

THE PHOTOCHEMICAL REACTION OF BENZOYLTRIMETHYLSILANE WITH ORGANOSILICON HYDRIDES

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SUMMARY

Photolysis of benzoyltrimethylsilane in various hydrosilanes was investigated. It was found that the benzoylsilane was subjected to photoisomerization under neutral conditions to give an open-chain siloxycarbene intermediate which was inserted into the silicon-hydrogen bond of hydrosilanes, yielding a new type of compounds (III). The verification of the nature of the new reaction by means of a series of competition photolyses in hydrosilanes showed that the attacking species toward hydrosilanes has nucleophilic and almost ionic character.

INTRODUCTION

It has been shown that cyclic carbon ketones give cyclic oxacarbenes on photoisomerization with ring enlargement, as evidenced by trapping with olefins^{1,2} and alcohols¹⁻⁶ or by separation of the dimers^{1,2,5}. In silicon chemistry, Brook *et al.* recently suggested similar photoisomerization of an acylsilane to the corresponding siloxycarbene in the presence of base catalysts⁷ and also found evidence for the isomerization of a silacyclohexanone to the cyclic siloxycarbene⁸.

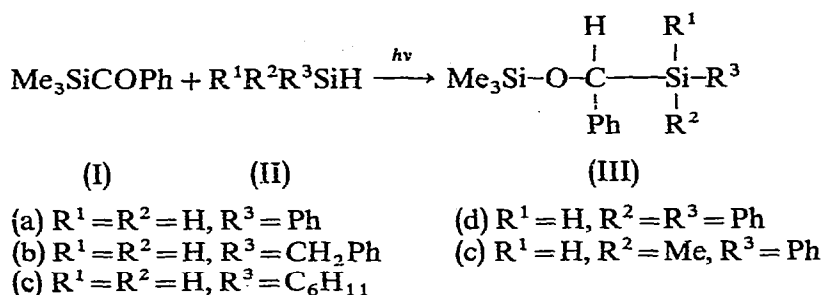
In connection with our study on structure/reactivity relationships in radical reactions of hydrosilanes⁹⁻¹⁵, it seemed of interest to investigate the photolysis of an acylsilane in hydrosilanes, since hydrosilanes are expected to be efficient trapping agents for the carbene¹⁶⁻²¹. We describe below the results of the photolysis of an open-chain acylsilane, benzoyltrimethylsilane, in various hydrosilanes, and the investigation of the nature of the reaction involving competition between various hydrosilanes. We show that the photolysis proceeds smoothly to give a high yield of compounds of a new type, *viz.* α -siloxysilicon derivatives, (III), which are not readily accessible by other methods. The reaction thus has not only mechanistic interest but also synthetic significance.

RESULTS AND DISCUSSION

Type of reaction

Photolysis of benzoyltrimethylsilane (I) in phenylsilane (IIa) proceeded readily to give the insertion product, [α -(trimethylsiloxy)benzyl]phenylsilane (IIIa)

in 93% yield. The results of elemental analysis and the molecular weight ($M^+ m/e$



286) of the product were consistent with the 1/1 adduct of the two reactants. The IR spectrum of (IIIa) exhibited characteristic bands at 2140 (Si-H), 1430 (Si-Ph), 1253 (Si-Me), 1119 (Si-Ph), 1050 (Si-O-C) and 848 (Si-Me) cm^{-1} . Structure (IIIa) was assigned on the basis of the NMR spectrum, which showed signals at : 7.34 (m); 7.16 (s) (PhSi and PhC, 10 H); 4.83 (t, HC, 1 H); 4.30 (d, HSi, 2 H) [$J(\text{HC-HSi}) 2.5 \text{ Hz}$]; -0.03 (s, MeSi, 9 H).

Similarly, photolysis of benzoyltrimethylsilane in hydrosilanes (IIb-d) gave the corresponding products, (IIIb-d), in high yields (84-98%), the products were characterized on the basis of the analysis and spectra. The reaction conditions and product yields are summarized in Table 1, while Tables 2, 3 and 4 list the analytical, IR, and NMR data, respectively.

