

## FREE-RADICAL CHLORINATION OF ALKYL SILANES V. THE ABSTRACTION OF HYDROGEN ATOMS FROM ARYLHYDRO- SILANES BY THE TRICHLOROMETHYL RADICAL\*

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### SUMMARY

The relative rate constants for Si-H hydrogen abstraction from substituted phenylsilanes, phenylmethylsilanes and phenyldimethylsilanes by the trichloromethyl radical have been determined from competitive chlorinations at 80° with carbon tetrachloride as the chlorinating agent. The relative rates for the three sets of arylhydrosilanes are well correlated with the Hammett  $\sigma$  constants for the ring substituents, with  $\rho$  values of -0.460, -0.372 and -0.453, respectively. It seems that there is electrophilic attack by the trichloromethyl radical at the Si-H bond but without much separation of charge in the transition state. The  $\rho$  values are compared with those for the benzylic hydrogen abstraction from the corresponding carbon analogs.

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Although the free radical abstraction of hydrogen atoms from various C-H bonds has received much attention<sup>2-5</sup>, detailed studies of the hydrogen abstraction from Si-H bonds have only recently been reported. Thus, Kerr *et al.*<sup>6</sup> and also Morris and Thynne<sup>7</sup> measured Arrhenius parameters for the gas phase reaction of the methyl and trifluoromethyl radicals with various silanes including alkylhydrosilanes, but to our knowledge kinetic data on solution reactions of organic hydrosilanes are still lacking. The present paper describes measurements of relative rates of hydrogen abstraction by the trichloromethyl radical from a variety of arylhydrosilanes in solution.

In order to determine the relative rates, we have utilised the free radical hydrogen-chlorine exchange reaction between a hydrosilane and carbon tetrachloride, which is known to proceed via a radical chain mechanism with moderate chain length involving alternate formation of silyl and trichloromethyl radicals<sup>8-11</sup>, as shown in eqns. (1) and (2) in which  $\equiv\text{SiH}$  and  $\equiv\text{SiCl}$  represent any hydrosilane and



\* For Part IV see ref. 1.

chlorosilane. This method is convenient since the hydrogen-chlorine exchange is not accompanied by serious side reactions, although homolytic disproportionation of arylhydrosilanes<sup>12</sup> or ring substitution in arenes by the trichloromethyl radical<sup>13</sup> are known to occur in other systems. The relative rates of hydrogen abstraction from Si-H bonds have thus been conveniently measured by allowing two hydrosilanes to compete with carbon tetrachloride under free radical conditions.

## RESULTS AND DISCUSSION

The possibility of hydrogen-hydrogen exchange reaction between two hydrosilanes under the conditions employed was first examined. For this purpose, an equimolar mixture of phenyldimethyldeuteriosilane and *m*-tolyl dimethylsilane was heated at 80° in the presence of benzoyl peroxide (10 mol% based on each component). After 13 h the phenyldimethyldeuteriosilane was fully recovered by preparative vapour phase chromatography, and was shown by infrared studies to be essentially free from phenyldimethylhydrosilane, as indicated by the absence of a Si-H absorption near 2110 cm<sup>-1</sup>. (Use of synthetic mixtures of authentic phenyldimethyldeuteriosilane and phenyldimethylhydrosilane showed that even 1% of the hydrosilane could have been detected in the deuteriosilane.) It is evident that no appreciable hydrogen exchange takes place between two hydrosilanes under the conditions used.

In the present investigation, *m*- and *p*-substituted phenylsilanes, phenylmethylsilanes and phenyldimethylsilanes were used and the competitive experiments were conducted in excess of carbon tetrachloride (see Experimental) at 80°, benzoyl peroxide being used as catalyst. The relative rate constants were calculated by the Ingold-Shaw<sup>14</sup> equation for competitive chain carrying steps in radical chain reactions involving the same attacking radicals, as shown in eqn. (3) in which [SiH]<sub>i</sub>,

$$\frac{k_1}{k_2} = \frac{\log [\text{SiH}]_i / [\text{SiH}]_f}{\log [\text{Si}'\text{H}]_i / [\text{Si}'\text{H}]_f} \quad (3)$$

[Si'H]<sub>i</sub> represent the initial concentrations of two hydrosilanes, [SiH]<sub>f</sub>, [Si'H]<sub>f</sub> the final concentrations, and  $k_1/k_2$  the ratio of rate constants for the attack of the abstracting reagent on the two species.

