Organosilicon Compounds. Part XLIX.[1] Some Reactions of Bis(triphenylsilyl)mercury

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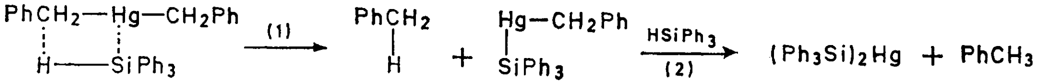
Bis(triphenylsilyl)mercury, prepared by the reaction of dibenzylmercury with triphenylsilane, decomposes on heating to give mercury and hexaphenyldisilane, along with traces of triphenylsilane, tetraphenylsilane, pentaphenyldisilane, and octaphenyltrisilane. Photolysis or pyrolysis in benzene gives the above products, with larger quantities of tetraphenylsilane; the reaction in toluene at 81 and at 220° gives additionally the tolyltriphenylsilanes (at the low temperature only), benzyltriphenylsilane (more at the higher temperature), and bibenzyl. Though the solid mercury compound is fairly stable to air and water, solutions in inert solvents react rapidly with air (to give mercury and hexaphenyldisiloxane) and with water (to give mercury, triphenylsilanol, and hydrogen as the major products). Radical and molecular reactions are proposed. The thermal decomposition of bis(triphenylsilyl)mercury appears to involve homolytic fission, in contrast to that of bis(trimethylsilyl)mercury, for which molecular reactions appear to be important.

BIS(TRIALKYL-SILYL and -GERMYL)MERCURY compounds may be photolysed to give the corresponding silyl or germyl radicals,[2,3,4] but most of the thermal reactions of these mercurials appear to be molecular in mechanism.[5,6] Reactions of bis(triphenylsilyl)mercury are of interest in this context, since there is considerably more steric hindrance at the Si and Hg atoms than in bis(trimethylsilyl)mercury, which should impede multicentre molecular reactions, and thereby make possible the observation of homolytic fission of the silicon–mercury bonds at high temperatures. Additionally, there is the possibility that triphenylsilyl radicals may be somewhat stabilized, relative to trimethylsilyl radicals, by delocalization of the unpaired electrons and this would make homolysis energetically more favourable.



$$\begin{matrix} PhCH_2\text{—}Hg\text{—}CH_2Ph \\ \vdots \qquad \vdots \\ H\text{———}SiPh_3 \end{matrix} \xrightarrow{(1)} \begin{matrix} PhCH_2 \\ | \\ H \end{matrix} + \begin{matrix} Hg\text{—}CH_2Ph \\ | \\ SiPh_3 \end{matrix} \xrightarrow[(2)]{HSiPh_3} (Ph_3Si)_2Hg + PhCH_3$$

RESULTS AND DISCUSSION

As already reported in outline,[7] bis(triphenylsilyl)mercury may be conveniently prepared by the reaction of dibenzylmercury with triphenylsilane at 125—130°l Diphenylmercury (this work) and diethylmercury (ref. 8) react similarly with triphenylsilane but require higher temperatures and give poorer yields of products.

Dibenzylmercury homolyses slowly in solution at 120—130°,[9] but since the reaction with triphenylsilane is faster than this, a molecular reaction is indicated [reactions (1) and (2)]. However, radical chain mechanisms, involving induced decomposition of the mercury compound, while unlikely, cannot be ruled out.

On the assumption that bond dissociation energies are similar for Ph_3Si and Me_3Si compounds, recent thermochemical estimates indicate that the above reactions (1) and (2) should be exothermic by about 20—30 kcal mol^{-1} overall;[10] alternatively the occurrence and nonreversibility of this reaction supports relatively high strengths for the silicon–mercury bonds in bis(triphenylsilyl)mercury.

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[1] Part XLVIII, M. A. Cook, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1971, **29**, 389.

[2] C. Eaborn, R. A. Jackson, and R. Pearce, *Chem. Comm.*, 1967, 920.

[3] S. W. Bennett, C. Eaborn, R. A. Jackson, and R. Pearce, *J. Organometallic Chem.*, 1968, **15**, P17.

[4] S. W. Bennett, C. Eaborn, R. A. Jackson, and R. Pearce, *J. Organometallic Chem.*, 1971, **28**, 59.

[5] C. Eaborn, R. A. Jackson, and R. W. Walsingham, *J. Chem. Soc.* (*C*), 1967, 2188.

