PHOTOCHEMICAL REACTION OF BENZOYLTRIMETHYLSILANE WITH SUBSTITUTED PHENYLSILANES

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Summary

Photochemical reaction of benzoyltrimethylsilane (I) with substituted phenylsilanes, $XC_6H_4SiH_3$ (X = m-CF_3, m-Cl, p-Cl, H, m-Me, p-Me-p-MeO) (II), gave [α-(trimethylsiloxy)benzyl]arylsilanes (III) in excellent yields, the formation of which can be accounted for in terms of the insertion reaction of the siloxycarbene, $Me_3SiO=\overset{+}{\overset{\bar{}}{C}}Ph$ (IV), derived by photoisomerization of I into the Si—H bond of the arylsilanes (II). Relative rates of m- and p-substituted phenylsilanes toward the attacking species correlated well with Hammett σ values and gave a ρ value of +1.82. The correlation with Taft σ* values for the aryl group on the central silicon gave a ρ* value of +2.34. It was found that hydrogen isotope effect in the reaction is very small (k_H/k_D = 1.26 ± 0.10). From these results the reaction mechanism is discussed.

Introduction

We have previously shown [1] that irradiation of benzoyltrimethylsilane in hydrosilanes such as phenylsilane, benzylsilane, cyclohexylsilane and diphenylsilane yielded organosilicon compounds which are not readily accessible by other methods. The reaction can be interpreted in terms of photoisomerization of the silyl ketone to phenyltrimethylsiloxycarbene [2,3], which inserts into the silicon—hydrogen bond. An alternative reaction path, which involves homolytic Si—H addition to the carbonyl bond, is not likely since it would give different products. It has been shown that the insertion reaction is governed by both polar and steric effects of the substituents on the silicon hydride by means of the Taft treatment [4] using these silanes [1].

We have carried out the photochemical reaction of benzoyltrimethylsilane with several m- and p-substituted phenylsilanes in order to examine the Hammett relationship in this reaction.

Results and discussion

The photochemical reaction of benzoyltrimethylsilane (I) with substituted phenylsilanes IIa-IIg proceeded readily to give [α-(trimethylsiloxy)benzyl]aryl-silanes IIIa-IIIg in excellent yields (Table 1). All the products thus obtained were characterized on the basis of analytical data and their spectra (Table 2).

$$Me_3SiCOPh + XC_6H_4SiH_3 \xrightarrow{h\nu} Me_3SiOCHPhSiH_2C_6H_4X$$
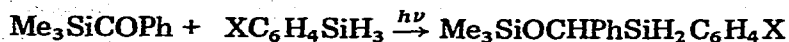
$$\text{(I)} \qquad\qquad \text{(II)} \qquad\qquad\qquad \text{(III)}$$

(a) X = m-CF$_3$
(b) X = m-Cl
(c) X = p-Cl
(d) X = H
(e) X = m-Me
(f) X = p-Me
(g) X = p-MeO

The reason why the formation of the trimethylsiloxycarbene rather than that of the trimethylsilyl radical predominates remains unclear, but the ob-served direction of the reaction might be due to the ease with which the hydro-silane reacts with the nucleophilic siloxycarbene using its readily accessible vacant d-orbitals.

Relative rates of the reactions of substituted phenylsilanes with the ben-zoylsilane were determined by means of a series of competitive reactions in which various pairs of the hydrosilanes competed for the active reagent. The relative rates were calculated by the Doering equation (eqn. 1) [5] where P_a and P_b represent the product concentrations derived from different hydrosilanes (a and b), S_a and S_b the initial concentrations of the two hydrosilanes and k_a/k_b

TABLE 1

PHOTOCHEMICAL REACTION OF BENZOYLSILANE (I) WITH SUBSTITUTED PHENYLSILANES $(XC_6H_4SiH_3)^a$

Reactants				Time (min)	Product	Yield [b] (%)
I (mmol)	Phenylsilane					
	No.	X	mmol			
1.00	IIa	m-CF$_3$	3.00	21	IIIa	80
0.99	IIb	m-Cl	3.02	40	IIIb	99
1.00	IIc	p-Cl	2.80	51	IIIc	80
1.23	IId	H	3.62	125	IIId	74
0.99	IIe	m-Me	2.03	135	IIIe	87
0.96	IIf	p-Me	1.96	170	IIIf	85
1.06	IIg	p-MeO	3.07	205	IIIg	91

[a]Irradiation was stopped when the yellow color of the initial solution disappeared and the product yield was determined by GLC analysis using the internal standard on a silicone column. [b]Based on benzoyl-trimethylsilane used.

