PHOTOLYTIC REACTIONS OF BIS(TRIMETHYLSILYL)MERCURY AND BIS(TRIMETHYLGERMYL)MERCURY WITH BENZENE, TOLUENE, AND ANISOLE. FREE-RADICAL AROMATIC SILYLATION AND GERMYLATION

S. W. BENNETT, C. EABORN, R. A. JACKSON AND R. PEARCE

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

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SUMMARY

Trimethylsilyl radicals produced by photolysis of bis(trimethylsilyl)mercury react with benzene or toluene to give the normal products of homolytic aromatic substitution. Thus the reaction with benzene gives, in addition to hexamethyldisilane, phenyltrimethylsilane and 2,5-cyclohexadienyltrimethylsilane, along with higher boiling products. With toluene the relative amounts of *o-*, *m-*, and *p-*tolyltrimethylsilanes are roughly in the statistically determined 2/2/1 ratio. The yield of hexamethyldisilane rises, and that of the aromatic substitution products falls when photolysis is carried out at higher temperatures.

The reaction of trimethylsilyl radicals with benzene appears to be in competition with induced decomposition of the mercurial, from which some of the hexamethyldisilane is thought to arise. For small extents of reaction the ratio of the amount of phenyltrimethylsilane to that of hexamethyldisilane formed is linearly related to the initial concentration of the mercurial, while the absolute amount of phenyltrimethylsilane found in a given time remains constant. Possible reaction schemes accounting for the main results are considered.

Analogous products are obtained from bis(trimethylgermyl)mercury, but the yields of aromatic substitution products are lower. Better yields of such products are obtained from naphthalene and phenanthrene.

Anisole also gives the expected aromatic substitution products with both mercurials, but there appears to be an accompanying molecular reaction in this case to give other products, and it is suggested that absorption of light by the mercurial gives an excited $[(Me_3M)_2Hg]^*$ molecule, which can either break up into free $Me_3M \cdot$ radicals or react directly with a reactive substrate.

INTRODUCTION

Photolysis of bis(trimethylsilyl)mercury appears to produce trimethylsilyl radicals[1], which can, for example, be trapped by olefins[2] or used to initiate addition of trichlorosilane to olefins[3]. We now give details of homolytic aromatic substitutions carried out by the radicals, which we reported briefly in a preliminary communication[1]. (The ability of organosilyl radicals to take part in such substitutions, which had

not previously been noted, was subsequently confirmed by Sakurai, Hosomi, and Kumada[4], who used radicals generated from organosilicon hydrides and di-tert-butyl peroxide at 135°.) We also describe the first free-radical aromatic substitutions involving germanium radicals, viz. trimethylgermyl radicals generated by photolysis of bis(trimethylgermyl)mercury.

RESULTS AND DISCUSSION

Reactions of bis(trimethylsilyl)mercury

Photolysis of bis(trimethylsilyl)mercury in benzene at 45° gives mercury (100%) along with hexamethyldisilane, phenyltrimethylsilane, 2,5-cyclohexadienyltrimethylsilane, and a large number of higher boiling products which are thought from their retention times to be mainly silylated biphenyls, phenylcyclohexadienes
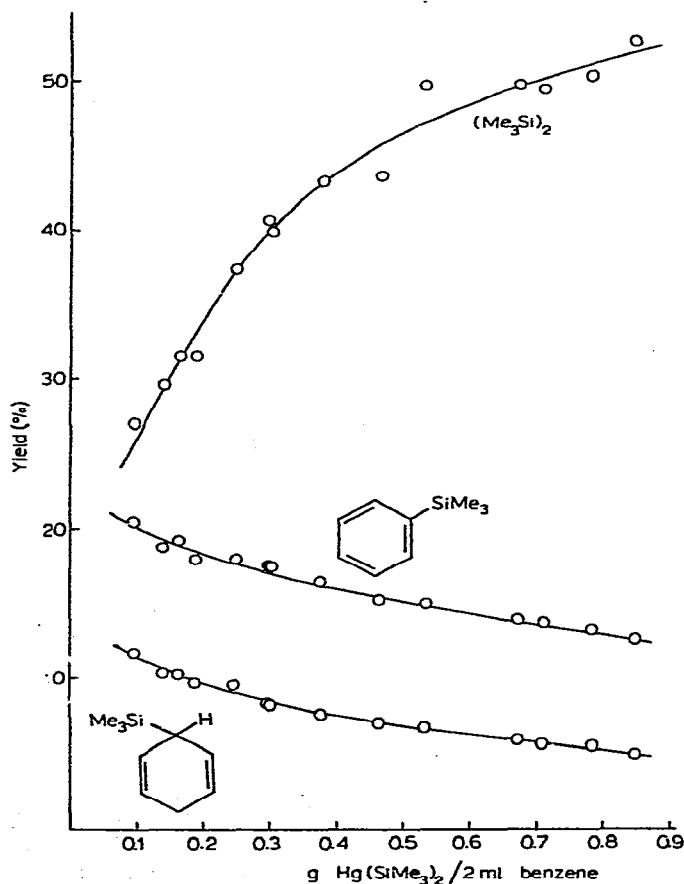

Fig. 1. Photolysis of (Me₃Si)₂Hg in benzene. Variation of product yields with initial mercurial concentration.

and bis(cyclohexadienyls)*. (See below for additional evidence in the case of the analogous germanium-containing products). These compounds are referred to below for convenience as biphenyl derivatives.

The yields of the major organic products hexamethyldisilane, phenyltrimethyl-silane and 2,5-cyclohexadienyltrimethylsilane depend on the initial concentration of the mercurial as shown in Fig. 1; the yields of phenyltrimethylsilane and 2,5-cyclo-hexadienyltrimethylsilane were highest (*viz.* 20 and 12% respectively) at the lowest mercurial concentrations studied, and the yield of hexamethyldisilane (*viz.* 27%) was correspondingly lowest at this concentration. The mole ratio of phenyltrimethyl-silane to the diene was ca. 1.9 over the whole range of concentrations studied. The ratio of hexamethyldisilane to phenyltrimethylsilane produced during the first 45 min (involving decomposition of the first 5–10% of the mercurial) varied considerably with the initial concentration of mercurial and was approximately linearly related to the latter, as shown in Fig. 2. Except possibly for the smallest initial concentration, the absolute amount of phenyltrimethylsilane produced in 45 min was independent of the initial concentration. (For details, see Table 3)

The above results can be satisfactorily accounted for in terms of the Scheme shown, which has much in common with schemes suggested for homolytic aromatic substitution involving carbon radicals.

