Polyfluoroarenes. Part XX.[1] Some Homolytic Arylations with Pentafluorophenylhydrazine

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

Oxidation of pentafluorophenylhydrazine in benzene by aqueous reagents ($CuSO_4$, NaOCl, H_2O_2, and H_2O_2–$FeSO_4$) gives 2,3,4,5,6-pentafluorobiphenyl. Use of solid potassium permanganate in pyridine or silver oxide in a solution of naphthalene in carbon tetrachloride gives low yields of the corresponding pentafluorophenylarenes, but a 57% yield of 2,3,4,5,6-pentafluoro(phenoxy)biphenyls is obtained from the hydrazine and silver oxide in molten diphenyl ether. The isomer ratio for the last reaction has been determined. Unambiguous syntheses of the two pentafluorophenylnaphthalenes and the three 2,3,4,5,6-pentafluoro(phenoxy)biphenyls are described.

THE oxidation of pentafluorophenylhydrazine in non-aqueous media was established some years ago as a useful route to the pentafluorophenyl radical,[2] and attempts to modify the procedure for application to solid substrates (biphenyls) have been described recently.[1] Although these met with only partial success, the method remains one of the most convenient means by which the pentafluorophenylation of arenes may be effected.[3a,b] and further investigation of its applicability [3b] is described here.

Oxidation in Aqueous Media.—Oxidation of pentafluorophenylhydrazine in aqueous media in the absence of an added substrate gives pentafluorobenzene by a mechanism which may be intramolecular or may involve free pentafluorophenyl radicals or (less likely) carbonium ions; if base is present some 1,2,4,5-tetrafluorobenzene is sometimes formed.[2,4] The ability of such systems to effect pentafluorophenylation of benzene has now been

---

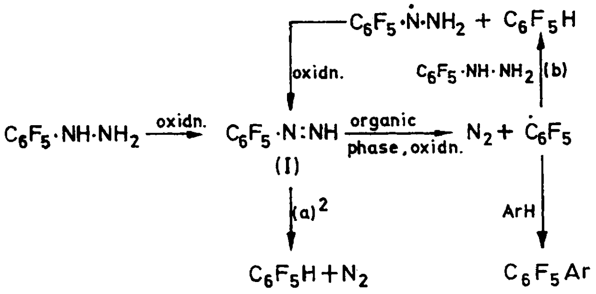
[1] Part XIX, J. M. Birchall, L. R. Evans, and R. N. Haszeldine, *J.C.S. Perkin I*, 1974, 1715.

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

[3] *Cf.* (*a*) P. H. Oldham, G. H. Williams, and B. A. Wilson, *J. Chem. Soc.* (*C*), 1971, 1094, and references cited therein; (*b*) J. M. Birchall, R. N. Haszeldine, and A. R. Parkinson, B.P. 1,054,622/1967.

[4] D. G. Holland, G. J. Moore, and C. Tamborski, *J. Org. Chem.*, 1964, **29**, 3042.

demonstrated in a series of reactions in which the hydrazine was oxidised by aqueous reagents [copper(II) sulphate, sodium hypochlorite, hydrogen peroxide, and Fenton's reagent ($FeSO_4$–H_2O_2 aq.)] mixed with an excess of the arene. The yields of pentafluorobiphenyl (37, 51, 18, and 18%, respectively) show that the use of such aqueous reagents does not provide an improved method for the synthesis of biaryls. However, these experiments do show that a significant proportion of the intermediates produced in the presence of an aqueous medium can react in the organic phase, in which it would be expected that the pentafluorophenyldi-imide (I) would be more soluble. The failure to detect more than traces of products which could be phenolic again[2] suggests that carbonium ions are not involved to a significant extent in the reactions, which under these conditions bear a strong resemblance to the more familiar Gomberg–Hey arylation[5] and may proceed as outlined in Scheme 1.



