γ-Ray- and UV-induced Generation of Methyl(phenyl)silylene and Silene Species from Heptamethyl-2-phenyltrisilane

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A benzene solution of heptamethyl-2-phenyltrisilane (**1**) has been irradiated with γ-rays in the presence of methanol. Hexamethyldisilane, methoxymethyl(phenyl)silane (**2**) and a 1-methoxytetramethyldisilanyl- and trimethylsilyl-substituted cyclohexadiene (**3**) were produced. The formation of **2** and **3** can be interpreted in terms of reactions of methanol with methyl(phenyl)silylene and a silicon–carbon double-bonded intermediate (silene), respectively. These intermediates are generated as follows. Benzene is first excited by γ-rays and by collisions the energy transfers to **1**. Excited **1** decomposes to give methyl(phenyl)silylene or undergoes rearrangement to a silene intermediate as when **1** is excited by UV light. A kinetic study revealed that the energy transfer in the γ-irradiated system is the same as that in a UV-irradiated system.

Poly(dimethylsilylene-co-methylphenylsilylene) is a potentially practical organic material owing to its solubility in common organic solvents and its mouldability when melted.[1] Interested by its application to microlithography, both we[2,3] and West *et al.*[1] have studied the γ- and photo-irradiation of the polymer, respectively. In the solid state both photo and γ-ray irradiation give rise to cross-linking but in solution both types of irradiations cause main-chain degradation. However, the mechanisms of the reactions induced by irradiation remain obscure.

In order to determine the detailed chemical behaviour of the polymers during the photolysis and radiolysis, we chose heptamethyl-2-phenyltrisilane as a model compound. The trisilane is reported to decompose with generation of methyl(phenyl)silylene and to rearrange into a silicon–carbon double-bonded intermediate by UV irradiation.[4] The silylene was confirmed spectroscopically by Gaspar *et al.*[5] In this paper we report a mechanistic study on the γ-radiolysis of the trisilane. It is expected that the information contained herein will be instrumental in elucidating the detailed chemical behaviour of irradiated polysilanes in general.

Results and Discussion

A degassed solution of heptamethyl-2-phenyltrisilane (**1**, 1.7×10^{-2} mol dm^{-3}), methanol (7.8×10^{-2} mol dm^{-3}) and octane (an internal standard for GLPC analysis) in benzene was irradiated with γ-rays. Hexamethyldisilane and methoxymethyl(phenyl)silane (**2**) were obtained in moderate yield, and a 1-methoxytetramethyldisilanyl- and trimethylsilyl-substituted cyclohexadiene (**3**) was produced in low yield. The dependence of the product yields on the irradiation doses is shown in Fig. 1. The production of hexamethyldisilane is given as experimental evidence of the generation of methyl(phenyl)silylene. The production of a silicon–carbon double-bonded intermediate arising from rearrangement of a trimethylsilyl group onto an *ortho* carbon atom in the phenyl ring by UV irradiation of **1** is documented.[4] It is clear that the products **2** and **3**† are formed by reactions of methanol with methyl(phenyl)silylene and the silicon=carbon intermediate, respectively (Scheme 1), since the

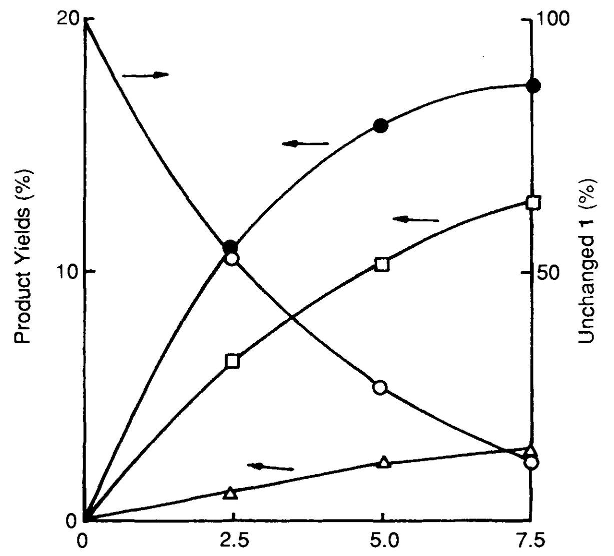
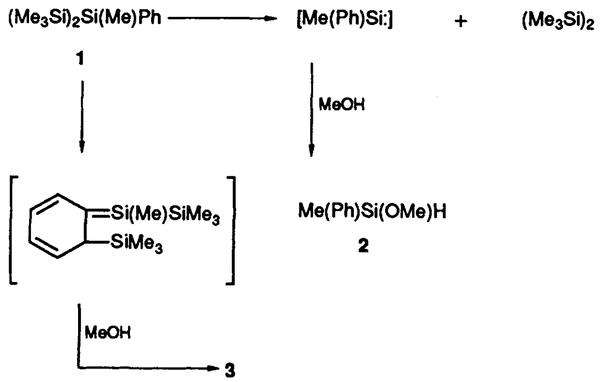


