Silyl Radicals. VIII. Directive Effects and Relative Reactivities of the Pentamethyldisilanyl Radical in Homolytic Aromatic Silylation[1,2]

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Abstract: Silyl radicals, generated by decomposition of di-*tert*-butyl peroxide at 135° in the presence of hydrosilanes, readily react with benzene to give substitution products in 15–30% yield. Reaction of the pentamethyldisilanyl radical with toluene yields ortho, meta, and para substituted toluenes as well as other expected products. The ratios of isomeric arylpentamethyldisilanes were determined to be 58% ortho : 34% meta : 8% para for anisole, 21% ortho : 52% meta : 27% para for toluene, and 0% ortho : 48% meta : 52% para for benzotrifluoride. The total rate factors, relative to benzene, are 0.45 for anisole, 0.62 for toluene, and 2.19 for benzotrifluoride. The partial rate factors for pentamethyldisilanylation are correlated with Hammett's σ constants, resulting in $\rho = +1.4$. From a combination of these data with data for other free radicals, the relative nucleophilicity of the organosilyl radical was estimated.

There is a substantial body of evidence for addition of hydrosilanes to carbon–carbon double and triple bonds involving free silyl radicals. Although it is well known that an aromatic ring effectively undergoes a homolytic substitution by carbon radicals,[4] no work has been reported to date about the reaction of aromatic compounds with hydrosilanes leading to homolytic aromatic silylations.

Recently, Eaborn, Jackson, and Pearce reported that aromatic silylations took place by trimethylsilyl radicals generated from bis(trimethylsilyl)mercury by photolysis in aromatic solvents.[5] More recently, in the course of a study on silyl radicals, it was reported[1d] that a triorganosilyl-substituted benzene was formed, along with the expected products, as one of the main products of thermolysis of di-*tert*-butyl peroxide (DTBP) in a benzene solution of a hydrosilane. It has been found further that in the reaction of (3-phenylpropyl)dimethylsilane with di-*tert*-butyl peroxide homolytic aromatic substitution took place intramolecularly, affording the cyclization product, 1,1-dimethyl-1-silatetralin, as a main product.[1e]

In this paper, the results of a study of the reactivity of the pentamethyldisilanyl radical in aromatic substitution are described. Although the behavior of organometallic radicals has been of current interest,[6,7] no detailed investigation of the structure and reactivity has been carried out. Our prime object was to elucidate the nature of the silyl radicals and it seems very interesting to compare the results with those of other radicals, especially of carbon radicals.

Results

Reaction of Hydrosilanes with Benzene Catalyzed by DTBP. When a benzene solution of an equimolar mixture of triethylsilane and di-*tert*-butyl peroxide (DTBP) was heated in a sealed tube under nitrogen at 135° for a period of 20 hr, triethylphenylsilane was obtained in 16.3% yield as a main product together with other polymeric products. The product was separated by preparative glc and its structure was determined unequivocally by comparing its ir, nmr, and uv spectra and its retention time on glc with those of the authentic sample prepared independently.

$$Et_3SiH \xrightarrow[\text{DTBP in PhH}]{135°,\ 20\ \text{hr}} Et_3SiPh$$

Similarly, the reaction of various hydrosilanes with DTBP in benzene afforded the corresponding phenylsilanes in 15–30% yields in all cases, the results being listed in Table I.

Table I. Reaction of Hydrosilanes with Di-*tert*-butyl Peroxide in Benzene at 135°

Hydrosilane	mmol	DTBP (mmol)	Product	Yield, %
Et_3SiH	4.36	4.52	$PhSiEt_3$	16.3
n-$PrMe_2SiH$	6.40	6.41	$PhSiMe_2$-n-Pr	29.5
$Me_3SiSiMe_2H$	3.34	2.88	$PhSiMe_2SiMe_3$	19.2
$Me_3SiSiMe_2SiMe_2H$	2.96	3.13	$PhSiMe_2SiMe_2SiMe_3$	15.0