The applicability of the Ingold-Shaw equation was tested by determining relative reactivities of (*m*-chlorophenyl)silane and phenylsilane at several concen-

TABLE I

THE COMPETITIVE REACTION OF PHENYLSILANE AND (*m*-CHLOROPHENYL)SILANE WITH CARBON TETRACHLORIDE AT 80°

Init. concn. C <sub>6</sub> H <sub>5</sub> SiH <sub>3</sub> (mmole)	Init. concn. <i>m</i> -ClC <sub>6</sub> H <sub>4</sub> SiH <sub>3</sub> (mmole)	$k(m\text{-ClC}_6\text{H}_4\text{SiH}_3)$ $k(\text{C}_6\text{H}_5\text{SiH}_3)$
1.17	2.00	0.75
1.02	1.52	0.71
2.05	2.01	0.68
1.51	1.02	0.73
2.02	1.00	0.71

TABLE 2

RELATIVE RATES FOR REACTIONS OF  $\text{ArMe}_n\text{SiH}_{3-n}$  ( $n=0,1,2$ ) WITH THE TRICHLOROMETHYL RADICAL AT 80°

X	$k_{\text{rel}}(\text{XC}_6\text{H}_4\text{SiH}_3)$	$k_{\text{rel}}(\text{XC}_6\text{H}_4\text{SiMeH}_2)$	$k_{\text{rel}}(\text{XC}_6\text{H}_4\text{SiMe}_2\text{H})$
<i>p</i> -CH <sub>3</sub>	1.33	1.28	1.25
<i>m</i> -CH <sub>3</sub>	1.08	1.13	1.16
H	1.00	1.00	1.00
<i>p</i> -Cl	0.84	0.89	0.83
<i>m</i> -Cl	0.71	0.78	0.71

trations (Table 1). The constancy of  $k_{\text{rel}}$  (within experimental error) in these experiments allows us to conclude that eqn. (3) does indeed apply. The relative rate constants of arylsilanes, arylmethylsilanes and aryl-dimethylsilanes towards the trichloromethyl radical thus calculated are expressed in terms of  $k(\text{PhSiH}_3) = 1$ ,  $k(\text{PhMeSiH}_2) = 1$  and  $k(\text{PhMe}_2\text{SiH}) = 1$ , respectively. The results are given in Table 2.

It will be seen from Table 2 that for the three sets of substrates an electron-donating substituent increases the rate of hydrogen abstraction. The relative rates are plotted against Hammett  $\sigma$  values for the substituents in Fig. 1, yielding three

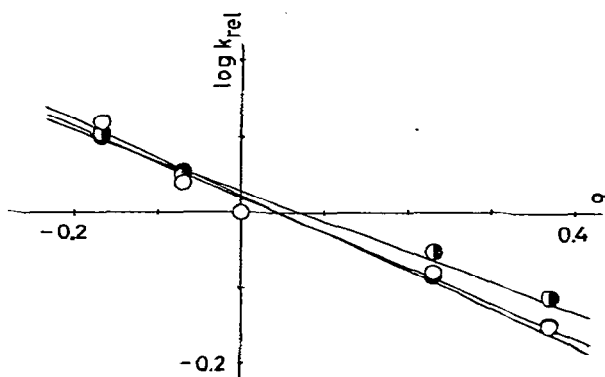
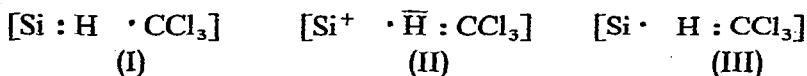


Fig. 1. Plots of relative rate constant *versus*  $\sigma$ . Open circles refer to reactions of substituted phenylsilanes, half solid circles to those of substituted phenylmethylsilanes and solid circles to those of substituted phenyl-dimethylsilanes.

It will be seen from Table 2 that for the three sets of substrates and electron-satisfactory straight lines. The results of the Hammett correlation are presented in Table 3. Utilising the  $\sigma^+$  function derived by Brown-Okamoto for carbonium ion reactions, similarly good correlations are obtained for arylsilanes and arylmethylsilanes. Correlation of aryl-dimethylsilanes with  $\sigma^+$  constants is somewhat poorer, but because of the limited range of substituents it seems of little interest to discuss these differences in further detail. The negative signs of the reaction constants are as expected on the basis of electron-seeking character of the trichloromethyl radical<sup>15</sup> which preferentially attacks hydrogens with higher electron densities. The activated complex for the hydrogen abstraction can be represented as a resonance hybrid of the following canonical structures, in which the silicon atom assumes some degree of siliconium ion character.