Scheme 1

It might be expected that aqueous reagents would be particularly effective for the pentafluorophenylation of water-soluble substrates, but the oxidation of pentafluorophenylhydrazine in pyridine with aqueous sodium hypochlorite at 60 °C gives pentafluorobenzene (86%) and nitrogen (93%). The intermediate pentafluorophenyldi-imide (I) may be particularly prone to intramolecular decomposition [step (a), Scheme 1] if it remains in an aqueous medium, or it may be that extraction of the intermediate into a separate hydrazine phase (pentafluorophenylhydrazine is only sparingly soluble in water) leads to the abstraction shown [step (b)]. Pyridine is unlikely to be particularly reactive towards the electrophilic pentafluorophenyl radical.

Reactions in Non-aqueous Systems.—The low reactivity of pyridine towards pentafluorophenylation is emphasised by an experiment in which oxygen was passed for 48 h through a solution of pentafluorophenylhydrazine in pyridine at 80 °C. The main product was again pentafluorobenzene (45%). Small amounts of pentafluoroaniline (the expected product of thermal decomposition of the hydrazine)[2] and decafluoroazobenzene were also formed, but no (pentafluorophenyl)pyridines were detected. However, the use of solid potassium permanganate as the oxidising agent for this reaction did give a low yield (*ca.* 5%) of (pentafluorophenyl)pyridines (identified mainly by mass spectrometry), the amount produced being insufficient to merit detailed analysis of the isomer ratio for the reaction.

In contrast, pentafluorophenylation of diphenyl ether (studied as a model compound for the development of thermally stable polyethers) in the neat liquid phase at 40 °C with a mixture of pentafluorophenylhydrazine and silver oxide gave the 2,3,4,5,6-pentafluoro(phenoxy)biphenyls (*o*-, *m*-, and *p*-$C_6F_5\cdot C_6H_4\cdot OPh$) in 57% yield. Pure specimens of the *m*- and *p*-isomers were separated by fractional crystallisation, and analysis of the crude product by g.l.c. gave an isomer ratio (*o* : *m* : *p*) of 1·56 : 1·00 : 1·80. Calibration and identification for this analysis were achieved by comparison with authentic specimens of the pentafluoro(phenoxy)biphenyls prepared from hexafluorobenzene and the *o*-, *m*-, or *p*-lithio-derivative of diphenyl ether. Comparison of the isomer ratio produced in the pentafluorophenylation of diphenyl ether with that for phenylation of this substrate is not possible since the latter reaction has not been reported. However, phenylation of the related anisole with benzoyl peroxide at *ca.* 80 °C gave the methoxybiphenyls in the ratio (*o* : *m* : *p*) 4·5 : 1·2 : 1·0.[6] The lower proportion of *ortho*-substitution obtained in the pentafluorophenylation reaction is consistent with the increased steric requirements of the reaction and the reduced *meta* : *para* ratio may be attributed to the electrophilic character of the attacking radical.

Treatment of a solution of pentafluorophenylhydrazine and an excess of naphthalene in carbon tetrachloride (*cf.* ref. 1) with silver oxide gave nitrogen (85%) and a 14% yield of 1- and 2-(pentafluorophenyl)naphthalene, separated by crystallisation and identified by comparison with specimens synthesised unambiguously from 1- or 2-naphthyl-lithium and hexafluorobenzene. The yield of arylated products was too low for isomer analysis to be meaningful, and a good deal of intractable material was produced.

Subsequent examination of the reaction between the hydrazine and refluxing carbon tetrachloride in the presence of silver oxide showed that nitrogen (83%), pentafluorobenzene (40%), chloropentafluorobenzene (9%), and decafluoroazobenzene (5%) were produced. The last three products were not detected during the experiment with naphthalene, but they must have been formed to some extent. Pentafluorobenzene (40%) is formed with traces of 1,2,4,5-tetrafluorobenzene[2,4] during treatment of neat pentafluorophenylhydrazine with silver oxide, and chloropentafluorobenzene is the expected product from the attack of pentafluorophenyl radicals on carbon tetrachloride (the residual trichloromethyl radical is detected as chloroform in the recovered solvent). Oxidation of the hydrazine with bleaching powder in carbon tetrachloride gave nitrogen (67%),