TABLE 1

PHOTOLYSIS OF BENZOYLTRIMETHYLSILANE IN HYDROSILANES^a

Reactants			Time (h) ^b	Product	Yield (%)
(I) (mmol)	Hydrosilane	(mmol)			
2.02	PhSiH ₃ (IIa)	6.10	2.5	(IIIa)	93
2.06	PhCH ₂ SiH ₃ (IIb)	6.00	3.25	(IIIb)	98
0.98	C ₆ H ₁₁ SiH ₃ (IIc)	3.21	74	(IIIc)	91
1.05	Ph ₂ SiH ₂ (IIc)	3.21	48	(IIIc)	84
2.13	PhMeSiH ₂ (IIe)	6.16	185	(IIIe)	52 ^c
2.07	Et ₂ SiH ₂	6.25	100	(I)	83 ^d
2.04	Et ₃ SiH	5.10	298	(I)	70 ^d

^a The solution was externally illuminated with light of wave-length longer than 3300 Å (see Experimental), and product yield was determined by GLC analysis on a silicone column. ^b Illumination was stopped when the yellow color of the solution disappeared. ^c Yield of crude product. ^d Recovery.

Isolation of the 1/1 adduct in a pure state from the photolysis in phenylmethylsilane was accomplished only with considerable difficulty, the crude product (IIIe) being contaminated with phenyl benzyl ketone (see Experimental). Moreover, the photolysis of the acylsilane in diethyl- and triethylsilane was so slow that the expected products could not be isolated in appreciable amounts after the times indicated and only the starting materials were recovered. The formation of the isomeric, simple

TABLE 2

ELEMENTAL ANALYSES, MOLECULAR WEIGHTS, AND REFRACTIVE INDICES OF THE PRODUCTS

Compd.	Analysis (%)				Mol. wt. ^a	n _D ²⁵
	Found		Calcd.			
	C	H	C	H		
(IIIa)	67.34	7.99	67.07	7.74	286	1.5301
(IIIb)	67.75	8.13	67.94	8.05	300	1.5332
(IIIc)	65.29	9.79	65.69	9.65	292	1.5020
(IIId)	73.19	7.80	72.89	7.22	362	1.5633

^a From mass spectrum.

TABLE 3

IR DATA FOR THE PRODUCTS

Compd.	Characteristic peak ^a (cm ⁻¹)			
	Si-H	Si-Me	Si-O-C	Others
(IIIa)	2153 vs	1255 vs 847 vs	1054 vs	1430 s (Si-Ph) 1120 s (Si-Ph)
(IIIb)	2123 s	1253 vs 850 vs	1053 vs	
(IIIc)	2133 s	1253 vs 842 vs	1053 vs	1100 m (Si-C)
(IIId)	2125 m	1250 s 840 vs	1050 s	1425 s (Si-Ph) 1112 s (Si-Ph)
(IIIe)	2125 m	1250 vs 840 vs	1050 vs	1428 m (Si-Ph) 1115 s (Si-Ph)

^a Abbreviations: m, medium; s, strong; w, weak; vs, very strong.

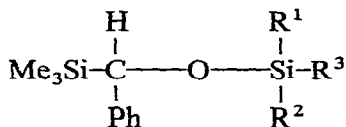
TABLE 4

NMR DATA FOR THE PRODUCTS

Compd.	Signal ^a (δ , ppm)
(IIIa)	7.34 (m); 7.16 (s) (PhSi and PhC, 10 H); 4.83 (t, HC, 1 H); 4.30 (d, HSi, 2 H) [$J(\text{HC-Si})$ 2.5 Hz]; -0.04 (s, MeSi, 9 H)
(IIIb)	7.14 (m, PhC, 10 H); 4.74 (t, HC, 1 H); 3.86 (d of t, HSi, 2 H) [$J(\text{HC-HSi})$ 3.7 Hz]; 2.18 (t, HC, 2 H); 0.03 (s, MeSi, 9 H)
(IIIc)	7.18 (s, PhC; 5 H); 4.78 (t, HC, 1 H); 3.61 (m, HSi, 2 H) [$J(\text{HC-Si})$ 2.5 Hz]; 1.95-0.88 (broad, H ₁₁ C ₆ , 11 H); 0.04 (s, MeSi, 9 H)
(IIId)	7.33 (m); 7.06 (s) (PhSi and PhC, 15 H); 4.98 (d, HSi, 1 H); 4.78 (d, HC, 1 H) [$J(\text{HC-Si})$ 2.1 Hz]; -0.08 (s, MeSi, 9 H)
(IIIe)	7.20 ^b (m, PhSi and PhC); 4.70 (d, HC, 1 H); 4.36 (m, HSi, 1 H); 0.25 (d, MeSi, 3 H); -0.03 (s, Me ₃ Si, 9 H)

^a Abbreviation: s, singlet; d, doublet; t, triplet; m, multiplet; J , coupling constant. ^b Integration could not be carried out because of overlapping with phenylprotons of the by-product, (see Table 1, footnote c).

addition products, (IV), in addition to (III) is also possible, but this type of compound could not be detected in any of the cases examined.