The dissociation of the mercurial, written in the simplest form in eqn. (1) could, of course, itself involve two steps (a) $Hg(SiMe_3)_2 \rightarrow \cdot HgSiMe_3 + Me_3Si\cdot$ and
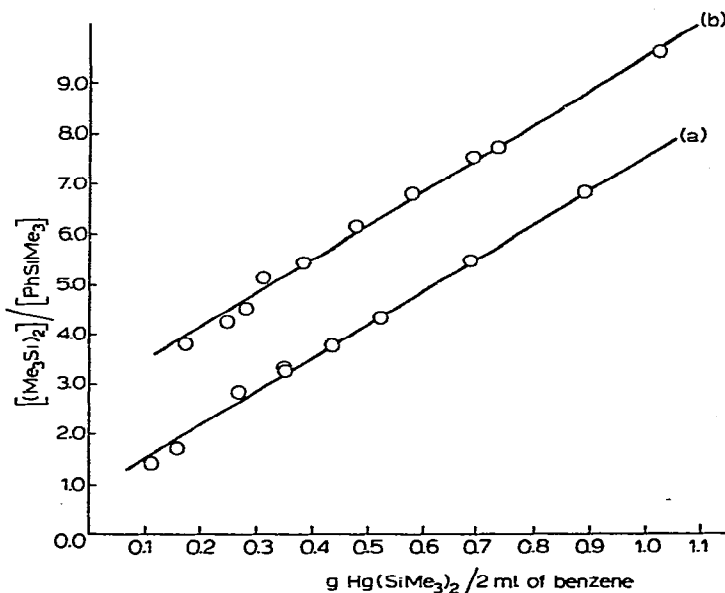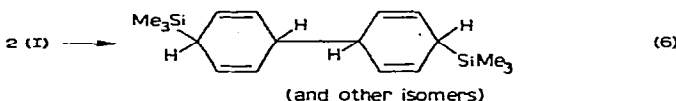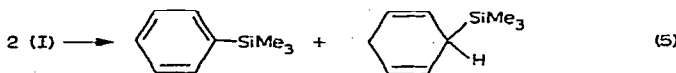

Fig. 2. Graph of mole ratio $[(Me_3Si)_2]/[PhSiMe_3]$ produced after 5–10% decomposition of a solution of bis(trimethylsilyl)mercury in benzene against initial $Hg(Me_3Si)_2$ concentration. (a), 45° for 45 min; (b), 80° for 20 min (points on this graph have been displaced upwards by 2.0 concn. units).

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* Small amounts of trimethylsilane and hexamethyldisiloxane were present in most reaction mixtures; these compounds may arise by hydrolysis or oxidation of the mercurial (see Experimental section.)

$$Hg(SiMe_3)_2 \xrightarrow{h\nu} Hg + 2\ Me_3Si\cdot \tag{1}$$

$$Me_3Si\cdot + Hg(SiMe_3)_2 \longrightarrow (Me_3Si)_2 + Hg + Me_3Si\cdot \tag{2}$$

$$2\ Me_3Si\cdot \longrightarrow (Me_3Si)_2 \tag{3}$$

$$Me_3Si\cdot + \left\langle \bigcirc \right\rangle \rightleftharpoons \overset{H}{\underset{SiMe_3}{\left\langle \bigcirc \right\rangle}} \tag{4}$$

(I)

$$2\ (I) \longrightarrow \left\langle \bigcirc \right\rangle\!\!-SiMe_3 + \overset{SiMe_3}{\underset{H}{\left\langle \bigcirc \right\rangle}} \tag{5}$$

$$2\ (I) \longrightarrow \overset{Me_3Si}{\underset{H}{\left\langle \bigcirc \right\rangle}}\!\!-\overset{H}{\underset{H}{\left\langle \bigcirc \right\rangle}}\!\!-\overset{H}{\underset{SiMe_3}{}} \tag{6}$$

(and other isomers)
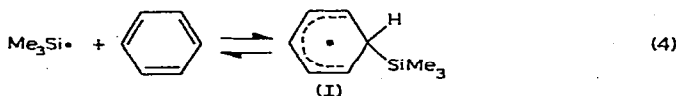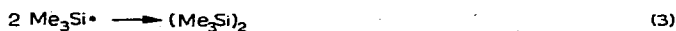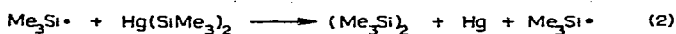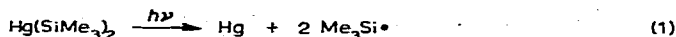
(b) $\cdot HgSiMe_3 \rightarrow Hg + Me_3Si\cdot$.

 On the basis of the Scheme above the $PhSiMe_3/C_6H_7SiMe_3$ product ratio should be 1.0, and the disagreement with the observed ratio of 1.9 can be attributed to loss of the cyclohexadienyl compound in further reactions.