TABLE 2

ANALYTICAL RESULTS AND PROPERTIES OF THE PRODUCTS

Compound	Formula	Analysis found (calcd.) (%)		Mass spec. M^+	IR (cm^{-1}) (neat)			NMR (δ, ppm)[a] (CCl_4)			n_D^{20}
					Characteristic peak						
		C	H		Si–H	Si–Me	Si–O–C	CHPh (t)[b]	SiH (d)[b]	SiMe₃ (s)[b]	
IIIa	$C_{17}H_{21}F_3OSi$	57.78 (57.60)	5.78 (5.97)	354	2150	1256	1055	4.94	4.41	0.02	1.4938
IIIb	$C_{16}H_{21}ClOSi$	60.27 (59.87)	6.63 (6.50)	320	2155	1252	1055	4.86	4.31	0.02	1.5390
IIIc	$C_{16}H_{21}ClOSi$	60.30 (59.87)	6.53 (6.59)	320	2150	1253	1054	4.88	4.33	0.05	1.5409
IIId	$C_{16}H_{22}OSi$	67.34 (67.07)	7.99 (7.74)	286	2153	1255	1054	4.88	4.36	0.03	1.5323
IIIe	$C_{16}H_{24}OSi$	67.88 (67.04)	7.76 (8.05)	300	2150	1251	1054	4.87	4.36	0.03	1.5308
IIIf	$C_{17}H_{24}OSi$	67.69 (67.94)	7.91 (8.05)	300	2150	1250	1053	4.86	4.33	0.04	1.5321
IIIg	$C_{17}H_{24}O_2Si$	64.80 (64.50)	7.34 (7.64)	316	2145	1254	1054	4.84	4.32	0.03	1.5424

[a] Proton chemical shift of $CHCl_3$ (436 Hz from TMS) was used as an internal standard. [b] t, triplet (1H), d, doublet (2H), s, singlet (9H).

TABLE 3

COMPETITION REACTION WITH VARIED MOLAR RATIO OF REACTANTS[a]

S_a	S_b	S_a/S_b	k_a/k_b
		0.505	0.732
p-MeC$_6$H$_4$SiH$_3$	C$_6$H$_5$SiH$_3$	0.839	0.754
		1.973	0.755

[a]Reaction conditions: $S_a + S_b$, 10-15 mmol; benzoyltrimethylsilane, 1 mmol.

the ratio of rate constants of the attack of the active species derived from the acylsilane.

$$k_{rel} = k_a/k_b = \frac{P_a/S_a}{P_b/S_b} \tag{1}$$

The applicability of the equation was tested by determining the relative reactivities of p-methylphenylsilane and phenylsilane at various concentrations (Table 3). The constancy of k_{rel} in the experiments allows us to conclude that eqn. 1 does apply.

The relative rate constants determined for various substituted phenylsilanes are listed in Table 4 and expressed in terms of $k(PhSiH_3) = 1$. Table 4 shows clearly that an electron-attracting substituent increases the relative rate constant of the hydrosilane. Figure 1, a plot of log k_{rel} vs. σ, shows that the values obtained fit the Hammett equation [4] quite well. The slope of the line obtained by the method of least squares gave a ρ value of +1.82 with a correlation coefficient of 0.981. The observed trend agrees well with our previous finding [1] that the photochemical reaction of benzoyltrimethylsilane with a set of hydrosilanes, including phenylsilane, benzylsilane, cyclohexylsilane and diphenylsilane, involves nucleophilic attack by the intermediate siloxycarbene, Me$_3$SiOC-Ph, on the hydrosilane. The magnitude of the ρ value suggests that charge separation in the transition state of the reaction is large. It is of interest to note at this point that the Hammett relationship found in the present system is accom-

