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POLAR EFFECTS ON THE CLEAVAGE REACTION OF SILICON-SILICON BONDS OF 1,2-DIARYLTETRAMETHYLDISILANE WITH 1,2-DIBROMOETHANE. STRUCTURE AND REACTIVITY IN S_H2 REACTION[1]

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Symmetrically substituted 1,2-diphenyltetramethyldisilane and hexamethyldisilane (the reference substrate) were reacted competitively with 1,2-dibromoethane in the presence of dibenzoyl peroxide at 30.0° with ultraviolet irradiation. The relative rates of bimolecular homolytic substitution increased with increasing electron-releasing power of the substituents, and a $\rho\sigma^+$ relationship was established with ρ=-1.55.

In a previous paper,[2] we reported that the reaction of organodisilanes with 1,2-dibromoethane afforded ethylene and the corresponding bromosilanes quantitatively in the presence of a catalytic amount of free-radical initiators, and that it was the first example of the liquid phase bimolecular homolytic substitution on silicon. The free-radical pathway has been established unequivocally and some synthetic applications were indicated. In this communication, the results of the structure and reactivity in this reaction are reported. Although S_H2 reactions are of current interest,[3] no detailed investigation on the structure and reactivity has been reported.

Symmetrically substituted 1,2-diphenyltetramethyldisilane and hexamethyldisilane as reference were reacted competitively with 1,2-dibromoethane and the relative reactivities were determined by the disappearance of the substrates.

$$\mathrm{Br}\cdot \quad + \quad \mathrm{X\text{-}C_6H_4SiMe_2SiMe_2C_6H_4\text{-}X} \xrightarrow{\underline{k}_X} \mathrm{X\text{-}C_6H_4SiMe_2Br} \quad + \quad \mathrm{X\text{-}C_6H_4SiMe_2}\cdot \qquad (1)$$

$$\mathrm{Br}\cdot \quad + \quad \mathrm{Me_3SiSiMe_3} \xrightarrow{\underline{k}_S} \mathrm{Me_3SiBr} \quad + \quad \mathrm{Me_3Si}\cdot \qquad (2)$$

$$\mathrm{X\text{-}C_6H_4SiMe_2}\cdot\,(\text{or } \mathrm{Me_3Si}\cdot) \quad + \quad \mathrm{BrCH_2CH_2Br}$$

$$\longrightarrow \quad \mathrm{X\text{-}C_6H_4SiMe_2Br}\ (\text{or } \mathrm{Me_3SiBr}) \quad + \quad \cdot\mathrm{CH_2CH_2Br} \qquad (3)$$

$$\mathrm{CH_2CH_2Br} \longrightarrow \mathrm{CH_2{=}CH_2} \quad + \quad \mathrm{Br}\cdot \qquad (4)$$

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Some of the required disilanes have been reported previously.[4] Details of preparation and properties of new compounds, *m*- and *p*-trifluoromethyl derivatives, will be reported in a future publication together with their spectral features.[5] The reaction gave very cleanly the expected products in quantitative yields as described in the previous paper,[2] no by-product due to the aryl-silicon cleavage being detected even in the most reactive *p*-methoxyl derivative.

The validity of the competitive method was demonstrated by the fact that the relative rate of a typical substrate such as 1,2-diphenyltetramethyldisilane to the standard substrate, hexamethyldisilane, was constant regardless of changing initial concentration of both substrates. Then 1,2-diaryltetramethyldisilane, hexamethyldisilane, 1,2-dibromoethane, cyclohexane (as an internal standard) and dibenzoyl peroxide in an approximate molar ratio of 1/1/1/0.5/0.05 were dissolved in benzene and the solution was placed in an nmr tube. It was irradiated at 30.0° in a constant temperature bath for 30 min, 30-50% of disilanes being consumed during irradiation. The relative rates, k_X/k_S, were calculated from both initial and final concentrations of substrates as determined by nmr.[6] The results are listed in Table 1.

Table 1

Reaction of 1,2-Diaryltetramethyldisilane with 1,2-Dibromoethane Catalyzed by Dibenzoyl Peroxide at 30.0° in Benzene

Substituent	$k_{rel.}$
p-CH_3O	8.47 ± 0.31
p-CH_3	0.736 ± 0.052
H	0.263 ± 0.027
p-Cl	0.208 ± 0.009
m-Cl	0.159 ± 0.013
m-CF_3	0.0666 ± 0.0095
p-CF_3	0.0622 ± 0.0188
$Me_3SiSiMe_3$	1.00 (Standard)

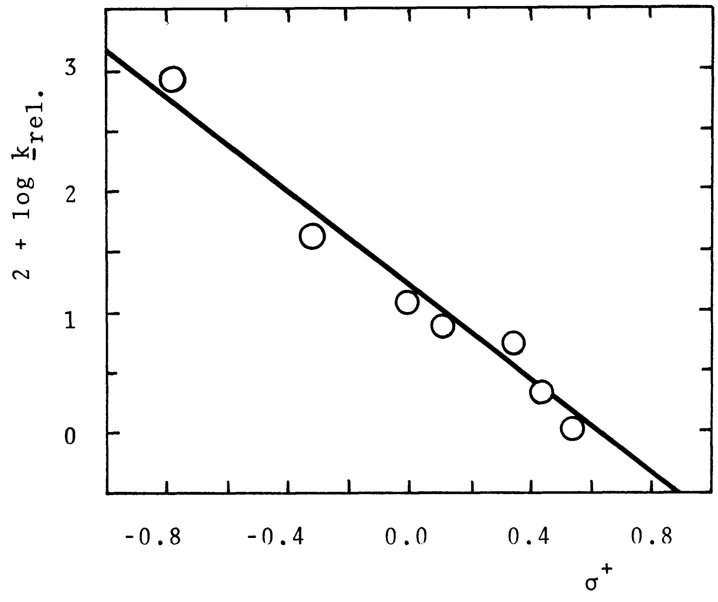
The relative rates increased with increasing electron releasing power of the substituents. The effect of substituents is, therefore, qualitatively in accord with the character of bromine atoms as "electrophilic" radicals. Furthermore, there is a quite satisfactory linear relationship between the logarithms of the relative rates and σ^+ constants[7] for the substituents, as shown in Figure 1. The equation is

