612. *Reactions of Polyfluoroaryl Bromides with Cuprous Salts in Dimethylformamide*

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Bromopentafluorobenzene reacts in dimethylformamide with cuprous cyanide, chloride, pentafluorothiophenoxide, and acetate to give pentafluorobenzonitrile, chloropentafluorobenzene, bis(pentafluorophenyl) sulphide, and pentafluorobenzene, respectively. Extension of these reactions to 1,4- and 1,2-dibromotetrafluorobenzene is reported.

PENTAFLUOROPHENYL compounds have been prepared from bromopentafluorobenzene by replacing the bromine atom, either with magnesium to form a Grignard reagent,[1] or with n-butyl-lithium to form pentafluorophenyl-lithium[2] and using these organometallic compounds for subsequent transformations. With nucleophilic reagents such as sodium methoxide, potassium hydroxide and ammonium hydroxide, bromopentafluorobenzene gives bromotetrafluorophenyl compounds,[3] *i.e.*, preferential replacement of a fluorine atom occurs.

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[1] E. Nield, R. Stephens, and J. C. Tatlow, *J.*, 1959, 166.

[2] P. L. Coe, R. Stephens, and J. C. Tatlow, *J.*, 1962, 3227.

[3] L. A. Wall, W. J. Pummer, J. E. Fearn, and J. M. Antonucci, *J. Res. Nat. Bur. Stand.*, 1963, **67**A, 481.

We now find that, when bromopentafluorobenzene reacts with cuprous salts in dimethylformamide, preferential replacement of the bromine atom occurs, giving a pentafluorophenyl compound, thereby greatly extending the value of bromopentafluorobenzene as an intermediate:

$$C_6F_5Br + CuY \longrightarrow C_6F_5Y + CuBr \quad (Y = CN, Cl, C_6F_5S, \textit{etc.})$$

Polyfluoroaryl dibromides undergo similar reactions.

Pentafluorobenzonitrile is prepared in 82—89% yield by heating either bromo- or iodo-pentafluorobenzene with cuprous cyanide in dimethylformamide according to the method of Friedman and Shechter;[4] small quantities of pentafluorobenzene and decafluorobiphenyl are also formed. Chloropentafluorobenzene was recovered after being kept with cuprous cyanide in dimethylformamide at 150° for 24 hours. The nitrile was identical with a sample prepared from pentafluorobenzaldehyde by the method of Pomeroy and Craig.[5]

1,4-Dibromotetrafluorobenzene reacts with cuprous cyanide in dimethylformamide giving tetrafluoroterephthalodinitrile in 61% yield. Similarly, 1,2-dibromotetrafluorobenzene gives tetrafluorophthalodinitrile; the highest yield (63%) is obtained when the reactants are kept at 160—170° for 2 hours; in this case, a considerable quantity of a fluorinated phthalocyanine is also formed. Impurities present in " laboratory reagent grade " dimethylformamide caused inhibition of the reactions of these dibromides with cuprous cyanide, but reproducible results were obtained by using dimethylformamide which had been treated with phosphoric oxide and distilled before use.

Aryl chlorides have been prepared by treating aryl bromides with cuprous chloride in a polar solvent.[6] This is an attractive route to polyfluoroaryl chlorides because bromopentafluorobenzene, the three dibromotetrafluorobenzenes, and other polyfluoroaryl bromides, are easily accessible. Treatment of bromopentafluorobenzene with cuprous chloride in dimethylformamide gives chloropentafluorobenzene in 61—64% yield; pentafluorobenzene and decafluorobiphenyl are also formed in considerable quantities. Similarly, 1,4-dibromotetrafluorobenzene gives 1,4-dichlorotetrafluorobenzene in 30% yield, together with several by-products.

The lack of a general route to highly fluorinated aryl sulphides prompted us to examine the reaction between a polyfluoroaryl bromide and a cuprous polyfluorothiophenoxide, a method used by Adams and his co-workers[7] for the preparation of hydrocarbon aromatic sulphides. Adams used pyridine as solvent, but our reactions, summarised below, were carried out in dimethylformamide.