 There is a marked rise in the hexamethyldisilane formation as the initial concentration of the mercurial is increased: since the amount of phenyltrimethylsilane formed in a given time in the partial decomposition experiments appears to be almost independent of the mercurial concentration, it is likely that much of the hexamethyldisilane formed in concentrated solution arises from induced decomposition, represented by step (2) in the above Scheme. It must be appreciated that except for the most dilute solutions used, the optical densities are greater than 2 in the relevant regions of the UV, so that effectively all the light falling on the solution is absorbed, and hence the rate of production of radicals is the same in all the solutions. This will result in the same stationary concentration of radicals in all the solutions, providing that the concentration of radicals is uniform through each solution. If hexamethyldisilane is formed only by reactions (2) and (3), and phenyltrimethylsilane by (4) [with an efficiency of α, to take account of the fact that not all of (I) is converted into phenyltrimethylsilane], then the initial rates of production of hexamethyldisilane and phenyltrimethylsilane, denoted $R(Si_2Me_6)$ and $R(PhSiMe_3)$, respectively, are given by:

$$R(Si_2Me_6) = k_2\cdot[Hg(SiMe_3)_2]\cdot[Me_3Si\cdot] + k_3\cdot[Me_3Si\cdot]^2,\ \text{and}$$
$$R(PhSiMe_3) = \alpha\cdot k_4\cdot[Me_3Si\cdot]\cdot[PhH].$$

 Thus, $R(Si_2Me_6)/R(PhSiMe_3) = a\cdot[Hg(SiMe_3)_2] + b$ {if $[Me_3Si\cdot]$, $[PhH]$ and $[Hg(SiMe_3)_2]$ are assumed to be constant}, and the ratio $R(Si_2Me_6)/R(PhSiMe_3)$ should be linearly related to the mercurial concentration, while the absolute amount of $PhSiMe_3$ formed in a given time should be independent of mercurial concentration, as observed.

While this simple picture satisfactorily accounts for the main features of the results, it cannot be wholly correct because it does not take account of the unevenness in the radical distribution which must exist in the reaction system. More radicals will be formed in the regions of the solution nearest the light source, and if it is assumed that $Me_3Si\cdot$ radicals are no more mobile than iodine atoms in solution, the average distance that a $Me_3Si\cdot$ radical could diffuse in its lifetime of $\sim 1/100$ sec would be $\sim 10^{-3}$ cm (*cf.* ref. 5)*. An approximate model based on this uneven distribution of radicals predicts a dependence of product ratios on mercurial concentration of the type:

$$R(Me_6Si_2)/R(PhSiMe_3) = a\cdot[Hg(SiMe_3)_2] + b\cdot[Hg(SiMe_3)_2]^{\ddagger}$$

Plots of $R(Me_6Si_2)/\{[Hg(SiMe_3)_2]\cdot R(PhSiMe_3)^{\ddagger}\}$ against $[Hg(SiMe_3)_2]^{\ddagger}$ do in fact, give satisfactorily straight lines, but this model has the disadvantage that it does not explain why the amount of phenyltrimethylsilane produced is independent of the initial mercurial concentration. Both this and the simple model require a substantial contribution from the induced decomposition reaction (2) in concentrated solutions of the mercurial.

The effect of varying the reaction temperature was studied, and the following observations were made:

(*a*). The rate of decomposition of the mercurial increases with temperature. The decomposition of the first 10% of the mercurial required only about 20 min at 80° compared with about 45 min at 45°, and the approximate times for complete decomposition at 45°, 145°, and 190°, were 24, 3, and 0.5 h respectively. (There is no question of any significant contribution from the simple pyrolytic decomposition even at 190°. In the absence of light, complete decomposition takes about 7 days at this temperature[6].)

(*b*). The ratio $(Me_3Si)_2/PhSiMe_3$ for the first 10% of decomposition varied with temperature in precisely the same way at 80° as at 45°, the slopes of the two lines in Fig. 2 being almost equal; the intercepts would not be expected to be exactly the same, since the light intensity was not kept rigidly constant when the temperature was raised. The amount of phenyltrimethylsilane formed during the decomposition of 10% of the mercurial was very similar to that observed at 45°, and was similarly independent of the initial concentration. (See Table 3).

(*c*). The overall yield of hexamethyldisilane increased and that of phenyltrimethylsilane decreased with increasing temperature; thus for initial concentrations of 0.22 g of mercurial per 2 ml of benzene, yields of hexamethyldisilane and phenyltrimethylsilane, respectively, are as follows: at 45°, 35% and 19%; at 145°, 78% and 8%; at 190°, 98% and 1.5%. With this same temperature variation the yield of 2,5-cyclohexadienyltrimethylsilane falls markedly from 10 to 0.5 to 0%, presumably as more of it disappears in secondary reactions.

There is not yet sufficient information to enable us to interpret these temperatu-

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* It has recently been suggested that the rate constants for combination of trimethylsilyl radicals[18] or silyl radicals[19] may be abnormally small. This would give longer radical lifetimes, so that the radicals could diffuse further before destruction, and the behaviour would be more in accord with the simple model; the rate constants proposed are not small enough, however, to lead to uniformity of radical concentration. Qualitative work in these laboratories suggests that the recombination of trimethylsilyl radicals in solution occurs at a much more "normal" rate than is proposed in the references cited.

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re effects, particularly since the reaction is undoubtedly more complex than is represented in the simple scheme of reactions (1)–(6). The rise in rate with increase in temperature may reflect an increasing quantum yield in the primary radical producing step (1) as well as an increasing contribution from the induced decomposition (2). The decrease in phenyltrimethylsilane formed at higher temperatures is probably due to the reversibility of reaction (4). Reaction (4) is probably a few kilocalories per mole exothermic; thus the rate of the reverse reaction will increase more rapidly than that of the forward reaction on increasing the temperature, and the concentration of the radical (I), and hence the rate of production of phenyltrimethylsilane, will be lowered.

Photolysis of the mercurial in toluene at 45° gives the expected products, as Table 1 shows; again high boiling products, assumed to be biphenyl derivatives, were

TABLE 1

PRODUCTS FROM PHOTOLYSIS OF $(Me_3Si)_2Hg$ IN TOLUENE

Temp. (°C)	Hg (%)	$(Me_3Si)_2$ (%)	$MeC_6H_4SiMe_3(\%)$			$MeC_6H_6SiMe_3{}^a$ (%)	$PhCH_2SiMe_3$ (%)	$(PhCH_2)_2$ (%)	Silyl "biphenyl" derivatives
			o	m	p				
45	100	30	8.2	9.0	4.0	8	0	0	Yes
145	100	70	1.0	4.5	1.8	0.5	0	Trace	Yes
190	100	96	0.5	2.0	0.7	0	0.5	0.5	Trace

^{a} A mixture of 2-, 3-, and 4-methyl-2,5-cyclohexadienyltrimethylsilane in the ratio 9.4/3.5/1 at 45° and 2.5/4.5/1 at 145°.