Reaction of Pentamethyldisilane with Toluene. The products of reaction of pentamethyldisilane with toluene were examined more thoroughly. The results are listed in Table II. When pentamethyldisilane or 1*H*-heptamethyltrisilane was used as a hydrosilane component, a dimerization product of the organosilyl radical, decamethyltetrasilane or tetradecamethylhexasilane, respectively, was also obtained. The structure

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[1] For previous papers in this series see: (a) I, H. Sakurai, A. Hosomi, and M. Kumada, *Bull. Chem. Soc. Jap.*, 40, 1551 (1967); (b) II, H. Sakurai, *et al.*, *J. Amer. Chem. Soc.*, **91**, 519 (1969); (c) III, H. Sakurai, M. Yamagata, A. Hosomi, and M. Kumada, *Bull. Chem. Soc. Jap.*, 42, 1746 (1969); (d) IV, H. Sakurai, A. Hosomi, and M. Kumada, *Tetrahedron Lett.*, 1757 (1969); (e) V, H. Sakurai, A. Hosomi, and M. Kumada, *ibid.*, 1759 (1969); (f) VI, H. Sakurai and M. Yamagata, *Chem. Commun.*, 1144 (1970); (g) VII, H. Sakurai and A. Hosomi, *J. Amer. Chem. Soc.*, **92**, 7507 (1970).

[2] Presented by H. S. at the Special Symposium of the Chemical Society of Japan on Recent Problems in Organic Reaction Mechanisms, Tokyo, Japan, Oct 25, 1969.

[3] F. W. Stacey and J. F. Harris, Jr., *Org. React.*, 13, 91 (1966).

[4] Walling "Free Radicals in Solution," Wiley, New York, N. Y., 1957.

[5] C. Eaborn, R. A. Jackson, and R. Pearce, *Chem. Commun.*, 920 (1967).

[6] For a pertinent review see R. A. Jackson, *Advan. Free-Radical Chem.*, 3, 231 (1969).

[7] Y. Nagai and H. Sakurai, "Free-Radical Chemistry," H. Sakurai and K. Tokumaru, Ed., Nankodo Publishing Co., Tokyo, 1967, Chapter 12.

Table II. Reaction of Pentamethyldisilane with Di-*tert*-Butyl Peroxide in Toluene at 135° for 20 hr

	Run 1 mmol	Run 1 % yield	Run 2 mmol	Run 2 % yield
Starting materials				
Me_5Si_2H	5.108		1.576	
DTBP	5.164		1.653	
$PhCH_3$				
Products				
$PhCH_3$ (recovered)	4.717		1.664	
o-$CH_3C_6H_4Si_2Me_5$	0.115	3.26[a]	0.0263	3.00[a]
m-$CH_3C_6H_4Si_2Me_5$	0.277	7.84[a]	0.0637	7.27[a]
p-$CH_3C_6H_4Si_2Me_5$	0.145	4.11[a]	0.0319	3.64[a]
$PhCH_2Si_2Me_5$	0.266	7.53[a]	0.0509	6.71[a]
$(PhCH_2)_2$	0.141	7.98[a]	0.0411	9.38[a]
$PhCH(Si_2Me_5)OC(CH_3)_3$	0.236	6.68[a]	0.0462	5.27[a]
$Me(SiMe_2)_4Me$	0.333	13.0[b]	0.0748	9.49[b]
$Me_5Si_2OC(CH_3)_3$	1.06	20.8[b]	0.239	15.1[b]
$(CH_3)_3COH$	3.13		1.801	
CH_3COCH_3	Trace		Trace	

[a] Based on the amount of consumed toluene. [b] Based on the amount of consumed pentamethyldisilane.

Table III. Yields in Homolytic Aromatic Substitution of Benzene-Substituted Benzene Mixture at 135°

Starting materials	Substrates(PhX) $PhOCH_3$, mmol	$PhCH_3$, mmol	$PhCF_3$, mmol
PhH	9.405	4.153	8.872
PhX	16.134	8.191	10.977
DTBP	2.893	1.710	2.227
Me_5Si_2H	2.674	1.629	2.371

Products	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
$PhSi_2Me_5$	0.2232	0.2414	0.0727	0.0759	0.0725	0.0718
o-$XPhSi_2Me_5$	0.1066	0.1056	0.0193	0.0193	0	0
m-$XPhSi_2Me_5$	0.0628	0.0623	0.0460	0.0470	0.0915	0.0956
p-$XPhSi_2Me_5$	0.0138	0.0153	0.0240	0.0254	0.1003	0.1029

of the dimerization product was determined by comparing its ir, nmr, and uv spectra with those of the corresponding authentic sample.