The observed values of  $\rho$  are rather small compared with the  $\rho$  values for the benzylic hydrogen abstraction by the trichloromethyl radical from substituted toluenes<sup>15</sup> ( $\rho = -1.46$ , with  $\sigma^+$ ) and cumenes<sup>16</sup> ( $\rho = -0.67$ , with  $\sigma^+$ ); the carbon analogs of arylsilanes and aryl dimethylsilanes. Small  $\rho$  values found for the present system suggest that the transition state is not highly charged. This is reasonable, since it has been shown that the Si-H bond is much more reactive than the C-H bond towards carbon radicals such as methyl and trifluoromethyl radicals<sup>6,7</sup> and hence the transition state would resemble the reactants, and involve little bond breaking of the silicon-hydrogen bond. It is noteworthy in this connection that the  $\rho$  values for the three sets of arylhydrosilanes do not differ much from each other. In the carbon series, *i.e.*, toluenes, ethylbenzenes and cumenes,  $\rho$  values for benzylic hydrogen abstraction decrease in absolute magnitude with successive substitution of methyl groups for  $\alpha$ -hydrogens in toluene. For example, abstraction by the bromine atom yields a  $\rho$  value of  $-1.39$  for substituted toluenes<sup>17</sup> and values for substituted ethylbenzenes<sup>18</sup> and cumenes<sup>16</sup> of  $-0.69$  and  $-0.38$ , respectively. These results have been explained in terms of the degree of bond breaking in the transition state, although an explanation based on steric requirement of reactions has been advanced for the unexpectedly large selectivity shown by reactions of the trichloromethyl radical with substituted cumenes<sup>16</sup> and neopentylbenzenes<sup>19</sup>. In the absence of complicating steric interaction, the  $\rho$  values for aralkylhydrocarbons appear to be related to the relative rates of reaction of the parent compounds. Thus, for hydrogen abstraction by the trichloromethyl radical a benzylic hydrogen in ethylbenzene is 50 times more reactive than a hydrogen in toluene whereas an  $\alpha$ -hydrogen of cumene reacts 260 times faster than that of toluene<sup>20</sup>. The results of competitive experiments which were carried out with pairs of  $\text{PhSiH}_3 + \text{PhMe}_2\text{SiH}$  and  $\text{PhMeSiH}_2 + \text{PhMe}_2\text{SiH}$  under the standard conditions showed that the ratio of the relative rates of phenylsilane, phenylmethylsilane and phenyldimethylsilane (on a per Si-H bond available basis) is 1.00/1.51/2.18. Replacement of a methyl group for an  $\alpha$ -hydrogen atom once again raises the reactivity, but the rate enhancement is markedly smaller than that in corresponding carbon series, and this is reflected in the difference in  $\rho$  values for reactions of the arylhydrosilanes.

It is not certain at this moment whether or not the slightly larger selectivity

TABLE 3

 $\rho$  VALUES FOR THE HYDROGEN ABSTRACTION BY  $\text{CCl}_3$  RADICALS FROM ARYLHYDROSILANES AT 80°

System	Substituent constant	$\rho$	$r$
ArSiH <sub>3</sub>	$\sigma$	-0.460	0.989
	$\sigma^+$	-0.412	0.990
ArSiMeH <sub>2</sub>	$\sigma$	-0.372	0.981
	$\sigma^+$	-0.330	0.982
ArSiMe <sub>2</sub> H	$\sigma$	-0.453	0.994
	$\sigma^+$	-0.389	0.945

for aryl dimethylsilanes compared with aryl methylsilanes is real, and discussion of this point must await a study of the influences of other factors, *e.g.*, solvent and change in structure of radical species, on the rates of the abstraction processes.