detected. The ratios of o-, m-, and p-isomers in the $MeC_6H_4SiMe_3$ products, viz. 2.05/2.25/1, are close to the statistically-determined ratios, the proportion of meta to para substitution thus being rather higher than in free radical methylation[7], possibly as a result of the greater electropositivity of silicon than carbon. The observed isomer-ratios have a limited significance, however, because the balance between the formation of tolyltrimethylsilane and that of alternative products may well differ for the different isomeric cyclopentadienyl radicals produced in the process analogous to step (4) of the Scheme. As with benzene, the rate of reaction with toluene increases markedly with temperature, and the yield of hexamethyldisilane increases at the expense of aromatic substitution products. The proportion of the ortho-isomer in the tolyltrimethylsilane products decreases. Very small amounts of benzyltrimethylsilane and dibenzyl are formed at the high temperatures; the abstraction of hydrogen from the methyl group of toluene, reaction (7), will be an endothermic reaction, probably with a high activation energy, but it is approximately neutral as far as entropy is concerned,

$$PhCH_2-H + \cdot SiMe_3 \rightarrow PhCH_2 \cdot + HSiMe_3 \qquad (7)$$

whereas the addition reaction analogous to (4) produces a decrease in entropy. Reaction (7) will therefore become significant at high temperatures, where addition to the aromatic nucleus is unfavourable for entropy reasons.

Photolysis of bis(trimethylsilyl)mercury in phenyltriethylsilane at 45° gave phenyltrimethylsilane in low yield (ca. 1%) along with several other compounds, the major two of which were identified as m- and p-(triethylsilyl)(trimethylsilyl)benzene. Photolysis at 145° gave an increased yield of phenyltrimethylsilane, with considerably smaller amounts of the other compounds. Mercury was obtained quantitatively in

both photolyses, and hexamethyldisilane was also present as a major product. Organosilyl radicals have previously been shown to displace organosilicon groups from aromatic compounds[8] : such reactions may have a substantial activation energy and thus may compete more effectively with other reactions at higher temperatures.

As Table 2 shows, photolysis of the mercurial in anisole at 45° gives mainly the

TABLE 2

PRODUCTS FROM PHOTOLYSIS OF $(Me_3Si)_2Hg$ IN ANISOLE[a]

Temp. (°C)	$(Me_3Si)_2$ (%)	$MeOC_6H_4SiMe_3$(%)			$MeOC_6H_6SiMe_3$[b]	Silyl "biphenyl" derivatives	$PhSiMe_3$ (%)	$PhOSiMe_3$ (%)	Hg (%)	Me_2Hg (%)
		o	m	p						
45	35	8	4	1	Yes	Yes	Trace	0.7	97	3
145	56	3	1	0.2	Yes	Yes	0.8	25	72	28
190	48	0.5	0.3	0	No	No	1.5	37	58	42

[a] Tetramethylsilane (traces) and trimethylmethoxysilane (ca. 1%) were also formed at all three temperatures. [b] Mixed methoxy-2,5-cyclohexadienyltrimethylsilanes.
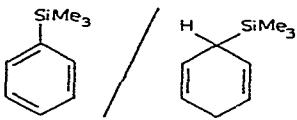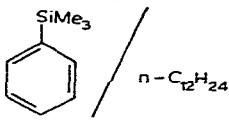
expected products, viz. hexamethyldisilane, (methoxyphenyl)trimethylsilanes, (methoxycyclohexadienyl)trimethylsilanes (the yields of which were not determined), and high-boiling compounds again assumed to be biphenyl derivatives. The high proportion of ortho-isomer in the (methoxyphenyl)trimethylsilanes is consistent with the high proportion of ortho-attack in free radical methylation of anisole[7], although the ratio of m/p substitution is distinctly smaller in the latter case. The reaction with anisole appears to be more complex, however, than those with benzene and toluene, because some methoxy- and phenoxytrimethylsilane are formed, and metallic mercury appears in only 97% yield, 3% of the element appearing in the form of dimethylmercury. The amounts of dimethylmercury and phenoxytrimethylsilane are much higher at higher temperatures, and, except for the persistence of a little o- and m-(methoxyphenyl)trimethylsilane, the product distribution at 190° approaches that observed in the thermal reaction[9]. The latter was originally found to require about 24 h for completion at 185° [9], but in later work the time required has been found to vary, sometimes being as short as that used in the photolysis, so that non-photolytic reactions may have contributed at the higher temperatures to the products listed in Table 2. However, there is no question of any significant thermal reaction at 45°, and we tentatively suggest that phenoxytrimethylsilane and dimethylmercury are formed as a result of a molecular reaction between anisole and bis(trimethylsilyl)mercury of the type discussed in ref. 9, but involving interaction of a thermally activated anisole molecule with a photoexcited molecule of bis(trimethylsilyl)mercury.

Reactions of bis(trimethylgermyl)mercury

The photolytic decomposition of bis(trimethylgermyl)mercury in benzene or toluene was complete in about 12 h at 40°, and 20 min at 180° ; the corresponding thermal reactions require about 24 h at 180°. It is noteworthy that only 2 h is required for the photolytic decomposition in cyclohexane at 40° ; photodecomposition of bis-(trimethylsilyl)mercury is likewise faster in cyclohexane than in aromatic solvents[6]. Such stabilisation by aromatic solvents is consistent with the reaction scheme proposed

TABLE 3

PHOTOLYSIS OF $Hg(SiMe_3)_2$ IN BENZENE SOLUTIONS: PRODUCT RATIOS ESTABLISHED BY GLC AFTER PARTIAL ($\sim 5-10\%$) DECOMPOSITION OF THE MERCURIAL