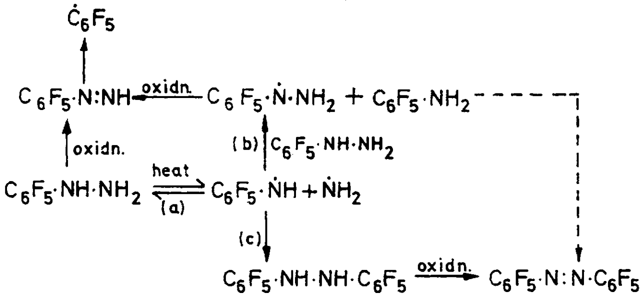
---

[5] G. H. Williams, 'Homolytic Aromatic Substitution,' Pergamon, New York, 1960. p. 29.

[6] C. S. Rondestvedt and H. S. Blanchard, *J. Org. Chem.*, 1956, **21**, 229; T. Suehiro, *Bull. Chem. Soc. Japan, Pure Chem. Sect.*, 1951, **72**, 301.

chloropentafluorobenzene (9%), and decafluoroazobenzene (19%).

The small amounts of decafluoroazobenzene detected among the products of some of the reactions described here could result from the oxidation of pentafluoroaniline formed by decomposition of the hydrazine.[2,7] However, it seems unlikely that all the azo-compound produced in the last reaction could have been formed in this way (decomposition of the neat hydrazine is slow even at 180 °C).[2] A more probable explanation is that dilution of the hydrazine retards effective cage-recombination of the primary fragments of thermal decomposition [step (a), Scheme 2] and the hydrogen-abstraction step (b), leading to an increased concentration of free pentafluorophenylaminyl radicals, which react as shown [step (c)].



SCHEME 2

Pentafluorophenylhydrazine reacts slowly with refluxing carbon tetrachloride in a vessel which is open to the atmosphere to give pentafluorobenzene and hydrogen chloride, isolated as the hydrazinium salt. The mechanism of this unexpected reaction has not been elucidated.[8]

EXPERIMENTAL

Unless otherwise stated, oxidations were carried out in closed vessels fitted with nitrometers.

Oxidation of Pentafluorophenylhydrazine with Aqueous Reagents.—(a) *In benzene*. (i) *Copper sulphate*. Copper sulphate (11·2 g, 70 mmol) in water (50 ml) was added during 130 min to a stirred solution of pentafluorophenylhydrazine (5·00 g, 25 mmol) in benzene (100 ml) and water (50 ml), maintained at 60 ± 2 °C; the mixture was then heated under reflux for 1 h. Nitrogen [531 ml (S.T.P.), 94%] was evolved. Water was added to the brown organic layer, the excess of benzene was removed by distillation, and the solid which separated from the wet residue was dried, sublimed *in vacuo* at 110 °C (bath), and recrystallised from light petroleum (b.p. 100—120 °C) to give 2,3,4,5,6-pentafluorobiphenyl (2·30 g, 37%), m.p. and mixed m.p. 111—113 °C (lit.,[2] 110·5—112 °C), identified by i.r. spectroscopy; sublimation of the residue at a higher temperature (<220 °C) gave traces of a red solid. The aqueous layer from the reaction was acidic, and extraction with ether followed by sublimation yielded a low-melting solid (0·02 g) with a phenolic odour, but tests with aqueous iron(III) chloride gave negative results.

(ii) *Sodium hypochlorite*. A similar experiment, in which aqueous sodium hypochlorite (39 ml; 10—14% w/v available chlorine) was added slowly to the hydrazine (5·00 g) in benzene (100 ml) and water (50 ml) at 60 °C and the mixture was then heated under reflux for 30 min, gave nitrogen (486 ml, 87%) and pentafluorobiphenyl (3·10 g, 51%).

