E. N. Gladyshev, L. O. Yuntila, G. A. Razuvaev, N. S. Vyazankin, and V. S. Sokolov

The properties of the silylmercury compounds,  $(R_3Si)_2Hg$ , are strongly dependent on the nature of the R radicals. Thus, in contrast to bis(trimethylsilyl)mercury, the thermolysis of which in cyclohexane is described by the kinetic equation of a second order reaction [1], the decomposition of bis(triphenylsilyl)mercury is a first order reaction, with the formation of  $(C_6H_5)_3Si$  radicals [2]. In view of this, it seemed interesting to study the properties of bis(phenyldimethylsilyl)mercury (I). This compound was obtained by the hydride method [3, 4], by the reaction of phenyldimethylsilane with di-tert-butylmercury in the absence of atmospheric oxygen and solvents, and using a 2:1 ratio of the reactants. At 100-105°C

$$2C_{6}H_{5}(CH_{3})_{2}SiH + (t-C_{4}H_{9})_{2}Hg \rightarrow [C_{6}H_{5}(CH_{3})_{2}Si]_{2}Hg + 2i-C_{4}H_{10}$$
(1)

the reaction is completed in 12-14 h. Replacement of the di-tert-butylmercury by other mercury derivatives [5], for example, either diethylmercury or  $\{[(CH_3)_3Si]_2N\}_2Hg$ , fails to give (I) even under more drastic conditions (150-160°, 70 h).

Compound (I) is a pale yellow-green crystalline substance that is readily soluble in the common organic solvents. Its solutions in hexane react exothermally with  $O_2$  to give mercury (92% yield) and 1, 1, 3, 3-tetram.ethyl-1, 3-diphenylsiloxane (86% yield). The principal photolysis products of (I) in benzene are mercury, 1, 1, 2, 2-tetramethyl-1, 2-diphenyldisilane, and phenyldimethylsilane (Table 1). Apparently, photolysis leads to homolytic cleavage of the Si-Hg bonds and the generation of  $C_6H_5(CH_3)_2Si$  radicals, which dimerize to disilane (II). A similar mechanism was postulated previously [6] for the photolysis of the optically active bis[methyl-(1-naphthyl)-phenylsilyl]mercury. Since the yield of  $(C_6H_5)_2Si(CH_3)_2$  is higher that that of phenyldimethylsilane (see Table 1), it must be assumed that the reaction of the  $C_6H_5$ - $(CH_3)_2Si$  radicals with benzene (which proceeds by the mechanism of homolytic hydrogen replacement in the aromatic ring) accompanies the reaction of the same radicals with disilane (II) according to equation (3). Analogous processes are realized during the photolysis of bis(triphenylsilyl)mercury in benzene so-

$$C_{6}H_{5} (CH_{8})_{2} \operatorname{Si} + C_{6}H_{6} \rightarrow C_{6}H_{5} (CH_{3})_{2} \operatorname{Si} \underbrace{\bullet}_{H} \underbrace{\bullet}_{H$$

 $\begin{array}{r} + C_{6}H_{5} (CH_{3})_{2} \operatorname{SiH} \\ C_{6}H_{5} (CH_{2})_{2} \operatorname{Si}^{*} + [C_{6}H_{5} (CH_{3})_{2} \operatorname{Si}]_{2} \rightarrow (C_{6}H_{5})_{2} \operatorname{Si} (CH_{3})_{2} + \\ + C_{6}H_{5} (CH_{3})_{2} \operatorname{SiSi} (CH_{3})_{2} \end{array}$ 

(3)

lution [2] and take place in other organosilicon system [7].

Together with mercury, disilane (II) was obtained in high yield during the photochemical decomposition of (I) in cyclohexane. In addition, traces of diphenyldimethylsilane, 1,3-diphenyl-1,1,2,2,3,3-hexamethyltrisilane (III), and phenyldimethylsilane (see Table 1) [due to the progress of side reactions (3), (4), and (5)] were identified by GLC, and also a number of other products of unestablished structure.