The structure of the sulphide (I), formed in 84% yield by reaction of bromopentafluorobenzene with cuprous pentafluorothiophenoxide, was proved by desulphurisation with Raney nickel which gave only pentafluorobenzene. Bis-2,3,5,6-tetrafluorophenyl sulphide (II), prepared in 83% yield from bromo-2,3,5,6-tetrafluorobenzene and cuprous 2,3,5,6-tetrafluorothiophenoxide, was identical with the specimen prepared from pentafluorobenzene and potassium 2,3,5,6-tetrafluorothiophenoxide by Tatlow and his co-workers.[8]

Desulphurisation of the dihydro-sulphide (II) gave only 1,2,4,5-tetrafluorobenzene. Reaction of bromopentafluorobenzene with cuprous 2,3,5,6-tetrafluorothiophenoxide gave pentafluorophenyl 2,3,5,6-tetrafluorophenyl sulphide (III) in 88% yield. Desulphurisation of compound (III) gave a 1 : 1 mixture of penta- and 1,2,4,5-tetra-fluorobenzene. Compound (III) was readily converted into 4-bromotetrafluorophenyl pentafluorophenyl sulphide (IV) in 72% yield by treatment with bromine and 65% oleum. No sulphone formation occurred during this reaction. Tatlow[8] also noted the resistance of highly

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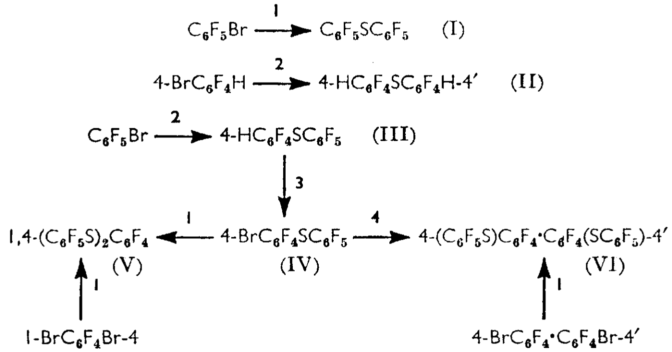
[4] L. Friedman and H. Shechter, *J. Org. Chem.*, 1961, **26**, 2522.

[5] J. H. Pomeroy and C. A. Craig, *J. Amer. Chem. Soc.*, 1959, **81**, 6340.

[6] W. B. Hardy and R. B. Fortenbaugh, *J. Amer. Chem. Soc.*, 1958, **80**, 1716.

[7] R. Adams, W. Reifschneider, and M. D. Nair, *Croat. Chem. Acta*, 1957, **29**, 277; R. Adams and A. Ferretti, *J. Amer. Chem. Soc.*, 1959, **81**, 4927.

[8] P. Robson, T. A. Smith, R. Stephens, and J. C. Tatlow, *J.*, 1963, 3692.



Reagents: 1, C_6F_5SCu; 2, $4\text{-}HC_6F_4SCu$; 3, Br_2–65% oleum; 4, Cu

fluorinated sulphides to oxidation. The structure of the bromo-sulphide (IV) was confirmed by treatment with cuprous pentafluorothiophenoxide to give an 80% yield of 1,4-bis(pentafluorophenylthio)tetrafluorobenzene (V), which was identical with the product obtained from cuprous pentafluorothiophenoxide and 1,4-dibromotetrafluorobenzene. Desulphurisation of the bis-sulphide (V) gave a 2 : 1 mixture of pentafluorobenzene and 1,2,4,5-tetrafluorobenzene. 4,4'-Bis(pentafluorophenylthio)-octafluorobiphenyl (VI) was prepared in two ways, (i) by heating the bromo-sulphide (IV) with copper bronze, (ii) by reaction of cuprous pentafluorothiophenoxide with 4,4'-dibromo-octafluorobiphenyl, thereby confirming its structure.

Selective replacement of the bromine atom is again observed when bromopentafluorobenzene is heated with cuprous oxide and acetic anhydride in dimethylformamide; pentafluorobenzene is formed in 73% yield. Similarly, 1,4-dibromotetrafluorobenzene is converted into 1,2,4,5-tetrafluorobenzene in 74% yield. Chloropentafluorobenzene is less reactive than bromopentafluorobenzene towards this reagent. Under conditions similar to those used to reduce the bromo-compound, little reduction of chloropentafluorobenzene occurs. Cuprous acetate in pyridine,[9] or a mixture of cuprous oxide and acetic anhydride in pyridine,[10,11] have been used previously to reduce aryl halides.