Wt. (g) $Hg(SiMe_3)_2$ per 2 ml of benzene	Mole ratio (SiMe₃-phenyl) / (cyclohexadienyl-SiMe₃)	Area ratio, (SiMe₃-phenyl) / $n-C_{12}H_{24}$
At 45° for 45 min		
0.112	1.8 ± 0.1	4.8 ± 0.1
0.159	1.9	3.9
0.268	1.9	3.5
0.351	1.8	3.5
0.353	2.1	3.5
0.439	1.9	3.6
0.523	2.4	3.7
0.684	1.8	3.5
0.890	1.9	3.5
At 80° for 20 min		
0.173	1.6	4.0
0.247	1.6	3.9
0.283	1.6	3.9
0.314	1.7	3.6
0.384	1.6	3.2
0.476	1.7	3.0
0.579	1.6	3.4
0.686	1.5	3.3
0.732	1.6_5	3.2
1.024	1.5_5	3.0

above, since trapping of $Me_3M \cdot$ radicals by the aromatic compound would reduce the amount of induced decomposition in reactions of type (2). Alternatively, the aromatic solvent molecules may be able to remove energy from photoexcited molecules of the mercurial. It is unlikely that the aromatic solvent retards the photolysis simply by absorbing the light, at least in the case of bis(trimethylsilyl)mercury, since Walsingham[6] found that ampoules containing bis(trimethylsilyl)mercury in cyclohexane decomposed more rapidly in sunlight than similar solutions of the mercurial in benzene even if the ampoules were immersed in a beaker of toluene.

The products from benzene at 40° were as follows: Hg (100%); $(Me_3Ge)_2$ (98%); Me_3GePh (1%); 2,5-cyclohexadienyltrimethylgermane (trace); trimethylgermane (trace), and high-boiling products (ca. 1%). (At 180° no phenyltrimethylgermane or cyclohexadienylmethylgermane was formed, and the yield of hexamethyldigermane was 99%.) No biphenyl was detected. The mass spectrum of a sample of the high-boiling products collected from the appropriate GLC effluents showed, in addition to many peaks at lower and higher values, complex patterns centred around m/e values of 394 and 274, corresponding to the ions $C_{18}H_{30}Ge_2^+$ and $C_{15}H_{20}Ge^+$, respectively, and this is consistent with the presence of substituted tetrahydrobiphenyl and phenylcyclohexadiene derivatives such as (II) and (III) and their isomers.

[Compound(III) may be formed indirectly from(II) by hydrogen atom abstraction from the 1-position, followed by loss of a $\cdot$GeMe$_3$ radical.]
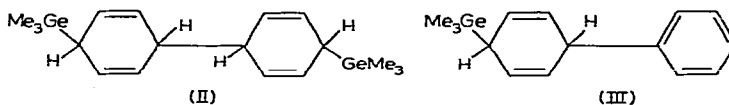
The products from toluene at 40 and 180° were as follows: Hg (100%); (Me$_3$Ge)$_2$ (96% at 40°; 98% at 180°); MeC$_6$H$_4$GeMe$_3$ (1% at 40°, with $o/m/p=$ 2/2/1; 0% at 180°); PhCH$_2$GeMe$_3$ (1% at 40°; 0.5% at 180°); dibenzyl (0% at 40°; trace at 180°); high-boiling products (ca. 1%). The high-boiling fractions showed patterns centred at m/e values of 420 and 301, attributable to the ions $C_{20}H_{34}Ge_2^+$ and $C_{17}H_{24}Ge^+$ and consistent with the presence of the expected analogues of compounds (II) and (III).

Photolytic decomposition of bis(trimethylgermyl)mercury in anisole at 40° was complete in 14 h, and the products were as follows: Hg (98–100%); (Me$_3$Ge)$_2$ (90%); MeOC$_6$H$_4$GeMe$_3$ (2%; $o/m/p=4/2/1$) Me$_3$GePh (trace); high-boiling products (ca. 2%); Me$_3$GeOMe (trace); Me$_3$GeH (trace).

The above results show that less aromatic substitution is brought about by the germanium than the silicon radicals, which is consistent with the lower strength of the Ge–C than of the Si–C bond. The ratio of $o/m/p$ substitution in toluene is virtually identical with that for trimethylsilyl radicals, but with anisole the germanium radicals give a somewhat higher proportion of p-substitution.

No significant displacement of triethylgermyl or trimethylsilyl groups from the corresponding phenyl compound by trimethylgermyl radicals occurred; photolysis of bis(trimethylgermyl)mercury in phenyltrimethylsilane at 40° gave only a trace of phenyltrimethylgermane, along with 1% of Me$_3$GeC$_6$H$_4$SiMe$_3$ ($o/m/p=2/3/1$), trimethylgermane (trace), and hexamethyldigermane (96%); likewise the reaction in phenyltriethylgermane gave only traces of Me$_3$GeH, Et$_3$GeH, and Me$_3$GePh, along with 1% of Me$_3$GeC$_6$H$_4$GeEt$_3$ ($o/m/p=2/3/2$), and Me$_6$Ge$_2$ (97%).

Because of the small amount of aromatic substitution observed with benzene, toluene, and anisole, we examined the photolytic reaction of bis(trimethylgermyl)-mercury with hydrocarbons known to undergo free radical substitution more easily, $viz.$ naphthalene and phenanthrene. Products from naphthalene at 100° were: Hg (100%); (Me$_3$Ge)$_2$ (91%); 1–C$_{10}$H$_7$GeMe$_3$ (5%); 2–C$_{10}$H$_7$GeMe$_3$ (trace); high-boiling products (ca. 3%); Me$_3$GeH (ca. 1%). Products from phenanthrene at 110° were: Hg (100%); (Me$_3$Ge)$_2$ (89%); 9-phenanthryltrimethylgermane (3%); high-boiling products (ca. 4%); Me$_3$GeH (trace). The amounts of aromatic substitution were thus larger than those with benzene derivatives, but were still small. The great predominance of 1-substitution with naphthalene is in agreement with results of free radical phenylation[10].
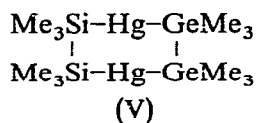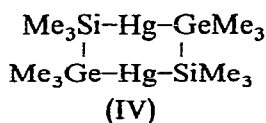
Production of free radicals from bis(trimethylsilyl)mercury and bis(trimethylgermyl)-mercury

The photo-initiated reactions of these mercurials can be explained most easily in terms of the reactions of Me$_3$M$\cdot$ radicals formed by photo-dissociation of the mercurial, as in process (1) or the two-step version of it. However, with anisole, pro-

ducts, similar to those produced in the higher temperature pyrolytic (molecular) reaction, were observed. Razuvaev and his colleagues showed that photolysis of the compound $Et_3SiHgGeEt_3$ as a neat liquid gave the mixed product $Et_3SiGeEt_3$ and no significant amount of the symmetrical products $(Et_3Si)_2$ and $(Et_3Ge)_2$, and concluded that the reaction proceeds molecularly without production of free radicals[11]. Similarly an equilibrium mixture of $(Me_3Si)_2Hg$, $Me_3SiHgGeMe_3$ and $(Me_3Ge)_2Hg$ in cyclopentane gave on photolysis predominantly the mixed product $Me_3SiGeMe_3$ rather than the statistical mixture of products expected from radical recombination reactions[12].