TABLE 4

RELATIVE RATE CONSTANTS FOR THE REACTIONS OF SUBSTITUTED PHENYLSILANES, XC$_6$H$_4$SiH$_3$

X	σ	$\Sigma\sigma^{*a}$	k_{rel}	Average
m-CF$_3$	0.415	1.87	8.28; 8.20	8.24
m-Cl	0.373	1.83	8.38; 8.01	8.20
p-Cl	0.227	1.73	3.50; 3.54	3.52
H	0.00	1.58	1.00	1.00
m-Me	—0.069	1.46	0.857;0.856	0.857
p-Me	—0.170	1.44	0.761;0.754	0.758
p-MeO	—0.268	1.34	0.619;0.612	0.616

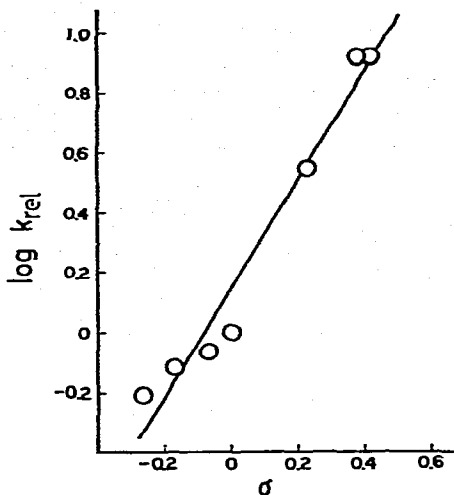[a]Sum of Taft σ^* values for the three substituents on silicon (see ref. 6 and 7).

Fig. 1. Plot of the relative rate constant vs. Hammett substituent constant σ.
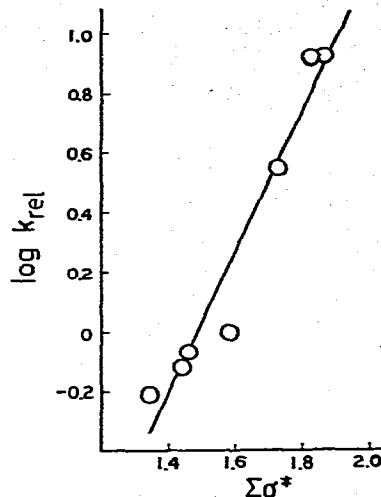
Fig. 2. Plot of the relative rate constant vs. sum of Taft $\sigma^\star$ values for three substituents on silicon.

modated with a ρ value of +1.82, whereas the Taft treatment of the previous rate data affords a $\rho^\star$ value of +2.13. Although these two values are sufficiently close to each other, the direct comparison of the two values is far less meaningful unless a common scale for the relationship·between the ρ and $\rho^\star$ scales is available. Quite recently, supporting evidence for the existence of such a scale has been offered [6] and $\rho^\star$ values for a number of substituted phenyl groups have been defined [6,7]. Thus, the relative rates were also plotted against the summation of Taft $\sigma^\star$ values for a substituted phenyl group and two hydrogens of silicon. Again, in Fig. 2 a linear correlation is found with a slope of +2.34 and a correlation coefficient of 0.973. The two values are in good agreement. Since in the present system the steric requirement in the transition state seems to be constant for all cases, it would appear that only the polar effects of the substituents at the reaction center are important. In the previous case [1], the relative rates of hydrosilanes were correlated well with the aid of the Taft equation [4] in which both polar ($\sigma^\star$) and steric (Es) effects of substituents on the silicon hydride were taken into account.

In order to gain further information about the reaction, the relative rate constant of $PhSiH_3$ versus $PhSiD_3$ was measured by allowing them to compete for the intermediate siloxycarbene. The relative yields were measured by the NMR method, in which, by integrating the signals of the methyl hydrogens of the trimethylsilyl group and the hydrogens at the tertiary carbon and secondary silicon of the product mixtures, which were isolated by means of preparative GLC, the relative amounts (P_H and P_D) of the two products derived from $PhSiH_3$ and $PhSiD_3$ could be determined. The value for k_H/k_D calculated from eqn. 1 by the use of P_H and P_D instead of P_a and P_b, respectively, was 1.26 ± 0.10, a rather small hydrogen isotope effect, as expected.

For the siloxycarbene insertion reaction into the Si—H bond, the following four mechanisms are possible: (a) an insertion of the carbene species into the

Si—H bond via a three-centered transition state [8-10]; (b) a radical abstraction of a hydrogen atom followed by a rapid radical coupling step [11]; (c) a hydride abstraction, followed by collapse of the resulting tight ion pair; (d) an attack of a nucleophilic carbene at silicon of the Si—H bond to form a pentavalent silicon complex.

