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## ON THE MECHANISM OF THE REACTION OF ORGANOSILICON HYDRIDES WITH DICHLOROCARBENE GENERATED FROM SODIUM TRICHLOROACETATE

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### Summary

The reaction of sodium trichloroacetate with various organosilicon hydrides in 1,2-dimethoxyethane was investigated and the products,  $\alpha$ -triorganosilyldichloromethanes, were formed in yields of 20-50%. The relative rate constants of these hydrosilanes in such insertion reactions of dichlorocarbene were determined by means of competition reactions. The relative reactivities of a series of alkyl substituted hydrosilanes correlate well with the Taft  $\sigma^*$  constants for the substituents on silicon, with a  $\rho^*$  value of -1.07, and a series of aryl substituted hydrosilanes also shows good linear correlation of the  $\log k_{rel}$  values with Taft  $\sigma^*$  constants, giving a  $\rho^*$  value of -1.18. The hydrogen isotope effect in the reaction,  $k_H/k_D$   $1.26 \pm 0.02$ . Based on the observed results, it was concluded that the insertion of  $CCl_2$  into the Si-H bond proceeds by a three-center concerted process in which charge separation in the transition state is not large, as suggested by Seyferth for the related  $PhHgCCl_2Br/XC_6H_4SiMe_2H$  reactions.

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### Introduction

In previous papers we have reported on the insertion into the Si-H bond by trimethylsilyloxycarbene, derived from benzoyl trimethylsilane by photochemical isomerization [1,2] and of carbomethoxycarbene, generated by the thermal decomposition of methyl diazoacetate in the presence of copper catalyst [3]. The characterization of these two reactions with the aid of the Hammett or Taft treatment showed that trimethylsilyloxycarbene is a nucleophilic species and that the reaction proceeds by an ionic pathway, while the carbomethoxycarbene is electrophilic, with only a small ionic contribution to the transition state.

It has been shown by Seyferth et al. that sodium trichloroacetate can be employed as a precursor of dichlorocarbene ( $CCl_2$ ) which inserts into the Si-H bond of triethylsilane [4]. However, no further studies of this reaction have



ferent hydrosilanes (a and b),  $S_a$  and  $S_b$  the initial

$$k_{rel} = k_a/k_b = \frac{P_a/S_a}{P_b/S_b} \quad (2)$$

concentration of the two hydrosilanes and  $k_a/k_b$  the ratio of rate constants for attack by the reactive species derived from the trichloroacetate. The applicability of the equation was tested by determining the relative rates of  $p\text{-ClC}_6\text{H}_4\text{-SiMe}_2\text{H}$  ( $S_a$ ) and  $\text{C}_6\text{H}_5\text{SiMe}_2\text{H}$  ( $S_b$ ) using different initial concentrations (the molar ratio,  $S_a/S_b$  0.5, 1.00 and 2.00), resulting in reasonably constant  $k_{rel}$  values (0.574, 0.545 and 0.553, respectively) which allow us to conclude that eq. 2 does apply.

Table 2 summarizes the relative rate constants determined for various substituted hydrosilanes, based on  $k_{\text{Et}_3\text{SiH}}$  as the standard, and lists the Hammett  $\sigma$  values for the substituent on the benzene ring of the aryldimethylsilanes and in the last column the sums of the Taft  $\sigma^*$  values for the three substituents on silicon for all the hydrosilanes tested. From Table 2 it is seen that in the series of aryldimethylsilanes an electron-donating substituent increases that relative rate of the reaction. In Fig. 1  $\log k_{rel}$  values are plotted against the Hammett  $\sigma$  values for the substituents. The slope of the line was found to be  $-0.970$  by the method of least squares, with a good correlation coefficient ( $\gamma$  0.996). Previously, Seyferth et al. had shown that in the  $\text{ArSiMe}_2\text{H}/\text{PhHgCCl}_2\text{Br}$  reaction in benzene the Hammett treatment of the  $k_{rel}$  correlated well with  $\sigma$  values, giving  $\rho$   $-0.632$  [6]. It is not surprising that the  $\rho$  value in the present study is greater than that of the phenylmercurial, since different reaction conditions were employed in the two systems. The greater  $\rho$  value in our system, despite the higher reaction temperature used, may be attributable to use of the more polar solvent DME, rather than to the different precursors of the attacking species, since in the solvent DME (dielectric constant  $\epsilon$ , 7.20) a stabilization of the ionic structure in the transition state by its solvation may be expected. This is not the case in benzene medium ( $\epsilon$ , 2.28).