A characteristic feature of these reactions of bromopentafluorobenzene with cuprous salts is the preferential replacement of the bromine atom with the formation of a pentafluorophenyl compound. Furthermore, chloropentafluorobenzene is much less reactive than either bromo- or iodo-pentafluorobenzene towards cuprous salts; thus, the order of displacement of halogen from a polyfluoroaryl halide is $I \sim Br > Cl \gg F$. This is the reverse of the order of reactivity usually found in fluoroaromatic nucleophilic substitutions. For example, either chloro-[12,13] or bromo-pentafluorobenzene[3] reacts with nucleophilic agents to give predominantly a 4-chloro- or 4-bromo-tetrafluorophenyl compound; in these cases the customary order[14] of halogen mobility $F \gg Cl \sim Br \sim I$ is observed. In view of this marked difference in halogen mobility, the reactions of bromopentafluorobenzene with cuprous salts must differ mechanistically from reactions with other nucleophiles, which probably involve charged σ-complexes.[14]

While our work was in progress, Bacon and Hill[11,15] published the results of a quantitative study of reactions of the type $ArHal + CuY \longrightarrow ArY + CuHal$, effected in polar organic solvents. In a detailed discussion,[15a] they postulate that the cuprous salt is solvated and that substitution is preceded by formation of a complex in which the copper

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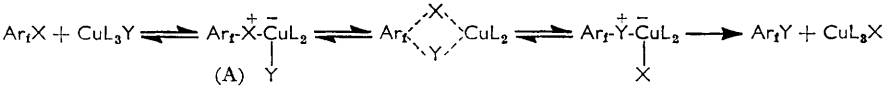
[9] W. G. H. Edwards and R. G. Stewart, *Chem. and Ind.*, 1952, 472.
[10] W. G. H. Edwards and G. K. McIndoe, *Chem. and Ind.*, 1953, 1091.
[11] R. G. R. Bacon and H. A. O. Hill, *J.*, 1964, 1112.
[12] F.P. 1,360,917/1963.
[13] G. M. Brooke, R. D. Chambers, J. Heyes, and W. K. R. Musgrave, *Proc. Chem. Soc.*, 1963, 213.
[14] J. F. Bunnett, *Quart. Rev.*, 1958, **12**, 1.
[15] R. G. R. Bacon and H. A. O. Hill, *J.*, 1964, (*a*) p. 1097; (*b*) p. 1108.

atom and the halogen of the aryl halide are bonded. Stephens and Castro[16] invoked the same mechanism to explain the reaction of an aryl iodide with cuprous phenylacetylide. By using the same concepts, the reaction of a polyfluoroaryl halide (Ar_fX) with a cuprous salt (CuY) in a ligand-forming solvent (L) can be interpreted by the scheme shown,



On the basis of the electronegativities of the halogens in Ar_fX, the tendency for formation of the complex (A) would be in the order $Ar_fI \sim Ar_fBr > Ar_fCl \gg Ar_fF$. This is, in fact, the order of reactivity observed with polyfluoroaryl halides and, in this respect, our results agree with those obtained by Bacon and Hill[15a] for 1-halogenonaphthalenes.

The presence of pentafluorobenzene and decafluorobiphenyl as by-products in the reaction of bromopentafluorobenzene with cuprous chloride and with cuprous cyanide requires comment. In the former reaction, when the reagents are not specially purified, the products are (yields in parentheses): C_6ClF_5 (61%); C_6HF_5 (15%); $C_{12}F_{10}$ (8%). Repetition of the reaction with purified cuprous chloride and purified dimethylformamide gives C_6ClF_5 (64%); C_6HF_5 (4%); $C_{12}F_{10}$ (15%). Bacon and Hill[15a] noted that the reaction of 1-bromonaphthalene with cuprous chloride was accompanied by reduction to naphthalene only when pyridine *N*-oxide was used as a solvent; nuclear coupling to 1,1′-binaphthyl was never detected in any solvent.

We suggest that decafluorobiphenyl is formed by the reaction of bromopentafluorobenzene with metallic copper, which is present as an impurity in cuprous chloride. Other work in this laboratory[17] has shown that bromopentafluorobenzene reacts with copper in dimethylformamide under mild conditions (150°/2 hr.) to give decafluorobiphenyl in about 90% yield. Hardy and Fortenbaugh,[6] who also used cuprous chloride for converting aryl bromides into aryl chlorides, noted that freshly prepared cuprous chloride contained about 2% of metallic copper. A smaller quantity of decafluorobiphenyl was obtained when we used commercial cuprous chloride, probably because disproportionation of the cuprous salt to copper and cupric ions would be hindered by cupric ions present as an impurity. The fact that Bacon and Hill[15a] detected no coupling in the reaction of 1-bromonaphthalene with cuprous chloride in a variety of solvents is not surprising, although it is likely that their reaction mixture contained metallic copper. 1-Bromonaphthalene is known to be resistant to coupling and undergoes little or no reaction when treated with copper powder in refluxing dimethylformamide for 24 hours.[18]

Pentafluorobenzene is possibly formed by the reduction of bromopentafluorobenzene by impurities in the reaction mixture of commercial cuprous chloride and dimethylformamide. Cuprous oxide may be formed, and we have shown that bromopentafluorobenzene is reduced by cuprous oxide in refluxing aqueous dimethylformamide. Removal of impurities by purification of the cuprous chloride and dimethylformamide reduced the amount of pentafluorobenzene formed from 15 to 4%.

