The Direct Synthesis of Fluoro-aromatic Derivatives of Metals and Non-metals

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POSSIBLY due to the ready availability and high reactivity of the corresponding fluoro-aromatic lithium and magnesium reagents,[1] the "direct" route for synthesising organometallic fluoroarenes seems to have been ignored except for the preparation of bis(pentafluorophenyl)mercury reported recently by Haszeldine:[2]

$$2C_6F_5I + 2Hg \rightarrow (C_6F_5)_2Hg + HgI_2$$

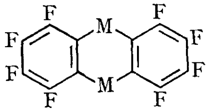
From several of our preliminary experiments it became apparent that the iodo-polyfluoroarenes were the most suitable reagents to use in direct syntheses and part of the wide range of compounds made available by this rather simple technique is indicated in the Table.

The element (in excess) and the corresponding iodo- or di-iodo-polyfluoroarenes were sealed into evacuated Pyrex tubes and heated at temperatures between 120 and 400° (the actual temperatures used in each case are given in parenthesis in the

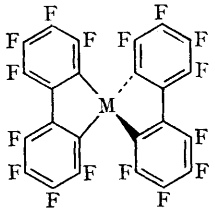
TABLE

Some fluoro-aromatic compounds prepared by "direct" synthesis: $Ar_FI + M$

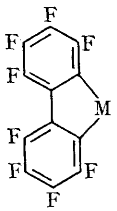
C_6F_5M :M = Cl, †(120°); Br, †(150°)
$(C_6F_5)_2M$:M = Hg, †(200°); S, m.p. 84—85°(230°) Se, m.p. 71—72°(230°)
$(C_6F_5)_3M$:M = P, †(220°); Sb, †(220°)
$(C_5F_6)_4M$:M = Ge, m.p. 245° (ref. 4) (325°); Sn, m.p. 220° (ref. 1) (240°)



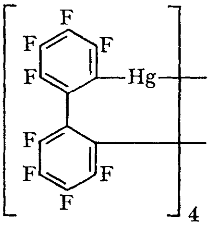
M = S, m.p. 102·5—104°(230°);
Se, m.p. 117—120°(320°)



M = Ge, m.p. 230·5—232° (390°);
Sn, m.p. 227—229° (230°)



M = Se, m.p. 118·5—120·5° (325°);
Te, m.p. 116—119° (325°)

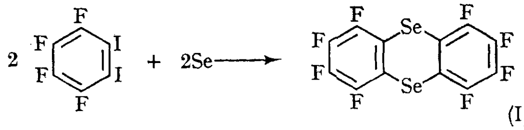


m.p. >380° (310°)

† Identity checked by infrared spectroscopy.

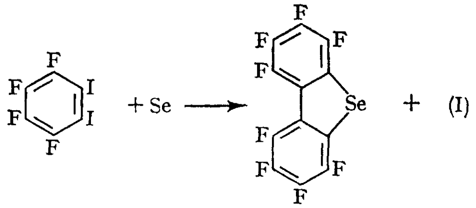
Table) for several hours, usually overnight; most of the organometallics were obtained in very high yield. The impurities (except in the cases of sulphur and selenium) appeared to be limited to unchanged starting material(s) and the element iodide (or iodine) so that sublimation in a vacuum was generally sufficient to produce analytically pure specimens.

The method is partially reliant on the high thermal stability of the organometallic derivatives once they are formed: as illustrated by the preparation of bis(octafluorobiphenylene)germane, where a temperature of 390° is required to initiate the reaction; though this compound, although sterically strained, was capable of withstanding temperatures up to 500° for some hours whilst undergoing only slight decomposition. An interesting variation in products with temperature is found in the reaction between selenium and 1,2-di-iodotetrafluorobenzene, which at 320° produces the product shown in the Table:



(I)

but at 375° some ring coupling simultaneously occurs giving rise to a mixture of organometallics:



Several of the compounds given in the Table have been prepared previously by more conventional means (*e.g.*, see ref. 1) whilst we have obtained some of the newer derivatives by alternative reactions such as 2,2'-$Li_2C_{12}F_8$ + $SeCl_4$ → $Se(C_{12}F_8)$. The corresponding mercury compound was prepared from the mercuric salt of the dicarboxylic acid.[3]

Typical Ullmann reactions occur with copper; however, one of the several products obtained on heating 1,2-di-iodotetrafluorobenzene and copper is perfluorotriphenylene (m.p. 102–104°), previously thought to be incapable of existence.[5]

(*Received March 6th*, 1967; *Com.* 218.)

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