TABLE 2  
RELATIVE RATES FOR THE REACTION OF VARIOUS HYDROSILANES

Hydrosilane	$k_{rel}^a$	Average	$\sigma$	$\Sigma\sigma^*$
$\text{Me}_3\text{SiSiMe}_2\text{H}$	248; 244	246		$-0.87^b$
$p\text{-MeOC}_6\text{H}_4\text{SiMe}_2\text{H}$	153; 150	152	$-0.27$	0.36
$p\text{-MeC}_6\text{H}_4\text{SiMe}_2\text{H}$	129; 125	127	$-0.17$	0.46
$\text{Et}_3\text{SiH}$	100	100		$-0.30$
$\text{C}_6\text{H}_5\text{SiMe}_2\text{H}$	95.0; 94.4	94.7	0.00	0.60
$p\text{-ClC}_6\text{H}_4\text{SiMe}_2\text{H}$	52.3; 50.8	51.6	0.23	0.75
$m\text{-CF}_3\text{C}_6\text{H}_4\text{SiMe}_2\text{H}$	34.9; 31.6	33.3	0.42	0.89
$\text{C}_6\text{H}_5\text{SiMeH}_2$	20.6; 18.1	19.4		1.09
$n\text{-Bu}_2\text{SiH}_2$	16.7; 17.8	17.3		0.23
$\text{PhCH}_2\text{SiMe}_2\text{H}$	9.96; 10.5	10.2		0.71
$\text{PhSiH}_3$	5.50; 7.00	6.25		1.58
$\text{PhCH}_2\text{SiH}_3$	1.83; 1.51	1.67		1.20

<sup>a</sup> Due to the differences in number of hydrogens bonded to silicon in hydrosilanes, consideration to reconcile the observed  $k_{rel}$  values was made. <sup>b</sup> Value calculated from  $J^{29}\text{Si-H}$  by the use of the equation in ref. 7.

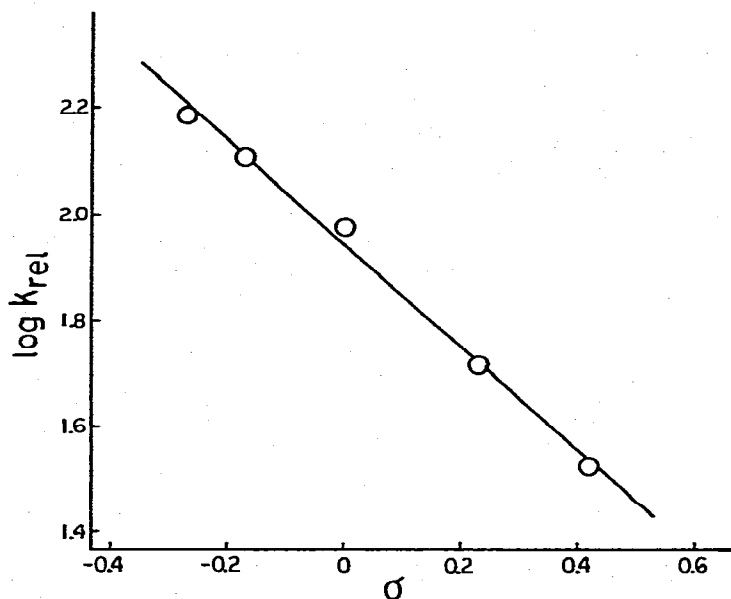


Fig. 1. Plot of the relative rate constant vs. Hammett substituent constant  $\sigma$ .