Further work is clearly necessary to confirm these suggestions about the formation of the by-products, pentafluorobenzene and decafluorobiphenyl. At this stage, we cannot exclude the possibility that they may arise from decomposition, by a radical mechanism, of the complex (A).[15a]

EXPERIMENTAL

Infrared spectra were measured with a Perkin-Elmer Infracord 137. Cuprous cyanide, chloride, and oxide were B.D.H. laboratory grade reagents; cuprous penta- and 2,3,5,6-tetrafluorothiophenoxides were prepared as previously described for the preparation of cuprous thiophenoxide.[7]

[16] R. D. Stephens and C. E. Castro, *J. Org. Chem.*, 1963, **28**, 3313.

[17] M. W. Buxton and G. Fuller, unpublished results.

[18] N. Kornblum and D. L. Kendall, *J. Amer. Chem. Soc.*, 1952, **74**, 5782.

Pentafluorobenzonitrile.—(*a*) Bromopentafluorobenzene (990 g.), cuprous cyanide (449 g.), and dimethylformamide (650 c.c.) were stirred together at 147—158° for 13 hr. A solution of ferric chloride (500 g.) in 1N-hydrochloric acid (2 l.) was added, the mixture stirred at 100° for 30 min., and then steam-distilled. The product was distilled through a $1\frac{1}{2}$ ft. vacuum-jacketed column packed with glass helices ($\frac{1}{8}$ in. × $\frac{1}{8}$ in.) to give (i) pentafluorobenzene (24·0 g.), b. p. 84·0—84·6°/765 mm., n_D^{20} 1·3920, with the expected infrared spectrum (Found: C, 42·8; H, 0·6; F, 56·1. Calc. for C_6HF_5: C, 42·9; H, 0·6; F, 56·5%), (ii) an intermediate fraction (38·2 g.), b. p. 84·6—162·5°/765 mm., (iii) *pentafluorobenzonitrile* (634·8 g.), b. p. 162·5°/757 mm., n_D^{20} 1·4429 (Found: C, 43·8; F, 49·0; N, 6·9. C_7F_5N requires C, 43·5; F, 49·2; N, 7·3%) (Pummer and Wall[19] give b. p. 185—190°, $n_D^{23\cdot8}$ 1·4764, for an impure sample of the nitrile) $\nu_{max.}$ 2241 (CN stretching) and 1649 and 1509 cm.$^{-1}$ (fluorinated benzene ring vibrations), (iv) a crystalline residue (21·2 g.); this was a steam-distilled and the distillate recrystallised from methanol, giving decafluorobiphenyl (12·8 g.), m. p. 67—68°, with an infrared spectrum closely similar to that of an authentic specimen. Gas chromatography revealed the presence of about 5% of an unidentified impurity.

(*b*) Iodopentafluorobenzene (589 g.), cuprous cyanide (224 g.), and dimethylformamide (325 c.c.) were stirred together at 160° for 11 hr., then worked up as above to give (i) a mixture (18·4 g.), b. p. 76—162·5°/769 mm., of pentafluorobenzene and pentafluorobenzonitrile, (ii) pentafluorobenzonitrile (345·9 g.), b. p. 162·5°/769 mm., and (iii) a crystalline residue (0·9 g.), m. p. 189—191°.

(*c*) Pentafluorobenzaldehyde[20] (10·0 g.), *O,N*-bis(trifluoroacetyl)hydroxylamine[5] (20·6 g.), benzene (72 c.c.), and pyridine (10 c.c.) were heated together on a steam-bath for 2 hr. The mixture was washed with 2·5N-sodium hydroxide, 5N-hydrochloric acid, sodium pyrosulphite, and water, and was distilled to give pentafluorobenzonitrile (7·5 g.), b. p. 98—101°/100 mm., n_D^{20} 1·4412 (Found: C, 43·2; F, 49·2; N, 6·8%).

Partial hydrolysis of pentafluorobenzonitrile gave pentafluorobenzamide, m. p. and mixed m. p. 150·5° (Found: C, 39·8; H, 1·2. Calc. for $C_7H_2F_5NO$: C, 39·8; H, 0·95%) and complete hydrolysis gave pentafluorobenzoic acid, m. p. and mixed m. p. 103—104·5°.

