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# AROMATIC POLYFLUORO COMPOUNDS
# LI*. REACTION OF (POLYFLUOROARYL)TRIMETHYLTIN COMPOUNDS WITH AROMATIC HALIDES

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## SUMMARY

The reactions of (pentafluorophenyl)trimethyltin and (*p*-methoxytetrafluorophenyl)trimethyltin with bromobenzene, *p*-iodotoluene and 1-bromo-2,3,4,5-tetrafluorobenzene are described. The use of one of these reactions in the specific synthesis of a biaryl is illustrated.

In the course of a study of nucleophilic displacement reactions of 2(*H*)-nonafluorobiphenyl it was impossible to distinguish with the required degree of certainty between isomers. One solution to the problem was unequivocal synthesis of one or more of these isomers.

Although most of syntheses of symmetrical polyfluorobiaryls give good yields[2], when two different aromatic halides are reacted, complex, difficulty separable mixtures result. A promising line of approach to overcome this problem was suggested by the report[3] of the reaction of a (tetrachlorophenyl)trimethyltin with *p*-iodotoluene to yield a tetrachloromethylbiphenyl. We now wish to report the use of this type of reaction using polyfluoroaryltin compounds.

The synthesis of polyfluoroaryltin alkyls[4] is well known and the tin compounds used were prepared by standard procedures.

It was found that reaction of bromobenzene with (pentafluorophenyl)trimethyltin afforded the known[5] 2,3,4,5,6-pentafluorobiphenyl in reasonable yield. A problem was found in the purification of the biphenyl due to its co-distillation with unreacted bromobenzene. This was overcome by conversion of the latter to benzene via a Grignard reagent. Similarly it was shown that *p*-iodotoluene reacted with the tin compound to yield the expected biaryl.

Thus it seemed that a specific biaryl could be synthesised by this route.

As an illustration of the usefulness of this procedure its application to a specific problem is now given. It was found that treatment of 2(*H*)-nonafluorobiphenyl with sodium methoxide afforded a mono-methoxy derivative, $^{19}$F NMR spectroscopy did not indicate with any degree of certainty the position of substitution. On the basis of previous reactions of polyfluorobiaryls with nucleophiles[6] it was thought that the

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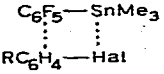
* For Part L, see ref. 1.

most likely isomer to be formed would be the 2(*H*)-4′-methoxy compound. A synthesis of this biphenyl specifically should be possible by reaction of (*p*-methoxytetrafluorophenyl)trimethyltin and bromo-2,3,4,5-tetrafluorobenzene. The two components were heated together in a Carius tube and it was found that a reasonably good yield of 2(*H*)-4′-methoxyoctafluorobiphenyl was obtained. This compound proved to be identical with the isomer obtained from the nucleophilic displacement.

The mechanism of the reaction seems likely to involve a four-centre of the type



$$\begin{array}{ccc} C_6F_5 & — & SnMe_3 \\ \vdots & & \vdots \\ RC_6H_4 & — & Hal \end{array}$$

with an exchange of halogen on the aromatic ring with the tin to form a tin–halogen bond.

Thus we suggest that this reaction represents a simple way of synthesis of mixed polyfluorobiaryls and which may be capable of more general application.

## EXPERIMENTAL

### *Preparation of (p-methoxytetrafluorophenyl) trimethyltin*

A solution of trimethyltin chloride (6.1 g) in dry ether (75 cm$^3$) was added to a solution of (*p*-methoxytetrafluorophenyl)magnesium bromide (from 4-MeOC$_6$F$_4$Br, 8.7 g, and Mg, 1.2 g) in dry ether (75 cm$^3$). The mixture was heated with stirring under reflux for 48 h, when after cooling, 4 *N* hydrochloric acid (50 cm$^3$) was added. The dried (MgSO$_4$) separated ether layer was distilled to leave a viscous liquid, distillation *in vacuo* afforded (*p*-methoxytetrafluorophenyl)trimethyltin (6.3 g), b.p. 90.92°/ 1.5 mm. (Found: C, 35.2; H, 3.4. C$_{10}$H$_{12}$F$_4$OSn calcd.: C, 35.2; H, 3.4%.) $^1$H NMR: $\tau$ 6.2 (t, OMe), 0.7 [complex, Sn(CH$_3$)$_3$], in the integral ratio 1/3.

In a similar experiment, but using the lithium derivative from 4-MeOC$_6$F$_4$Br (1.1 g) the tin compound (0.9 g) was obtained.

### *Reaction of (pentafluorophenyl) trimethyltin[4] with haloarenes*

(*a*). *With bromobenzene.* Bromobenzene (25 g) and (pentafluorophenyl)trimethyltin (4.0 g) were heated together at 160° for 5 days. The reaction mixture was then filtered and slowly added to magnesium turnings (5 g) activated by 1,2-dibromoethane (0.4 g) in dry ether (200 cm$^3$) and the mixture refluxed for 2 h, water (2 cm$^3$) and then 4 *N* sulphuric acid (200 cm$^3$) was added, the ether layer separated, dried (MgSO$_4$) and the ether distilled to yield a crude product (5.1 g). Separation by column (8″ × 1″) chromatography on silica gel using light petroleum as eluant afforded 2,3,4,5,6-pentafluorobiphenyl (1.3 g), m.p. 110°–111° alone and in admixture with an authentic sample[5] and with an identical IR spectrum to this latter.

(*b*). *With p-iodotoluene.* *p*-Iodotoluene (5.0 g) and (pentafluorophenyl)trimethyltin (3.5 g) were heated together under reflux for 5 days. The product mixture in ether (10 cm$^3$) was examined by GLC and showed all the tin compound had been consumed. The ether solution was then added to magnesium turnings (2.0 g) and the reaction mixture refluxed for 1 h when 4 *N* sulphuric acid (40 cm$^3$) was added. Distillation of the dried (MgSO$_4$) separated organic layer afforded an oil (2.3 g) which partly solidified on cooling, filtration followed by sublimation of the residue yielded

2,3,4,5,6-pentafluoro-4'-methylbiphenyl (0.8 g), m.p. alone and in admixture with an authentic sample[5] 117°–118°, and with identical IR spectrum to the latter.

*Reaction of (p-methoxytetrafluorophenyl) trimethyltin with 1-bromo-2,3,4,5-tetrafluorobenzene*

(*p*-Methoxytetrafluorophenyl)trimethyltin (2.0 g) and 1-bromo-2,3,4,5-tetrafluorobenzene (2.0 g) were heated together in a Carius tube at 210° for 50 h. The reaction products were dissolved in ether (100 cm$^3$) and washed with 4 *N* hydrochloric acid (2 × 50 cm$^3$). The ether layer was dried ($MgSO_4$) and distilled to give a brown liquid (2.0 g). Distillation *in vacuo* followed by alumina chromatography yield a crystalline solid (0.6 g) which on recrystallisation from light petroleum gave 2(*H*)-4'-methoxyoctafluorobiphenyl (0.4 g), m.p. 71°–72°. (Found: C, 47.9; H, 1.5. $C_{13}H_4F_8O$ calcd.: C, 47.6; H, 1.2%.)

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