[6] R. Fields, R. N. Haszeldine, and R. E. Hutton, *J. Chem. Soc.* (*C*), 1967, 2559.

[7] R. A. Jackson, *Chem. Comm.*, 1966, 827.

[8] N. S. Vyazankin, O. A. Kruglaya, G. S. Kalinina, and E. N. Gladyshev, *J. Gen. Chem.* (*U.S.S.R.*), 1968, **38**, 1544.

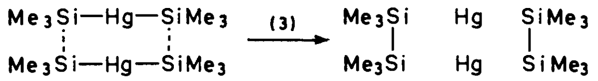
[9] R. A. Jackson and D. W. O'Neill, *Chem. Comm.*, 1969, 1210; K. C. Bass and G. M. Taylor, *J. Chem. Soc.* (*B*), 1970, 1615.

[10] R. A. Jackson, *Chem. Soc. Special Publ.*, 1970, **24**, 295; C. Eaborn, R. A. Jackson, and R. W. Walsingham, unpublished results, quoted by A. G. Beaumont, C. Eaborn, and R. A. Jackson, *J. Chem. Soc.* (*B*), 1970, 1624.

The lower temperature required for reaction of triphenylsilane with dibenzylmercury rather than with diethylmercury or diphenylmercury is interesting. Steric hindrance to approach of the reacting molecules cannot be of over-riding importance, otherwise diethylmercury would be the most reactive. However, treatment of the reaction as a ' forbidden ' molecular reaction by the method of ref. 11 indicates that the reaction with dibenzylmercury should be favoured because the benzyl radical possesses low-lying unfilled orbitals whose effect should be to lower the energy of the transition state for the molecular reaction.

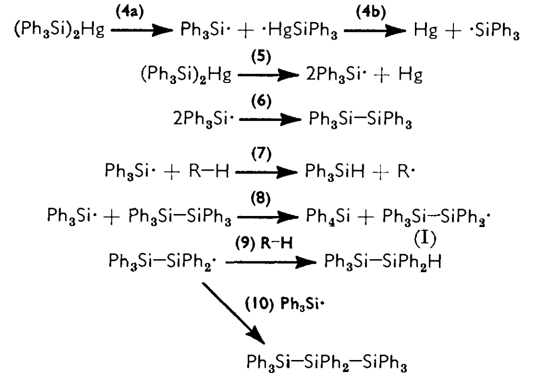
Bis(triphenylsilyl)mercury was also prepared satisfactorily by the reaction of triphenylsilyl-lithium with mercury, but attempts to make the mercury compound from triphenylbromosilane by the sodium amalgam method [5,12] gave a mixture of bis(triphenylsilyl)mercury and hexaphenyldisilane which could not easily be separated.

Decomposition.—Bis(triphenylsilyl)mercury decomposes slowly at its melting point, but rapidly at 250°. At 300° the decomposition (judged visually) is complete within a minute. Pyrolysis at 220 or 260° for 7 days gives an almost quantitative yield of mercury, along with over 90% of hexaphenyldisilane, and traces of triphenylsilane, tetraphenylsilane, pentaphenyldisilane, and octaphenyltrisilane. Decomposition in saturated hydrocarbons such as cyclohexane is slower, but produces similar products, with no appreciable attack on the solvent. At 219·5°, a solution of bis(triphenylsilyl)-mercury in cyclohexane decomposed with approximately first-order kinetics, and a rate constant of $4{\cdot}1 \times 10^{-6}\ \mathrm{s^{-1}}$. The rate of decomposition is much slower than for similar concentrations of bis(trimethylsilyl)mercury (which gives second-order kinetics [13]). We believe that, in contrast with bis(trimethylsilyl)mercury, bis(triphenylsilyl)mercury decomposes homolytically on heating, in either one or two stages, to produce triphenylsilyl radicals. The difference in behaviour is probably due to the greater size of the $\mathrm{Ph_3Si}$ than of the $\mathrm{Me_3Si}$ group, which would make reactions analogous to (3) difficult for $(\mathrm{Ph_3Si})_2\mathrm{Hg}$.



$$\begin{matrix}\mathrm{Me_3Si{-}Hg{-}SiMe_3} \\ \mathrm{Me_3Si{-}Hg{-}SiMe_3}\end{matrix} \xrightarrow{(3)} \begin{matrix}\mathrm{Me_3Si} & \mathrm{Hg} & \mathrm{SiMe_3} \\ | & & | \\ \mathrm{Me_3Si} & \mathrm{Hg} & \mathrm{SiMe_3}\end{matrix}$$