(IV)

These results appear to provide evidence for the formation of siloxycarbene intermediate by isomerization under neutral conditions of the photochemically excited acylsilane molecule having an open-chain system, this contrasts with the results obtained by Brook *et al.*, who isolated only the solvolysis product under neutral conditions⁷.

Relative reactivities and the nature of the reaction

In order to examine the trend of reactivity of various hydrosilanes and to throw light on the nature of the reaction, a series of competitions was carried out with various pairs of the compounds phenylsilane, benzylsilane, cyclohexylsilane and diphenylsilane, competing for the intermediate siloxycarbene. The relative rates of the reaction were calculated by the Doering equation (1)²² where R_a and R_b represent the peak

$$k_{\text{rel}} = \frac{k_a}{k_b} = \frac{P_a/R_a}{P_b/R_b} \quad (1)$$

areas of the analytical gas chromatography for two products derived from different hydrosilanes (a and b), P_a and P_b the initial concentrations of the two hydrosilanes and k_a/k_b the ratio of rate constants toward the attack of the active species from the acylsilane.

Table 5 summarizes the relative reactivities and lists also the sums of the relevant polar and steric substituent constants.

Obviously, the reactivity order of the hydrosilanes investigated toward the attacking species cannot be explained on the basis of polar effects alone, since phenylsilane reacts faster than cyclohexylsilane whereas diphenylsilane reacts slower than phenylsilane. The results can be correlated nicely, however, with the aid of the Taft²³ equation (2), in which both polar (σ^*) and steric (E_s) effects of substituents on silicon are taken into account.

TABLE 5

RELATIVE RATES FOR REACTIONS OF HYDROSILANES

Silane	k_{rel}^a	$\Sigma\sigma^*$	ΣE_s	$(\log k_{\text{rel}} - s \cdot \Sigma E_s)^b$
PhSiH ₃	26.90	+1.58	+1.58	+0.055
PhCH ₂ SiH ₃	16.90	+1.20	+2.10	-0.599
C ₆ H ₁₁ SiH ₃	1.00	+0.83	+1.69	-1.470
Ph ₂ SiH ₂	0.849 ^c	+1.69	-0.56	+0.416

^a Average from duplicated runs. ^b $s=0.87$. ^c The value was calculated by multiplying the observed k_{rel} values by 1.5 to take account of the presence of two hydrogens in diphenylsilane and three in cyclohexylsilane.

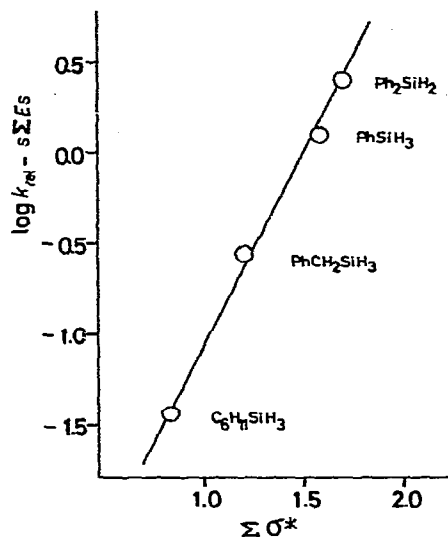
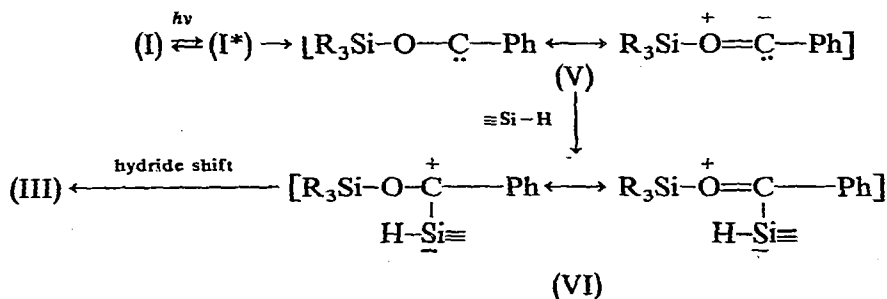


Fig. 1. Plot of $(\log k_{rel} - s \cdot \Sigma E_s)$ versus $\Sigma \sigma^*$.

$$\log \frac{k_a}{k_b} = \rho^* \cdot \Sigma \sigma^* + s \cdot \Sigma E_s \quad (2)$$