 $C_{6}H_{5}(CH_{3})_{2}Si^{*} + C_{6}H_{5}(CH_{3})_{2}Si\dot{S}i(CH_{3})_{2} \rightarrow C_{6}H_{5}[(CH_{3})_{2}Si]_{2}C_{6}H_{5}$   $C_{6}H_{5}(CH_{3})_{2}Si^{*} + cyclo-C_{6}H_{12} \rightarrow C_{6}H_{5}(CH_{3})_{2}SiH + cyclo-C_{6}H_{11}$  (4)

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(I), mmoles	Reaction conditions			Reaction products, mmoles (%)					
	solvent, ml	Т <b>.</b> , °С	Time h	Hg	Ph2SiMe2	Ph Me <sub>2</sub> SiH	PhMe∘Si ∙SiMe₂Ph	Ph(SiMe₂)₃Ph	
1,00	Benzene,10	40	4	1,00 (~100)	0,91(46)	0,27(14)	0,23(23)		
1,03	Benzene, <u>10</u>	80	2	1,03 (~100)	0,70(34)	0,39(19)	0,45(44)	<u> </u>	
1,64	Cyclohexane, 10	40	1	1,64 (~100)	0,06(2)	0,07(2)	0,84(51)	0,03(2)	
1,60	Cyclohexane, 10	80	0,5	1,50(94)	0,09(3)	0,03(1)	1,07(67)	0,04(3)	

TABLE 1. Photodecomposition of Bis(phenyldimethylsilyl)mercury (I)

TABLE 2. Reactions of Bis(phenyldimethylsilyl)mercury (I)

Starting reactants, mmoles		Reaction	condi	tions		Yield,
		Toluene solvent, ml	т., ℃	Time, h	Reaction products	mmoles (%)
(I) CH3CO2H	4,46 4,83	12	60	4	Hg C6H5(CH3)2SiH * C6H5(CH3)2SiOCOCH3 †	4,29 (96) 3,29 (74) 4,17 (94)
(I) (C6H5CO2)2	$3,84 \\ 3,84$	7	60	20 min	Hg C6H5(CH3)2SiOCOC6H5 ‡	$3,64 (95) \\ 6,67 (87)$
(I) 1,2-Br <sub>2</sub> C <sub>2</sub> H <sub>4</sub>	6,75 10,75	10	20	120	Hg C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>2</sub> SiBr * CH <sub>2</sub> ==CH <sub>2</sub> *	6,68 (99) 12,50 (93) 5,49 (81)
(I) HgCl <sub>2</sub>	$3,82 \\ 3,90$	10	40	24	Hg C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>2</sub> SiCl	7,28 (95) 6,21 (81)

\*Identified by GLC.

<sup>†</sup> mp 94-96° (7 mm);  $n_D^{20}$  1.4921; cf. [12]. <sup>‡</sup> mp 130-131° (1 mm);  $n_D^{20}$  1.5475; Found: C 70.33; H 6.22; Si 10.24%. C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>Si. Calculated: C 70.27; H 6.29; Si 10.95%.

The photoreaction of (I) with excess triethylgermane leads in high yields to mercury, phenyldimethylsilane, and hexaethyldigermane. The reaction mixture does not contain disilane (II) and C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>2</sub>SiGe(C<sub>2</sub>- $H_5$ )<sub>3</sub>, which is not in agreement with the concept regarding the intermediate formation of the  $C_6H_5(CH_3)_2Si$ free radicals in the given system. It is most probable that the  $C_{g}H_{5}(CH_{3})_{2}Si$  fragments in the (I) molecules are replaced by triethylgermyl radicals in the first step, with subsequent decomposition of the formed bis-(triethylgermyl)mercury.

$$[C_{6}H_{5} (CH_{3})_{2} Si]_{2} Hg + 2 (C_{2}H_{5})_{3} GeH \xrightarrow{a} 2C_{6}H_{5} (CH_{3})_{2} SiH + [(C_{2}H_{5})_{3} Ge]_{2} Hg$$

$$b \downarrow h_{\nu} \\ Hg + (C_{2}H_{5})_{6} Ge_{2}$$
(6)

Reactions, similar to (6a), are common for many types of organobimetallic compounds [8-10]. Reaction (6b) proceeds with the quantitative formation of mercury and hexaethyldigermane, which permits its use as an analytical reaction [3].