Competitive Silylations. The reaction of pentamethyldisilane with a mixture of benzene and the appropriate aromatic compound in the presence of DTBP at 135° for 20 hr was carried out in a sealed tube. The reaction mixtures were analyzed by glc to identify the isomers of arylpentamethyldisilanes and then the isomer distribution was determined. All of the arylpentamethyldisilanes were separated by preparative glc.

The structure of ortho isomers was confirmed by their uv, ir, and nmr spectra, and glc analysis. The meta and para isomers were also identified by comparing their uv, ir, and nmr spectra and the retention times on glc with those of the authentic samples which were prepared from chloropentamethyldisilane and the corresponding Grignard reagents. Since complete resolution of *o*- and *m*-methoxyphenylpentamethyldisilane could not be attained by glc techniques, the isomer distribution was determined quantitatively by ir and nmr techniques.

In Table III are given the yields of substitution products for the homolytic aromatic silylation in a mixture of benzene and a substituted benzene under the same condition described in the previous section. As can be seen, virtually the same meta:para ratios of the product from toluene (1.91, 1.99, 1.92, and 1.85) were obtained in spite of diverse reaction conditions, indicative of the validity of competitive treatment.

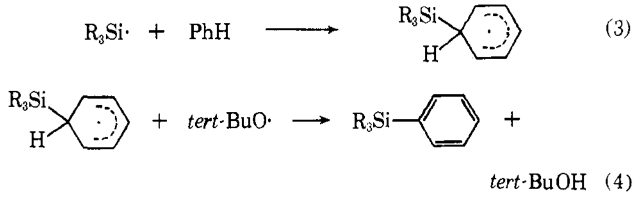
When halobenzenes were used as aromatic compounds, no halophenyl derivatives were detected in spite of careful examination, but benzene, phenylpentamethyldisilane, and bis(pentamethyldisilanyl) oxide were obtained. Thus, as shown earlier,[1c,8] it has been observed that halobenzenes were effectively reduced to benzene without undergoing homolytic aromatic silylations.

Discussion

Aromatic substitution by radical mechanisms has been an interesting problem from both the theoretical and practical point of view and has been investigated extensively by many workers. In homolytic aromatic substitution the formation of a substituted cyclohexadienyl radical, arising from the addition of a free radical to an aromatic compound, is generally the rate-determining step.[9] The products of the silylation reaction are similarly in accord with a homolytic process involving addition of organosilyl radicals to an aromatic ring (eq 1-5).

$$(tert\text{-BuO})_2 \longrightarrow 2tert\text{-BuO}\cdot \qquad (1)$$

$$tert\text{-BuO}\cdot + R_3SiH \longrightarrow tert\text{-BuOH} + R_3Si\cdot \qquad (2)$$



$$2R_3Si\cdot \longrightarrow R_3SiSiR_3 \qquad (5)$$

Thus, the formation of permethylated polysilanes is attributed to the recombination of organosilyl radicals. This is consistent with the result reported previously; silyl radicals formed by the reaction of cyclopropyldimethylsilane with di-*tert*-butyl peroxide gave 1,2-dicyclopropyltetramethyldisilane as a result of recombination.[10] Decomposition of DTBP and pentamethyl-

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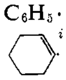
(8) J. Curtice, H. Gilman, and G. S. Hammond, *J. Amer. Chem. Soc.*, **79**, 4754 (1957).

(9) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, Oxford, 1960.

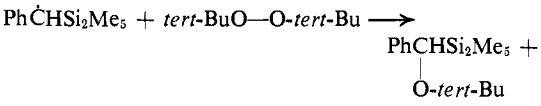
(10) J. R. Shelton and C. W. Uzelmeier, *J. Amer. Chem. Soc.*, **88**, 5222 (1966).

