74. *Phenyl-group Migration in Compounds Containing* Si–O–Hg *Linkages.*

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Reaction of sodium triphenylsilyl oxide (2 mol.) with mercury chloride (1 mol.) yields bistriphenylsiloxymercury, $(Ph_3Si{\cdot}O)_2Hg$, which undergoes a spontaneous rearrangement involving migration of a phenyl group from silicon to mercury, to form $Ph_3Si{\cdot}O{\cdot}HgPh$, the first pure compound containing an Si–O–Hg bond to be isolated. When this product is heated gently, further migration of phenyl groups occurs to give diphenylmercury. Polymeric phenylsilicone derivatives are also formed during the rearrangements.

When the original reactants are mixed in an equimolar ratio, an analogous reaction appears to take place, to yield phenylmercuric chloride.

Interest has been shown recently in the preparation and properties of monomeric and polymeric materials containing Si–O–M linkages (M = a metal or non-metal). The present investigation was carried out to prepare, and examine the thermal stability of, a compound containing a Si–O–Hg bond, since no pure compound containing such a bond had been reported previously. It has been stated that bistrimethylsiloxymercury $(Me_3Si{\cdot}O)_2Hg$ may be obtained by the interaction of sodium trimethylsilyl oxide $Me_3Si{\cdot}ONa$ with mercuric chloride, but the material formed underwent reaction so readily with traces of moisture that it was always contaminated with mercuric oxide and no analysis of the substance was given.[1] A somewhat similar reaction employing $Ph_2Si(ONa)_2$ and mercuric chloride gave only octaphenylcyclotetrasiloxane and an unidentified product.[2]

In the present investigation, it was found that sodium triphenylsilyl oxide $Ph_3Si{\cdot}ONa$ and mercuric chloride reacted instantly when mixed in ethereal solution in the molar ratio 2 : 1 to form what was believed to be bistriphenylsiloxymercury:

$$2Ph_3Si{\cdot}ONa + HgCl_2 \longrightarrow (Ph_3Si{\cdot}O)_2Hg + 2NaCl \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

Even when the ether was evaporated *in vacuo* below room temperature, partial decomposition occurred (according to reaction 2) to give a sticky solid from which the compound $(Ph_3SiO)_2Hg$ could not be isolated in the pure state. The colourless ethereal solutions of the bistriphenylsiloxymercurysiloxymercury were hydrolysed instantly, even by moisture in the air, with precipitation of mercuric oxide.

$$x(Ph_3Si{\cdot}O)_2Hg \longrightarrow (x - 1)Ph_3Si{\cdot}O{\cdot}HgPh + Ph_3Si{\cdot}O{\cdot}[Ph_2Si{\cdot}O]_x{\cdot}HgPh \quad . \; . \; . \; . \; . \quad (2)$$

When ethereal solutions of bistriphenylsiloxymercury were left at room temperature, or when the sticky solid obtained by complete removal of the ether was heated gently, a phenyl group migrated from silicon to mercury with the formation of the new compound phenyl(triphenylsiloxy)mercury $Ph_3Si{\cdot}O{\cdot}HgPh$. Up to 34% of the mercury used could be recovered as this compound, but no trustworthy analysis or molecular-weight data could be obtained for the polymeric material since it obviously still contained some solid $Ph_3Si{\cdot}O{\cdot}HgPh$ from which it could not be separated. No sign of hydrolysis was detected when ethereal solutions of the compound $Ph_3Si{\cdot}O{\cdot}HgPh$ were treated with water.

When equimolar ratios of sodium triphenylsilyl oxide and mercuric chloride were used in the initial reaction, none of the compound $Ph_3Si{\cdot}O{\cdot}HgPh$ was formed on heating; instead, large quantities of phenylmercuric chloride were produced together with viscous polymeric material.

$$Ph_3Si{\cdot}ONa + HgCl_2 \longrightarrow Ph_3Si{\cdot}O{\cdot}HgCl + NaCl \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$(x + 1)Ph_3Si{\cdot}O{\cdot}HgCl \longrightarrow xPhHgCl + Ph_3Si{\cdot}O{\cdot}[Ph_2Si{\cdot}O]_x{\cdot}HgCl \quad . \; . \; . \; . \; . \quad (4)$$