Tetrafluoroterephthalodinitrile.—1,4-Dibromotetrafluorobenzene (308 g.), cuprous cyanide (225 g.), and dry, freshly distilled dimethylformamide (200 c.c.) were stirred together at 160—170° for $2\frac{1}{2}$ hr. The mixture was poured into a solution of ferric chloride (500 g.) in 2N-hydrochloric acid (1400 c.c.) and stirred at 70—80° for 30 min. Decantation of the aqueous layer and repeated washing with water of the residual black sludge gave a solid, which was sublimed at 200—210°/2 mm. The sublimate was recrystallised from acetone to give *tetrafluoroterephthalodinitrile* (123 g.), m. p. 196—198° (Found: C, 47·8; F, 37·6; N, 14·0. $C_8F_4N_2$ requires C, 48·0; F, 38·0; N, 14·0%), $\nu_{max.}$ (CCl_4) 2242 (CN) and 1490 cm.$^{-1}$ (fluorinated aromatic ring).

Partial hydrolysis of tetrafluoroterephthalodinitrile gave *tetrafluoroterephthalodiamide*, m. p. 320° (decomp.) (Found: C, 40·5; H, 2·0; F, 31·8. $C_8H_4F_4N_2O_2$ requires C, 40·7; H, 1·7; F, 32·2%) and complete hydrolysis gave tetrafluoroterephthalic acid, m. p. 285—287° (lit.,[21] 283—284°) (Found: C, 40·6; H, 1·0; F, 31·2%; Equiv., 119. Calc. for $C_8H_2F_4O_4$: C, 40·3; H, 0·8; F, 31·9%; Equiv., 119).

Tetrafluorophthalodinitrile.—1,2-Dibromotetrafluorobenzene (123 g.), cuprous cyanide (86 g.), and dry, freshly distilled dimethylformamide (140 c.c.) were stirred at 160—170° for 2 hr., and then poured into a solution of ferric chloride (165 g.) in 2N-hydrochloric acid (500 c.c.). The mixture was stirred at 80° for 30 min. and then steam-distilled. Recrystallisation of the steam-distillate from aqueous ethanol gave *tetrafluorophthalodinitrile* (50 g.), m. p. 88—89° (Found: C, 48·0; F, 37·6; N, 14·0. $C_8F_4N_2$ requires C, 48·0; F, 38·0; N, 14·0%), $\nu_{max.}$ (CCl_4) 2251 (CN stretching) and 1625, 1520, and 1494 cm.$^{-1}$ (fluorinated benzene ring).

Partial acidic hydrolysis of tetrafluorophthalodinitrile gave tetrafluorophthalimide, m. p. 220—222° (from benzotrifluoride) (lit.,[21] 210—211°) (Found: C, 44·1; H, 0·6; F, 34·6. Calc. for $C_8HF_4NO_2$: C, 43·8; H, 0·5; F, 34·7%) and complete hydrolysis gave tetrafluorophthalic acid, m. p. 154—156° (lit.,[21] 153—154°) (Found: C, 39·9; H, 1·2; F, 31·3%; Equiv., 119).

Chloropentafluorobenzene.—Bromopentafluorobenzene (989 g.) was added during 75 min. to a stirred suspension of cuprous chloride (795 g.) in dimethylformamide (650 c.c.) held at 130—140°. The mixture was stirred for 13 hr. longer at 130—140°, while a liquid distillate (686 g.),

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[19] W. J. Pummer and L. A. Wall, *J. Res. Nat. Bur. Stand.*, 1959, **63**A, 167; U.S.P. 3,046,313/1962.
[20] A. K. Barbour, M. W. Buxton, P. L. Coe, R. Stephens, and J. C. Tatlow, *J.*, 1961, 808.
[21] B. Gething, C. R. Patrick, and J. C. Tatlow, *J.*, 1961, 1574.

b. p. 85—120°, was collected from the top of a 12 in. vacuum-jacketed column, packed with $\frac{1}{16}$ in. × $\frac{1}{16}$ in. Dixon gauzes, attached to the apparatus. Addition of water (750 c.c.) to the residue and steam-distillation gave a white solid distillate (54·8 g.). Two recrystallisations of the solid from ethanol gave decafluorobiphenyl (29·8 g.), m. p. 66·5—69·5° (lit.,[1] 68—69°) with the expected infrared spectrum (Found: C, 43·1; F, 56·3. Calc. for $C_{12}F_{10}$: C, 43·1; F, 56·8%). The liquid product was distilled through a 2 ft. vacuum-jacketed column packed with Dixon gauzes ($\frac{1}{16}$ in. × $\frac{1}{16}$ in.) giving (i) pentafluorobenzene (100·5 g.), b. p. 85—86°/775 mm., $n_D^{20.5}$ 1·3918 with the expected infrared spectrum (Found: C, 42·6; H, 0·6; F, 55·8. Calc. for C_6HF_5: C, 42·9; H, 0·6; F, 56·5%), (ii) an intermediate fraction (23·0 g.), b. p. 86—117°, (iii) chloropentafluorobenzene (496 g.), b. p. 117°/750 mm., $n_D^{20.5}$ 1·4244 (Found: C, 35·3; Cl, 17·4; F, 46·1. Calc. for C_6ClF_5; C, 35·6; Cl, 17·5; F, 46·9%).