Table IV. Orientation and Meta to Para Ratios in Homolytic Aromatic Substitution

Attacking radicals	IP,[a] eV	$C_6H_5OCH_3$ Ortho	$C_6H_5OCH_3$ Meta	$C_6H_5OCH_3$ Para	$C_6H_5OCH_3$ Meta/para	$C_6H_5CH_3$ Ortho	$C_6H_5CH_3$ Meta	$C_6H_5CH_3$ Para	$C_6H_5CH_3$ Meta/para	$C_6H_5CF_3$ Ortho	$C_6H_5CF_3$ Meta	$C_6H_5CF_3$ Para	$C_6H_5CF_3$ Meta/para	ρ[b]
n-$PrMe_2Si\cdot$	(7.31)[c]					16	64	20	1.7	0	40	60	0.34	+1.6
$Me_5Si_2\cdot$		58	34	8	4.3	21	52	27	1.9	0	48	52	0.92	+1.4
c-$C_6H_{11}\cdot$[d]	7.76	67	28	5	5.6	32	43	25	1.7	6	52	42	1.2	+1.1
$CH_3\cdot$[e]	9.86	74	15	11	1.4	56	27	17	1.6					
$C_6H_5\cdot$	9.90	69[f]	18[f]	13[f]	1.4	66[g]	22[g]	13[g]	1.4	29[h]	41[h]	30[h]	1.4	+0.05
 [i]	(9.45)[j]	68	16	16	1.0	67	33[k]							
$PhC{\equiv}C\cdot$[l]						53	25	21	1.2					
$HOOCCH_2\cdot$[m]	(10.87)[n]	78	5	17	0.29									

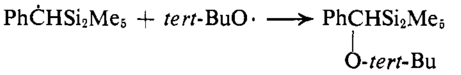
[a] Ionization potentials of attacking radicals. Values are taken from A. Streitwieser, Jr., *Progr. Phys. Org. Chem.*, **1**, 1 (1963), unless otherwise stated. [b] Hammett's ρ values where correlation was examined. [c] Value for $Me_3Si\cdot$, M. F. Lappert, J. Simpson, and T. R. Spalding, *J. Organometal. Chem.*, **17**, 1 (1969). [d] Reference 10. [e] Reference 14. [f] T. Inukai, K. Kobayashi, and O. Simamura, *Bull. Chem. Soc. Jap.*, **35**, 1576 (1966). [g] Reference 22. [h] D. Hey, F. Saunders, and G. H. Williams, *J. Chem. Soc.*, 554 (1961). [i] Reference 17. [j] Value for $CH_2{=}\dot{C}H$. [k] Not separated. [l] Reference 18, isomer distribution for ethylbenzene. [m] Reference 19. [n] Value for $NCCH_2\cdot$, see ref 19

disilane in excess toluene for 20 hr resulted in almost complete conversion of the peroxide to *tert*-butoxy radicals. The latter species mainly abstracted hydrogen from pentamethyldisilane, forming *tert*-butyl alcohol and pentamethyldisilanyl radicals, which subsequently coupled to form decamethyltetrasilane or attacked the aromatic solvent. Minor amounts of acetone were produced by the β scission of the *tert*-butoxy radicals. Formation of every possible termination product between pentamethyldisilanyl and benzyl radicals further supports a homolytic process. Formation of α-*tert*-butoxybenzylpentamethyldisilane may be rationalized by induced decomposition of DTBP, as suggested recently by Huang, *et al.*, in decomposition of DTBP in benzylic systems.[11] The facts, however, that the reaction of benzylpentamethyldisilane with DTBP at 80° in the presence of



$$Ph\dot{C}HSi_2Me_5 + tert\text{-}BuO\text{—}O\text{-}tert\text{-}Bu \longrightarrow \underset{\displaystyle O\text{-}tert\text{-}Bu}{PhCHSi_2Me_5} + tert\text{-}BuO\cdot$$

other free-radical initiators such as dibenzoyl peroxide gave no α-*tert*-butoxybenzylpentamethyldisilane, suggests that induced decomposition is unlikely in the present case. A coupling reaction between pentamethyldisilanylbenzyl radicals and *tert*-butoxy radicals seems likely.