An Arrhenius study was not made, but if A ($\mathrm{s^{-1}}$) lies between 10^{15} and 10^{18} as is usual for homolytic dissociations, an activation energy in the region of 46—53 kcal $\mathrm{mol^{-1}}$ is indicated. This activation energy may be equated with the energy required to dissociate one (reaction 4a) or both (reaction 5) of the Hg–Si bonds; the high value indicated suggests that there is little stabilization of the triphenylsilyl radicals by the phenyl groups (contrast the triphenylmethyl radical).



$$(\mathrm{Ph_3Si})_2\mathrm{Hg} \xrightarrow{(4a)} \mathrm{Ph_3Si\cdot} + \cdot\mathrm{HgSiPh_3} \xrightarrow{(4b)} \mathrm{Hg} + \cdot\mathrm{SiPh_3}$$

$$(\mathrm{Ph_3Si})_2\mathrm{Hg} \xrightarrow{(5)} 2\mathrm{Ph_3Si\cdot} + \mathrm{Hg}$$

$$2\mathrm{Ph_3Si\cdot} \xrightarrow{(6)} \mathrm{Ph_3Si{-}SiPh_3}$$

$$\mathrm{Ph_3Si\cdot} + \mathrm{R{-}H} \xrightarrow{(7)} \mathrm{Ph_3SiH} + \mathrm{R\cdot}$$

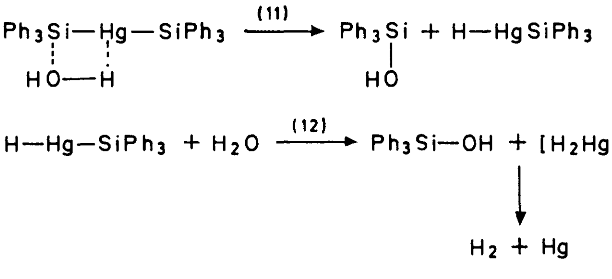
$$\mathrm{Ph_3Si\cdot} + \mathrm{Ph_3Si{-}SiPh_3} \xrightarrow{(8)} \mathrm{Ph_4Si} + \underset{(\mathrm{I})}{\mathrm{Ph_3Si{-}SiPh_2\cdot}}$$

$$\mathrm{Ph_3Si{-}SiPh_2\cdot} \xrightarrow{(9)\ \mathrm{R{-}H}} \mathrm{Ph_3Si{-}SiPh_2H}$$

$$\mathrm{Ph_3Si{-}SiPh_2\cdot} \xrightarrow{(10)\ \mathrm{Ph_3Si\cdot}} \mathrm{Ph_3Si{-}SiPh_2{-}SiPh_3}$$

Triphenylsilane may be expected from hydrogen abstraction by the $\mathrm{Ph_3Si\cdot}$ radicals, especially from solvent molecules (7). The tetraphenylsilane probably arises from reaction (8) in which a triphenylsilyl radical attacks hexaphenyldisilane at the C–Si bond, displacing the pentaphenyldisilyl radical (I), a type of reaction which is known to occur in other silicon systems,[14] followed by reaction of pentaphenyldisilyl radicals by reactions (9) and (10) to produce pentaphenyldisilane and octaphenyltrisilane respectively.

Reactions with Air and Water.—Crystals of bis(triphenylsilyl)mercury are moderately stable to air [contrast $(\mathrm{Me_3Si})_2\mathrm{Hg}$]. However, solutions of bis(triphenylsilyl)-mercury in inert solvents react rapidly with oxygen or air, to give hexaphenyldisiloxane and mercury in almost quantitative yield. Reaction of solid $(\mathrm{Ph_3Si})_2\mathrm{Hg}$ with water is likewise very slow, but in solution in benzene saturated with water it decomposes rapidly to give mercury (quantitative), triphenylsilanol, and hydrogen as major products, along with lesser amounts of triphenylsilane, hexaphenyldisiloxane, and hexaphenyldisilane. Molecular reactions (11) and (12) are likely to be responsible for the formation of the major products; other reactions of the postulated $\mathrm{HHgSiPh_3}$ intermediate may be responsible for the production of triphenylsilane and hexaphenyldisilane.