These results can be accounted for by assuming that the light is absorbed by the mercurial to form the photo-excited molecule $Hg(SiMe_3)_2^*$, which dissociates into free $Me_3Si\cdot$ radicals only in the absence of other reactive molecules; when formed these radicals enter into other reactions, including induced decomposition of the mercurial. When reactive substances, such as anisole or bromobenzene[13] (or even the mercurial itself if it is present in sufficiently high concentration), are present, the excited mercurial molecule is assumed to be able to react with them by a molecular reaction before it can dissociate into radicals.

The predominance of mixed products R_3SiGeR_3 (rather than R_3SiSiR_3 and R_3GeGeR_3) when unsymmetrical mercurials[11] or mixtures of mercurials[12] are photolysed is not inconsistent with such a scheme. If induced decompositions such as reaction (2) are important, there should be a tendency for silyl radicals to attack at a germanium centre or *vice versa*. Alternatively, if a multi-centre molecular reaction takes place between an excited and a normal mercurial molecule, the formation of Si–Ge bonds should be more favoured than that of Si–Si and Ge–Ge bonds: for example (IV) would be expected to be a transition state of lower energy than (V), since the strength of a covalent M–M' bond is normally greater than the arithmetic mean of M–M and M'–M'.

$$\begin{array}{cc}
\text{Me}_3\text{Si-Hg-GeMe}_3 & \text{Me}_3\text{Si-Hg-GeMe}_3 \\
\quad\mid\qquad\mid & \quad\mid\qquad\mid \\
\text{Me}_3\text{Ge-Hg-SiMe}_3 & \text{Me}_3\text{Si-Hg-GeMe}_3 \\
(\text{IV}) & (\text{V})
\end{array}$$

Quantum yield studies now in progress should provide more detailed information about the nature of the initial photolytic process.

EXPERIMENTAL

Bis(trimethylsilyl)mercury

This mercurial was prepared and handled as described previously[9]. In typical photolysis experiments 2 ml of the degassed organic solvent was added to 0.3 g of the mercurial in a Pyrex ampoule in a nitrogen-filled glove box, after which the ampoule was sealed under vacuum. Photolyses were carried out using a 500 watt medium pressure mercury-arc lamp (Engelhard–Hanovia UVS 500/A) at a distance of 20 cm. For high temperature photolytic reactions the ampoules were suspended in a quartz jacket and heated by the vapour from a refluxing hydrocarbon. In the ambient temperature photolyses the reaction mixtures were at temperatures of 40–45°.

Bis(trimethylgermyl)mercury

This mercurial, m.p. 120–122° (lit.[14] 120–122°), was prepared by the method of ref. 14, but with sublimation at a lower temperature, *viz.* 55–65°/0.01 mm. Solutions in cyclohexane showed UV absorption maxima at 313 and 361 nm. In the photolyses, ca. 0.1 g mercurial was dissolved in 1 ml of solvent as described above.

Analysis of reaction mixtures

Products were identified by GLC, using at least two different columns (normally one polar and one non-polar) to establish retention times for comparison with those of authentic compounds. For quantitative analyses internal standards (*e.g.* dodecane, as indicated in Table 3) were used. Mercury was weighed.

Reaction mixtures involving bis(trimethylsilyl)mercury were found to contain small amounts of hexamethyldisiloxane (usually $< 3\%$) both before and after the photolyses; this compound was presumably formed either by decomposition during manipulation, or from traces of impurities (*e.g.* O_2, H_2O) in the solvent. Traces of trimethylsilane were also found in almost constant amount before and after photolysis, indicating that this product too was formed before the photolysis.

Preparations of new organosilicon and organogermanium compounds

Many of the organosilicon compounds required for reference standards are well known, but most of the organogermanium compounds had not previously been reported.

(a). Conventional Grignard syntheses

Reactions were carried out in ether, with 3–4 h reflux after addition of the organogermanium halide to the Grignard reagent. Treatment with saturated aqueous ammonium chloride solution was followed by extraction with ether, and drying (MgSO$_4$) and fractional distillation of the extract. The following organogermanium compounds were obtained:

o-Tolyltrimethylgermane. 4.7 g, 90%, from *o*-bromotoluene (4.3 g, 0.025 mole), bromotrimethylgermane (4.9 g, 0.025 mole), and magnesium (0.7 g, 0.028 g-atom), b.p. 72–75°/7 mm, n_D^{25} 1.5033. (Found: C, 57.7; H, 7.80. $C_{10}H_{16}Ge$ calcd.: C, 57.5; H, 7.71%.)

m-Tolyltrimethylgermane. 1.7 g, 85%, from *m*-bromotoluene (1.7 g, 0.01 mole), bromotrimethylgermane (2.0 g, 0.01 mole), and magnesium (0.3 g, 0.012 g-atom), b.p. 83–84°/14 mm, n_D^{25} 1.4951. (Found: C, 57.4; H, 7.61. $C_{10}H_{16}Ge$ calcd.: C, 57.5; H, 7.71%.)

p-Tolyltrimethylgermane. 2.1 g, 85%, from *p*-bromotoluene (2.1 g, 0.012 mole), bromotrimethylgermane (2.4 g, 0.012 mole), and magnesium (0.35 g, 0.014 g-atom), b.p. 62–64°/5 mm, n_D^{25} 1.4972. (Found: C, 57.3; H, 7.59. $C_{10}H_{16}Ge$ calcd.: C, 57.5; H, 7.71%.)

