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POLYFLUOROARYL ORGANOMETALLIC COMPOUNDS—VI

SOME REACTIONS OF PENTAFLUOROPHENYL- AND *ORTHO*-BROMOTETRAFLUOROPHENYL-ORGANOMETALLIC COMPOUNDS[1]

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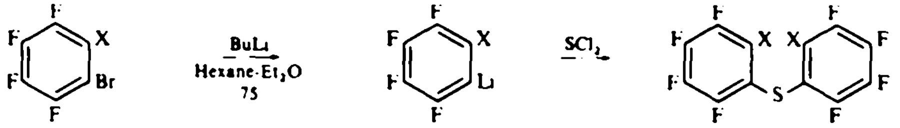
Abstract Pentafluorophenyl-lithium and *ortho*-bromotetrafluorophenyl-lithium react with sulphur dichloride, in ether hexane, to give the corresponding aryl sulphides; various polyfluoroaryl sulphides are reported, including the new heterocycle octafluorothianthren. Reaction of the lithium reagents with sulphur monochloride or with organic disulphides leads to S–S bond cleavage; and a nucleophilic displacement of CF_3^- from sulphur is reported. Cleavage of pentafluorophenyl- and *ortho*-bromotetrafluorophenyl-tin compounds occurs with iodide ion but is not a useful route to polyfluorobenzynes.

THE reaction of alkyl-lithium derivatives and Grignard reagents with sulphur halides[2] had not hitherto been applied to the synthesis of polyfluoroarylsulphur compounds. Previous work in this area has utilized nucleophilic displacement of fluorine in polyfluoroaromatic compounds using thiol anions,[3,4] heating polyfluoroaryl-organometallic compounds with sulphur,[5] reactions of copper thiophenolate salts with bromopolyfluoroaromatic compounds,[6] and the addition of sulphur to polyfluoroaryl-lithiums.[7] We describe here reactions of polyfluoroaryl-lithiums with sulphur halides which were studied in connection with the synthesis of some fused-ring polyfluoroheterocyclic compounds.[8]

Bromopentafluorobenzene (1) undergoes easy exchange of bromine for lithium, using a hydrocarbon solvent at low temperatures and addition of sulphur dichloride to this reagent gave bis(pentafluorophenyl)sulphide (3). Attempts to prepare the latter compound had been unsuccessful when the present work began but two successful syntheses, different from the present one, have since been reported.[5,6] The yield of bis(pentafluorophenyl)sulphide was highest when the sulphur dichloride used was freshly distilled after addition of a small amount of PCl_3 and a mixture of hexane-ether was found to be the most effective solvent. Pentafluorophenyl-lithium is also conveniently prepared by reaction of pentafluorobenzene with butyl-lithium.[9] Corresponding reaction of pentafluorophenyl-lithium with sulphur monochloride gave, again, (3). This indicated that nucleophilic attack on the S–S bond had occurred and, indeed, it was shown that the latter occurs quite readily because pentafluorophenyl-lithium with dimethyl disulphide and diphenyl disulphide gave the corresponding methyl- and phenyl-pentafluorophenyl sulphides respectively. In fact the latter reactions provide alternative routes to these sulphides

$$C_6F_5Li + R{-}S{-}S{-}R \rightarrow C_6F_5{-}S{-}R$$

since their preparation by nucleophilic aromatic displacements of fluorine, using the appropriate anions (PhS^- and MeS^-) is complicated by polysubstitution.[3,4] Reaction