(iii) *Hydrogen peroxide*. Aqueous hydrogen peroxide (20 vol.; 28·6 ml, 50 mmol) was added slowly to the hydrazine (5·00 g) in benzene (100 ml) and water (50 ml) at 60 °C, and the mixture was heated under reflux for 1 h. Evolution of nitrogen (total 107 ml, 25%) began after a short induction period, and the organic layer from the reaction yielded (separation by sublimation and extraction with dilute acid) pentafluorophenylhydrazine (1·37 g, 27% recovery) and pentafluorobiphenyl (0·81 g, 18% based on hydrazine consumed). Extraction of the acidic aqueous layer with ether gave a solid (0·02 g), which may have been a polyfluorophenol (i.r.) but which did not give a colour with aqueous iron(III) chloride.

(iv) *Fenton's reagent*. The rate of addition of aqueous hydrogen peroxide (100 vol.; 11·2 ml, 100 mmol) to the hydrazine (5·00 g) and iron(II) sulphate heptahydrate (2·80 g, 10 mmol) in benzene (100 ml) and water (50 ml) was controlled to keep the exothermic mixture at 60—65 °C. Gaseous products (652 ml, 115% of the theoretical volume of nitrogen) were evolved. The mixture was basified (NaOH), and the organic layer yielded pentafluorobiphenyl (1·15 g, 18%) and a residue (1·92 g), which would not sublime at 190 °C *in vacuo*. Acidification of the filtered aqueous layer and extraction with ether and benzene gave a phenolic oil (0·35 g), which gave a violet colour with aqueous iron(III) chloride.

(b) *In pyridine*. Aqueous sodium hypochlorite (37 ml; 10—14% available chlorine) was added during 110 min to pentafluorophenylhydrazine (5·00 g) in pyridine (100 ml) at 60 ± 2 °C. Nitrogen (522 ml, 93%) was evolved, and fractional distillation of the liquid products gave a fraction, b.p. <114 °C, which was washed with 5M-hydrochloric acid and dried by distillation from phosphorus pentaoxide to give pure (g.l.c.) pentafluorobenzene (3·65 g, 86%), identified by i.r. spectroscopy.

Oxidation of the Hydrazine with Non-aqueous Reagents.—(a) *In pyridine*. (i) *Oxygen*. Oxygen (*ca.* 50 ml min^{-1}) was passed through the hydrazine (10·0 g, 50 mmol) in pyridine (200 ml), kept at 80 ± 2 °C under an efficient reflux condenser, for 48 h. Fractional distillation then gave a fraction, b.p. <114 °C, which was washed with 5M-hydrochloric acid and dried to give pentafluorobenzene (3·80 g, 45%). The excess of pyridine was removed under reduced pressure and the liquid residue was steam-distilled; extraction of the distillate with ether yielded an oil (0·38 g), b.p. 50—51 °C at 19 mmHg, shown by i.r. and mass spectroscopy to be pentafluoroaniline contaminated with pyridine. The residue from the steam-distillation was basified (NaOH) and extracted with ether, leaving a black brittle solid (2·10 g), and the red oily extract (0·30 g) was shown by i.r. and mass spectroscopy to contain decafluoroazobenzene and unidentified components.

(ii) *Potassium permanganate*. The hydrazine (9·00 g, 45 mmol) in pyridine (50 ml) was added during 105 min to a suspension of finely powdered potassium permanganate (10·0 g) in pyridine at 80 °C. The exothermic reaction maintained the temperature at 80—85 °C, and after the addition was complete, potassium permanganate (3·0 g) was added to the mixture, which was kept at 80 °C for a

---

[7] J. M. Birchall, R. N. Haszeldine, and J. E. G. Kemp, *J. Chem. Soc.* (*C*), 1970, 449.

[8] For suggestions, see M. Wilkinson, Ph.D. Thesis, Manchester, 1966, p. 53.

further 30 min. Nitrogen (860 ml, 85%) was evolved, and pentafluorobenzene (3·95 g, 52%) was isolated from the mixture as before. Careful distillation of the less volatile liquid products gave pentafluoroaniline (0·31 g), identified by i.r. spectroscopy, and a solid fraction (0·55 g), b.p. *ca.* 100 °C at 1 mmHg, m.p. 57—87 °C, shown by mass spectroscopy to contain (pentafluorophenyl)pyridine(s) (Found: C, 52·0; H, 1·9; N, 6·0. Calc. for $C_{11}H_4F_5N$: C, 53·9; H, 1·7; N, 5·7%).

