2,2′-Disubstituted Octafluorobiphenyls

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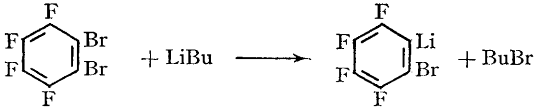
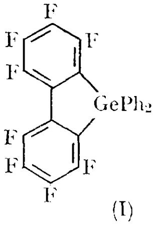
BY exploiting the known instability of titanium–carbon bonds we have synthesised 2,2′-dibromo-octafluorobiphenyl in high yield which opens up the possibility of forming many perfluoro-heterocyclic derivatives of the elements.

1,2-Dibromotetrafluorobenzene is first lithiated by treatment with an equimolecular quantity of n-butyl-lithium at −78° in an ether–hexane solvent:

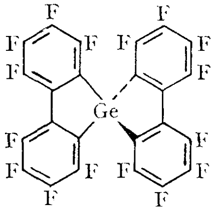


and an excess of titanium tetrachloride added to this stirred solution still held at −78°; the temperature is then allowed to rise slowly to about 20° and stirring continued for 15 hours to decompose the intermediate C_6F_5–Ti species before the addition of distilled water. The ether–hexane mixture, containing the 2,2′-dibromo-octafluorobiphenyl, is separated, dried with magnesium sulphate, and the solvent removed under vacuum; yield of essentially pure product, m.p. 98—99°, is 80—88%. The most efficient method of purification is vacuum sublimation at 85° (10^{-2} mm.). There is little doubt that the corresponding Grignard reagent and other metal halides could be used in place of 2-bromo-1-lithiotetrafluorobenzene and titanium tetrachloride[1] but the ease of formation of the lithium reagent coupled to the ready availability, ease of handling and ether-solubility of titanium tetrachloride make these the most suitable reagents. The titanium tetrachloride coupling reaction is obviously superior to the Ullman reaction when polyhalogenobenzene derivatives are used because no polymeric materials or mixtures of products are formed.

Depending on the ratio of reactants employed, either one or both bromine atoms in 2,2′-dibromo-octafluorobiphenyl will undergo lithium–bromine exchange when treated with butyl-lithium at −78° in an ether–hexane solvent. The formation of 2′-bromo-2-lithio-octafluorobiphenyl was demonstrated by the addition of water to the reagent and identifying its hydrolysis product, 2′-bromo-2-hydro-octafluorobiphenyl; dilithiation was proved by the formation of the hydrolysis product 2,2′-dihydro-octafluorobiphenyl (m.p. 80·5—81·5°) on the addition of distilled water and by the formation of the germanium heterocycles (I) and (II) when treated with diphenylgermanium dichloride or germanium tetrachloride respectively. These germanium compounds are interesting since in them the biphenyl rings must be essentially planar and will thus introduce considerable steric strain in the 6- and 6′-positions; we are at present investigating the possible consequences of this steric interaction.

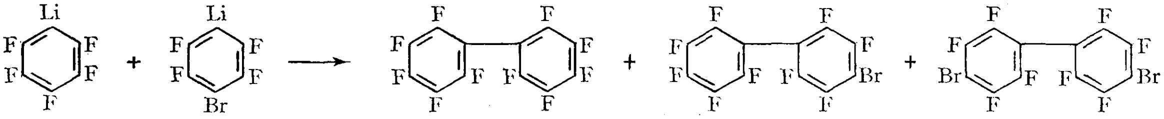


(I)



(II)

The titanium coupling reaction can be used to prepare, in about 75% yield, the 2,2′-dihydro-octafluorobiphenyl mentioned above; in this case, however, tetrahydrofuran is used as the solvent since 1,2-dihydrotetrafluorobenzene is difficult to lithiate in diethyl ether.[2] We have also obtained good yields of 3,3′- and 4,4′-disubstituted biphenyls by this coupling procedure and have shown that "crossed" coupling reactions give the three expected products (often in about 20% yield of *each* component) which can usually be separated easily by vapour-phase chromatography or fractional crystallisation: *e.g.*,



m.p. 67·5—69° m.p. 97—99° m.p. 112—114°

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[1] A. G. Massey and M. R. Wiles, unpublished work.

[2] R. J. Harper, E. J. Soloski, and C. Tamborski, *J. Org. Chem.*, 1964, **29**, 2385.