Chloropentafluorobenzene, Prepared with Purified Reagents.—Bromopentafluorobenzene was washed with 2N-potassium hydroxide solution and with water, dried (phosphoric oxide), and distilled (b. p. 136—138°) before use. Cuprous chloride (AnalaR) was purified as described elsewhere.[22] Dimethylformamide was dried (phosphoric oxide) and distilled before use.

Repetition of the previous experiment, under nitrogen, with bromopentafluorobenzene (575 g.), cuprous chloride (454 g.), and dimethylformamide (450 c.c.) gave, in addition to decafluorobiphenyl (54·5 g.), a liquid product, which was distilled to give (i) an intermediate fraction (31·0 g.), b. p. 86—116°, consisting of a mixture of pentafluorobenzene (55%) and chloropentafluorobenzene (45%), (ii) chloropentafluorobenzene (302·4 g.), b. p. 116—116·5°, and (iii) a residue (27·0 g.).

1,4-*Dichlorotetrafluorobenzene.*—A solution of 1,4-dibromotetrafluorobenzene (460 g.) in dimethylformamide (500 c.c.) containing a stirred suspension of cuprous chloride (303 g.) was heated to 80°. An exothermic reaction set in, and the mixture was then kept under reflux for 6 hr., diluted with water (750 c.c.), and steam-distilled. Dichloromethane (200 c.c.) was added to the distillate and the organic layer separated and dried. Fractional distillation through a 2 ft. vacuum-jacketed column packed with Dixon gauzes ($\frac{1}{16}$ in. × $\frac{1}{16}$ in.) gave, after the removal of solvent, (i) an intermediate fraction (6·2 g.), b. p. 40—125°, (ii) 1-*chloro*-2,3,5,6-*tetrafluorobenzene* (15·1 g.), b. p. 125—126·5°/759 mm., n_D^{20} 1·4423 (Found: C, 38·9; H, 0·6; Cl, 19·1; F, 40·6. C_6HClF_4 requires C, 39·0; H, 0·5; Cl, 19·2; F, 41·2%), $\nu_{max.}$ 3070 (C–H stretching) and 1639, 1518, and 1457 cm.$^{-1}$ (fluorinated aromatic ring), (iii) an intermediate fraction (43·5 g.), b. p. 126·5—157°, (iv) 1,4-*dichlorotetrafluorobenzene* (99·1 g.), b. p. 157—158°/759 mm., m. p. 52—54° (after two recrystallisations from ethanol) (Found: C, 32·5; Cl, 32·0; F, 34·7. $C_6Cl_2F_4$ requires C, 32·9; Cl, 32·4; F, 34·7%), $\nu_{max.}$ (CCl_4) 1496 and 1460 cm.$^{-1}$ (C–C stretching in a flourinated aromatic ring), (v) an intermediate fraction (14·1 g.), b. p. 158—160°, and (vi) a residual solid (76·1 g.).

By vapour-phase reduction [23] at 280° with hydrogen over a 10% palladium–active carbon catalyst, 1,4-dichlorotetrafluorobenzene (10·9 g.) gave a liquid product (5·5 g.), which was distilled to give 1,2,4,5-tetrafluorobenzene (2·6 g.) and 1-chloro-2,3,5,6-tetrafluorobenzene (2·4 g.), identified by gas chromatography and infrared spectroscopy.

Bispentafluorophenyl Sulphide (I).—A mixture of bromopentafluorobenzene (17·4 g.), cuprous pentafluorothiophenoxide (20·0 g.), and dimethylformamide (100 c.c.) was stirred at 150° for 5 hr. under nitrogen and filtered hot, and the filtrate was poured into water (300 c.c.). The precipitate was washed with water, dried, and extracted with ether. Evaporation of the extract and recrystallisation of the residue from ethanol gave *bispentafluorophenyl sulphide* (21·6 g.), m. p. 85—86° (Found: C, 39·3; F, 51·8%; *M*, 350. $C_{12}F_{10}S$ requires C, 39·35; F, 51·9%; *M*, 366), $\nu_{max.}$ (Nujol and hexachlorobutadiene mulls) 1638, 1518, and 1496 cm.$^{-1}$ (C–C stretching in a fluorinated aromatic ring).

