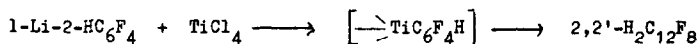
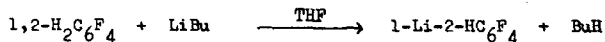


3,3',4,4',5,5',6,6'-OCTAFLUOROBIPHENYL

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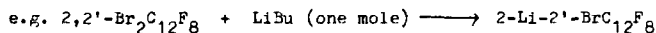
(Received 4 July 1966)

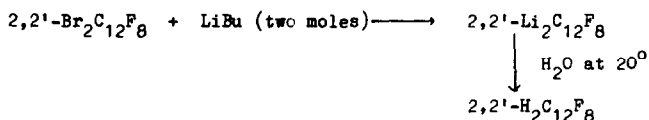
3,3',4,4',5,5',6,6'-Octafluorobiphenyl (m.p. 80.5 - 81.5°) can be made in about 75% yield by treating 3,4,5,6-tetrafluorophenyllithium with an excess of titanium tetrachloride at -78° in a tetrahydrofuran-hexane solvent and then stirring the mixture at 20° for 15 hours to decompose the intermediate Ti-C<sub>6</sub>F<sub>4</sub>H species :



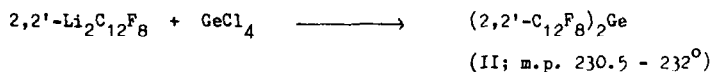
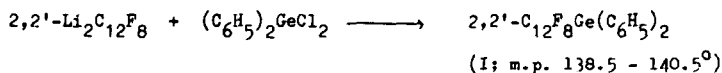
(Found: C, 48.3; H, 0.5; F, 50.8; M, 289. Calc. for C<sub>12</sub>H<sub>2</sub>F<sub>8</sub>: C, 48.35; H, 0.7; F, 51.1; M, 298). This biphenyl is a very useful starting material for the synthesis of other polyfluoro-aromatic derivatives: in oleum, treatment with either bromine or iodine gives the respective 2,2'-dihalo-octafluorobiphenyl in 60 - 80% yield (Found: C, 31.8; H, 0.05; F, 33.1; Br, 35.3; M, 458. Calc. for C<sub>12</sub>Br<sub>2</sub>F<sub>8</sub>: C, 31.6; H, 0.00; F, 33.3; Br, 35.1; M, 456. Found: C, 26.5; H, 0.0; F, 27.6; I, 46.3. Calc. for C<sub>12</sub>I<sub>2</sub>F<sub>8</sub>: C, 26.2; H, 0.0; F, 27.6; I, 46.15).

2,2'-Dibromo- and 2,2'-diiodo-octafluorobiphenyl both undergo lithium-halogen exchange on treatment with n-butyllithium in an ether-hexane solvent :





2,2'-Dilithio-octafluorobiphenyl can be used to synthesise heterocyclic organometallic derivatives of, for example, germanium by treatment with the appropriate metal halide :



( Found: C, 55.0; H, 2.1; F, 28.9; M, 517. Calc. for  $\text{C}_{24}\text{H}_{10}\text{F}_8\text{Ge}$  (I): C, 55.1; H, 1.93; F, 29.1; M, 523. Found: C, 43.5; H, 0.0; F, 45.9; Calc. for  $\text{C}_{24}\text{F}_{16}\text{Ge}$  (II) : C, 43.4; H, 0.0; F, 45.7).

2,2'-Diiodo-octafluorobiphenyl loses iodine on heating and when heated in a sealed tube at 200° with copper powder gives octafluorobiphenylene, m.p. 100 - 101.5° (Found: C, 48.7; H, 0.00; F, 51.25; M, from the mass spectrum, 296. Calc. for  $\text{C}_{12}\text{F}_8$  : C, 48.7; H, 0.00; F, 51.3; M, 296) in about 5% yield; polymeric phenylenes and trace amounts of 3,3',4,4',5,5',6,6'-octafluorobiphenyl and 2-iodo-3,3',4,4',5,5',6,6'-octafluorobiphenyl are also formed along with cuprous iodide. We are now studying the thermal decomposition of 2,2'-diiodo-octafluorobiphenyl and its coupling products in the Ullman reaction in more detail.