The thermal decomposition of (I) in cyclohexane (200°, 6 h) leads chiefly to disilane (II) (84% yield). From this it follows that the possibility of the C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)<sub>2</sub>Si radicals taking part in side reactions is minimum under the adopted conditions.

Finally, we studied the typical reactions of compound (I) with CH<sub>3</sub>COOH, benzoyl peroxide, 1,2dibromoethane, and HgCl<sub>2</sub>, which, in contrast to the above-discussed reactions, proceed by the molecular mechanism with a heterolysis of the Si-Hg bonds [6,11]. The reaction conditions, and the composition of the products and their yields, are summarized in Table 2.

## EXPERIMENTAL METHOD

All of the photoreactions were run in evacuated sealed Pyrex glass ampuls. A PRK-2 lamp served as the light source, and the distance from the lamp was 10 cm. The reaction products were analyzed by GLC on a Tswett-4 chromatograph, equipped with a detector based on the heat conductivity. Helium was the carrier gas. The  $300 \times 0.4$  cm glass column was packed with 5% Silicone SE - 30 deposited on Chromatone N-AW-DMCS.

<u>Bis(phenyldimethylsily)mercury (I)</u>. A mixture of 3.30 g of di-tert-butylmercury and 5.20 g of phenyldimethylsilane was heated at 100-105° for 12-14 h. Here 300 ml (64%) of isobutane was liberated. The excess silane was removed in vacuo, and 10 ml of hexane was added to the residue. On cooling to 0° we obtained 2.20 g (45% yield) of crystalline (I), mp 88-89.5°. Found: Hg 43.00%.  $C_{16}H_{22}HgSi_2$ . Calculated: Hg 42.58%.

Oxidation of (I). Oxygen was passed through a solution of 1.35 g of (I) in 10 ml of hexane. Exothermic reaction ceased after 15-20 min. The amount of separated Hg was 0.53 g (92%), the solvent was removed by fractional distillation. From the residue we isolated 0.71 g (86%) of 1,1,3,3-tetramethyl-1,3diphenylsil.oxane, bp 151-153° (13 mm);  $n_D^{20}$  1.5190, which is in agreement with [12].

<u>Photoreaction of (I) with Triethylgermane</u>. A mixture of 1.42 g of (I) and 7.06 g of triethylgermane was exposed to UV light for 6 h at 8-10°. Here 0.64 g (~ 100%) of Hg was formed. The excess triethyl-germane was removed by fractional distillation. Employing GLC, the residue contained 0.58 g (71%) of phenyldimethylsilane and 0.94 g (97%) of hexaethyldigermane.

Thermal Decomposition of (I) in Cyclohexane. A solution of 0.77 g of (I) in 10 ml of cyclohexane was heated in a sealed ampul for 6 h at 200°. Here 0.32 g (98%) of Hg separated. The excess solvent was removed in vacuo. Employing GLC, we identified 0.37 g (84%) of 1,1,2,2-tetramethyl-1,2-diphenyldisilane in the residue, and also traces of diphenyldimethylsilane, phenyldimethylsilane, and trisilane (III).

## CONCLUSIONS

1.  $\operatorname{His}(\operatorname{phenyldimethylsilyl})$  mercury was synthesized, the reactions of which with molecular oxygen, benzoyl peroxide, 1,2-dibromoethane,  $\operatorname{HgCl}_2$ , and acetic acid proceed with cleavage of the Si-Hg-Si fragment.

2. A study was made of the photodecomposition reactions of bis(phenyldimethylsilyl)mercury in either benzene or cyclohexane medium at 40 and  $80^{\circ}$ , and also its thermal decomposition in cyclohexane at  $200^{\circ}$ .

3. The photoreaction of bis(phenyldimethylsilyl)mercury in triethylgermane solution gives mercury, phenyldimethylsilane, and hexaethyldigermane.

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