$$\begin{matrix}\mathrm{Ph_3Si{-}Hg{-}SiPh_3} \\ \mathrm{HO{-}H}\end{matrix} \xrightarrow{(11)} \begin{matrix}\mathrm{Ph_3Si} \\ | \\ \mathrm{HO}\end{matrix} + \mathrm{H{-}HgSiPh_3}$$

$$\mathrm{H{-}Hg{-}SiPh_3} + \mathrm{H_2O} \xrightarrow{(12)} \mathrm{Ph_3Si{-}OH} + [\mathrm{H_2Hg}] \longrightarrow \mathrm{H_2} + \mathrm{Hg}$$

Reactions with Aromatic Hydrocarbons.—The products of the reaction of bis(triphenylsilyl)mercury with benzene and with toluene under both thermal and photolytic conditions are shown in the Table. It will be seen that similar products are formed under the two sets of conditions, which provides further support for the thermal homolysis of bis(triphenylsilyl)mercury. The low pro

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[11] R. A. Jackson, *J. Chem. Soc.*, (*B*) 1970, 58.

[12] E. Wiberg, O. Stecher, H. J. Andrascheck, L. Kreuzbichler, and E. Staude, *Angew. Chem. Internat. Edn.*, 1963, **2**, 507.

[13] C. Eaborn, R. A. Jackson, and R. W. Walsingham, unpublished work.

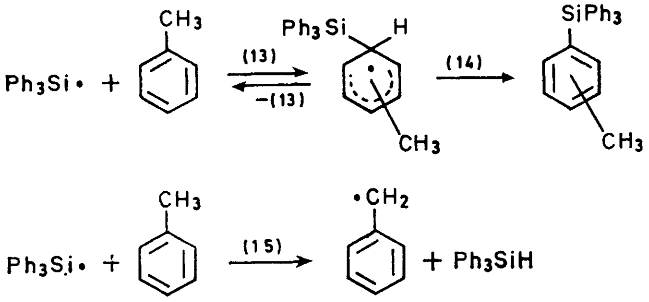
[14] L. E. Nelson, N. C. Angelotti, and D. R. Weyenberg, *J. Amer. Chem. Soc.*, 1963, **85**, 2662.

portion of *ortho* isomer in the tolyltriphenylsilanes produced by attack of the triphenylsilyl radical on toluene is probably attributable to the large size of the triphenylsilyl radical. The decrease in aromatic substitution products and increase in benzyl products with increasing temperature has been noted before with trimethylsilyl radicals.[4] The aromatic substitution reaction (13), though exothermic and presumably having a moderate activation energy, proceeds with loss of entropy. At high temperatures, this will make the reverse reaction more favourable, and no aromatic substitution is in fact observed at 220°. Attack of triphenylsilyl radicals at the methyl group in toluene (reaction 15) is possibly slightly endothermic, but there is no loss of entropy in this reaction which will therefore be more favoured at higher temperatures.

Reactions of bis(triphenylsilyl)mercury with benzene and toluene

	Benzene †			Toluene ‡		
Thermal/ photolytic	*hν* *	*hν* *	Δ	*hν*	*hν*	Δ
Temp. (°C)	40	81	220	81	220	220
Time	9 h	6 h	3 wks.	6 h	¾ h	3 wks.
Products (%)						
Hg	100	96·5	96	99·3	100	99
Ph_3SiH	12·8	11·3	7·8	10·4	19·8	22·5
Ph_4Si	16·4	11·8	5·8	1·0	1·9	4·0
Ph_6Si_2	41·6	38·3	81·9	46·4	66·1	61·0
Ph_8Si_3	Trace	Trace	Trace	Trace	Trace	Trace
o-$MeC_6H_4SiPh_3$				1·4	0	0
m-$MeC_6H_4SiPh_3$				5·2	0	0
p-$MeC_6H_4SiPh_3$				2·2	0	0
$(PhCH_2)_2$				Trace	19·7	15·2
$PhCH_2SiPh_3$				0·4	3·6	3·5

* Traces of at least 15 other high boiling products were detected in these reactions; these products were not looked for in the corresponding pyrolysis. † Biphenyl, diphenylsilane, and pentaphenyldisilane were not produced in detectable amounts in these reactions. ‡ Pentaphenyldisilane was not produced in detectable amounts in these reactions.