$$Ph\dot{C}HSi_2Me_5 + tert\text{-}BuO\cdot \longrightarrow \underset{\displaystyle O\text{-}tert\text{-}Bu}{PhCHSi_2Me_5}$$

Evidence concerning the rate-determining step of the silylation may be obtained by a study of the kinetic isotope effect.[12] The silylation of hexadeuteriobenzene was carried out competitively with benzene. Isotope effects, k_H/k_D, of 1.50 ± 0.05 and 1.45 ± 0.05 were obtained for n-propyldimethylsilyl and pentamethyldisilanyl radical, respectively. The unexpected large value of isotope effect at a first glance appears to indicate that the addition process of silyl radicals is reversible. However, a rather large isotope effect $k_H/k_D = 1.33 \pm 0.05$ was also obtained in cyclohexylation under the same condition. Accordingly it can be considered that the isotope effect might in part include secondary isotope effect reflecting the inductive effect of the deuterio group. A sort of investigation to elucidate such a kind of secondary isotope effect originating in the change of hybridization at a reaction center of the deuteriobenzene system is now under way and the implication of such effects will be discussed in subsequent papers.

Table IV shows the isomer distributions for the reaction with substituted benzenes, along with available data from the literature on cyclohexylation,[10] methylation,[13–15] phenylation,[16] 1-cyclohex-1-enylation,[17] phenylethynylation,[18] and carboxymethylation.[19] Table IV also contains the preliminary results for n-propyldimethylsilyl radicals,[20] which revealed almost the same reactivity as pentamethyldisilanyl radicals. The high meta:para isomer ratio of the aromatic silylation products for toluene and anisole compared with other homolytic aromatic substitutions is noteworthy.

By comparing the orientation for homolytic aromatic substitution by pentamethyldisilanyl radicals with that for various other free radicals, it may be seen that for aromatic compounds containing an electron-releasing substituent such as methyl or methoxyl, the ratios of meta to para isomer decrease in the order: silylation > cyclohexylation > methylation > phenylation > 1-cyclohex-1-enylation > phenylethynylation > carboxymethylation. On the other hand, for aromatic compounds containing an electron-withdrawing group such as trifluoromethyl, the ratios increase in this order.

If the resonance effect does not play an important role in the transition state of free-radical addition to a benzene ring, these facts seem to indicate that for the aromatics substituted by an electron-releasing group, the greater the nucleophilicity of the attacking radicals, the larger the meta:para ratios, since the electron density of the para position is larger than that of the meta position. The reverse is the case for the aromatics substituted by an electron-withdrawing group.[10] Thus, in the silyla-

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(11) R. L. Huang, F. W. Lee, and S. H. Ong, *Chem. Commun.*, 1251 (1968).

(12) H. Zollinger, *Advan. Phys. Org. Chem.*, **2**, 163 (1964).

(13) E. L. Eliel, K. Rabindran, and S. H. Wilen, *J. Org. Chem.*, **22**, 859 (1957).

(14) B. Cowley, R. O. C. Norman, and W. A. Waters, *J. Chem. Soc.*, 1799 (1959).

(15) G. E. Corbelt and G. H. Williams, *ibid.*, 3437 (1964).

(16) D. H. Hey, *Advan. Free-Radical Chem.*, **2**, 47 (1967).

(17) P. Spagnolo and M. Tiecco, *Tetrahedron Lett.*, 2313 (1968).

(18) G. Martelli, P. Spagnolo, and M. Tiecco, *Chem. Commun.*, 282 (1969).

(19) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Amer. Chem. Soc.*, **91**, 138 (1969).

(20) The results for n-propyldimethylsilyl radical were obtained very recently by F. Mita in this laboratory. It is found from these data that this radical is slightly more nucleophilic than pentamethyldisilanyl radical (ρ value was +1.6).