(b) *In diphenyl ether.* (i) *Qualitative.* The hydrazine (10·0 g, 50 mmol) was added during 2 h to a stirred suspension of silver oxide (23·4 g, 100 mmol) in diphenyl ether (150 ml) at 40 ± 2 °C, and the mixture was then stirred at 90 °C for 30 min. Nitrogen (1100 ml, 98%) was evolved, and fractional distillation of the filtered products gave a mixture of 2,3,4,5,6-pentafluoro(phenoxy)biphenyls (9·63 g, 57%), b.p. 126—170 °C at 2 mmHg. Redistillation yielded the impure (g.l.c.) 2′-phenoxy-isomer (2·73 g), b.p. 106—112 °C at 1 mmHg, and a fraction (4·52 g), b.p. 158—160° at 1 mmHg, fractional crystallisation of which from methanol gave pure samples of 2,3,4,5,6-*pentafluoro-4′-phenoxybiphenyl* (Found: C, 64·1; H, 2·8. $C_{18}H_9F_5O$ requires C, 64·3; H, 2·8%), m.p. 78—79 °C, and 2,3,4,5,6-*pentafluoro-3′-phenoxybiphenyl* (Found: C, 64·3; H, 2·8%), m.p. 107—109 °C. The biphenyls were identified by comparison (i.r.; mixed m.p.) with specimens synthesised unambiguously (see later).

(ii) *Quantitative.* The hydrazine (10·0 g) in diphenyl ether (50 ml) was added during 90 min to a stirred suspension of silver oxide (23·4 g) in diphenyl ether (100 ml) at 80 °C, and the mixture was stirred at 80 °C for 1 h. The excess of diphenyl ether was removed by fractional distillation at 125 °C and 10 mmHg [the distillate contained no biphenyls (g.l.c.)], and the residue (26·1 g) was analysed directly by g.l.c. (4 m Apiezon L; 250 °C; Griffin and George Gas density balance) and shown to contain the 2,3,4,5,6-pentafluoro-2′-, -3′-, and -4′-phenoxybiphenyls in the ratio 1·56 : 1·00 : 1·80, respectively. Calibration with a synthetic mixture of the pure isomers showed that the response of the instrument was the same for all three compounds.

(c) *In carbon tetrachloride containing naphthalene.* The exothermic reaction which occurred when silver oxide (15·0 g, 65 mmol) was added during 210 min to pentafluorophenylhydrazine (10·0 g, 50 mmol) and naphthalene (50·0 g, 390 mmol) in carbon tetrachloride (170 ml) was controlled by external cooling to maintain the mixture at <30 °C. The mixture was then heated under reflux for 75 min. Nitrogen (953 ml, 85%) was evolved, and at the end of the reaction, the mixture was filtered and dried (Na_2SO_4). The solvent was distilled off and most of the excess of naphthalene was removed by distillation at 25 mmHg and then sublimation at 1 mmHg. The residue from the sublimation yielded a fraction (4·10 g), b.p. *ca.* 120 °C at 1 mmHg, which solidified and was fractionally recrystallised from ethanol to give crude 1-(*pentafluorophenyl*)*naphthalene* (1·09 g), m.p. 81—84 °C, and 2-(*pentafluorophenyl*)*naphthalene* (1·02 g), m.p. 166—170 °C. Pure specimens were obtained by repeated recrystallisation: the 1-isomer (Found: C, 65·0; H, 2·5. $C_{16}H_7F_5$ requires C, 65·3; H, 2·4%) had m.p. 92—93 °C (from aqueous ethanol) and the 2-isomer (Found: C, 65·3; H, 2·5%) had m.p. 171—172 °C (from ethanol). Identification was achieved by comparison with specimens synthesised unambiguously (see later). The (pentafluorophenyl)naphthalenes have been mentioned recently as products of the photolysis of a mixture of hexafluorobenzene and naphthalene, but no yields or physical constants are reported.[9]