Generally, if a direct comparison of reaction constants obtained in some related reactions is possible on a common scale, it is very convenient and helpful in the elucidation of the nature of the reactions. Recently, we have been successful in obtaining such a common scale for the relationship between the  $\sigma$  and  $\sigma^*$  scale and to determine the Taft  $\sigma^*$  constants for substituted phenyl groups [7,8]. Hence, the relative rates were again plotted against the sum of the Taft  $\sigma^*$  values for the three substituents on silicon in the hydrosilanes. Employing the  $\sigma^*$  values for the series of aryl dimethylsilanes, the plots of  $\log k_{rel}$  vs.  $\Sigma\sigma^*$  shown in Fig. 2 demonstrate that all the hydrosilanes are accommodated by two separate lines. One of these is for the series of the hydrosilanes with alkyl group(s) and the other for the series with aryl group(s) on silicon. The two lines are parallel to each other and fit the Taft equation quite well in each series. The slope of the lines, obtained by the method of least squares, gave a  $\rho^* -1.07$  with  $\gamma$  0.970 for the alkyl series and  $\rho^* -1.18$  with  $\gamma$  0.997 for the aryl series, respectively.

From the sign and magnitude of the  $\rho^*$  values, it is clear that the reaction involves electrophilic attack by  $\text{CCl}_2$  at the Si-H bond to form the insertion products and that the charge separation in the transition state of the reaction is not so large. On the other hand, as seen in Fig. 2, the relative rates of the aryl hydrosilanes are greater than those of the alkylhydrosilanes by approximately one log unit for the same  $\sigma^*$  values. This acceleration in the rates of the reactions for the series of arylsilanes may be interpreted in terms of a mesomeric electron-donating effect of the ring  $\pi$  system toward the adjacent positive silicon via (p-d)  $\pi$  interaction during the electrophilic attack by  $\text{CCl}_2$  on the Si-H bond.

In order to obtain further information concerning the reaction, the kinetic isotope effect,  $k_H/k_D$ , was determined by allowing  $\text{PhSiMeH}_2$  and  $\text{PhSiMeD}_2$  to

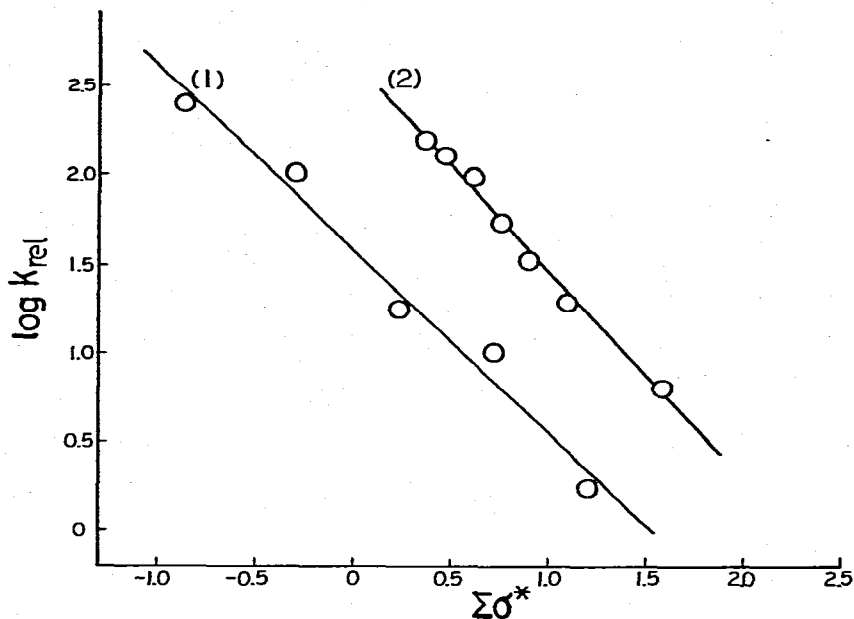


Fig. 2. Plot of the relative rate constant vs. sum of Taft  $\sigma^*$  values for three substituents on silicon: (1) alkyl substituted hydrosilanes; (2) aryl substituted hydrosilanes.

compete for the active species,  $\text{CCl}_2$ . The relative amounts of the two products were determined by the NMR method as previously reported [2] and the value for  $k_{\text{H}}/k_{\text{D}}$  calculated by eq. 2 was  $1.26 \pm 0.02$ . This is a small hydrogen isotope effect, as expected from the literature, in which the isotope effect for insertion reaction of  $\text{CCl}_2$  with  $n\text{-Bu}_3\text{SiH}$  and  $n\text{-Bu}_3\text{SiD}$  was found to be  $k_{\text{H}}/k_{\text{D}}$  1.23 [9,10].

