the mixture consisted of 2,3,4,5,6-pentafluorobiphenyl and the three isomeric 2,2″,3,3″,4,4″,5,5″,6,6″-decafluoroterphenyls in the proportions shown in Tables 1 and 2. G.l.c. of a sample of the product mixture on an Aerograph Autoprep instrument (4 m Silicone Gum Rubber SE-52; 250 °C), which did not give a complete separation of the isomers, led to the isolation of a specimen of each terphenyl, the identity of which was confirmed by i.r. spectroscopy.

(b) *Biphenyl.* Pentafluoroiodobenzene (5·0 g, 17 mmol), biphenyl (2·62 g, 17 mmol), and carbon tetrachloride (50 ml) were irradiated for 400 h at 80 ± 2 °C, and the resulting mixture was analysed as in (a) to give impure hydrogen chloride [17 mmol (*M*, 39·6); 16 mmol (*M*, 39·4)], iodine (6·2 mmol; 6·0 mmol), chloropentafluorobenzene (0·08 g; 0·07 g), pentafluoroiodobenzene (1·25 g; 1·35 g), a mixture (2·40 g and 2·39 g after division of the ethereal solutions into two), 92% of which consisted of biphenyl and the isomeric 2,3,4,5,6-pentafluoroterphenyls in the proportions shown in Tables 1 and 2, and residual tar (0·71 g; 0·71 g). The structures of the products were confirmed by i.r. spectroscopy following the isolation of samples from the Autoprep instrument.

Reference Compounds.—(a) *2,2″,3,3″,4,4″,5,5″,6,6″-Decafluoro*-p-*terphenyl.* Bromopentafluorobenzene (4·92 g, 20 mmol), *p*-dibromobenzene (1·57 g, 6·7 mmol), and copper-bronze (10 g) were heated *in vacuo* in a sealed Pyrex tube (30 ml) in a rocking furnace at 200 °C for 24 h. The volatile product was identified (i.r.) as pentafluorobenzene (0·26 g, 7%), and the solid products were extracted continuously with boiling benzene for 24 h. The benzene was evaporated off to leave a pale brown solid (3·8 g), which was washed with cold ether and recrystallised from benzene to give pure (g.l.c.; 4 m Apiezon L; 250 °C) 2,2″,3,3″,4,4″,5,5″,6,6″-decafluoro-*p*-terphenyl (1·72 g, 63%) [Found: C, 52·7; H, 0·9%; *M* (mass spec.), 410. Calc. for $C_{18}H_4F_{10}$: C, 52·7; H, 1·0%; *M*, 410], m.p. 207·5—208 °C, $\lambda_{max.}$ (hexane) 255 nm (log ε 4·37).

(b) *2,2″,3,3″,4,4″,5,5″,6,6″-Decafluoro*-m-*terphenyl.* A similar experiment on the same scale, but with *m*-dibromobenzene, gave pentafluorobenzene (0·29 g), but the solid extracted with benzene was difficult to crystallise and was initially purified by sublimation at 90 °C (bath) *in vacuo*. The sublimate was crystallised from aqueous ethanol and gave the pure (g.l.c.) *m*-terphenyl (1·50 g, 55%) (Found: C, 25·7; H, 1·0%; *M*, 410), m.p. 99—100 °C, $\lambda_{max.}$ (hexane) 235 nm (log ε 4·47).

(c) *2,2″,3,3″,4,4″,5,5″,6,6″-Decafluoro*-o-*terphenyl.* Bromopentafluorobenzene (9·80 g, 40 mmol), *o*-dibromobenzene (3·14 g, 13·4 mmol), and copper-bronze (20 g) were heated in a sealed tube (60 ml) at 200 °C for 85 h and gave pentafluorobenzene (0·21 g) contaminated with a trace of bromopentafluorobenzene. Extraction of the involatile products with boiling benzene gave a mixture, crudely separated into fraction (*a*) (4·0 g), which distilled and sublimed at *ca.* 80 °C and <1 mmHg, and fraction (*b*) (2·4 g), which sublimed above 120 °C at <1 mmHg. Fractional crystallisation of fraction (*a*) from aqueous methanol gave decafluorobiphenyl (2·07 g, 16%), m.p. and mixed m.p. 67—68 °C (lit.,[9] 68—69 °C), identified by i.r. spectroscopy, and *2′-bromo-2,3,4,5,6-pentafluorobiphenyl* (0·55 g, 13%) [Found: C, 44·8; H, 1·2%; *M* (mass spec.), 323. $C_{12}H_4BrF_5$ requires C, 44·6; H, 1·2%; *M*, 323], m.p. 39·5—41 °C, identical with a specimen obtained from an Ullmann reaction between 1-bromo-2-iodobenzene and pentafluoroiodobenzene.[10] Fraction (*b*) was recrystallised from ethanol to give pure (g.l.c.) 2,2″,3,3″,4,4″,5,5″,6,6″-*decafluoro*-o-*terphenyl* (1·94 g, 35%) (Found: C, 52·6; H, 1·0%; *M*, 410), m.p. 149—150 °C, $\lambda_{max.}$ 212 nm (log ε 4·49), $\lambda_{infl.}$ 238 and 265 nm (log ε, 4·09 and 3·38).

