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THE RAPID INTERACTION OF BIS(TRIMETHYLSILYL)MERCURY AND BIS(TRIMETHYLGERMYL)MERCURY

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SUMMARY

The compounds $(Me_3Si)_2Hg$ and $(Me_3Ge)_2Hg$ have been shown to interact in solution to give the unsymmetrical compound $Me_3SiHgGeMe_3$. An equilibrium is rapidly established.

INTRODUCTION

Redistribution of alkyl groups between dialkylmercury compounds is a slow process; for example, little exchange occurred between $(CH_3)_2Hg$ and $(CD_3)_2Hg$ in tetrahydrofuran during 8 days at 28°, although exchange did take place[1] on prolonged heating at 65°. Consistently, disproportionation of $EtHgSiEt_3$ to Et_2Hg and $(Et_3Si)_2Hg$ took place[2] only on heating to 170°. By contrast, we find that exchange of groups occurs rapidly between $(Me_3Si)_2Hg$ and $(Me_3Ge)_2Hg$ to establish the equilibrium (1), in which the mixed compound $Me_3SiHgGeMe_3$ is a substantial component.

$$(Me_3Si)_2Hg + (Me_3Ge)_2Hg \rightleftarrows 2\ Me_3SiHgGeMe_3 \tag{1}$$

RESULTS AND DISCUSSION

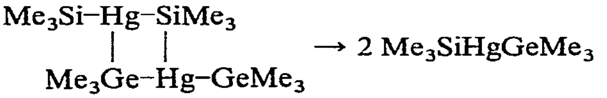
The interaction (1) was first suspected when pyrolysis (at 210°) or photolysis (at 40°) of a roughly equimolar mixture of $(Me_3Si)_2Hg$ and $(Me_3Ge)_2Hg$ was found to give $Me_3SiGeMe_3$ in 87 or 78% yield, respectively, along with only small amounts of the compounds $Me_3SiSiMe_3$ and $Me_3GeGeMe_3$, which are obtained in essentially quantitative yield in the separate decompositions of $(Me_3Si)_2Hg$ and $(Me_3Ge)_2Hg$ under the same conditions. (The compound $Et_3SiHgGeEt_3$ has been shown to give predominantly the mixed compound $Et_3SiGeEt_3$ on photolysis[2].) Again, treatment of the equimolar mixture with air gave the mixed $Me_3SiOGeMe_3$ in 90% yield, along with only small amounts of $(Me_3Si)_2O$ and $(Me_3Ge)_2O$.

The existence of equilbrium (1) was confirmed by Raman spectroscopy. The Raman spectrum of bis(trimethylsilyl)mercury in cyclopentane at room temperature is similar to that of hexamethyldisilane except that the symmetric Me_3Si–$SiMe_3$

stretching vibration is replaced by a strong polarized band at 159 cm^{-1}, which can be assigned to the $Me_3Si{-}Hg{-}SiMe_3$ symmetric stretch. Similarly a strong polarized band at 139 cm^{-1} in the spectrum of bis(trimethylgermyl)mercury can be assigned to the $Me_3Ge{-}Hg{-}GeMe_3$ symmetric stretch. Treating the $Me_3Si{-}Hg{-}GeMe_3$ molecule as a linear triatomic system, with the Me_3Si and Me_3Ge "atoms" having effective masses of 73 and 118, respectively, and assuming no interaction between the $Me_3Si{-}Hg$ and $Me_3Ge{-}Hg$ bonds, it can be calculated very simply (*cf.* ref. 3) that the symmetrical stretching should have a frequency of about 149 cm^{-1}[*], and an equimolar mixture of $(Me_3Si)_2Hg$ and $(Me_3Ge)_2Hg$ did, indeed, show a very strong polarized band at 146 cm^{-1}, although the natural width of all the bands precluded complete separation of this band from those at 139 and 159 cm^{-1}. An identical spectrum was given by a solution of a separately prepared sample of $Me_3SiHgGeMe_3$. In both cases the spectrum underwent no change during the three days after the first recording, which was made within 10 min of the preparation of the solution, and so equilibrium (1) must be established within a few minutes.

In view of the results obtained, it might be expected that exchange of Me_3M groups between different molecules of the separate $(Me_3M)_2Hg$ compounds would occur fairly rapidly. However, the NMR spectrum of bis(trimethylsilyl)mercury in carbon disulphide or dichloromethane shows a coupling of 40 Hz between the ^{199}Hg atom and the methyl protons[4], which means that a Me_3Si group must remain attached to a specific mercury atom for at least 0.01 sec.

