γ-Induced Generation of Dimethylsilylene from Dodecamethylcyclohexasilane

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γ-Irradiation of dodecamethylcyclohexasilane (**I**) generates dimethylsilylene in 65% yield when benzene is used as a solvent. Kinetic studies using anthracene as quencher are consistent with a mechanism proposed for the generation of dimethylsilylene. Benzene is first excited by γ-rays and energy is transferred to (**I**). Excited (**I**) decomposes to give dimethylsilylene presumably in a way similar to (**I**) excited by u.v. light. The ratio of the rate constant for self-deactivation of benzene to that for energy transfer from benzene to (**I**), k_2/k_3, is 5.1×10^{-2} mol l^{-1} at room temperature. Energy transfer to (**I**) is hindered by added anthracene. The ratio of the rate constant for energy transfer to anthracene to that for energy transfer to (**I**), k_6/k_3, is *ca.* 6 at room temperature. A similar energy transfer is possible in the case of u.v. irradiation.

A large number of methods for generation of silylenes have been reported.[1,2] Almost all these methods are based on pyrolysis or photolysis of precursors. Consequently, high reaction temperatures or a quartz vessel and a limited range of solvents must be employed. It is well known that γ-irradiation, as well as heating and u.v. irradiation, gives free radicals, but the γ-induced generation of silylenes has not so far been reported.† Dodecamethylcyclohexasilane (I) is one of the most convenient precursors for dimethylsilylene and the effect of u.v. irradiation has been fully studied.[4] It is of interest to investigate the generation of dimethylsilylene from (I) upon γ-irradiation,

$[(CH_3)_2Si]_6$
(I)

which can be carried out with few experimental restrictions, *viz.*, in any vessel at any temperature. From this point in view, γ-radiolysis of (I) was carried out in several solvents and the generation of dimethylsilylene was studied kinetically.

Results and Discussion

It is known that photolysis of (I) gives dimethylsilylene and decamethylcyclopentasilane, which in turn gives two more silylenes successively.[4] A degassed ethanol solution of (I) was irradiated with u.v. light and ethoxydimethylsilane,[5] an insertion product of dimethylsilylene into the O–H bond of ethanol, was obtained in 160% yield based on the consumption of (I). On the other hand, γ-irradiation of the same solution gave the product in only 6% yield even after all (I) was consumed. The results may be interpreted by means of the preferential reaction of (I) with radicals produced in the γ-radiolysis of ethanol.

To depress the contribution of the free-radical reactions, benzene which is stable against γ-irradiation was used as a solvent. Benzene solutions of (I) and ethanol were irradiated with various doses. The yields of ethoxydimethylsilane and decamethylcyclopentasilane are shown in Figure 1. The yield of ethoxydimethylsilane reaches 65%. Results for benzene, n-hexane, or ethanol as solvent are given in the Table for the purpose of comparison. As expected, benzene proved to be more favourable for dimethylsilylene generation than n-hexane or ethanol, both of which readily decompose giving free radicals by γ-irradiation.[6]

Dependence of $C_2H_5O(CH_3)_2SiH$ yield on solvent and its amount[a]

Solvent	Weight (g)	Yield of $C_2H_5O(CH_3)_2SiH$ (%)
Benzene	1.0	13.8
Benzene	2.0	20.2
Benzene	4.0	32.3
n-Hexane	2.0	9.2
Ethanol	3.2[b]	4.3

[a] (I) 0.04 mmol; C_2H_5OH 0.3 mmol; irradiation dose 44.8 Mrad. [b] Total amount of ethanol as reactant and solvent.