## EXPERIMENTAL

### Materials

Substituted phenylsilanes, phenyl methylsilanes and phenyl dimethylsilanes were prepared by lithium aluminium hydride reduction of the corresponding aryl trichlorosilanes, aryl methyl dichlorosilanes and aryl dimethyl chlorosilanes which were obtained by reaction of the appropriate Grignard reagent with silicon tetrachloride, methyl trichlorosilane and dimethyl dichlorosilane. Physical properties of the hydro-silanes are tabulated in Table 4. Phenyl dimethyl deuteriosilane (b.p. 155.0–155.5°) was prepared by reducing phenyl dimethyl chlorosilane with lithium aluminium deuteride. Its infrared spectrum in neat was devoid of a characteristic absorption

TABLE 4

PHYSICAL PROPERTIES OF *m*- AND *p*-SUBSTITUTED ARYLHYDROSILANES (XC<sub>6</sub>H<sub>4</sub>SiRR'H)

X	R	R'	B.p. [°C (mm)]	n <sub>D</sub> <sup>20</sup>	Formula	Calcd. (%)		Found (%)	
						C	H	C	H
<i>p</i> -Me	H	H	55.5(34)	1.5122	C <sub>7</sub> H <sub>10</sub> Si	68.89	8.24	68.64	8.25
<i>m</i> -Me	H	H	68.3–69.0(43)	1.5150	C <sub>7</sub> H <sub>10</sub> Si	68.89	8.24	69.48	8.35
H	H	H	119–119.5(760) <sup>a</sup>	1.5128 <sup>a</sup>	C <sub>6</sub> H <sub>8</sub> Si				
<i>p</i> -Cl	H	H	65.0–65.5(30)	1.5378	C <sub>6</sub> H <sub>7</sub> ClSi	50.51	4.94	50.67	4.80
<i>m</i> -Cl	H	H	163.5(760)	1.5363	C <sub>6</sub> H <sub>7</sub> ClSi	50.51	4.94	50.67	5.13
<i>p</i> -Me	Me	H	164(760)	1.5067	C <sub>8</sub> H <sub>12</sub> Si	70.51	8.87	70.82	9.01
<i>m</i> -Me	Me	H	80.0–81.0(36)	1.5080	C <sub>8</sub> H <sub>12</sub> Si	70.51	8.87	70.23	8.68
H	Me	H	142(760) <sup>b</sup>	1.5059 <sup>b</sup>	C <sub>7</sub> H <sub>10</sub> Si				
<i>p</i> -Cl	Me	H	81.0–81.1(25)	1.5271	C <sub>7</sub> H <sub>9</sub> ClSi	53.65	5.78	53.96	5.93
<i>m</i> -Cl	Me	H	180–182(760)	1.5280	C <sub>7</sub> H <sub>9</sub> ClSi	53.65	5.78	53.79	5.62
<i>p</i> -Me	Me	Me	107–108(80) <sup>c</sup>	1.4997 <sup>c</sup>	C <sub>9</sub> H <sub>14</sub> Si				
<i>m</i> -Me	Me	Me	76(21) <sup>d</sup>	1.5011 <sup>d</sup>	C <sub>9</sub> H <sub>14</sub> Si				
H	Me	Me	157(760) <sup>e</sup>	1.4986 <sup>e</sup>	C <sub>8</sub> H <sub>12</sub> Si				
<i>p</i> -Cl	Me	Me	101.0–101.1(40) <sup>f</sup>	1.5190 <sup>f</sup>	C <sub>8</sub> H <sub>11</sub> ClSi				
<i>m</i> -Cl	Me	Me	95–96(30) <sup>g</sup>	1.5186 <sup>g</sup>	C <sub>8</sub> H <sub>11</sub> ClSi				

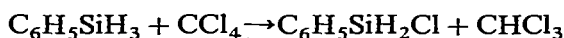
<sup>a</sup> Lit.<sup>21</sup> b.p. 120° (760 mm), n<sub>D</sub><sup>20</sup> 1.5125. <sup>b</sup> Lit.<sup>22</sup> b.p. 53° (30 mm), n<sub>D</sub><sup>25</sup> 1.505. <sup>c</sup> Lit.<sup>23</sup> b.p. 180° (760 mm), n<sub>D</sub><sup>20</sup> 1.5000. <sup>d</sup> Lit.<sup>24</sup> b.p. 69.5–71° (21 mm), n<sub>D</sub><sup>20</sup> 1.5018. <sup>e</sup> Lit.<sup>25</sup> b.p. 157° (760 mm), n<sub>D</sub><sup>20</sup> 1.4992. <sup>f</sup> Lit.<sup>26</sup> b.p. 78–80° (12 mm), n<sub>D</sub><sup>20</sup> 1.5187. <sup>g</sup> Lit.<sup>24</sup> b.p. 197–201° (760 mm), n<sub>D</sub><sup>20</sup> 1.5185.