The assignment of the structure $Ph_3Si{\cdot}O{\cdot}HgPh$ to the compound isolated in reaction (2) is consistent with the fact that with hydrochloric acid reaction (5) took place almost quantitatively:

$$Ph_3Si{\cdot}O{\cdot}HgPh + HCl \longrightarrow Ph_3Si{\cdot}OH + PhHgCl \quad . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

and that it could be formed from PhHgCl as shown in reaction (6):

$$PhHgCl + Ph_3Si{\cdot}OK \longrightarrow Ph_3Si{\cdot}O{\cdot}HgPh + KCl \quad . \; . \; . \; . \; . \; . \; . \quad (6)$$

Phenyl(triphenylsiloxy)mercury appears to be completely stable at room temperature but just above its melting point (140—141°) rapid migration of another phenyl group from silicon to mercury occurred with the formation of diphenylmercury and large quantities of viscous polymer:

$$(x + 1)Ph_3Si{\cdot}O{\cdot}HgPh \longrightarrow xPh_2Hg + Ph_3Si{\cdot}O{\cdot}[Ph_2Si{\cdot}O]_x{\cdot}HgPh \quad . \; . \; . \; . \; . \; . \quad (7)$$

The results of this investigation show that the Si–O–Hg linkage has the interesting property of causing spontaneous migration of phenyl groups from silicon to mercury and in this respect the reaction is somewhat analogous to those involving cleavage of Si–aryl bonds by means of mercuric acetate.[3] The direct reaction of a Si–Ph bond with a Hg–Cl bond to give phenylmercuric chloride which then reacts with sodium triphenylsilyl oxide to give the compound $Ph_3Si{\cdot}O{\cdot}HgPh$ is unlikely since precipitation of sodium chloride was instantaneous in the reactions studied, and the order of addition of reactants was such

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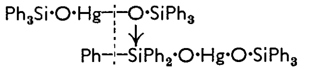
[1] Tatlock and Rochow, *J. Org. Chem.*, 1952, **17**, 1555.

[2] Hornbaker and Conrad, *J. Org. Chem.*, 1959, **24**, 1858.

[3] Benkeser, Hoke, and Hickner, *J. Amer. Chem. Soc.*, 1958, **80**, 5294.

that the sodium salt was present in excess as the reaction took place. Also, no phenylmercuric chloride or hydrogen chloride was formed when ethereal solutions of triphenylsilanol and mercuric chloride were refluxed together. Similarly no reaction occurred on refluxing ethereal solutions of PhHgCl and Ph_3SiOH together in the presence of triethylamine.

The rearrangement may occur by means of an intermolecular $>O \longrightarrow$ Si interaction, *viz.*:



with cleavage at the broken line as shown. This process could then recur to give larger molecules. A similar type of interaction could be used to explain the conversion of $Ph_3Si{\cdot}O{\cdot}HgPh$ into diphenylmercury. However, the information available does not indicate whether this mechanism is to be preferred to one involving electrophilic displacement at a carbon as postulated for reactions between Si–aryl bonds and mercuric acetate.[3]

EXPERIMENTAL

Reagents.—" Baker Analyzed " mercuric chloride was heated at 110° for 2 hr. in a stream of dry nitrogen. Triphenylsilanol (K. and K. Laboratories, Inc., recrystallized from 1 : 1 light petroleum–ether, had m. p. 152—153° (lit.,[4] 148—150°,[5] 150·5—151·1°). "Baker Analyzed " anhydrous diethyl ether and phenylmercuric chloride (Eastman Kodak) were used without further purification. An ~45% sodium dispersion in xylene was kindly given by the Ethyl Corporation, New York.

Phenyl(triphenylsiloxy)mercury.—Apparatus used was heated in an oven at 110° for ~15 hr. and was flushed with dry nitrogen while cooling. Sodium triphenylsilyl oxide was prepared most conveniently by the use of sodium dispersion. The xylene sodium dispersion, mixed with an approximately equal volume of ether, was added slowly to triphenylsilanol (17·0 g.) in ether (100 ml.) stirred in a dry nitrogen atmosphere. Consumption of all the silanol was signalled by cessation of evolution of hydrogen on addition of a drop of the dispersion. Approximately 0·1 g. of the silanol was then added to remove any slight excess of sodium.