(m-Chlorophenyl)trimethylgermane. 1.7 g, 75%, from 1-bromo-3-chlorobenzene (1.9 g, 0.01 mole), bromotrimethylgermane (2.0 g, 0.01 mole), and magnesium (0.3 g, 0.012 g-atom), b.p. 85–87°/3.5 mm, n_D^{25} 1.5013. (Found: C, 47.2; H, 5.56. $C_9H_{13}ClGe$ calcd.: C, 47.1; H, 5.72%.)

(p-Chlorophenyl)trimethylgermane. 2.4 g, 75%, from 1-bromo-4-chlorobenzene (2.7 g, 0.014 mole), bromotrimethylgermane (2.8 g, 0.014 mole) and magnesium (0.4 g,

0.016 g-atom), b.p. 89–91°/6 mm, n_D^{25} 1.5092. (Found: C, 47.0; H, 5.64. $C_9H_{13}ClGe$ calcd.: C, 47.1; H, 5.72%.)

(m-Methoxyphenyl)trimethylgermane. 2.0 g, 75%, from 1-bromo-3-methoxy-benzene (2.2 g, 0.012 mole), bromotrimethylgermane (2.4 g, 0.012 mole) and magnesium (0.35 g, 0.014 g-atom), b.p. 87–88°/5 mm, n_D^{25} 1.5151. (Found: C, 53.5; H, 7.12. $C_{10}H_{16}$-GeO calcd.: C, 53.4; H, 7.18%.)

(p-Methoxyphenyl)trimethylgermane. 2.1 g, 80%, from 1-bromo-4-methoxy-benzene (1.9 g, 0.01 mole), bromotrimethylgermane (2.0 g, 0.01 mole), and magnesium (0.3 g, 0.012 g-atom), b.p. 102–104°/11 mm, n_D^{25} 1.5144. (Found: C, 53.4; H, 7.31. $C_{10}H_{16}GeO$ calcd.: C, 53.4; H, 7.18%.)

(2,4,6-Trimethylphenyl)trimethylgermane. 1.8 g, 75%, from bromomesitylene (2.0 g, 0.01 mole), bromotrimethylgermane (2.0 g, 0.01 mole), and magnesium (0.3 g, 0.012 g-atom) in tetrahydrofuran, b.p. 84–86°/1.5 mm., n_D^{25} 1.5212. (Found: C, 60.9; H, 8.40. $C_{12}H_{20}Ge$ calcd.: C, 60.8, H, 8.51%.)

(b). "In situ" Grignard syntheses

The organic halide in ether was added slowly to the magnesium and the group IVB halide in ether. After 3–4 h reflux, work up was as above. The following compounds were obtained:

(o-Chlorophenyl)trimethylgermane. 2.1 g, 65%, from 1-bromo-2-chlorobenzene (2.7 g, 0.014 mole), bromotrimethylgermane (2.8 g, 0.014 mole), and magnesium (0.4 g, 0.016 g-atom), b.p. 46–47°/0.3 mm, n_D^{25} 1.5136. (Found: C, 47.3; H, 5.72. $C_9H_{13}ClGe$ calcd.: C, 47.1; H, 5.72%.)

1-Naphthyltrimethylgermane. 1.8 g, 75%, from 1-bromonaphthalene (2.1 g 0.01 mole), bromotrimethylgermane (2.0 g, 0.01 mole) and magnesium (0.3 g, 0.012 g-atom), b.p. 98–99°/1 mm, n_D^{25} 1.5902. (Found: C, 63.5; H, 6.49. $C_{13}H_{16}Ge$ calcd.: C, 63.7; H, 6.59%.)

2-Naphthyltrimethylgermane. 1.7 g, 70%, from 2-bromonaphthalene (2.1 g, 0.01 mole), bromotrimethylgermane (2.0 g, 0.01 mole), and magnesium (0.3 g, 0.012 g-atom), b.p. 85–87°/0.4 mm, n_D^{25} 1.5856. (Found: C, 63.6; H, 6.56. $C_{13}H_{16}Ge$ calcd.: C, 63.7; H, 6.59%.)

(9-Trimethylgermyl)phenanthrene. 1.6 g, 55%, after crystallisation from ethanol, from 9-bromophenanthrene (2.6 g, 0.01 mole), bromotrimethylgermane (2.3 g, 0.012 mole), and magnesium (0.4 g, 0.016 g-atom) in tetrahydrofuran, m.p. 75–77°. (Found: C, 69.6; H, 6.27, $C_{17}H_{18}Ge$ calcd.: C, 69.2; H, 6.15%.)

(c). Wurtz reactions

A few drops of a solution of the Group IV halide and the organic halide in sodium-dried toluene were added to sodium sand in warm toluene. Reaction was initiated with a few drops of ethyl acetate, the remainder of the halide solution was added dropwise during 30 min, and the reaction mixture was refluxed for a further 30 min. The reaction mixture was cooled, the sodium halide and excess sodium were filtered off, and the solution was fractionally distilled. Thus obtained were:

m-(Triethylsilyl)(trimethylsilyl)benzene. 2.5 g, 50%, from m-(chlorophenyl)-trimethylsilane (4.1 g, 0.022 mole), bromotriethylsilane (4.4 g, 0.023 mole), and sodium (0.6 g, 0.026 g-atom), b.p. 75°/0.01 mm. (Found: C, 68.4; H, 10.85. $C_{15}H_{28}Si_2$ calcd.: C, 68.1; H, 10.7%.)

p-(Triethylsilyl)(trimethylsilyl)benzene. 2.5 g, 60%, from (*p*-chlorophenyl)-trimethylsilane (3.7 g, 0.02 mole), bromotriethylsilane (3.9 g, 0.02 mole) and sodium (0.5 g, 0.022 g-atom), b.p. 78°/0.005–0.01 mm. (Found: C, 68.4; H, 10.8. $C_{15}H_{28}Si_2$ calcd.: C, 68.1; H, 10.7%.)