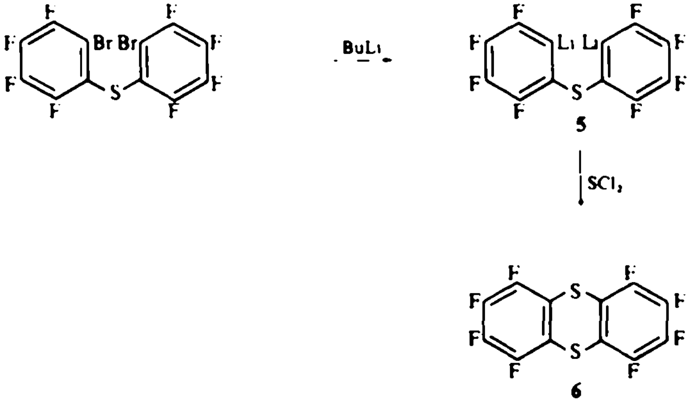
1: X = F
2: X = Br

3: X = F
4: X = Br

of pentafluorophenyl-lithium with bis(trifluoromethyl)disulphide was carried out with the possibility of obtaining the unknown $C_6F_5SCF_3$. However, not only nucleophilic attack at the S—S bond took place but, also, displacement of $^-CF_3$ occurred, giving bis(pentafluorophenyl) sulphide.

$$C_6F_5Li + CF_3{\cdot}S{\cdot}S{\cdot}CF_3 \rightarrow [C_6F_5{\cdot}S{\cdot}CF_3] \xrightarrow{C_6F_5Li} (C_6F_5)_2S + [LiCF_3] \rightarrow LiF + \text{polymer}$$

Derivatives via 1,2-dibromotetrafluorobenzene. Exchange of bromine for lithium occurs in 1,2-dibromotetrafluorobenzene (2) and the corresponding lithio derivative with sulphur dichloride gave bis(orthobromotetrafluorophenyl) sulphide (4) which is a useful precursor to octafluorodibenzothiophen.[8] Also, the bromine atoms in (4) are available for further exchange with butyl-lithium giving a di-lithio derivative (5)



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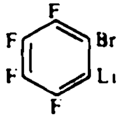
which in turn reacted with sulphur dichloride to give the new heterocycle octafluorothianthren (6), the chemistry of which will be discussed in a later publication.

ortho-Bromotetrafluorophenyl-lithium reacts with metal halides in the usual way, e.g. giving bis(*ortho*-bromotetrafluorophenyl)mercury (7) or (*ortho*-bromotetrafluorophenyl)trimethyltin (8).



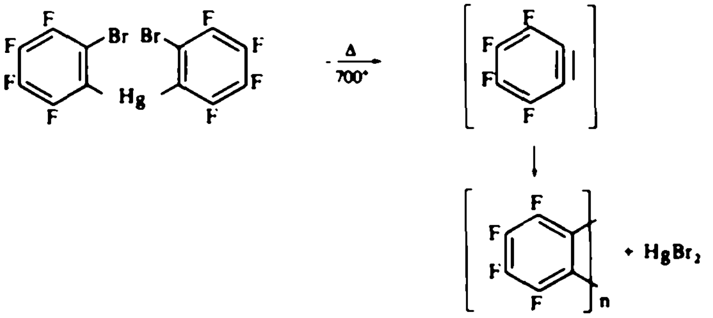
$+ HgCl_2 \longrightarrow Hg(C_6F_4Br)_2$

7

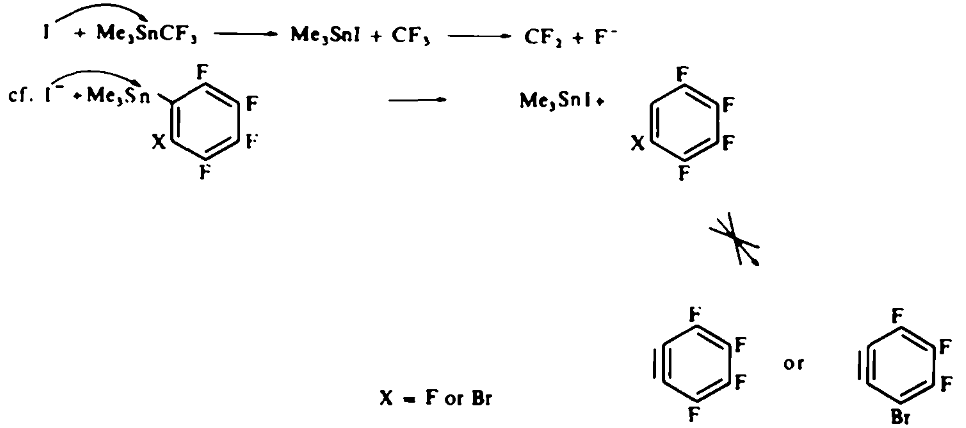
$C_6F_4BrLi + (Me_3)SnCl \longrightarrow (Me_3)SnC_6F_4Br$