of Si-H grouping near 2110 cm<sup>-1</sup>, but instead showed a strong Si-D stretching absorption at 1520 cm<sup>-1</sup>. NMR analysis showed absorption of a singlet at τ9.67 ppm for the SiMe<sub>2</sub> and a multiplet at 2.64 ppm for the phenyl group. The ratio of integrated area was 6/5. Phenyl dichlorosilane, b.p. 90–91°/40 mm, n<sub>D</sub><sup>20</sup> 1.5266 (lit.<sup>26</sup> b.p. 203.1°/749 mm, n<sub>D</sub><sup>20</sup> 1.5257), and phenyl methyl dichlorosilane, b.p. 199°/760 mm, n<sub>D</sub><sup>20</sup> 1.5192 (lit.<sup>27</sup> b.p. 203.1°/749 mm, n<sub>D</sub><sup>20</sup> 1.5188), were prepared according to the literature procedures. Phenyl chlorosilane was prepared as follows. A mixture

of 85 g (0.55 mole) of carbon tetrachloride and 2 g of benzoyl peroxide was added dropwise into 55 g (0.5 mole) of phenylsilane at 80°. After the addition was complete, the reaction mixture was further heated at 80° for 12 h. Fractional distillation gave 44 g (56% based on phenylsilane consumed) of phenylchlorosilane together with 11 g of the starting silane recovered. B.p. 89–90°/101 mm,  $n_D^{20}$  1.5354 (lit.<sup>28</sup> b.p. 160°/760 mm). Phenylmethylchlorosilane, b.p. 92.0–92.5°/65 mm,  $n_D^{20}$  1.5171 (lit.<sup>29</sup> b.p. 176°/760 mm,  $n_D^{20}$  1.5171), was obtained in a similar fashion from a combination of phenylmethylsilane and carbon tetrachloride<sup>30</sup>. Yield was 51%. Phenyltrichlorosilane and benzoyl peroxide were commercial samples. Carbon tetrachloride was purified according to the standard procedure. VPC analysis of the materials used for kinetic runs showed that they contained negligible amounts of impurities.

### Product studies

The primary reaction of phenylsilane with excess of carbon tetrachloride at 80° in the presence of benzoyl peroxide can be expressed by the following equation



In practice the reaction also gave further chlorination products, phenyldichlorosilane and phenyltrichlorosilane, the structures of which were confirmed by comparing their physical properties with those of the respective authentic sample after collection and purification by VPC. However, since the material balance was excellent and the use of excess of carbon tetrachloride was found to suppress completely further reduction of chloroform to dichloromethane, as shown by the results given in Table 5, it was concluded that the Ingold–Shaw equation would be applicable to the data obtained in competitive experiments under such conditions. The situation is almost identical with phenylmethylsilane. Table 5 also indicates that the reaction of phenyldimethylsilane gives cleanly the expected pair of products, phenyldimethylchloro-

TABLE 5

THE REACTION OF PHENYLSILANES WITH CARBON TETRACHLORIDE AT 80°<sup>a</sup>

Reactants (mmole) <sup>b</sup>	Reactants (mmole) <sup>c</sup>	Reactants (mmole) <sup>d</sup>
PhSiH <sub>3</sub> (6.25)	PhMeSiH <sub>2</sub> (5.69)	PhMe <sub>2</sub> SiH (5.03)
CCl <sub>4</sub> (19.90)	CCl <sub>4</sub> (15.32)	CCl <sub>4</sub> (15.52)
Bz <sub>2</sub> O <sub>2</sub> (0.06)	Bz <sub>2</sub> O <sub>2</sub> (0.09)	Bz <sub>2</sub> O <sub>2</sub> (0.08)
Products (mmole)	Products (mmole)	Products (mmole)
PhSiH <sub>3</sub> (2.18)	PhMeSiH <sub>2</sub> (2.24)	PhMe <sub>2</sub> SiH (1.89)
PhSiH <sub>2</sub> Cl (2.91)	PhMeSiHCl (2.30)	PhMe <sub>2</sub> SiCl (3.02)
PhSiHCl <sub>2</sub> (0.75)	PhMeSiCl <sub>2</sub> (1.20)	CCl <sub>4</sub> (12.30)
PhSiCl <sub>3</sub> (0.50)	CCl <sub>4</sub> (11.98)	CHCl <sub>3</sub> (3.15)
CCl <sub>4</sub> (16.00)	CHCl <sub>3</sub> (3.41)	CH <sub>2</sub> Cl <sub>2</sub> (–) <sup>e</sup>
CHCl <sub>3</sub> (4.21)	CH <sub>2</sub> Cl <sub>2</sub> (–) <sup>e</sup>	Ph <sub>2</sub> Me <sub>2</sub> Si <sup>f</sup> (–) <sup>e</sup>
CH <sub>2</sub> Cl <sub>2</sub> (–) <sup>e</sup>	Ph <sub>2</sub> MeSiH <sup>f</sup> (–) <sup>e</sup>	
Ph <sub>2</sub> SiH <sub>2</sub> <sup>f</sup> (–) <sup>e</sup>		