(d) *In carbon tetrachloride.* (i) *With silver oxide.* The hydrazine (5·00 g, 25 mmol) in carbon tetrachloride (40 ml) was added during 45 min to silver oxide (14·9 g, 63 mmol) in refluxing carbon tetrachloride, and the mixture was heated under reflux for a further 90 min. Nitrogen (466 ml, 83%) was evolved. The mixture was filtered, the inorganic residue was washed with carbon tetrachloride, and the combined organic phases were dried ($MgSO_4$) and distilled; the distillate was shown by g.l.c. (4 m Apiezon L; 125 °C) to contain pentafluorobenzene (1·71 g, 40%), chloropentafluorobenzene (0·44 g, 9%), and a trace of chloroform, and the residue was shown by i.r. and mass spectroscopy to contain decafluoroazobenzene (*ca.* 0·3 g, 5%) and a trace of decafluorobiphenyl.

(ii) *With bleaching powder.* A similar reaction, in which the hydrazine (5·00 g) in carbon tetrachloride (50 ml) was added to bleaching powder (12·5 g) in refluxing carbon tetrachloride (50 ml) gave nitrogen (380 ml, 67%). The excess of carbon tetrachloride was removed by careful fractionation and shown by g.l.c. to contain pentafluorobenzene and chloroform. Steam-distillation of the higher-boiling material gave chloropentafluorobenzene (*ca.* 0·4 g, 9%), and recrystallisation of the residue from ethanol gave decafluoroazobenzene (0·85 g, 19%), m.p. and mixed m.p. 143—144 °C (lit.,[7] 143 °C). An unidentified tar (1·17 g) was also formed.

(e) *Neat pentafluorophenylhydrazine.* Silver oxide (9·40 g, 40 mmol) was added during 1 h to the hydrazine (4·00 g, 20 mmol), kept at 100 °C. Nitrogen (460 ml, 100%) was evolved, and extraction with ether gave pentafluorobenzene (1·31 g, 40%), 1,2,4,5-tetrafluorobenzene (0·12 g, 4%) (identified by i.r. and g.l.c.), and an oily residue (1·39 g), which partially sublimed *in vacuo* at 90—95 °C (bath) but was not identified.

Reaction of the Hydrazine with Carbon Tetrachloride.—The hydrazine (3·00 g, 15 mmol) was heated under reflux in carbon tetrachloride (25 ml) in air for 2 h. Filtration of the resulting cold suspension gave pentafluorophenylhydrazine hydrochloride (0·27 g, 52% based on hydrazine transformed) (i.r.),[2] and distillation of the filtrate gave carbon tetrachloride containing pentafluorobenzene (0·05 g, 14%) (g.l.c.); the residue was the unchanged hydrazine (2·56 g, 86%).

Reference Compounds.—(a) *Pentafluoro(phenoxy)biphenyls.* Ethereal *o*-phenoxyphenyl-lithium [from ethereal n-butyllithium (0·74M; 77 ml, 113 mmol) and diphenyl ether (8·50 g, 50 mmol) in ether (100 ml)] [10] was added under nitrogen during 95 min to hexafluorobenzene (14·0 g, 75 mmol) in refluxing ether (50 ml). The mixture was heated under reflux for 72 h, then hydrolysed with aqueous 2M-hydrochloric acid (100 ml) and extracted with ether to give 2,3,4,5,6-*pentafluoro-2′-phenoxybiphenyl* (4·57 g) [Found: C, 64·3; H, 2·9%; *M* (mass spec.), 336. $C_{18}H_9F_5O$ requires C, 64·3; H, 2·7%; *M*, 336], b.p. 104—105 °C at 1 mmHg, $\lambda_{max.}$ (hexane) 278 nm (log ε 3·47), $\lambda_{infl.}$ 222 (4·39) and 271 nm (3·43). The higher-boiling products were shown by mass spectroscopy to contain 2,3,4,5,6-pentafluoro-2′-(2-pentafluorophenylphenoxy)biphenyl.