$$\log(k_X/k_S) = -1.55\ \sigma^+ - 0.47 \qquad (r=0.975)$$

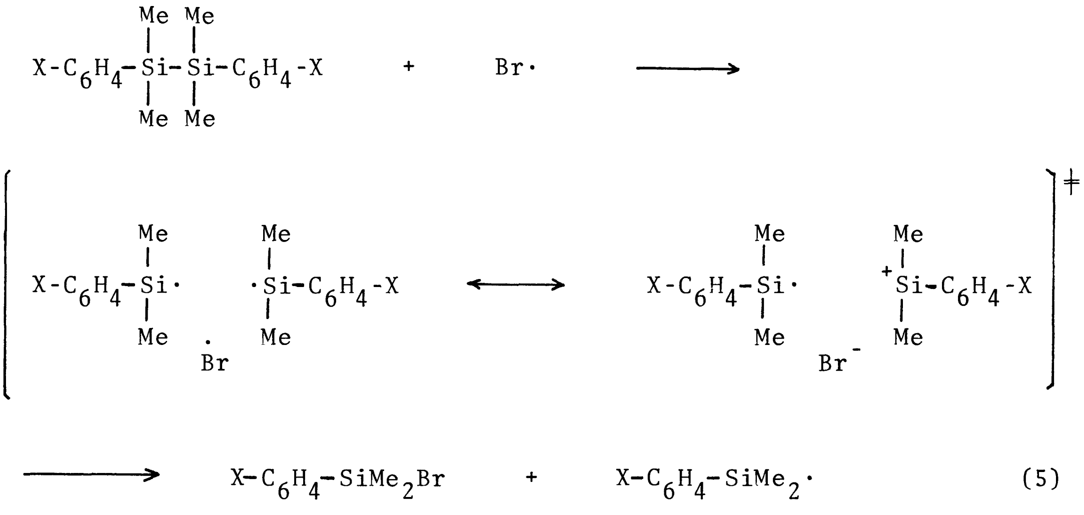
The correlation of $\log(k_X/k_S)$ with σ is less satisfactory (r=0.904). The negative ρ value is consistent with the view that the bromine atom is of an

Figure 1

Correlation of 2 + log $k_{rel.}$ and σ^+ for the Reaction of 1,2-Diaryltetramethyldisilane with 1,2-Dibromoethane Catalyzed by Benzoyl Peroxide at 30.0° in Benzene



"electrophilic" nature and the following polar structure may contribute at the transition state of bromine attack.



$$X\text{-}C_6H_4\text{-}\underset{Me}{\overset{Me}{Si}}\text{-}\underset{Me}{\overset{Me}{Si}}\text{-}C_6H_4\text{-}X \quad + \quad Br\cdot \quad \longrightarrow$$

$$\left[X\text{-}C_6H_4\text{-}\underset{Me}{\overset{Me}{Si}}\cdot \quad \underset{Br}{\cdot} \quad \cdot\underset{Me}{\overset{Me}{Si}}\text{-}C_6H_4\text{-}X \longleftrightarrow X\text{-}C_6H_4\text{-}\underset{Me}{\overset{Me}{Si}}\cdot \quad Br^- \quad {}^{+}\underset{Me}{\overset{Me}{Si}}\text{-}C_6H_4\text{-}X \right]^{\ddagger}$$

$$\longrightarrow X\text{-}C_6H_4\text{-}SiMe_2Br \quad + \quad X\text{-}C_6H_4\text{-}SiMe_2\cdot \tag{5}$$

The transition-state model described above does not imply the geometry at the attack of a bromine atom. It can be a flank-side or a back-side attack. Further work is in progress on this problem and will be reported at a later date.

Note that the data do correlate with σ^+ constants. The σ^+ constants were originally conceived on the basis of solvolysis results for substituted 2-phenyl-2-propyl chlorides[7] and have found wide applicability, especially in a variety of reactions of aromatic side chains in which a positive charge capable of direct resonance interaction with the aromatic ring is developed. In many free-radical reactions, particulary in abstraction of benzylic hydrogen atoms with electrophilic radicals, rate data are also best correlated by σ^+ parameters.[8,9] It should be emphasized that the $\rho\sigma^+$ relationship observed in these hydrogen-abstraction reaction is concerned with the polar effects of substituents in stabilizing the benzylic carbonium ions that contribute to the resonance hybrid in the transition state and not with the resonance stabilization of the benzylic radicals.[10,11]

All the solvolytic reactions of organosilicon compounds are thought to proceed via associative pentacovalent species as intermediates,[12] and substituent effects on the formation of trivalent "true" siliconium ions are unknown. However, the apparent applicability of the σ^+ constants to the present reaction suggests that certain substituents on the phenyl ring can interact with a silicon atom through resonance, as observed in carbonium ions, to make the silicon-silicon bond more nucleophilic.[13]

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