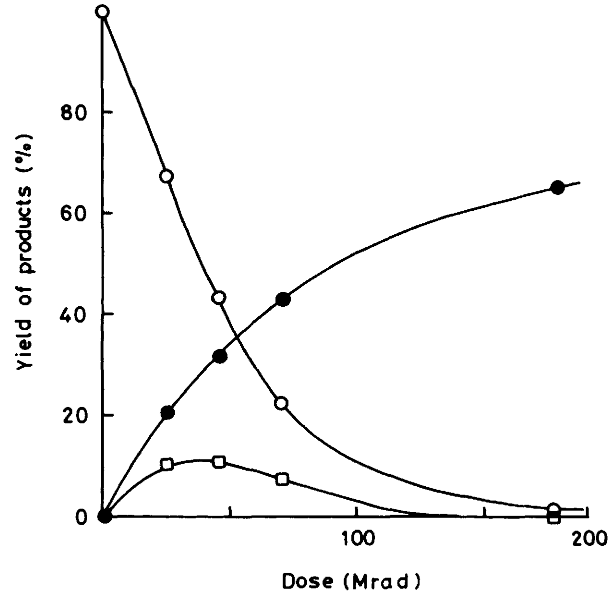

Figure 1. Dependence of the yield of the product on dose for γ-induced reaction of (I) (0.04 mmol) with ethanol (0.15 mmol) in benzene (0.4 g): ○, (I); ●, ethoxydimethylsilane; □, decamethylcyclopentasilane

Benzene is resistant to decomposition and it has a u.v. absorption band at *ca.* 255 nm which overlaps that of (I). The overlapping of the absorption band probably facilitates the energy-transfer process from benzene to (I). Therefore we can

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† Ref. 2 reported that silylene is generated by high-energy radiation[3] but the method is not suitable for general use because the nuclear reaction of gaseous phosphin, $^{31}P(n, p) \longrightarrow {}^{31}Si$, takes place.

explain the above results as follows. Benzene was first excited by γ-rays and the energy transferred to (**I**). Excited (**I**) decomposed to give dimethylsilylene and decamethylcyclopentasilane as with (**I**) subjected to u.v. irradiation. The fact that the yield of ethoxydimethylsilane increases with increasing amount of benzene as shown in the Table is consistent with our assumption that the reaction is induced by excitation of benzene by γ-rays.

Confirmation of Energy Transfer by Kinetic Studies using Anthracene as a Quencher.—The reactions described above can be denoted as equations (1)—(4).* Steady-state treatment of

$$C_6H_6 \xrightarrow{\gamma\text{-rays}} C_6H_6^* \quad (1)$$

$$C_6H_6^* \xrightarrow{k_2} C_6H_6 \quad (2)$$

$$C_6H_6^* + (\mathbf{I}) \xrightarrow{k_3} C_6H_6 + (\mathbf{I})^* \quad (3)$$

$$(\mathbf{I})^* \xrightarrow{k_4} (CH_3)_2Si\colon + \text{Cyclo}[(CH_3)_2Si]_5 \quad (4)$$

these reactions gives equation (5), where $R^0_{[(CH_3)_2Si]_5}$ is the production rate of decamethylcyclopentasilane, and R_1 denotes the rate of initiation [equation (1)] and is constant if the

$$\frac{1}{R^0_{[(CH_3)_2Si]_5}} = \frac{1}{R_1} + \frac{k_2}{R_1k_3}\cdot\frac{1}{[(\mathbf{I})]} \quad (5)$$

conditions of irradiation are constant. Benzene solutions of (**I**) were irradiated with 4.9 Mrad h^{-1} for 1 h and the $1/R^0_{[(CH_3)_2Si]_5}$ value obtained was plotted against $1/[(\mathbf{I})]$ in Figure 2.† The plot gave a straight line. From the values of the intercept and the slope, k_2/k_3 is 5.1×10^{-2} mol l^{-1}. This value implies that the rate of deactivation of $C_6H_6^*$ [equation (2)] is equal to that of energy transfer from $C_6H_6^*$ to (**I**) [equation (3)] when the concentration of (**I**) is 5.1×10^{-2} mol l^{-1}.