Thus, an excellent correlation (Fig. 1) was found to exist between the reactivities listed in Table 5 and the polar substituent constants by solving eqn. (2) for ρ^* and s on the basis of the method of least squares²⁴. The linear relationship can be expressed in terms of $\rho^* = +2.13$ and $s = 0.87$, with a correlation coefficient of 0.997. The steric effects of substituents are not unexpected in view of the bulk of the attacking carbene species. With respect to the polar effect, the sign and the value of ρ^* indicate that the reaction has a nucleophilic character, and approaches an ionic nature. These observations lead us to interpret the photochemical reaction as proceeding as represented in Scheme 1, in which nucleophilic attack of the siloxycarbene (V) on the silicon atom of hydrosilanes occurs to form a pentavalent silicon complex (VI) with the *d*-orbital participation. The complex then undergoes a hydride shift²⁵ from the silicon to the adjacent carbon atom, leading to the neutral product (III).

SCHEME 1



The fact that in a control experiment without a hydrosilane, the starting acyl-

silane remained almost unchanged, even after illumination for a long time, has an important implication. The formation of the complex (VI), which is possible only when a hydrosilane is present, might be energetically favorable, since pentavalent silicon intermediates have been proposed in many other cases involving nucleophilic substitution reaction for a variety of organosilicon compounds²⁶.

Finally, it should be noted that the results of the Taft correlations are in accord with the qualitative observation by Brook *et al.*⁸ that a cyclic siloxycarbene adds to an electron-deficient olefin rather in preference to a simple olefin.

EXPERIMENTAL

All the boiling points are uncorrected. The IR spectra were recorded with neat liquid films, by the sandwich method, on a Hitachi EPI-G3 spectrometer. The NMR spectra were measured on a Varian A-60D spectrometer in CCl₄ solution with tetramethylsilane as internal standard. Mass spectra were obtained with a Hitachi RMU-6L spectrometer.

Materials

Benzoyltrimethylsilane (b.p. 68°/0.5 mmHg, lit.²⁷ 42–44°/0.02 mmHg) was prepared according to the method described by Brook *et al.* Phenylsilane (b.p. 118°, lit.²⁸ 120°), benzylsilane (b.p. 149°, lit.²⁹ 65–68°/35–40 mmHg), cyclohexylsilane (b.p. 117°, lit.³⁰ 118°), diphenylsilane (b.p. 113–114°/9 mmHg, lit.³¹ 75–76°/0.5 mmHg), phenylmethylsilane (b.p. 140°, lit.¹⁶ 120°/730 mmHg), and diethylsilane (b.p. 54.5°, lit.²⁸ 55.9°) were prepared by lithium aluminum hydride reduction of the corresponding chlorosilanes, as described in the literature. Triethylsilane (b.p. 107°, lit.³² 108.7°) was obtained from the reaction of trichlorosilane and ethylmagnesium bromide in ether. Physical constants and GLC analyses confirmed the purity of the materials.

Typical preparative photolysis

Benzoyltrimethylsilane(I) (2.02 mmol) and phenylsilane (IIa) (6.10 mmol) were placed in a Pyrex tube (6 mm internal diameter) in which the clear yellow solution was degassed several times, sealed, and then externally illuminated through a filter (0.1 M naphthalein solution in cyclohexane; 10 mm thick) for 2½ h using a 400 W high-pressure lamp, after which time the color had disappeared, indicating that the acylsilane was completely consumed. The resulting solution was subjected to GLC analysis with a silicone column. Among the many products formed, the major product, giving rise to the largest peak, was isolated by preparative GLC. From the elemental analysis, IR spectrum, NMR spectrum and the mol. wt. (from mass spectrum), the product was identified as [α -(trimethylsiloxy)benzyl]phenylsilane (IIIa).

In separate experiments involving photolyses without the use of the filter, under otherwise identical conditions, the yields of the product (III) were generally somewhat (ca. 10%) lower. We were unable to obtain a pure 1/1 adduct from the photolysis of benzoyltrimethylsilane in phenylmethylsilane; the GLC peak for this adduct showed a shoulder arising from a minor impurity. The fraction corresponding to the partially resolved peak was isolated by GLC, and part of it crystallized on standing (m.p. 55.5°). An IR spectrum of the solid material was superposable on that of an authentic sample. The NMR and IR spectra of the main component are consis-

tent with structure (IIIe), though the collected sample was not pure enough to give accurate analytical data.

Competition photolyses

Benzoyltrimethylsilane was mixed with approximately 6- to 10-fold excess of two different hydrosilanes, and the resulting solution was subjected to photolysis as described above. The reactivity ratio for the two hydrosilanes was calculated from eqn. (1), and the relative reactivities are expressed by taking cyclohexylsilane as the standard (see Table 5).

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