Fig. 1 γ-Induced reaction of **1** (0.017 mol dm^{-3}) with methanol (0.078 mol dm^{-3}) in benzene. Dose rate: 30.4 kGy h^{-1}. ○, Heptamethyl-2-phenyltrisilane (**1**); ●, hexamethyldisilane; □, methoxymethyl(phenyl)silane (**2**); △, 1-methoxytetramethyldisilanyl- and trimethylsilyl-substituted cyclohexadiene (**3**).



Scheme 1

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† For the product **3**, three isomers, 5-(1-methoxytetramethyldisilanyl)-6-trimethylsilylcyclohexa-1,3-diene, 1-(1-methoxytetramethyldisilanyl)-6-trimethylsilylcyclohexa-1,3-diene and 1-(1-methoxytetramethyldisilanyl)-6-trimethylsilylcyclohexa-1,4-diene, are possible from the addition of methanol to the silicon=carbon intermediate. Unfortunately we are unable to distinguish which is produced in practice.

Table 1 Effect of the amount of benzene on product yields[a]

Amount of benzene (V/cm^3)	Consumed **1** (%)	Product yield (%)		
		$Me_3SiSiMe_3$	**2**	**3**
16	86.5	17.5	12.8	2.8
8	74.2	12.2	6.2	1.3
4	58.0	8.1	2.8	0.5

[a] **1**, 0.27 mmol; CH_3OH, 1.25 mmol; irradiation dose, 228 kGy.

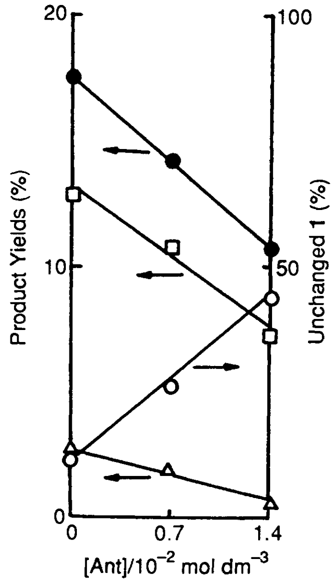

Fig. 2 Effect of the amount of added anthracene (Ant) on product yields. Dose rate: 30.4 kGy h^{-1}; dose, 228 kGy. **1**, 0.017 mol dm^{-3}; CH_3OH 0.078 mol dm^{-3} in benzene; ○, **1**; ●, hexamethyldisilane; □, **2**; △, **3**.

same products are obtained by UV irradiation of a cyclohexane solution of the same mixture. That the yield of **2** is lower than that of hexamethyldisilane is probably due to the formation of poly[methyl(phenyl)silylene] and 1-methoxy-1,2-dimethyl-1,2-diphenyldisilane, $MeO(SiMePh)_2H$. Formation of the latter was confirmed by means of GC–MS.

We previously reported that γ irradiation of dodecamethylcyclohexasilane in benzene generated dimethylsilylene by a mechanism in which the energy transfer from benzene to the hexasilane initiated the reaction.[6] By analogy with this process, methyl(phenyl)silylene and silene species are assumed to be generated from **1** by the following mechanism. Benzene is first excited by γ-rays and the energy is transferred to **1**. Excited **1** decomposes to give methyl(phenyl)silylene and hexamethyldisilane and/or undergoes rearrangement to give the double-bonded intermediate. The fact that the amount of **1** consumed and the product yields increase with increased amounts of benzene, as shown in Table 1, is consistent with our assumption that the reactions are induced by excitation of benzene by γ-rays. For further confirmation of the energy transfer, anthracene, which is a good quencher, was added to the reaction system. As shown in Fig. 2, the amount of **1** consumed and the product yields decrease with increased amounts of anthracene. This shows that anthracene competes with benzene for excitation energy and diminishes the energy transfer to **1**.