The mechanism for the insertion of  $\text{CCl}_2$ , as generated from  $\text{PhHgCCl}_2\text{Br}$ , into the Si-H bond of hydrosilanes was proposed to be a three-center concerted process by Seyferth et al. [6] and Sommer et al. [11], in which the transition state involves attack by the electrophile at the Si-H bond through a three-center array of atoms rather than a linear array so as to lose the Si-H bending modes with the retention of configuration around the silicon. This proposed triangular transition state process is quite compatible with the observations of our present study of  $\text{CCl}_3\text{CO}_2\text{Na}/\text{R}^1\text{R}^2\text{R}^3\text{SiH}$  reactions. Recently, Seyferth and Cheng have reported that the isotope effect in the insertion of  $\text{CCl}_2$  into a benzylic C-H bond was  $k_{\text{H}}/k_{\text{D}}$  2.5 and this reaction also proceeds to form the products via a three-center concerted process similar to that of the  $\text{CCl}_2$ -insertion into the Si-H bond [12,13].

It is of interest to compare the reaction constants in the present study with those of previously studied related reactions of other carbenes and carbenoid intermediates. All the pertinent data are listed in Table 3. Also included are the sums of Taft  $\sigma^*$  values for X and Y in  $\text{CXY}$  which represents the divalent species to be inserted into the Si-H bond. Since this value reflects the polar character (i.e., electrophilicity or nucleophilicity) of the  $\text{CXY}$  species, the comparisons of the  $\Sigma\sigma^*$  values and the reaction constants between the reactions listed are useful in obtaining an understanding of the nature of the reactions. As shown pre-

TABLE 3

COMPARISON OF REACTION CONSTANTS ( $\rho$  AND  $\rho^*$ ) FOR THE INSERTION REACTION OF CXY INTO Si—H BOND OF HYDROSILANES

No.	Reaction system and conditions (Solvent; Temp.; etc.)	Attacking species		Reaction constants		Ref.
		CXY	$\Sigma\sigma^*$	$\rho^a$	$\rho^*^b$	
1	$N_2CHPh/R^1R^2R^3SiH$ (none; 22°C; $h\nu$ )	CHPh	+1.09	—	0	17
2	$N_2CHCO_2Me/XC_6H_4SiMe_2H$ (none; 90°C; Cu cat.)	CHCO <sub>2</sub> Me	+2.49	-0.26	-0.36	3
3	$PhHgCCl_2Br/XC_6H_4SiMe_2H$ (PhH; 79°C)	CCl <sub>2</sub>	+5.88	-0.63	-0.95 <sup>c</sup>	6
4	$CCl_3CO_2Na/XC_6H_4SiMe_2H$ (DME; 100°C)	CCl <sub>2</sub>	+5.88	-0.97	-1.18	this work
5	$CCl_3CO_2Na/R^1R^2R^3SiH$ (DME; 100°C)	CCl <sub>2</sub>	+5.88	—	-1.07	this work
6	$Hg(CH_2Br)_2/XC_6H_4SiMe_2H$ (PhH; 80°C)	Carbenoid	—	-1.31	-1.83 <sup>c</sup>	15
7	$ZnEt_2-CH_2I_2/XC_6H_4SiMe_2H$ (Et <sub>2</sub> O; 24°C)	Carbenoid	—	-1.11	-1.56 <sup>c</sup>	16
8	$Me_3SiCOPh/XC_6H_4SiH_3$ (none; 22°C; $h\nu$ )	C(Ph)OSiMe <sub>3</sub>	—	+1.82	+2.32	2
9	$Me_3SiCOPh/R^1R^2R^3SiH$ (none; 22°C; $h\nu$ )	C(Ph)OSiMe <sub>3</sub>	—	—	+2.13	1