o-Bis(trimethylgermyl)benzene. 8.4 g, 50%, from (*o*-chlorophenyl)trimethyl-germane (12.4 g, 0.054 mole), bromotrimethylgermane (12.6 g, 0.064 mole), and sodium (2.8 g, 0.12 g-atom), b.p. 85–87°/0.8 mm, n_D^{25} 1.5081. (Found: C, 46.4; H, 7.14. $C_{12}H_{22}$-Ge_2 calcd.: C, 46.3; H, 7.12%). [Small quantities of benzyltrimethylgermane and *m*-bis(trimethylgermyl)benzene were also formed, and were removed by careful fractionation].

m-Bis(trimethylgermyl)benzene. 2.0 g, 65%, from (*m*-chlorophenyl)trimethyl-germane (2.3 g, 0.01 mole), bromotrimethylgermane (2.4 g, 0.012 mole), and sodium (0.7 g, 0.03 g-atom), b.p. 73–75°/0.3 mm, n_D^{25} 1.5060. (Found: C, 46.5; H, 7.17. $C_{12}H_{22}$-Ge_2 calcd.: C, 46.3; H, 7.12%.)

p-Bis(trimethylgermyl)benzene. 2.6 g, 85%, after recrystallisation from ethanol, from (*p*-chlorophenyl)trimethylgermane (2.3 g, 0.01 mole), bromotrimethylgermane (2.4 g, 0.012 mole), and sodium (0.7 g, 0.03 g-atom), m.p. 106–107°, lit.[15] 91–92°. (Found: C, 46.5; H, 7.12 $C_{12}H_{22}Ge_2$ calcd.: C, 46.3; H, 7.12%.)

1-(Trimethylgermyl)-2-(trimethylsilyl)benzene. 2.5 g, 45%, from (*o*-chloro-phenyl)trimethylsilane (3.7 g, 0.02 mole), bromotrimethylgermane (4.3 g, 0.022 mole), and sodium (1.2 g, 0.05 g-atom), b.p. 108–110°/9 mm, n_D^{25} 1.5016. (Found: C, 54.3; H, 8.39. $C_{12}H_{22}GeSi$ calcd.: C, 54.0; H, 8.31%.) [Small amounts of benzyltrimethylger-mane and 1-(trimethylgermyl)-3-(trimethylsilyl)benzene were also formed and were removed by careful fractionation].

1-(Trimethylgermyl)-3-(trimethylsilyl)benzene. 0.8 g, 60%, from (*m*-chloro-phenyl)trimethylsilane (0.9 g, 0.005 mole), bromotrimethylgermane (1.2 g, 0.006 mole), and sodium (0.35 g, 0.015 g-atom), b.p. 81–82°/2.5 mm, n_D^{25} 1.5002. (Found: C, 53.9; H, 8.26. $C_{12}H_{22}GeSi$ calcd.: C, 54.0; H, 8.31%.)

1-(Trimethylgermyl)-4-(trimethylsilyl)benzene. 1.0 g, 75%, from (*p*-chloro-phenyl)trimethylsilane (0.9 g, 0.005 mole), bromotrimethylgermane (1.2 g, 0.006 mole), and sodium (0.35 g, 0.015 g-atom), b.p. 91–94°/4 mm, m.p. 33–37°. (Found: C, 54.4; H, 8.49. $C_{12}H_{22}GeSi$ calcd.: C, 54.0; H, 8.31%.)

1-(Triethylgermyl)-2-(trimethylgermyl)benzene. 1.7 g, 40%, from (*o*-chloro-phenyl)triethylgermane (3.25 g, 0.012 mole), bromotrimethylgermane (2.8 g, 0.014 mole), and sodium (0.7 g, 0.03 g-atom), b.p. 89–91°/0.1 mm, n_D^{25} 1.5102, (Found: C, 50.8; H, 7.89. $C_{15}H_{28}Ge_2$ calcd.: C, 50.9; H, 7.99%.)

1-(Triethylgermyl)-3-(trimethylgermyl)benzene. 1.6 g, 65%, from (*m*-chloro-phenyl)triethylgermane (1.9 g, 0.007 mole), bromotrimethylgermane (2.0 g, 0.01 mole) and sodium (0.5 g, 0.02 g-atom), b.p. 83–85°/0.07 mm, n_D^{25} 1.5092. (Found: C, 50.8; H, 8.06. $C_{15}H_{28}Ge_2$ calcd.: C, 50.9; H, 7.98%.)

1-(Triethylgermyl)-4-(trimethylgermyl)benzene. 2.5 g, 70%, from (*p*-chloro-phenyl)triethylgermane (2.7 g, 0.01 mole), bromotrimethylgermane (2.4 g, 0.012 mole), and sodium (0.65 g, 0.028 g-atom), b.p. 72–74°/0.02 mm, m.p. 26–31°. (Found: C, 50.4; H, 8.12. $C_{15}H_{28}Ge_2$ calcd.: C, 50.9; H, 7.98%.)

(d). Miscellaneous preparations

(i). *(o-Methoxyphenyl)trimethylgermane*. (*o*-Methoxyphenyl)lithium[16] prepa-

red from 1-bromo-2-methoxybenzene (5.2 g, 0.028 mole) and lithium (0.5 g, 0.065 g-atom) in ether, was added dropwise during 30 min to bromotrimethylgermane (4.9 g, 0.025 mole) in ether at $-5°$. The mixture was refluxed for 2 h, treated with dilute hydrochloric acid, and extracted with ether. The ethereal extracts were dried ($MgSO_4$) and fractionated to give (o-methoxyphenyl)trimethylgermane (3.4 g, 60%), b.p. 94–96°/10 mm, n_D^{25} 1.5172. (Found: C,53.7; H, 7.29. $C_{10}H_{16}GeO$ calcd.: C, 53.4; H, 7.18%.)

(ii). *2,5-Cyclohexadienyltrimethylgermane*. Electrolysis[17] (0.8 A, 90 V for 3 h at $-5°$) of phenyltrimethylgermane (3.2 g, 0.016 mole) and lithium chloride (10 g) in methylamine (300 ml) afforded 2,5-cyclohexadienyltrimethylgermane (1.5 g, 50%), b.p. 63–64°/10 mm, n_D^{25} 1.4936. (Found: C, 54.9; H, 8.4. $C_9H_{16}Ge$ calcd.: C, 54.9; H, 8.2%)

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