The trisilane **1** has a UV absorption maximum at 243 nm and may favourably accept the energy from benzene, the absorption band of which overlaps with that of **1**. In contrast, energy transfer from a solvent which does not have an overlapping absorption band with **1** would be slow. In fact, γ-radiolysis of **1**, using cyclohexane as the solvent instead of benzene, gave the products mentioned above only in trace amounts together with many unidentified products. The result can be interpreted as a slow energy transfer due to the absence of a co-absorption band and by a preferential reaction of **1** with radicals produced by γ-radiolysis of cyclohexane.†

Energy Transfer in a UV-irradiated System.—Although energy levels of benzene excited by UV- and γ-irradiation are obscure, the transfer of energy from benzene to **1** in a UV-irradiated system is expected to take place similarly to that in the γ-irradiated system. In order to understand the energy-transfer process, a solution of **1** in benzene was irradiated at 254 nm and the results are discussed in terms of the kinetics. In this case, both **1** and benzene absorb the light. If the energy of the excited benzene is transferred to **1**, as expected, and **1** excited both by the energy transfer and direct irradiation decomposes to hexamethyldisilane and methyl(phenyl)silylene, the overall reactions can be described by eqns. (1)–(8), where M represents a third body capable of accepting the excess of energy.

$$\mathbf{1} \xrightarrow{h\nu} \mathbf{1}^* \qquad (1)$$

$$C_6H_6 \xrightarrow{h\nu} C_6H_6^* \qquad (2)$$

$$C_6H_6^* \xrightarrow{k_3} C_6H_6 \qquad (3)$$

$$C_6H_6^* + M \xrightarrow{k_4} C_6H_6 + M^* \qquad (4)$$

$$C_6H_6^* + \mathbf{1} \xrightarrow{k_5} C_6H_6 + \mathbf{1}^* \qquad (5)$$

$$\mathbf{1}^* \xrightarrow{k_6} \mathbf{1} \qquad (6)$$

$$\mathbf{1}^* + M \xrightarrow{k_7} \mathbf{1} + M^* \qquad (7)$$

$$\mathbf{1}^* \xrightarrow{k_8} Me(Ph)Si\colon + (Me_3Si)_2 \qquad (8)$$

The compounds marked with an asterisk are those in excited states, and eqns. (3), (4), (6) and (7) represent deactivation reactions with no generation of the silylene. Under the conditions where the absorbance of **1** is extremely small compared with that of benzene, the steady state treatment of these reactions leads to eqn. (9), where R_{Si_2} is the rate of

$$\frac{1}{R_{Si_2}} = \frac{k_5}{c} + \frac{k}{c} \cdot \frac{1}{[Si_3]} \qquad (9)$$

formation of hexamethyldisilane, and c is a constant which is determined by k_3 to k_8, the extinction coefficient of **1** and the incident light intensity. The parameter k, a rate constant for the deactivation reactions of benzene [eqns. (3) and (4)], is defined as $k_3 + k_4[M]$ which can be regarded as constant. Benzene solutions of **1**, in various concentrations, were irradiated with UV light under defined conditions and $1/R_{Si_2}$ values obtained are plotted against $1/[Si_3]$ in Fig. 3. The linear correlation is consistent with eqn. (9) which is derived from the assumption of energy transfer from benzene to **1**. From the values of the intercept and the slope, k_5/c is 5.7×10^2 dm^3 mol^{-1} min and k/c is 0.32×10^2 min, respectively. These values imply that a half of the excited benzene serves to excite **1** [eqn. (5)] and the remaining half is deactivated according to eqns. (3) and (4) when $[Si_3]$ is 5.6×10^{-2} mol dm^{-3}.