<sup>a</sup> From Hammett treatment. <sup>b</sup> From Taft treatment using the  $\sigma^*$  constants of aryl substituents (see ref. 7 and 8). <sup>c</sup> By calculation using the data in ref. 6, 15 and 16, respectively.

viously [3], it is reasonable to consider that the magnitude of the  $\Sigma\sigma^*$  values for CXY are approximately proportional to the reaction constants,  $\rho$  and/or  $\rho^*$  values (in the absolute sense). The observed  $\rho$  and  $\rho^*$  values for the  $CCl_3CO_2Na/XC_6H_4SiMe_2H$  (No. 4) and  $R^1R^2R^3SiH$  (No. 5) reactions agree well with that found for the  $PhHgCCl_2Br/XC_6H_4SiMe_2H$  reactions (No. 3) [6]. The good agreement of the kinetic isotope effects has been mentioned above, and this concordance in the two  $\rho$  values, although different carbene precursors are employed, is as expected since the attacking species is  $CCl_2$  in each case [6,14].

With this approach to the interpretation of the reaction mechanism, the two reactions of  $Hg(CH_2Br)_2$  [15] (No. 6) and  $ZnEt_2-CH_2I_2/XC_6H_4SiMe_2H$  [16] (No. 7) were confirmed to proceed via carbenoids rather than free carbenes, as had already been demonstrated by the original authors. Similarly, it was shown that the  $N_2CHCO_2Me/XC_6H_4SiMe_2H$  reactions (No. 2) occur by way of free  $CHCO_2Me$ -insertion into the Si—H bond and that the copper used thus served only as the decomposition catalyst for the diazoacetate ester [3].

Interestingly, for the two reactions of  $Me_3SiCOPh/XC_6H_4SiH_3$  (No. 8) [2] and  $Me_3SiCOPh/R^1R^2R^3SiH$  [1] (No. 9), the reaction constants  $\rho$  (and  $\rho^*$ ) indicate that the sum of the Taft  $\sigma^*$  for the substituents of C(Ph)OSiMe<sub>3</sub> should have a large negative value, although a definite value is not yet available, and that the electron-donating resonance effect of oxygen of the trimethylsiloxy group on the adjacent carbon contributes significantly to the nucleophilic character of the attacking species. Similarly, the values of  $\Sigma\sigma^*$  for the carbenoid species in

$\text{Hg}(\text{CH}_2\text{Br})_2/\text{XC}_6\text{H}_4\text{SiMe}_2\text{H}$  (No. 6) and  $\text{ZnEt}_2-\text{CH}_2\text{I}_2/\text{XC}_6\text{H}_4\text{SiMe}_2\text{H}$  (No. 7) reactions should also be large and positive according to the magnitude of their reaction constants. However, as to the nature of phenylcarbene (CHPh) as an attacking species, which was generated photochemically from phenyldiazomethane (No. 1) [17], the relative reactivities of a series of hydrosilanes did not show a linear correlation with the Taft  $\sigma^*$  constants for the substituents on silicon. Thus, the calculated  $\rho^*$  value was found to be zero, as seen in Table 3. Therefore, it may be inferred that in this reaction system the reactive intermediate (CHPh) behaves as a radical species. This assumption is supported by the fact that, together with the expected product, toluene and 1,2-diphenylethane, which were presumably formed by radical processes, were found in most cases. The details of these reactions will be discussed elsewhere.

### Experimental

All boiling points are uncorrected. The reactions were carried out under an atmosphere of dry nitrogen. IR spectra were recorded using neat liquid films with a Hitachi EPI-G3 spectrometer, and NMR spectra were measured in  $\text{CCl}_4$  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.

