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THE REACTION OF BIS(TRIMETHYLSILYL)MERCURY WITH BROMOPENTAFLUOROBENZENE OR BROMOTRIFLUOROETHYLENE: ISOLATION OF INTERMEDIATE ARYL- AND VINYL-SILYLMERCURY COMPOUNDS

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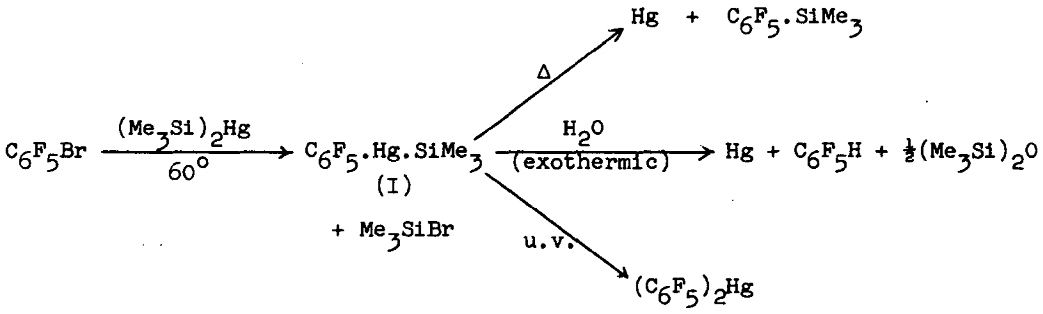
The reaction of bis(trimethylsilyl)mercury with bromopentafluorobenzene has previously been reported[1] to give trimethylpentafluorophenylsilane in the dark at 20°. In continuation of our studies of the reactions of this mercurial with halogenobenzenes[2] and with fluoro-olefins,[3] we now report the detection of pentafluorophenyl(trimethylsilyl)mercury (I) spectroscopically and chemically by its thermal decomposition to mercury and trimethylpentafluorophenylsilane, by its photochemical conversion to bis(pentafluorophenyl)mercury, and by its hydrolysis to hexamethyldisiloxane and pentafluorobenzene.



Thus after 2 days at 60°, bromopentafluorobenzene and bis(trimethylsilyl)mercury gave bromotrimethylsilane (33%), mercury (48%), and unchanged bis(trimethylsilyl)mercury, and the ^{19}F n.m.r. spectrum of the liquid products showed the presence of pentafluorobenzene, bromopentafluorobenzene, and trimethylpentafluorophenylsilane, but the major absorptions comprised an AA'BB'X pattern showing mercury satellite peaks associated with the AA' part. When the sample was kept for a further 3 days at 60°, this pattern disappeared, the bands due to trimethylpentafluorophenylsilane increased in intensity, and mercury was deposited. Bis(trimethylsilyl)mercury similarly reacts with pentafluoroiodosilane, exothermically at room temperature, to give high yields of (I) and iodotrimethylsilane together with a small amount of trimethylpentafluorophenylsilane.

The detection of the aryl silyl-mercury intermediate provides support for a four-centre mechanism of the type previously proposed[2a] for the replacement of bromine in bromobenzene by the Me_3Si-group, and argues against a free-radical substitution or electron-transfer mechanism.[1a] Russian workers have previously suggested[4] that unsymmetrical mercury-silicon compounds of this type might be stable if the alkyl or aryl group attached to mercury were highly electronegative, but do not appear to have reported their isolation.

In a similar manner, the thermal (60°) reaction of bromotrifluoroethylene with bis(trimethylsilyl)mercury gave mercury (85%), bromotrimethylsilane, and trimethyltrifluorovinylsilane (79%), together with fluorotrimethylsilane (6%) and hexamethyldisilane (20%); the ^{19}F n.m.r. spectrum of the high-boiling product fraction (which contained no trimethyltrifluorovinylsilane) showed the presence of a mercury-containing trifluorovinyl compound. When this material was kept at 60° (3 days) mercury was deposited, and the ^{19}F n.m.r. spectrum showed that the original compound had decomposed and that the only fluorine-containing compound was now trimethyltrifluorovinylsilane. Photochemical reaction of bromotrifluoroethylene and bis(trimethylsilyl)mercury gave the same products in similar yields.

When a sample of the intermediate trifluorovinylmercury compound was allowed to warm to room temperature in the presence of water, a mildly exothermic reaction gave trifluoroethylene, hexamethyldisiloxane, trimethyltrifluorovinylsilane, and mercury, thus providing further evidence for the formulation of the intermediate as trifluorovinyl(trimethylsilyl)mercury (II).

$$\begin{tikzcd}[column sep=large]
CF_2{:}CFBr \arrow[r, "(Me_3Si)_2Hg", "60^\circ\text{, or u.v.}"'] & \begin{matrix}CF_2{:}CF.Hg.SiMe_3\\ \text{(II)}\\ + Me_3SiBr\end{matrix} \arrow[r, "60^\circ", "\text{or u.v.}"'] \arrow[dr, "H_2O"] & CF_2{:}CF.SiMe_3 + Hg \\
& & \begin{matrix}CF_2{:}CHF + Hg + \tfrac{1}{2}(Me_3Si)_2O\\ + CF_2{:}CF.SiMe_3\end{matrix}
\end{tikzcd}$$

It thus appears that bis(trimethylsilyl)mercury may react with fluoro-olefins either by addition to the double bond (e.g.,[3] with C_2F_4, $CF_2{:}CFCl$, C_3F_6, etc.) or by substitution of a vinylic bromine, as here, in each case to give a mercury-containing intermediate. Eaborn et al.[5] have recently reported the reaction of the silyl- and germylmercurials with vic-dibromoalkanes, and suggested an analogous alkyl intermediate, but preferred a concerted reaction.

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