A small deficit of mercuric chloride (7·7 g.) in ether (400 ml.) was added to the above solution which was stirred for 2—3 min. A very pale yellow precipitate was formed instantly. After rapid removal of all the ether from the reaction vessel by means of a high-vacuum mechanical pump (which caused the vessel to become very cold) it was placed in an oven at 110° for 35 min. The heating time required was determined in preliminary experiments by removing small quantities of the material from time to time, adding ether, filtering, and then adding water to the filtrate. When the conversion was complete a yellow precipitate of mercury oxide was no longer formed upon addition of water. 400 ml. of ether were added to the reaction vessel and the material was filtered, another 400 ml. of ether being used to wash the residue on the filter. The ether was removed from the filtrate by a mechanical pump and after reduction of the volume to 400 ml. the small precipitate which had been formed was removed by filtration. On evaporation of the filtrate to 200—250 ml., a heavy precipitate began to be formed. After 15 hr. it was removed by centrifugation and washed alternately with methanol and ether several times and then dried *in vacuo*. This was the pure *product* (5·3 g.), m. p. 140—141° (Found, for different preparations: C, 51·9, 52·4, 52·0; H, 3·5, 3·5; Hg, 36·5, 36·1, 35·9; Si, 5·3. $C_{24}H_{20}HgOSi$ requires C, 52·1; H, 3·6; Hg, 36·2; Si, 5·1%). The above quantity of product contained 34% of the mercury used.

The infrared spectrum of the compound was measured with a Perkin-Elmer Infracord spectrophotometer (model 137 B) employing a sodium chloride optical system. The material (2—3 mg.), in a 300 mg. potassium bromide disc, gave the following bands ($cm.^{-1}$) (relevant page nos. of Bellamy's book[6] in parentheses): 3100m and 3050m (C–H) stretch, 66), 2340vw, 1975w, 1900w, 1830w, 1775vw, 1660w, 1590w and 1487m (C=C stretch, 342), 1430s (Si–Ph, 338), 1383w, 1330vw, 1301w, 1265w, 1185m (Si–Ph, 342), 1155vw, 1114s (Si–Ph, 338), 1070w

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[4] Ladenburg, *Ber.*, 1907, **40**, 2274.

[5] Marsden and Kipping, *J.*, 1908, **93**, 198.

[6] Bellamy, " The Infrared Spectra of Complex Molecules," Methuen, London, 2nd edn., 1958.

(Si–O–Si, impurity, 340), 1030m and 1000m (Si–Ph, 342), 885vs (Si–O–Hg *), 736s and 702vs (out-of-plane C–H bend, 76, 338; 65, 77, 338), 675vw.

Further reduction of the volume of the ethereal solution to 100 ml. yielded a substance (0·4 g.), melting at 135—250°. On reduction of the volume to 25 ml., a very viscous solution was obtained which contained small crystals. Repeated efforts to obtain either pure crystals or pure viscous material from this mixture were unsuccessful. The infrared spectrum of this material (in $CHCl_3$) showed very strong absorption at 1070 (Si–O–Si stretch) 1113, and 1422 cm.$^{-1}$ (Si–Ph) which strongly suggested a phenylsilicone type of structure.

In many preliminary attempts to obtain pure solid $(Ph_3Si{\cdot}O)_2Hg$ the compound apparently commenced to decompose as soon as it was formed and in attempts to recrystallise it material obtained was always slightly sticky and gave slightly incorrect analyses. Ethereal solutions of this material were extremely sensitive to traces of water which caused the instantaneous precipitation of mercuric oxide.

Reaction of Phenyl(triphenylsiloxy)mercury with Hydrogen Chloride.—(*a*) A stream of dry gas was passed into a solution of the mercurial (0·8494 g.) in ether (75 ml.) for 4 min. The precipitated phenylmercuric chloride (0·4341 g., 90%) had m. p. 253—254° after recrystallization (lit.,[9] 251°,[10] 258°) (Found: C, 22·9; H, 1·5; Hg, 63·9. Calc. for C_6H_5ClHg: C, 23·0; H, 1·6; Hg, 64·1%).

(*b*) Hydrogen chloride was passed into a solution of the mercurial (0·8615 g.) in ether (60 ml.) and water (3 ml.). After removal of the precipitate by centrifugation, the liquid was evaporated and the solid obtained recrystallized from ether–light petroleum. This was triphenylsilanol (0·3794 g., 88%), m. p. 147—149° (lit.,[4] 148—150°,[5] 150·5—151·5°) (identity confirmed by infrared spectrum [11]) (Found: C, 78·0; H, 5·9; Si, 10·6. Calc. for $C_{18}H_{16}OSi$: C, 78·2; H, 5·85; Si, 10·2%).