### Materials

Anhydrous sodium trichloroacetate was prepared by neutralization of trichloroacetic acid with sodium methoxide in methanol according to the literature [14,18–20] and recrystallization from a mixture of anhydrous dioxane/DME below 45°C. DME was freshly distilled from lithium aluminum hydride before use.

Triethylsilane, benzylsilane, phenylsilane, diphenylsilane, phenylmethylsilane and substituted phenyldimethylsilanes were made as described previously [1–3, 21]. Pentamethyldisilane (b.p. 98–99°C; lit. 97°C [22], benzylmethylsilane (b.p. 163–164°C;  $n_D^{25}$  1.5111 [23] and di-*n*-butylsilane (b.p. 165°C; lit. 160°C [24]) were obtained by lithium aluminum hydride reduction of the corresponding chlorosilanes, as described in the literature. Similarly, phenylmethyldeuteriosilane was obtained by reduction of the corresponding chlorosilane with lithium aluminum deuteride (b.p. 130°C). This compound showed an IR absorption peak at  $1555\text{ cm}^{-1}$  [ $\nu(\text{Si}-\text{D})$ ] and NMR signals at  $\delta$  7.41 (mc, 5H, phenyl hydrogens) and 0.41 ppm (s, 3H, Si–Me). No absorption band and signal due to Si–H were detected in the IR and NMR spectra, respectively.

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

### Typical preparative reaction of $\alpha$ -silyldichloromethanes, $\text{R}^1\text{R}^2\text{R}^3\text{SiH}$

These compounds were prepared by the  $\text{R}^1\text{R}^2\text{R}^3\text{SiH}-\text{CCl}_3\text{CO}_2\text{Na}$  reaction and the method used for dichloromethylpentamethyldisilane is representative. Pentamethyldisilane (Ia, 3.97 g, 30.0 mmol), sodium trichloroacetate (II, 1.85 g, 10.0 mmol), and DME (6 ml) were placed in a dry, small round-bottomed flask fitted with a reflux condenser which was previously flushed with dry nitrogen. The mixture was immersed in an oil bath maintained at 100°C and heated with

TABLE 4  
ELEMENTAL ANALYSIS AND MOLECULAR WEIGHT

Compound	Formula	Analysis found (calcd.) (%)		
		C	H	Mol. wt. <sup>a</sup>
IIIa	C <sub>6</sub> H <sub>16</sub> Cl <sub>2</sub> Si <sub>2</sub>	33.50 (33.47)	7.33 (7.49)	214 (215.3)
IIIb <sup>b</sup>	C <sub>7</sub> H <sub>16</sub> Cl <sub>2</sub> Si	42.46 (42.20)	8.01 (8.10)	198 (199.2)
IIIc <sup>c</sup>	C <sub>9</sub> H <sub>12</sub> Cl <sub>2</sub> Si	49.40 (49.32)	5.49 (5.52)	218 (219.2)
IIId	C <sub>8</sub> H <sub>10</sub> Cl <sub>2</sub> Si	46.58 (46.84)	4.65 (4.91)	204 (205.2)
IIIe	C <sub>7</sub> H <sub>8</sub> Cl <sub>2</sub> Si	43.53 (43.93)	4.16 (4.21)	190 (191.1)
IIIf	C <sub>9</sub> H <sub>20</sub> Cl <sub>2</sub> Si	48.06 (47.57)	8.85 (8.87)	— <sup>d</sup> (227.3)
IIIg	C <sub>9</sub> H <sub>12</sub> Cl <sub>2</sub> Si	49.59 (49.32)	5.56 (5.52)	218 (219.2)
IIIh	C <sub>8</sub> H <sub>10</sub> Cl <sub>2</sub> Si	46.58 (46.84)	4.89 (4.91)	204 (205.2)
IIIi	C <sub>10</sub> H <sub>14</sub> Cl <sub>2</sub> OSi	48.12 (48.20)	5.69 (5.66)	248 (249.2)
IIIj <sup>c</sup>	C <sub>10</sub> H <sub>14</sub> Cl <sub>2</sub> Si	51.83 (51.50)	5.95 (6.05)	232 (233.2)
IIIk <sup>c</sup>	C <sub>9</sub> H <sub>11</sub> Cl <sub>3</sub> Si	42.89 (42.62)	4.43 (4.37)	252 (253.7)
III <sup>c</sup>	C <sub>10</sub> H <sub>11</sub> Cl <sub>2</sub> F <sub>3</sub> Si	41.70 (41.82)	4.11 (3.86)	— <sup>d</sup> (287.2)