The production of tetraphenylsilane in the toluene reactions implies a reaction of triphenylsilyl radicals with hexaphenyldisilane. In the benzene reaction, part of the tetraphenylsilane no doubt arises in this manner, and part by the aromatic substitution reaction. The decrease, but not disappearance, of tetraphenylsilane with increasing temperature supports this interpretation.

EXPERIMENTAL

Bis(triphenylsilyl)mercury.—A mixture of dibenzylmercury (2·0 g, 5·2 mmol) and triphenylsilane (5·34 g, 20·5 mmol) in a 100 ml flask was degassed by freezing and melting *in vacuo*, and was heated (in the dark) in a silicone oil bath at 125—130° for 6 h. The reaction mixture was set aside for 3 days, when lemon yellow crystals of bis(triphenylsilyl)mercury separated. Precipitation was completed by distilling in dry and degassed cyclohexane (15 ml). The solid product was filtered off under dry nitrogen in a Schlenk tube, washed with further dry and degassed cyclohexane, and transferred into a vacuum sublimator in a glove box. Volatile materials (cyclohexane, toluene) were pumped off, after which the cold finger of the sublimator was filled with acetone–solid CO_2, and the sublimator was heated at 140—150° at 10^{-3} mmHg, when mercury, bibenzyl, and unchanged triphenylsilane sublimed off, leaving pure bis(triphenylsilyl)mercury as a residue, m.p. 210—212° (35—45%) (Found: C, 60·45; H, 4·25; Hg, 28·2. Calc. for $C_{36}H_{30}HgSi_2$; C, 60·1; H, 4·2; Hg 27·9%). The u.v. spectrum showed, in addition to aromatic absorption between 240 and 280 nm, weaker bands at 345 and 388 nm. The mass spectrum (130°, 15 eV) showed a group of peaks, in a pattern characteristic of one mercury and two silicon atoms, centred around *m/e* 718, due to the parent ion.

Solid $(Ph_3Si)_2Hg$ is quite stable in air, and the yellow solid becomes greyish only after several weeks exposure. However, when dry oxygen was bubbled through a toluene solution of the mercury compound, the mixture became warm, and mercury was quantitatively precipitated. Hexaphenyldisiloxane was the major product (90—95%), along with traces of hexaphenyldisilane, triphenylsilane, tetraphenylsilane, and triphenylsilanol.

When diphenylmercury was used instead of dibenzylmercury in the above preparation, the reaction proceeded slowly at 160° and the yield of bis(triphenylsilyl)mercury was poor even after 12 h. Attempts to make bis(triphenylsilyl)mercury from triphenylbromosilane by the action of sodium amalgam (*cf.* refs. 5 and 12) gave a mixture of the mercury compound and hexaphenyldisilane which could not readily be separated, either by crystallization or by sublimation. Triphenylsilyl-lithium [15] in dry THF however reacted with an excess of mercury on stirring under nitrogen for 2 days to give a yellow suspension of bis(triphenylsilyl)mercury, which was transferred to a vacuum sublimator and purified as above. Maximum yields of *ca.* 60% were obtained.

Reaction Mixtures.—These were made up in a glove-box filled with purified dry nitrogen. To bis(triphenylsilyl)-mercury (*ca.* 0·05 g) in a Pyrex ampoule was added the appropriate solvent (*ca.* 1 ml) which had previously been fractionally distilled from $LiAlH_4$ and degassed. The ampoules were degassed further, and sealed. Pyrolyses were carried out in a silicone oil bath, the temperature of which could be maintained within ±2°; for photolyses, the ampoule was placed 25 cm from a medium pressure Engelhard Hanovia UVS 500/A mercury lamp. For photolyses above ambient temperature, the ampoule was suspended in the vapour of a refluxing solvent.

Analysis.—Mercury was estimated either as the element by weighing, or complexometrically.[16] Hexaphenyldisilane was almost insoluble in the solvent used. It was estimated

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[15] H. Gilman and G. D. Lichtenwalter, *J. Amer. Chem. Soc.*, 1958, **80**, 608.