Mechanisms (a) and (b) are less likely since the large values of ρ or $\rho^{\star}$ would reflect a considerable charge separation in the transition state. Of the remaining two mechanisms, we prefer mechanism (d) because of the observed small hydrogen isotope effect, although the mechanism (c) might not be ruled out, as long as there was little Si—H bond breaking in the transition state.

Thus, as previously proposed [1], the mechanism may be depicted as follows:

$$Me_3Si\underset{\underset{O}{\parallel}}{C}Ph \xrightarrow{h\nu} \left[Me_3SiO\underset{\cdot\cdot}{C}Ph \longleftrightarrow Me_3Si\overset{+}{O}=\overset{-}{C}Ph \right]$$

(IV)

$$\equiv SiH \downarrow$$

$$III \xleftarrow{\text{hydride shift}} \left[Me_3SiO\overset{+}{\underset{\underset{HS\underline{i}\equiv}{|}}{C}}Ph \longleftrightarrow Me_3Si\overset{+}{\underset{\underset{HS\underline{i}\equiv}{|}}{O}}=CPh \right]$$

(V)

In this scheme a nucleophilic attack of siloxycarbene IV at the silicon atom of the hydrosilane to form the Si—C bond is rate-determining, and the subsequent hydride shift of the pentavalent silicon complex V [12] to give the product III appears to be fast, as evidenced by the hydrogen isotope effect of only 1.26 [13].

Recently, it has been shown that photolysis of acylsilanes in non-polar solvents forms a silyl and an acyl radical [14,15], while photolysis in polar solvents such as alcohols [2,3] gives rise to a siloxycarbene intermediate as an active species. In the present reaction, however, the product can be explained only by the insertion of the trimethylsiloxycarbene into the Si—H bond.

Experimental

All the boiling points are uncorrected. IR spectra were recorded on neat liquid films with a Hitachi EPI-G3 spectrometer, and NMR spectra were measured in CCl_4 solution using a Varian A-60D spectrometer. Mass spectra were obtained with a Hitachi RMU-6L spectrometer. GLC analyses were conducted using an Okhura Model 1700 gas chromatograph. Irradiation was performed by means of a 400 W high pressure mercury lamp in a cooling bath with running water at 21°C.

Materials

Benzoyltrimethylsilane and the substituted phenylsilanes were prepared as described previously [1,6,16]. *m*-Trifluoromethylphenylsilane is a new compound and was prepared by the reduction of the corresponding chlorosilane with lithium aluminium hydride (b.p. 128-129.5°C; n_D^{20} 1.4446; Anal. found: C, 48.06; H,

3.68. $C_7H_7F_3Si$ calcd.: C, 47.71; H, 4.00%). This compound showed an IR absorption peak at 2170 cm^{-1} [ν(Si—H)] and NMR signals at δ 4.26 (Si—H) and 7.28-7.98 ppm (phenyl protons).

Physical constants and GLC analyses confirmed the purity of these materials.

Typical preparative reaction

A mixture of benzoyltrimethylsilane (I) (0.99 mmol) and *m*-chlorophenylsilane (IIb) (3.02 mmol) was placed in a Pyrex tube (6 mm internal diameter) in which the clear yellow solution was degassed several times, sealed, and then irradiated for 40 min using a 400 W high pressure mercury lamp, after which time the color had disappeared, indicating that the benzoylsilane was completely consumed. The resulting solution was subjected to GLC analysis with a silicone column (2 m × 4 mm, 20% SE-30 on Celite 545, 200-230°C). The product was isolated by preparative GLC using the same column. From the elemental analysis and the spectral data (IR, NMR and mass spectra), the product was identified as [α-(trimethylsiloxy)benzyl]-*m*-chlorophenylsilane (IIIb). The yield by GLC was 99% (based on I), thermal conductivity correction being applied.

Competition reactions

Benzoyltrimethylsilane was mixed with two different substituted phenylsilanes in molar ratio 1/5/5 and the resulting solution was irradiated and then analyzed by GLC as described above. The relative reactivities for the two hydrosilanes were calculated from eqn. 1, and are expressed by taking phenylsilane as the standard (Table 4).

Acknowledgement

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