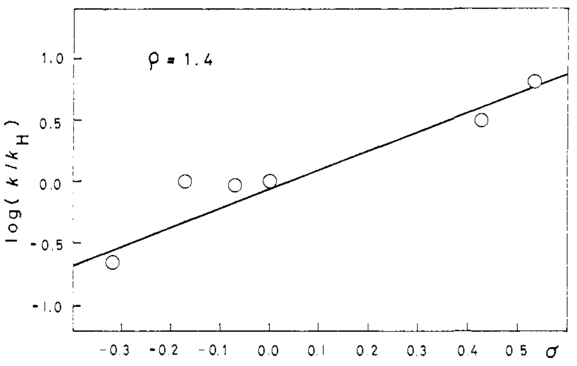
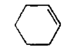
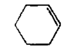


Figure 1. Relationship between log k/k_H and Hammett's σ parameters.

tion process the directional effects are similar to those in the case of the cyclohexylation and opposite to those normally observed in electrophilic aromatic substitution, and in the homolytic aromatic substitution the nucleophilicity of attacking radicals systematically increases in the order: *n*-propyldimethylsilylation > pentamethyldisilanylation > cyclohexylation > methylation > phenylation > 1-cyclohex-1-enylation > phenylethynylation > carboxymethylation.

Table V presents the relative reactivities and partial rate factors of homolytic aromatic silylation along with data from the literature for other free radicals. Inspection of these partial rate factors supports the arguments above. Thus, the para partial rate factors for the substrates containing an electron-releasing substituent such as *p*-CH$_3$O and *p*-CH$_3$ gradually increase in the series: silylation < cyclohexylation < phenylation < 1-cyclohex-1-enylation < phenylethynylation. However, for the compound substituted by an electron-withdrawing substituent such as *p*-CF$_3$ the para partial rate factors decrease in this series as the attacking radical becomes more electron seeking. Furthermore, the k_m/k values for these substrates also clearly demonstrate that the homolytic aromatic substitution by silyl radicals involves the attack of nucleophilic species upon the aromatic ring.

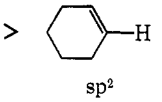
Table V. Relative Rates (k_X/k_H) and Partial Rate Factors (f_X)

Radical	Temp, °C	k_X/k_H[a]	f_X k_o/k	k_m/k	k_p/k
$C_6H_5OCH_3$					
Me_5Si_2·	135	0.45	0.81	0.47	0.22
c-C_6H_{11}	90	2.3	4.6	1.9	0.69
C_6H_5·	20	1.7	3.6	0.93	1.3
	80	1.5	3.06	0.72	1.44
HOOCCH$_2$·	90	3.0	7.0	0.45	3.1
$C_6H_5CH_3$					
n-PrMe$_2$Si·	135	0.53	0.21	0.85	0.53
Me_5Si_2·	135	0.62	0.39	0.95	1.01
c-C_6H_{11}·	90	0.76	0.73	0.98	1.1
	80	1.2	2.41	Not separated	
C_6H_5·	20	1.68	3.30	1.09	1.27
$C_6H_5C≡C$·[b]		(2.00)	(3.15)	(1.53)	(2.52)
$C_6H_5CF_3$					
n-PrMe$_2$Si·	135	2.67	0	2.60	7.74
Me_5Si_2·	135	2.19	0	3.15	6.81
c-C_6H_{11}·	90	2.0	0.36	3.1	5.0
C_6H_5·	80	1.0	0.87	1.2	1.8

[a] $k_X = 2k_o + 2k_m + k_p$; $k_H = 6k$. [b] Value for ethylbenzene.

That the ·CH$_2$COOH radical has a high ionization potential is suggested by the fact that the radical is oxidized with difficulty[19] and that the gas-phase ionization potential of the cyanomethyl radical, which should be similar to that of ·CH$_2$COOH, is 10.87 eV. These facts combined with the data of meta:para ratio in homolytic aromatic substitution rank the ·CH$_2$COOH radical as the least nucleophilic radical among the radicals discussed here.

For α,β unsaturation the nucleophilicity of radicals may parallel the assumed hybridization of the α carbon atom. In the following series nucleophilicity decreases as the s character of the α carbon increases. In other words the larger the s character of orbitals involving an unpaired electron becomes, the higher the electronegativity of a carbon atom in the free-radical center increases. These arguments and consideration of the relative electronegativities of free radicals[21] suggest that the nucleophilicities of these radicals would be the reverse of the order of electronegativities; that is, as in Table V: organosilyl > cyclohexyl > methyl > phenyl > 1-cyclohex-1-enyl > phenylethynyl.