When anthracene (Ant) is added to the reaction system as a quencher, equations (6) and (7) take place.‡ From equations

$$C_6H_6^* + \text{Ant} \xrightarrow{k_6} C_6H_6 + \text{Ant}^* \quad (6)$$

$$(\mathbf{I})^* + \text{Ant} \xrightarrow{k_7} (\mathbf{I}) + \text{Ant}^* \quad (7)$$

(1)—(4), (6), and (7), the ratio of the rate of formation of decamethylcyclopentasilane in the absence of anthracene to that in its presence, $R^0_{[(CH_3)_2Si]_5}/R^A_{[(CH_3)_2Si]_5}$, is represented by equation (8). The solutions containing a fixed

$$\frac{R^0_{[(CH_3)_2Si]_5}}{R^A_{[(CH_3)_2Si]_5}} = \left\{1 + \frac{k_6[\text{Ant}]}{k_2 + k_3\,[(\mathbf{I})]}\right\}\cdot\left(1 + \frac{k_7}{k_4}[\text{Ant}]\right) \quad (8)$$

amount of (**I**) and varying amounts of anthracene were irradiated in the same way as above. The ratio, $R^0_{[(CH_3)_2Si]_5}/R^A_{[(CH_3)_2Si]_5}$, was plotted against [Ant]. Figure 3 presents such plots for two different values of [(**I**)]. First-order relations were obtained individually. These first-order relations, combined with the fact that the slopes are clearly dependent on [(**I**)], demand that the term $k_7[\text{Ant}]/k_4$ should be neglected. It follows that equation (8), a quadratic equation with respect to [Ant], is reduced to equation (9). The slopes, $k_6/\{k_2 + k_3[(\mathbf{I})]\}$, in Figure 3 were 41 and 67 l mol^{-1} for [(**I**)] 8.8×10^{-2} and 4.4×10^{-2}M, respectively. By using k_2/k_3 5.1×10^{-2} mol l^{-1}

$$\frac{R^0_{[(CH_3)_2Si]_5}}{R^A_{[(CH_3)_2Si]_5}} = 1 + \frac{k_6[\text{Ant}]}{k_2 + k_3\,[(\mathbf{I})]} \quad (9)$$

obtained above (Figure 2), the respective slopes give k_6/k_3 5.6 and 6.4. These two values are in satisfactory agreement, lending further support to the mechanism proposed here, *i.e.*, the formation of dimethylsilylene is well substantiated by energy transfer from benzene to (**I**).

Energy transfer seems to occur when the benzene solution of (**I**) is u.v.-irradiated. Cyclohexane (A) and benzene (B) solutions of (**I**) (0.1 mol l^{-1}) and hexamethylcyclotrisiloxane were irradiated with u.v. light for 15 min. The insertion product of di-

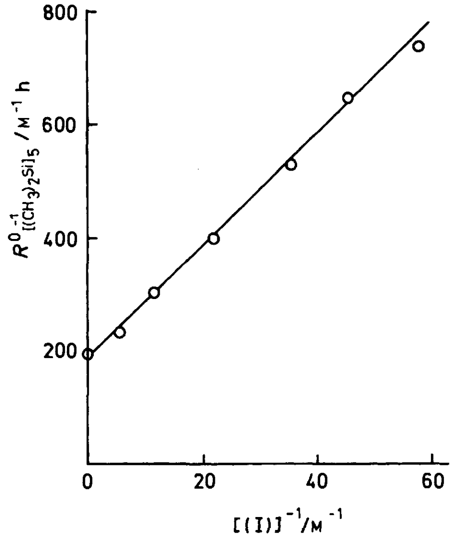

Figure 2. Plot of $1/R^0_{[(CH_3)_2Si]_5}$ *versus* $1/[(\mathbf{I})]$ for γ-induced reaction of (**I**) in benzene