Application to Polysilanes.—It is reported that dialkyl- and methylphenyl-substituted polysilanes, $(R_2Si)_n$ and $(MePhSi)_n$,

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† Cyclohexane decomposes *ca.* six times faster to give radicals than benzene.[7]

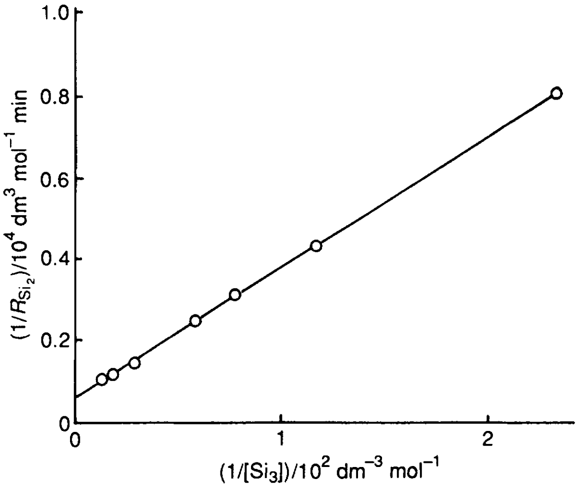

Fig. 3 Plot of $1/R_{Si_2}$ *versus* $1/[Si_3]$ for the photoinduced reaction of **1** in benzene

degraded extruding silylene units, R_2Si: or Me(Ph)Si:, on photolysis.[8] Dodecamethylcyclohexasilane is a well-known photochemical precursor of dimethylsilylene.[9] The same silylene is generated by γ-irradiation of the cyclohexasilane in benzene.[6] Although neither photo- nor γ-induced generation of silylene species from poly(dimethylsilylene-co-methylphenylsilylene) has been reported so far, the results obtained here, combined with the knowledge of the other polysilanes mentioned above, suggest that generation of silylene(s) plays an important role in photolysis and radiolysis of poly(dimethylsilylene-co-methylphenylsilylene), particularly in benzene.

Experimental

Materials.—Heptamethyl-2-phenyltrisilane (**1**) was prepared from methyl(phenyl)dichlorosilane and chlorotrimethylsilane using lithium metal in THF. Solvents and methanol were treated with molecular sieves 3 Å to remove water and were distilled under vacuum. The other commercially available reagents were used without further purification.

Procedure for Irradiation.—Prescribed amounts of the reagents dissolved in benzene or cyclohexane were degassed and irradiated with γ-rays from a ^{60}Co source in Pyrex tubes or with a 20 W ozoneless low-pressure mercury lamp in quartz tubes. It was confirmed that light of wavelength 254 ± 5 nm and >290 nm was emitted by the lamp by means of a photon counting spectrometer (Unisoku PCS-400).

Identification and Estimation of Products.—Identification and measurement of the products were performed by GC–MS and GLPC. Mass spectra were taken with a JEOL DX302 and GLPC analyses were made by a Yanagimoto G-3800 with a methylsilicon bonded-type column ($\phi = 0.75$ mm; 30 m; Supelco).

Product **2**: *m/z* 152 (M^+, 56%), 151 [$(M - H)^+$, 34], 137 [$(M - CH_3)^+$, 73], 121 [$(M - OCH_3)^+$, 36], 107 [$(137 - CH_2{=}O)^+$, 50], 91 [$(C_6H_5CH_2)^+$, 31], 74 [$(151 - C_6H_5)^+$, 100], 59 [$(137 - C_6H_5 - H)^+$, 75].

Product **3**: *m/z* 298 (M^+, 6%), 283 [$(M - CH_3)^+$, 28], 267 [$(M - OCH_3)^+$, 53], 209 {$[283 - (CH_3)_3SiH]^+$, 13}, 193 {$[267 - (CH_3)_3SiH]^+$, 32}, 151 {$[M - SiOCH_3(CH_3)Si(CH_3)_3]^+$, 18}, 147 [$(M - 151)^+$, 95], 135 {$[C_6H_5Si(CH_3)_2]^+$, 68}, 73 {$[Si(CH_3)_3]^+$, 100}.

$MeO(SiMePh)_2H$: *m/z* 272 (M^+, 13%), 271 [$(M - H)^+$, 18], 257 [$(M - CH_3)^+$, 45], 151 [$(SiPhMeOMe)^+$, 100], 121 [$(SiPhMeH)^+$, 54].

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Paper 0/03938A
Received 30*th August* 1990
Accepted 11*th December* 1990