Desulphurisation of Bispentafluorophenyl Sulphide.—A mixture of the sulphide (8·4 g.) and Raney nickel (grade W4; 25 g.) was heated in boiling butan-1-ol (200 c.c.) for 5 hr., and fractionally distilled, giving pentafluorobenzene (5·7 g.), b. p. 84—85°/763 mm., n_D^{20} 1·3925, with the expected infrared spectrum.

Bis-2,3,5,6-*tetrafluorophenyl Sulphide* (II).—A mixture of 1-bromo-2,3,5,6-tetrafluorobenzene (11·5 g.), cuprous 2,3,5,6-tetrafluorothiophenoxide (12·2 g.), and dimethylformamide (60 c.c.) was stirred at 150° for 3½ hr. The product, isolated as before, was distilled to give

[22] W. C. Fernelius, *Inorg. Synth.*, 1946, **2**, 1.

[23] R. E. Florin, W. J. Pummer, and L. A. Wall, *J. Res. Nat. Bur. Stand.*, 1959, **62**, 119; U.S.P. 2,967,894/1961.

bis-2,3,5,6-tetrafluorophenyl sulphide (13·8 g.), b. p. 106°/2·5 mm., m. p. 44—45° (lit.,[8] m. p. 44·5°) (Found: C, 43·6; H, 0·6; F, 46·4%; *M*, 308. Calc. for $C_{12}H_2F_8S$: C, 43·6; H, 0·6; F, 46·0%; *M*, 330), $\nu_{max.}$ (CCl_4) 3080 (C–H stretching) and 1634, 1500, and 1439 cm.$^{-1}$ (C–C stretching in a fluorinated aromatic ring).

Desulphurisation of the sulphide (9·9 g.) gave 1,2,4,5-tetrafluorobenzene (5·2 g.), b. p. 89—90°/756 mm., n_D^{20} 1·4079, with the expected infrared spectrum.

Pentafluorophenyl 2,3,5,6-*Tetrafluorophenyl Sulphide* (III).—A mixture of bromopentafluorobenzene (56·9 g.), cuprous 2,3,5,6-tetrafluorothiophenoxide (57·0 g.), and dimethylformamide (250 c.c.) was stirred at 140° for 3 hr., then worked up as in the previous case to give *pentafluorophenyl* 2,3,5,6-*tetrafluorophenyl sulphide* (70·5 g.), b. p. 100—102°/1·5 mm., m. p. 52·5—53·5° (Found: C, 41·4; H, 0·2; F, 48·4. $C_{12}HF_9S$ requires C, 41·4; H, 0·3; F, 49·1%), $\nu_{max.}$ (CCl_4) 3060 (C–H stretching), and 1630, 1613, 1512, and 1496 cm.$^{-1}$ (C–C stretching in a fluorinated aromatic ring).

Desulphurisation of the sulphide (8·3 g.) gave a fraction (7·0 g.), b. p. 87·5—89°/761 mm., which was shown by gas chromatography and infrared spectroscopy to be a 1 : 1 mixture of pentafluorobenzene and 1,2,4,5-tetrafluorobenzene.

Pentafluorophenyl 4-*Bromotetrafluorophenyl Sulphide* (IV).—To a stirred mixture of pentafluorophenyl 2,3,5,6-tetrafluorophenyl sulphide (22·3 g.) and bromine (7·3 g.), heated to 60—70°, was added 65% oleum (6 c.c.) during 15 min. The mixture was kept at 60° for 30 min. longer, then poured on ice (100 g.). The precipitate was recrystallised twice from ethanol, giving *pentafluorophenyl* 4-*bromotetrafluorophenyl sulphide* (19·7 g.), m. p. 70—71° (Found: C, 33·6; Br, 19·2; F, 40·1. $C_{12}BrF_9S$ requires C, 33·75; Br, 18·7; F, 40·0%), $\nu_{max.}$ (CCl_4) 1638, 1508, 1487, and 1442 cm.$^{-1}$ (C–C stretching in fluorinated aromatic rings).