[16] G. Schwarzenbach, 'Complexometric Titrations,' Methuen, London, 1957, pp. 87—88.

by weighing, and an allowance was made for its known solubility in the solvent used for the reaction. This gave results reproducible within ±7%. Other products were estimated gas chromatographically to within ±3%. Octaphenyltrisilane and other high boiling products were identified and estimated using a 23 cm column packed with 5% silicone gum rubber on silanized Chromosorb G at 270°. For lower-boiling materials a 2·13 m column containing the same packing was used. Octane, dodecane, and octacosane were used as internal standards. Benzyltriphenylsilane and *o*-tolyltriphenylsilane, and *m*- and *p*-tolyltriphenylsilanes were not separable on the standard column. The *m*- and *p*-tolyltriphenylsilanes were separated on a 15-m Perkin-Elmer, Support Coated Open Tubular column at 230°, but since no conditions could be found for gas-chromatographic separation of benzyl- and *o*-tolyl-triphenylsilanes their combined yield was estimated (using octacosane as the internal standard), and the reaction mixture was then refluxed with a 5M-KOH in 4 : 1 ethanol–water for 2 days, which selectively cleaved the carbon–silicon bond in benzyltriphenylsilane, leaving the tolyltriphenylsilanes unaffected. Benzyltriphenylsilane was thus estimated by difference.

Decomposition of Bis(triphenylsilyl)mercury.—Samples of bis(triphenylsilyl)mercury were pyrolysed for 7 days at 220 and at 260°, giving (low temperature yields first) mercury (97, 96%), hexaphenyldisilane (95·8, 90·4%), tetraphenylsilane (0·02, 0·05%), triphenylsilane (0·01, 0·25%), pentaphenyldisilane (0·01, 0·01%), along with traces of octaphenyltrisilane and higher boiling products. Pyrolysis at 300° for 1 h gave the same products, but the yield of hexaphenyldisilane had dropped to 80%. Photolysis of the solid at ambient temperature either by daylight or by u.v. light proceeded only slowly and was incomplete after several months.

Pyrolysis of solutions of bis(triphenylsilyl)mercury in cyclohexane at 220° was complete in 3 weeks, and photolysis by u.v. light at 81° within 6 h. Yields of products (pyrolysis first, photolysis second), were hexaphenyldisilane (75·6, 70·4%), tetraphenylsilane (4·1, 3·2%), triphenylsilane (4·9, 5·6%), pentaphenyldisilane (0, 0), octaphenyltrisilane (trace, trace), cyclohexyltriphenylsilane (possibly a trace in both cases, but not positively identified), bicyclohexyl (0, 0), and mercury (96, 98%).

Pyrolysis of bis(triphenylsilyl)mercury in decane at 220° was complete within 3 weeks, giving hexaphenyldisilane (85·3%), triphenylsilane (2·6%), tetraphenylsilane (3·6%), and mercury (97%). Small peaks possibly attributable to triphenylsilyldecanes and decyl dimers were observed. Pentaphenyldisilane was absent, octaphenyltrisilane was not looked for.

Pyrolysis of bis(triphenylsilyl)mercury in triphenylsilane at 250° was complete within 3 days, giving tetraphenylsilane as the major organic product, along with hexaphenyldisilane and diphenylsilane, and a trace of pentaphenyldisilane. A compound with a retention time less than Ph_2SiH_2, which was probably $PhSiH_3$, was detected. When the ampoule was opened with a red hot glass rod, ignition took place, probably due to SiH_4. Octaphenyltrisilane was absent. Mercury was recovered quantitatively.

Blanks.—Various experiments were performed to ascertain the stability of some of the reaction products under our reaction conditions. A 5% solution of triphenylsilane in benzene was recovered unchanged after pyrolysis at 220° for 3 weeks. No traces of other materials were detected. A 5% solution of hexaphenyldisilane in benzene was also unaffected by this treatment. Neat triphenylsilane, after 3 days at 250°, gave tetraphenylsilane (*ca.* 10%) along with traces of phenylsilane and diphenylsilane (hexaphenyldisilane was not looked for).

Kinetics.—The rate of decomposition of solutions of $(Ph_3Si)_2Hg$ (*ca.* 0·01M) in cyclohexane was followed at 388 nm with a Unicam SP 500 spectrometer. The reaction mixtures, in Pyrex ampoules, were degassed, sealed, and heated in a thermostatted aluminium block. At intervals, the ampoules were removed, centrifuged to precipitate mercury, the optical density was measured, and the ampoules were returned to the thermostat. The ampoules were always placed in the cell holder in the same orientation. This technique will be discussed in more detail elsewhere.[13]

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