The exchange of groups in compounds RHgR′ or $R_3MHgM'R_3$ is probably a 4-centre molecular process, of type (2). The readier exchange of Me_3M groups



$$\begin{array}{l} Me_3Si{-}Hg{-}SiMe_3 \\ \qquad\ \ | \quad\ | \\ Me_3Ge{-}Hg{-}GeMe_3 \end{array} \longrightarrow 2\ Me_3SiHgGeMe_3 \qquad (2)$$

compared with that of alkyl groups is in accord with a generalisation, based on orbital symmetry arguments, that for reactions of this type lower activation energies should be found for systems containing heavier elements[5].

EXPERIMENTAL

Decomposition of a mixture of $(Me_3Si)_2Hg$ and $(Me_3Ge)_2Hg$

(*i*). A mixture of $(Me_3Si)_2Hg$ (0.38 g) and $(Me_3Ge)_2Hg$ (0.51 g) in cyclohexane (2 ml) was kept in a sealed tube at 210° for 15 h. Mercury was produced in 100% yield, and analysis by GLC showed that $Me_3SiGeMe_3$ had been formed in 87% yield, along with $Me_3SiSiMe_3$ and $Me_3GeGeMe_3$ in 12 and 13% of the theoretically possible yields.

(*ii*). Photolysis for 10 h at 40° of a mixture of $(Me_3Si)_2Hg$ (0.35 g) and $(Me_3Ge)_2Hg$ (0.42 g) in cyclopentane gave mercury (100%), $Me_3SiGeMe_3$ (78%), $Me_3SiSiMe_3$ (10%), and $Me_3GeGeMe_3$ (11%).

(*iii*). Dry air was passed into a mixture of $(Me_3Si)_2Hg$ (0.21 g) and $(Me_3Ge)_2Hg$

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[*] There should also be an unsymmetrical stretching vibration at about 207 cm^{-1} but this is a forbidden transition which would be very weak in the Raman spectrum; no scattering was detected at this frequency.

(0.26 g) in cyclopentane (2 ml) to give mercury (100%), $Me_3SiOGeMe_3$ (90%), $(Me_3Si)_2O$ (3%), and $(Me_3Ge)_2O$ (4%); the compound $Me_3SiOGeMe_3$, n_D^{25} 1.4007, b.p. 118–120°/761 mm (lit.,[4] 116.5–117.5/723 mm) was isolated from the products by preparative GLC on a column of 20% SE 30 on 85–100 mesh Chromosorb (Found: C, 35.1; H, 8.85. $C_6H_{18}GeOSi$ calcd.: C, 34.8; H, 8.8%.) Essentially the same mixture of products was obtained when a solution of the compound $Me_3SiHgGeMe_3$ was similarly treated.

(Trimethylgermyl)(trimethylsilyl)mercury (impure)

A solution of bromotrimethylgermane (9.8 g, 0.05 mole) and chlorotrimethylsilane (5.4 g, 0.05 mole) in dry degassed cyclohexane (20 ml) was shaken under nitrogen for 3 weeks with sodium amalgam (450 g, 0.5% w/w). The cyclohexane layer was filtered under nitrogen (No. 4 glass-sinter filter), and the solvent was removed under reduced pressure to give bright yellow crystals (4.8 g, 25%). Sublimation at 60°/0.01 mm gave material of m.p. 106–110°. (Found: C, 18.9; H, 4.85. $C_6H_{18}GeHgSi$ calcd.: C, 18.4; H, 4.6%.) The mass spectrum showed peaks of expected isotope pattern centred around *m/e* 348 and 438, attributed to the ions $C_6H_{18}Si_2Hg^+$ and $C_6H_{18}Ge_2Hg^+$, in addition to the peak at 392 attributed to $C_6H_{18}GeSiHg^+$, indicating that there was some contamination by $(Me_3Si)_2Hg$ and $(Me_3Ge)_2Hg$. Attempts to remove these impurities by fractional sublimation met with only partial success.

Raman spectra

A Coderg Type PH1 helium–neon laser Raman spectrometer was used. Solutions of the mercurials in degassed anhydrous cyclopentane were filtered under nitrogen into the cell to ensure the absence of metallic mercury.

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