8

These compounds were particularly interesting with respect to the ease of formation of the corresponding metal-bromine bond and the production of tetrafluorobenzyne because, while pentafluorophenyltin[10] and -mercury[11] compounds are not susceptible to decomposition by formation of bonds from fluorine to the metal the decomposition of organo-mercury derivatives by formation of mercury-bromine or iodine bonds is now well known.[12, 13] Pyrolysis of the mercurial (7) in a sealed tube at 300° gave only an intractable tar but pyrolysis in a flow system at 700° and 10^{-1} mm gave mercuric bromide and viscous liquid, which could not be sublimed, but the IR spectrum was consistent with a polytetrafluorophenylene.[14]



We have also attempted the displacement of pentafluorophenyl and bromotetrafluorophenyl from tin and mercury using iodide ion in glyme solvents, analagous to the method which Seyferth *et al.* used for the generation of dihalocarbenes.[15]



However, although it was found that both pentafluorophenyl and bromotetrafluorophenyl are cleaved from tin by iodide ion, no evidence for the intermediacy of a benzyne could be obtained. Unless solvents were rigorously dried, then pentafluorobenzene or bromotetrafluorobenzene and trimethyltin hydroxide were obtained, indicating a halide-ion catalysed hydrolysis of the type previously studied.[10, 16] On exclusion of moisture then more drastic conditions were required for cleavage (~200°) but although trimethyltin iodide was obtained the organic product consisted of tars. Attempts to trap a benzyne by carrying out the displacements in the presence of furan or anthracene were also unsuccessful. Therefore it appears that this type of displacement is unlikely to prove a useful route to benzynes.

EXPERIMENTAL

Bis(pentafluorophenyl)sulphide (3)

Pentafluorobenzene (8·4 g, 50 mmoles) in hexane–ether soln (20 : 30 ml) was cooled to -70 in a 250 ml flask fitted with stirrer, dropping funnel, N_2 inlet, and solid CO_2 condenser. n-Butyl-lithium (22 ml of a hexane soln, 50 mmoles) in hexane (20 ml) was added, dropwise, over ½ hr. The mixture was then stirred at this temp for 3 hr and then sulphur dichloride (2·58 g, 25 mmoles) (freshly distilled from PCl_3) in ether (10 ml) was slowly added (0·5 hr) and, after a further 2 hr at $-70°$, the reaction mixture was allowed to reach room temp. Hydrolysis (H_2O), followed by separation of the organic layer, which was then dried ($MgSO_4$) and finally removal of the solvent by vacuum transfer, left bis(pentafluorophenyl)sulphide (5·5 g, 60%), m.p. 83° (lit. 85–86°[6]). (Found: C, 39·4; F, 51·5. Calc. for $C_{12}F_{10}S$: C, 39·3; F, 51·9%.)