<sup>a</sup> Each run was carried out in a sealed tube. <sup>b</sup> For 2 h. <sup>c</sup> For 2½ h. <sup>d</sup> For 5 h. <sup>e</sup> Not detectable. <sup>f</sup> Expected redistribution products.

silane and chloroform, without appreciable formation of other products. That ring substituents do not greatly disturb the hydrogen-chlorine exchange reaction is clearly shown by the results in Table 6, which presents a comparison of results obtained with (*m*-chlorophenyl)dimethylsilane and *m*-tolyl dimethylsilane.

TABLE 6

THE REACTION OF SUBSTITUTED PHENYLDIMETHYLSILANES WITH CARBON TETRACHLORIDE 80° (5 h)<sup>a</sup>

Reactants (mmole)	Reactants (mmole)
<i>m</i> -ClC <sub>6</sub> H <sub>4</sub> Me <sub>2</sub> SiH (5.29)	<i>m</i> -MeC <sub>6</sub> H <sub>4</sub> Me <sub>2</sub> SiH (3.02)
CCl <sub>4</sub> (15.25)	CCl <sub>4</sub> (10.33)
Bz <sub>2</sub> O <sub>2</sub> (0.08)	Bz <sub>2</sub> O <sub>2</sub> (0.07)
Products (mmole)	Products (mmole)
<i>m</i> -ClC <sub>6</sub> H <sub>4</sub> Me <sub>2</sub> SiH (2.31)	<i>m</i> -MeC <sub>6</sub> H <sub>4</sub> Me <sub>2</sub> SiH (1.49)
<i>m</i> -ClC <sub>6</sub> H <sub>4</sub> Me <sub>2</sub> SiCl (3.24)	<i>m</i> -MeC <sub>6</sub> H <sub>4</sub> Me <sub>2</sub> SiCl (1.61)
CCl <sub>4</sub> (11.93)	CCl <sub>4</sub> (8.64)
CHCl <sub>3</sub> (3.36)	CHCl <sub>3</sub> (1.70)
CH <sub>2</sub> Cl <sub>2</sub> (-) <sup>b</sup>	CH <sub>2</sub> Cl <sub>2</sub> (-) <sup>b</sup>

<sup>a</sup> Each run was carried out in a sealed tube. <sup>b</sup> Not detectable.

*Hydrogen exchange reaction between phenyldimethyldeuteriosilane and (m-chlorophenyl)dimethylhydrosilane*

To a mixture of 0.137 g (1.00 mmole) of phenyldimethyldeuteriosilane and 0.151 g (1.00 mmole) of (*m*-chlorophenyl)dimethylsilane was added 0.027 g (0.11 mmole) of benzoyl peroxide. The degassed mixture was heated at 80° for 13 h in a sealed tube and then the material responsible for a peak of phenyldimethylsilane was collected by preparative VPC (KF-96, 2m, 90°). An IR spectrum of the collected sample showed no peak near 2110 cm<sup>-1</sup>.

*Procedure for kinetic runs*

A solution of two arylhydrosilanes, carbon tetrachloride and benzoyl peroxide in an approximate molar ratio of 1/1/6/0.01 was introduced into a tube which was sealed after the mixture was carefully degassed. Then the reaction tube was maintained at 80° in a constant temperature bath for 1-5 h, by which time 40-70% of the arylhydrosilanes had reacted. The reaction mixtures were subjected to VPC analysis, using column materials such as DOS, XF-1105, KF-96 and so on. Corrections were made for thermal conductivity of the various components. The relative rates were calculated from original data by use of eqn. (3).

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