<sup>a</sup> By mass spectrum. <sup>b</sup> Known compound (see ref. 4). <sup>c</sup> Known compound (see ref. 6). <sup>d</sup> No molecular peak was observed.

TABLE 5  
NMR CHEMICAL SHIFTS OF THE PRODUCTS <sup>a</sup>

Com- pound	ArH	CCl <sub>2</sub> H	SiH	CH <sub>2</sub>	SiMe	Others
IIIa	—	5.37(s, 1)	—	—	0.25(s) 0.16(s) <sup>(15)</sup>	—
IIIb	—	5.35(s, 1)	—	—	—	1.30—0.30(m, 15) <sup>b</sup>
IIIc	7.75—7.20(m, 5)	5.33(s, 1)	—	—	0.53(s, 6)	—
IIId	7.80—7.10(m, 5)	5.38(d, 1)	4.61(m, 1)	—	0.61(d, 3)	—
IIIe	7.90—7.10(m, 5)	5.44(t, 1)	4.67(d, 2)	—	—	—
IIIf	—	5.36(d, 1)	4.01(m, 1)	—	—	1.75—0.45(m, 18) <sup>c</sup>
IIIg	7.50—6.85(m, 5)	5.22(d, 1)	4.18(m, 1)	2.37(d, 2)	0.28(d, 3)	—
IIIh	7.14(s, 5)	5.25(t, 1)	4.20(m, 2)	2.48(t, 2)	—	—
IIIi	7.63—6.68(q, 4)	5.29(s, 1)	—	—	0.50(s, 6)	3.80(s, 3) <sup>d</sup>
IIIj	7.43 7.13 <sup>(q, 4)</sup>	5.30(s, 1)	—	—	0.51(s, 6)	2.38(s, 3) <sup>e</sup>
IIIk	7.63—7.21(q, 4)	5.32(s, 1)	—	—	0.53(s, 6)	—
III	7.99—7.29(m, 4)	5.36(s, 1)	—	—	0.58(s, 6)	—

<sup>a</sup> CCl<sub>4</sub> solution; TMS internal standard;  $\delta$  ppm. <sup>b</sup> Ethyl hydrogens. <sup>c</sup> Butyl hydrogens. <sup>d</sup> *p*-Methoxy hydrogens. <sup>e</sup> *p*-Methyl hydrogens.



magnetic stirring for 15 h, after which time gas evolution ceased. After cooling, the resulting mixture was subjected to GLC analysis with a silicone column (2 m X 4 mm; 20% KF-96 on Celite 545; column temp. 160–200°C). Only one product was formed and it was isolated by preparative GLC. From the elemental analysis and IR, NMR and mass spectra, the product was identified as dichloromethylpentamethyldisilane (IIIa). The yield by GLC was 42% (based on II). Pertinent physical, spectral and analytical data for all the compounds thus prepared are given in Table 4 and 5.

#### *Procedure for competition reactions*

Sodium trichloroacetate was mixed with two different hydrosilanes in millimolar ratio of 2 : 10 : 10 in 6 ml of DME and the mixture was heated at 100°C with stirring until gas evolution almost ceased (15 h). After cooling, the reaction mixture was subjected to GLC analysis using the silicone column described above. Corrections were made for the differing thermal conductivities of the various compounds by means of an internal standard (high boiling n-alkane or diphenylmethane). The reactivity ratio for the two hydrosilanes was calculated from eq. 2 and relative reactivities are expressed by taking that for triethylsilane as the standard (Table 2). Due to the differences in the number of hydrogens bonded to silicon in hydrosilanes, consideration to reconcile the observed  $k_{rel}$  values was made.

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