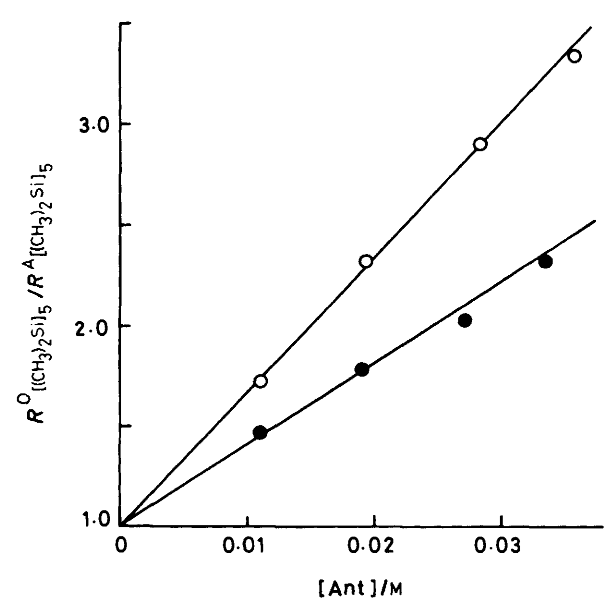

Figure 3. Plots of $R^0_{[(CH_3)_2Si]_5}/R^A_{[(CH_3)_2Si]_5}$ *versus* [Ant] for γ-induced reaction of (**I**) in the presence of anthracene in benzene: ○, [(**I**)] 4.4×10^{-2} mol l^{-1}; ●, [(**I**)] 8.8×10^{-2} mol l^{-1}

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* Direct production of excited (**I**) by γ-irradiation was neglected, since the concentration of (**I**) was low (*ca.* 3%).

† The decomposition of decamethylcyclopentasilane was negligible, because the conversion of (**I**) was smaller than 7%.

‡ Energy transfer from excited anthracene to (**I**) might occur, but this can be ruled out, since (**I**) was not reduced when a benzene solution of (**I**) and anthracene was irradiated with u.v. light which could be absorbed only by anthracene.

methylsilylene into the Si–O bond of the trisiloxane, octamethyl-3,5,7-trioxa-1,2,4,6-tetrasilacycloheptane,[7] was obtained in 120 and 78% from solutions A and B, respectively. Light of wavelength 254 ± 5 nm is absorbed by these solutions. The ε value of (I) is 2 000 at 255 nm ($\lambda_{max.}$) and that of benzene is *ca.* 100 at 255 nm ($\lambda_{max.}$). From these values and the concentration of (I), it is obvious that light of *ca.* 254 nm is completely absorbed by the solutions. A simple calculation shows that in solution B 15% of the incident light is absorbed by (I). Therefore, it is worth noting that (I) absorbed only 15% of the light and yet the insertion product amounted to 65% of that produced in solution A. This can be recognized as the result of energy transfer from benzene to (I) as in γ-irradiation, although the characterization of the excitation levels of benzene in the respective cases is not possible at present. Therefore, photo-induced reactions of (I) can be achieved efficiently even in benzene.

Experimental

Materials.—Dodecamethylcyclohexasilane (I) was prepared from dichlorodimethylsilane and lithium metal in THF.[8] Solvents were treated with molecular sieves 3A to remove water and were distilled under vacuum. The other commercially available reagents were used without further purification.

Procedure for Irradiation and Analysis.—Compound (I) (0.04 mmol) was dissolved in solvent (0.4 g) unless otherwise noted, and varying amounts of ethanol or anthracene was added in some experiments. The solutions in Pyrex or quartz tubes were degassed and were irradiated with γ-rays from a ^{60}Co or with a 100 W low-pressure mercury lamp, respectively. It was confirmed that the lamp emits light mainly at 254 ± 5 nm and at >290 nm by means of a photon-counting spectrometer (Unisoku PCS-400).

Identification and estimation of the products were carried out by g.l.c. using Yanagimoto G-3800 with a 3 m column containing 25% silicone DC-200 on Celite 545.

Photolyses of (I) *in the Presence of Hexamethylcyclotrisiloxane.*—Compound (I) (0.04 mmol) and the siloxane (0.23 mmol) were dissolved in cyclohexane (A) or benzene (B) (0.4 ml). Solutions A and B were irradiated with u.v. light for 15 min. Unchanged (I) was recovered in 24% (A) and 51% (B).

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