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Preliminary communication

Polyfluoroarylorganometallic compounds XIII*. Pentachlorophenylpentafluorophenylmercury

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There is much interest in the chemistry of halocarbon organometallic compounds, particularly polyhaloaryl derivatives. Bis(pentafluorophenyl)mercury (I), bis(pentachlorophenyl)mercury (II) and corresponding $C_6H_5HgC_6X_5$ (X = F, Cl) derivatives have been synthesised and their chemistry investigated[2,3]. We now describe a synthesis of the interesting pentachlorophenylpentafluorophenylmercury, $C_6Cl_5HgC_6F_5$ (III), and its reaction with HCl where the two groups are in competition for electrophilic cleavage.

The obvious methods of synthesis, reaction between an aryllithium and the appropriate arylmercury(II) halide, gave only (I) and (II) in essentially quantitative yields.

$$\begin{tikzcd}
C_6F_5Li + C_6Cl_5HgCl \arrow[dr, "\text{ether} \; -78^\circ"] & \\
& \underset{\text{(I)}}{(C_6F_5)_2Hg} + \underset{\text{(II)}}{(C_6Cl_5)_2Hg} \\
C_6Cl_5Li + C_6F_5HgBr \arrow[ur, "\text{ether} \; -15^\circ"'] &
\end{tikzcd}$$

The mercurial (III) was eventually synthesised by an exchange reaction between pentachlorophenylmercury(II) chloride[3] and methylpentafluorophenylmercury[2] and, when pure, shows no sign of disproportionation in the solid phase or in solution.

$$C_6Cl_5HgCl + CH_3HgC_6F_5 \xrightarrow[\text{benzene}\\ \text{30 min}]{\text{refluxing}} \underset{\text{(III)}}{C_6Cl_5HgC_6F_5} + CH_3HgCl$$

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*For part XII see ref. 1.

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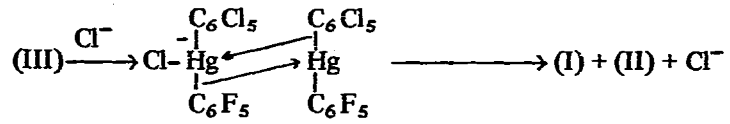
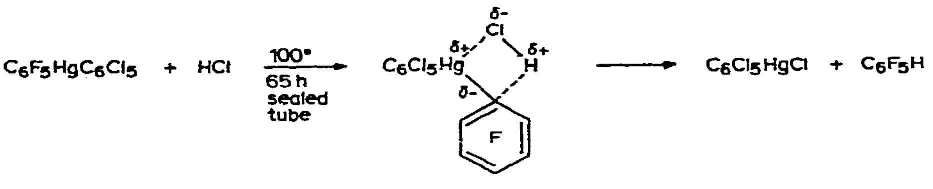
In view of these interesting observations we investigated the effect of catalytic amounts of lithium chloride and mercury(II) chloride on the disproportionation of (III). A solution of (III) in acetone/methanol (4/1) containing LiCl gave a precipitate of (II) after 1 hour while, under identical conditions, the solution containing $HgCl_2$ gave a precipitate only after 7–10 days. Clearly, the influence of the lithium chloride accounts for the disproportionation observed in the reactions involving aryllithiums. While the action of $HgCl_2$ in catalysing disproportionation is relatively well understood[4], the different effect of LiCl probably involves initial coordination of Cl^- to mercury.



$$(\mathrm{III}) \xrightarrow{\mathrm{Cl}^-} \mathrm{Cl}\text{-}\overset{C_6Cl_5}{\underset{C_6F_5}{\mathrm{Hg}}} \rightleftarrows \overset{C_6Cl_5}{\underset{C_6F_5}{\mathrm{Hg}}} \longrightarrow (\mathrm{I}) + (\mathrm{II}) + \mathrm{Cl}^-$$

Electrophilic cleavage of (III) with anhydrous HCl gave, exclusively, pentachlorophenylmercury(II) chloride (identified by IR and melting point)[3].



(IV)

It is generally accepted[4] that cleavage of organomercurials, by HCl, occurs via an S_Ei or S_E2 reaction mechanism which involves a four-centre transition state (IV). This is, in effect, an electrophilic aromatic substitution reaction[5], a process which rarely occurs with highly halogenated aromatic systems, except in cleavage of organometallic compounds. Therefore, this reaction provides, for the first time, a direct competition between pentachlorophenyl and pentafluorophenyl for electrophilic attack. Exclusive attack at pentafluorophenyl occurs, showing that the cumulative effect of five halogen atoms parallels the influence of a single halogen on similar processes[6]. It is also probable that steric effects operate to limit the reactivity at the pentachlorophenyl–mercury bond.

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