Thermal Decomposition of Phenyl(triphenylsiloxy)mercury.—The mercurial (0·9597 g.) was heated in dry nitrogen at 145° for 75 min. Extraction of the viscous product with ether yielded crude diphenylmercury (0·3392 g.), m. p. 118—123° (lit.,[12] 121·8°) which contained 55% of the mercury used. Recrystallization yielded a sample of m. p. 121·5—122·5° (Found: C, 40·9, 41·0; H, 2·9, 2·95; Hg, 56·1. Calc. for $C_{12}H_{10}Hg$: C, 40·6; H, 2·85; Hg, 56·6%).

Triphenylsiloxymercury Chloride.—Attempts to isolate this product pure were unsuccessful since it apparently began to decompose spontaneously as soon as it was formed. Its complete decomposition was investigated as above: Triphenylsilanol (11·3 g.) and mercuric chloride (10·9 g.) were allowed to react and the products were heated at 110°. Extraction with ether (~1 l.) and chloroform (~1 l.) gave crude phenylmercuricchloride (7·63 g.; m. p. 253—258°) that crystallized from the organic solvents on partial evaporation. This material contained 61% of the mercury used. A large quantity of very viscous material was obtained after complete removal of the organic solvents. Recrystallization of the crude phenylmercuric chloride yielded pure material, m. p. 254—255° (infrared spectrum correct). No evidence for the formation of the compound $Ph_3SiO{\cdot}HgPh$ was obtained.

Triphenylsilanol and Mercuric Chloride.—Triphenylsilanol (17·0 g.) and mercuric chloride (7·7 g.) were dissolved in ether (500 ml.) which was then refluxed for 1 hr. while hydrogen was passed through it and into silver nitrate solution. No hydrogen chloride was evolved. Evaporation of the ether yielded only unchanged starting materials.

Reaction of Phenylmercuric Chloride with Potassium Triphenylsilyl Oxide.—Metallic potassium (1 g.), in the form of thin sheets, was added to triphenylsilanol (6·9 g.) dissolved in ether (200 ml.) and after the initial brisk reaction the mixture was refluxed greatly. When hydrogen evolution ceased the small particles of unchanged metal were removed mechanically and a suspension of phenylmercuric chloride (7·8 g.) in ether (150 ml.) was added to the potassium triphenylsilyl oxide solution. After 2 days' stirring the solution was filtered and evaporated

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* The values of the Si–O–Si, Si–O–Ti,[7] and Si–O–As [8] stretching frequencies suggest that the Si–O–Hg stretch should appear in this region.

[7] Zeitler and Brown, *J. Phys. Chem.*, 1957, **61**, 1174.

[8] Chamberland and MacDiarmid, *J. Amer. Chem. Soc.*, 1961, **83**, 549.

[9] Kharasch and Grafflin, *J. Amer. Chem. Soc.*, 1925, **47**, 1948.

[10] Nesmejanow, *Ber.*, 1929, **62**, 1010.

[11] Richards and Thompson, *J.*, 1949, 124.

[12] "Handbook of Chemistry and Physics," 40th edn., Chemical Rubber Co., 1958—1959, pp. 1088—1089.

and the resulting solid recrystallized from hot benzene. The second fraction of crystalline material removed was $Ph_3Si{\cdot}O{\cdot}HgPh$, m. p. 137—139°, with an infrared spectrum similar to compound obtained above (Found: C, 52·4; H, 3·4; Hg, 36·0; Si, 5·3. Calc. for $C_{24}H_{20}HgOSi$: C, 52·1; H, 3·64; Hg, 36·2; Si, 5·1%). Further crystallization yielded a small amount of triphenylsilanol and a solid material believed to be the addition compound $Ph_3Si{\cdot}O{\cdot}HgPh{\cdot}Ph_3Si{\cdot}OH$, m. p. 114—117° (Found: Si, 6·65, 6·7. Calc. for $C_{42}H_{36}HgO_2Si_2$: Si, 6·8%). The infrared spectrum of this material indicated conclusively that it was not a physical mixture of $Ph_3Si{\cdot}O{\cdot}HgPh$ and $Ph_3Si{\cdot}OH$.

Analyses were done by Galbraith Laboratories, Knoxville, Tennessee.

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