1,4-*Bis*(*pentafluorophenylthio*)*tetrafluorobenzene* (V).—(*a*) A mixture of 1,4-dibromotetrafluorobenzene (10·0 g.), cuprous pentafluorothiophenoxide (17·2 g.), and dimethylformamide (70 c.c.) was stirred at 140° for 2 hr. The product, isolated as before, was recrystallised twice from dimethylformamide to give 1,4-*bis*(*pentafluorophenylthio*)*tetrafluorobenzene* (11·2 g.), m. p. 164·5—166° (Found: C, 40·0; F, 31·8%; *M*, 564. $C_{18}F_{14}S_2$ requires C, 39·6; F, 48·7%; *M*, 546), $\nu_{max.}$ (KBr) 1644, 1518, 1488, and 1463 cm.$^{-1}$ (C–C stretching in fluorinated aromatic rings).

(*b*) A mixture of pentafluorophenyl 4-bromotetrafluorophenyl sulphide (4·3 g.), cuprous pentafluorothiophenoxide (2·6 g.), and dimethylformamide (30 c.c.), stirred at 130—140° for 90 min., gave 1,4-bis(pentafluorophenylthio)tetrafluorobenzene (4·4 g.), m. p. 163·5—164·5°, after recrystallisation from butan-1-ol. The melting point was not depressed on admixture with the sulphide prepared in the previous experiment and the infrared spectra of the two samples were identical.

Desulphurisation of the sulphide (10·0 g.) gave a fraction (6·7 g.), b. p. 85—87°/761 mm., which was shown by gas chromatography and infrared spectroscopy to be a 2 : 1 mixture of pentafluorobenzene and 1,2,4,5-tetrafluorobenzene.

4,4′-*Bis*(*pentafluorophenylthio*)-*octafluorobiphenyl* (VI).—(*a*) A mixture of 4,4′-dibromooctafluorobiphenyl (9·1 g.), cuprous pentafluorothiophenoxide (11·3 g.), and dimethylformamide (60 c.c.) was stirred at 150° for 5 hr. Isolation of the product and recrystallisation from dimethylformamide and then from butan-1-ol gave 4,4′-*bis*(*pentafluorophenylthio*)-*octafluorobiphenyl* (7·9 g.), m. p. 164—167° (Found: C, 41·5; F, 49·5. $C_{24}F_{18}S_2$ requires C, 41·5; F, 49·2%), $\nu_{max.}$ (CCl_4) 1630, 1505, 1488, and 1466 cm.$^{-1}$ (fluorinated aromatic ring).

(*b*) Pentafluorophenyl 4-bromotetrafluorophenyl sulphide (8·2 g.) was heated with copper bronze (10 g.) in a sealed ampoule at 200° for 24 hr., then at 260° for 20 hr. The mixture was extracted with ether and the extract evaporated to give 4,4′-bis(pentafluorophenylthio)-octafluorobiphenyl (5·1 g.), m. p. 165—166·5° (from butan-1-ol), undepressed in admixture with the sample described above, and the infrared spectra of the two specimens were identical.

Pentafluorobenzene.—A mixture of bromopentafluorobenzene (98 g.), cuprous oxide (114 g.), acetic anhydride (166 g.), and dimethylformamide (200 c.c.) was stirred and kept at 140—150° under reflux for 6 hr., then poured into water (1500 c.c.) and steam-distilled. The product was distilled to give pentafluorobenzene (48·6 g.), b. p. 86°/763 mm., n_D^{20} 1·3920 (Found: C, 43·4; H, 0·9; F, 56·0. Calc. for C_6HF_5: C, 42·9; H, 0·6; F, 56·5%), with the expected infrared spectrum, and a liquid residue consisting of pentafluorobenzene (7·5 g.) and bromopentafluorobenzene (1·1 g.), as shown by analysis on a calibrated gas-chromatographic column.

1,2,4,5-*Tetrafluorobenzene*.—1,4-Dibromotetrafluorobenzene (51·4 g.) was stirred with cuprous oxide (47·7 g.), acetic anhydride (34·6 g.), and dimethylformamide (90 c.c.) at 150—160° in a flask fitted with a 6 in. vacuum-jacketed column packed with $\frac{1}{16}$ in. × $\frac{1}{16}$ in. Dixon gauzes. During 2 hr. a distillate (22·2 g.), b. p. 90—120°, was collected from the top of the column. The product was washed with water and distilled from phosphoric oxide to give 1,2,4,5-tetrafluorobenzene (18·5 g.), b. p. 88—90°/765 mm., n_D^{20} 1·4075, with the expected infrared spectrum.

Reduction of Bromopentafluorobenzene with Cuprous Oxide.—A mixture of bromopentafluorobenzene (20·7 g.), cuprous oxide (16·3 g.), water (3 c.c.), and dimethylformamide (47 c.c.) was stirred under reflux for 17 hr., and then poured into water. The product, isolated by steam-distillation, was pentafluorobenzene (8·1 g.), b. p. 82—85°, with the expected infrared spectrum.

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