Reaction of pentafluorophenyl-lithium

(a) *With diphenyl disulphide*. Pentafluorobenzene (2·02 g, 12 mmoles) in ether (20 ml) was added slowly to a soln of n-butyl-lithium (5 ml, 12 mmoles) in ether (20 ml) at $-70°$. After stirring for 0·75 hr, diphenyl disulphide (2·18 g, 10 mmoles) in ether (20 ml) was added slowly at $-80°$ and the mixture was allowed to warm to room temp. After hydrolysis (H_2O) the organic layer was separated, dried ($MgSO_4$) and the solvent evaporated leaving a pale yellow solid (2·6 g, 94%), *phenylpentafluorophenyl sulphide*, m.p. 47–48° from MeOH. (Found: C, 52·3; H, 1·9. $C_{12}H_5F_5S$ requires: C, 52·1; H, 1·8%.)

(b) *With dimethyl disulphide*. Dimethyl disulphide (2·1 g, 22 mmoles) in ether (20 ml) was added to a cooled soln ($-80°$) of pentafluorophenyl-lithium (23·7 mmoles), made by exchange between bromopentafluorobenzene and butyl-lithium in ether hexane. After hydrolysis the organic layer was separated, dried ($MgSO_4$) and solvent was removed by distillation leaving pentafluorophenylmethyl sulphide[4] (2·7 g, 57%) which was distilled, b.p. 170° (mic. cap.) (Found: C, 39·3. Calc. for $C_7H_3F_5S$: C, 39·2%.) The mass spectrum showed a parent peak at 214, as required for $C_7H_3F_5S$. The distillation residue contained *para-bis-(methylthio)tetrafluorobenzene* (0·1 g), m p. 89 91° (from MeOH). (Found: C, 39·2. $C_8H_6F_4S_2$ requires 39·6.) The mass spectrum showed a parent peak at 242, as required for $C_8H_6F_4S_2$ and the ^{19}F NMR spectrum showed a single resonance at -27 ppm (from C_6F_6) indicating *para* orientation.

(c) *With bis(trifluoromethyl)disulphide*. Bis(trifluoromethyl)disulphide (1·7 g, 8·4 mmoles) in ether (20 ml) was added to a cooled soln ($-80°$) of pentafluorophenyl-lithium (8·8 mmoles) in ether, prepared from pentafluorobenzene and butyl-lithium (see above). After hydrolysis, the organic layer was separated, dried ($MgSO_4$) and solvent removed by distillation leaving a dark solid (0·42 g) from which bis(pentafluorophenyl) sulphide (0·26 g) (see above) was obtained by crystallization from MeOH and sublimation. The IR spectrum of the residual material indicated that it was highly fluorinated.

Reactions with ortho-*bromotetrafluorophenyl-lithium*

Bis(ortho-*bromotetrafluorophenyl*)*sulphide*. *o*-Dibromotetrafluorobenzene (9·2 g, 30 mmoles) in hexane ether soln (30 : 20 ml) was cooled to $-75°$ and n-butyl-lithium (12·8 ml of a hexane soln, 30 mmoles) in hexane (20 ml) was added, dropwise over ½ hr. The mixture was stirred for 3 hr at -75 and then sulphur dichloride (1·55 g, 15 mmoles) in ether (10 ml) was added over ½ hr. After a further 1·5 hr at $-75°$ the mixture was allowed to reach room temp, hydrolysed (H_2O) and the organic layer was separated and dried ($MgSO_4$). Solvent was then removed under vacuum to yield a yellow oily solid (7·7 g). The solid was carefully washed on a sintered funnel with several small volumes of b.p. 40° petroleum ether and air dried before being sublimed (80°/10^{-3} mm) giving *bis*(ortho-*bromotetrafluorophenyl*)*sulphide* (4·5 g, 62%), as a white crystalline solid, m.p 100° (Found: C, 29·4; F, 31·2; Br, 32·7. $C_{12}F_8Br_2S$ requires: C, 29·5; F, 31·1, Br, 32·8%.)