A similar experiment, in which ethereal *m*-phenoxyphenyl-lithium [from *m*-bromophenoxybenzene (4·75 g,

---

[9] D. Bryce-Smith, A. Gilbert, and P. J. Twitchett, *J.C.S. Chem. Comm.*, 1973, 457.

[10] K. Oita and H. Gilman, *J. Org. Chem.*, 1965, **21**, 1009.

19 mmol) and butyl-lithium (18 mmol)][11] and hexafluorobenzene (6·68 g, 36 mmol) were heated under reflux for 2 h, gave a fraction, b.p. 138—148 °C at 1 mmHg, which was recrystallised from methanol to give 2,3,4,5,6-pentafluoro-3′-phenoxybiphenyl (2·42 g) (Found: C, 64·2; H, 2·9%; *M*, 336), m.p. 107—109 °C, $\lambda_{max.}$ (hexane) 226 (log ε 4·38) and 278 nm (3·38), $\lambda_{infl.}$ 268 nm (3·42). Use of *p*-phenoxyphenyl-lithium [from *p*-bromophenoxybenzene (7·55 g, 30 mmol)][12] and hexafluorobenzene (7·47 g, 40 mmol) similarly gave the 4′-phenoxy-compound (4·10 g) (Found: C, 64·4; H, 2·9%; *M*, 336), b.p. 164—168 °C at 1 mmHg, m.p. 78—79 °C (from aqueous methanol), $\lambda_{max.}$ (hexane) 258 nm (log ε 4·28).

(b) *Pentafluorophenylnaphthalenes*. Ethereal 1-naphthyl-lithium [from 1-bromonaphthalene (5·00 g, 24 mmol) and lithium (0·67 g, 96 mmol) in refluxing ether (90 ml)] was added to hexafluorobenzene (4·02 g, 22 mmol) in refluxing ether (60 ml), and the mixture was heated under reflux for 1 h and then kept overnight at room temperature. Hydrolysis with 2M-hydrochloric acid, extraction with ether, and distillation–sublimation gave hexafluorobenzene (1·90 g), b.p. 79—80 °C; naphthalene (0·90 g), subliming at 50 °C at 1 mmHg (bath), m.p. 80—81 °C; and 1-pentafluorophenylnaphthalene (0·37 g) [Found: C, 65·6; H, 2·5%; *M* (mass spec.), 294. Calc. for $C_{16}H_7F_5$: C, 65·3; H, 2·4%; *M*, 294], b.p. *ca.* 120 °C at 1 mmHg, m.p. 91·5—93 °C (from ethanol), $\lambda_{max.}$ (hexane) 222 (log ε 4·82) and 281 nm (3·87), $\lambda_{infl.}$ 270 (3·76), 286 (3·83), 312 (2·81), and 316 nm (2·58). 2-Naphthyl-lithium [from 2-bromonaphthalene (5·00 g) and lithium (0·65 g)] and hexafluorobenzene (5·00 g) in ether, mixed slowly at room temperature and then heated under reflux for 9 h, similarly gave hexafluorobenzene, naphthalene (0·70 g), 2-pentafluorophenylnaphthalene (0·30 g) (Found: C, 65·5; H, 2·4%; *M*, 294), subliming *in vacuo* at 90—95 °C (bath), m.p. 171—172 °C (from ethanol), $\lambda_{max.}$ (hexane) 225 (log ε 4·35), 240 (4·58), 272 (3·91), and 279 nm (3·91), $\lambda_{infl.}$ 320 nm (2·58), and 2,2′-binaphthyl (0·14 g), m.p. 186—188 °C, identified by i.r. spectroscopy.

We thank Pennwalt Corporation for financial support.

[4/240 *Received, 7th February* 1974]

---

[11] H. Gilman and O. L. Marrs, *J. Org. Chem.*, 1960, **25**, 1194.

[12] H. Gilman and J. J. Goodman, *J. Org. Chem.*, 1957, **22**, 45.