(d) *2,3,4,5,6-Pentafluoro*-p-*terphenyl.* Biphenyl-4-yl-lithium (17 mmol) in ether (230 ml) [solution prepared from 4-bromobiphenyl (8·75 g, 37·5 mmol)[11] and lithium (1·56 g, 223 mmol) in ether and analysed by the double-titration method[12] with hexafluorobenzene in place of benzyl chloride] was added dropwise during 1·5 h, under nitrogen, to a stirred solution of hexafluorobenzene (20·0 g, 108 mmol) in ether, maintained at −45 ± 5 °C. The mixture was allowed to warm to room temperature, heated under reflux for 2 h, and carefully distilled to remove the solvent and the excess of hexafluorobenzene (16·7 g). The solid product was treated with boiling ether (400 ml) and the mixture (ethereal solution and residue) was poured into water (500 ml) containing 5N-hydrochloric acid (30 ml); filtration then gave *p*-quaterphenyl (0·46 g) (Found: C, 94·1; H, 5·8. Calc. for $C_{24}H_{14}$: C, 94·1; H, 5·9%), m.p. 318—320 °C (lit.,[13] 320 °C), identified by i.r. spectroscopy. The aqueous and ethereal layers were separated, the aqueous layer was extracted with ether (3 × 50 ml), and the combined ethereal layers were dried ($MgSO_4$) and concentrated. The solid which separated during this process was recrystallised from ethanol to yield off-white plates of pure (g.l.c.) 2,3,4,5,6-*pentafluoro*-p-*terphenyl* (1·64 g) [Found: C, 67·6; H, 2·6%; *M* (mass spec.), 320. $C_{18}H_9F_5$ requires C, 67·5; H, 2·8%; *M*, 320], m.p. 193—194 °C, $\lambda_{max.}$ (hexane) 268 nm (log ε 4·40). Complete removal of the ether by distillation and continued distillation of the residue gave a fraction (1·74 g), b.p. 74—78° at <1 mmHg, which was recrystallised from aqueous ethanol to give pure (g.l.c.) biphenyl (1·35 g), m.p. 69—70 °C (lit.,[14] 69—70 °C), identified by i.r. spectroscopy, and sublimation of the final residue *in vacuo* at 180 °C (bath), followed by recrystallisation from ethanol, gave a further sample of the pentafluoro-*p*-terphenyl (0·50 g, total yield 2·14 g, 41% based on C_6F_6 transformed), m.p. and mixed m.p. 193—194 °C.

(e) *2,3,4,5,6-Pentafluoro*-m-*terphenyl.* A similar experiment in which biphenyl-3-yl-lithium (12 mmol) [from 3-bromobiphenyl (8·75 g, 37·5 mmol)[15] and lithium (1·56 g, 223 mmol) in ether (230 ml)] reacted with hexafluorobenzene (20·0 g, 108 mmol) in ether (50 ml) gave unchanged hexafluorobenzene (15·6 g, 78%) and a solid product. The latter was treated with boiling ether and dilute hydrochloric acid as before and evaporation of the ether gave a brown semi-solid (9·13 g); this was extracted with cold ether (50 ml) and the insoluble material was recrystallised from ethanol to give white needles of pure (g.l.c.) 2,3,4,5,6-*pentafluoro*-m-*terphenyl* (1·65 g) (Found: C, 67·6; H, 2·8%; *M*, 320), m.p. 152—153 °C, $\lambda_{max.}$ (hexane) 243 nm (log ε 4·48). Distillation of the ethereal solution gave biphenyl (1·78 g), b.p. 79—80 °C at <1 mmHg, m.p. 69—70 °C (from aqueous ethanol), and a fraction (1·83 g), b.p. 142—143 °C at <1 mmHg, which crystallised from ethanol to give the pentafluoro-*m*-terphenyl (1·00 g, total yield 2·65 g, 35% based on C_6F_6 consumed) (Found: C, 67·3; H, 2·7%).

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(f) 2,3,4,5,6-*Pentafluoro*-o-*terphenyl*. (i) A similar experiment with biphenyl-2-yl-lithium (8·5 mmol) [from 2-bromobiphenyl (17·5 g, 75 mmol) and lithium (3·2 g, 450 mmol)] in ether (230 ml) and hexafluorobenzene (40·0 g, 216 mmol) in ether (100 ml) gave hexafluorobenzene (36·0 g, 90% recovery) and a solid residue, which was treated with ether and hydrolysed as before. Distillation of the product *in vacuo* gave crude biphenyl (6·45 g; 4·20 g after purification) and a fraction (2·75 g), b.p. 99—130 °C at <1 mmHg, which was purified by a difficult fractional crystallisation from aqueous methanol to give white needles (pure by g.l.c.) of 2,3,4,5,6-*pentafluoro*-o-*terphenyl* (1·50 g, 22% based on C_6F_6 consumed) (Found: C, 67·3; H, 2·7%; *M*, 320), m.p. 86·5—87·5 °C, $\lambda_{\text{infl.}}$ (hexane) 221 and 244 nm (log ε 4·34 and 4·01).

(ii) Bromopentafluorobenzene (4·92 g, 20 mmol), 2-bromobiphenyl (4·66 g, 20 mmol), and copper bronze (10 g) were heated *in vacuo* in a sealed Pyrex tube (30 ml) in a rocking furnace at 200 °C for 24 h. Pentafluorobenzene (0·75 g) was produced, and continuous extraction of the residual products with benzene followed by distillation *in vacuo* and repeated recrystallisation from aqueous methanol gave decafluorobiphenyl (0·31 g) (Found: C, 43·0. Calc. for $C_{12}F_{10}$: C, 43·1%), m.p. 67·5—68·5 °C, and 2,3,4,5,6-pentafluoro-*o*-terphenyl (1·59 g, 25%) (Found: C, 67·3; H, 2·6%), m.p. 86·5—87·5 °C.

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