Octafluorothianthren. n-Butyl-lithium (2 ml hexane soln, 4·6 mmoles) in hexane–ether (1 : 1, 20 ml) was cooled to $-78°$ and bis-(*ortho*-bromotetrafluorophenyl)sulphide (1·1 g, 2·3 mmoles) in hexane ether (1 : 1, 10 ml) was slowly added over 1 hr. The mixture was stirred for 2 hr at $-78°$ before sulphur dichloride (0·24 g, 2·3 mmoles) in ether (5 ml) was added over 15 min. After a further 1 hr at this temp the mixture was allowed to warm to 0° and was then hydrolysed; the organic layer was separated, washed with water and dried ($MgSO_4$). Solvent was removed by vacuum transfer to leave a yellow semi-solid (0·8 g) which sublimed (80°/10^{-3} mm) giving colourless crystals (0·3 g) of *octafluorothianthren*. (Found: F, 42·4. $C_{12}F_8S_2$ requires F, 42·2%), m.p. 100°. The mass spectrum gave a parent ion at 360, as required for $C_{12}F_8S_2$. High resolution ^{19}F NMR gave two peaks of equal intensity (shifts 134 and 155 ppm w.r.t. $CFCl_3$) as required for octafluorothianthren, and these shifts are identical to those observed for fluorine atoms in corresponding orientations in octafluorodibenzothiophen.

Bis(ortho-bromotetrafluorophenyl)mercury. *o*-Dibromotetrafluorobenzene (9·2 g, 30 mmoles) in hexane–ether solution (30 20 ml) was cooled to −75° and n-butyl-lithium (12·8 ml, 30 mmoles) in hexane (20 ml) was added over ~3 hr. Mercury(II)bromide (5·0 g, 14 mmoles) in suspension in ether (~70 ml) was slowly added. After ~1·5 hr the mixture was allowed to reach room temp, hydrolysed (H_2O) and the organic layer was separated, dried ($MgSO_4$) and solvent removed under vacuum, giving *bis(ortho-bromotetrafluorophenyl)mercury* (7·4 g), which on sublimation (140°/10^{-3} mm) gave (6·5 g, 71%) m.p. 152 154°. (Found: C, 21·9; F, 23·2. $C_{12}Br_2F_8Hg$ requires C, 21·9; F, 23·1%.)

Trimethyl(ortho-bromotetrafluorophenyl)tin. Trimethyltin chloride (4·6 g, 23·2 mmoles) in ether (30 ml) was added to *ortho*-bromotetrafluorophenyl-lithium (23 mmoles) in ether (60 ml) as described above, and the reaction mixture was worked up in an analogous fashion giving *trimethyl(ortho-bromotetrafluorophenyl)tin* which was distilled under reduced press (~83 0·05 mm), (7·4 g, 82%). (Found: C, 27·0 $C_9H_9BrF_4Sn$ requires C, 27·6%.) The mass-spectrum gave a parent peak at 391, as required for $C_9H_9BrF_4Sn$. High resolution ^{19}F NMR gave four peaks of equal intensity as required for this compound. Analysis of these peaks showed that two fluorine atoms had *ortho*, *meta*, and *para* F–F coupling (viz. 20–25, 2·5–3·5, and 12·0–13·0 cycles/sec.), whilst the remaining two, showed two *ortho* and one *meta* F F couplings, and these results are wholly consistent with the proposed structure

Cleavage with iodide ion. Trimethylpentafluorophenyltin in monoglyme was warmed in a sealed tube to 80° with NaI and a high recovery of pentafluorobenzene and trimethyltin hydroxide resulted. When the solvent was rigorously dried, then a higher reaction temp ~200° was required to effect the cleavage and trimethyltin iodide (isolated as the ammonia complex) was obtained but only a tar and a small amount of pentafluorobenzene were the other products. These experiments were also carried out in the presence of furan and also using the latter as the solvent, but no adducts could be obtained.

Similar experiments to that described above were carried out using trimethyl(*ortho*-bromotetrafluorophenyl)tin; cleavage occurred readily in the presence of moisture but, again, more drastic conditions were required when strictly anhydrous materials were used and no adducts with furan could be isolated.

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