RCH$_2$· >  ≃ C_6H_5· > R—C≡C·
sp^3 sp^2 sp^2 sp

Plots of the para and meta partial rate factors in pentamethyldisilanylation against Hammett's σ values are shown in Figure 1. It can be seen that the partial rate factors correlate satisfactorily, although not perfectly, with σ. The best line for the plots determines a slope of +1.4 by a least-squares method. The *m*-methoxy was excluded in this computation owing to rather poor analysis of ortho and meta isomer distributions by nmr techniques. The correlation factor is 0.945.

Recent investigations of homolytic arylation to substituted benzenes by Simamura and coworkers[22] have shown that the influence of a substituent can be divided into resonance and inductive effects. For meta substitution, only the latter term was important, while, for para substitution, partial rate factors were expressed as $\log(k/k_0) = \rho\sigma_p + \tau_p$, where τ_p is the term for stabilization related to the difference of the resonance energy for the substrate and the substituted cyclohexadienyl radical. The observed correlation with Hammett's σ parameters alone for homolytic aromatic silylation indicates that this reaction is mainly controlled by the polar effect of the substituent, contrary to homolytic arylation. Such polar effects presumably originate in the charge-transfer interaction in the transition state between the attacking radicals and substrates. The low ionization potential of the silyl radical makes the contribution of ionic structures in the transition state, due to a charge-transfer interaction, more significant than in the case of phenylation. In homolytic phenylation (ρ = 0.05) the attacking radical has an ionization potential and orbital energies of almost the same magnitude as the substrate, due to the σ radical of the phenyl radical.[23]

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(21) H. Pritchard and H. Skinner, *Chem. Rev.*, **55**, 745 (1955).

(22) R. Itô, T. Migita, N. Morikawa, and O. Simamura, *Tetrahedron*, **21**, 955 (1965).

Table VI. Physical Properties of Arylpentamethyldisilanes

	Bp, °C (mm)	n^{20}D	$d^{20}{}_4$
p-$CH_3C_6H_4Si(CH_3)_2Si(CH_3)_3$	119 (21)	1.5060	0.8651
m-$CH_3C_6H_4Si(CH_3)_2Si(CH_3)_3$	106 (14)	1.5080	0.8699
p-$CH_3OC_6H_4Si(CH_3)_2Si(CH_3)_3$	117–118 (9)	1.5159	0.9156
m-$CH_3OC_6H_4Si(CH_3)_2Si(CH_3)_3$	131 (14)	1.5125	0.9179
p-$CF_3C_6H_4Si(CH_3)_2Si(CH_3)_3$	100 (13)	1.4700	1.0096
m-$CF_3C_6H_4Si(CH_3)_2Si(CH_3)_3$	94–95 (15)	1.4686	1.0103

Table VII. Nmr Data of Some New Organosilicon Compounds

Compound	Chemical Shift (δ) in CCl_4				
	a	b	c	d	e
o-$\overset{a}{CH_3}\overset{b}{C_6H_4}Si(\overset{c}{CH_3})_2Si(\overset{d}{CH_3})_3$	2.38	6.95–7.35	0.38	0.06	
m-$CH_3C_6H_4Si(CH_3)_2Si(CH_3)_3$	2.34	7.05–7.20	0.28	0.03	
p-$CH_3C_6H_4Si(CH_3)_2Si(CH_3)_3$	2.33	6.95–7.30	0.29	0.04	
o-$\overset{a}{CH_3}O\overset{b}{C_6H_4}Si(\overset{c}{CH_3})_2Si(\overset{d}{CH_3})_3$	3.74	6.55–7.30	0.29	0.03	
m-$CH_3OC_6H_4Si(CH_3)_2Si(CH_3)_3$	3.72	6.60–7.29	0.32	0.07	
p-$CH_3OC_6H_4Si(CH_3)_2Si(CH_3)_3$	3.69	6.65–7.31	0.32	0.08	
m-$CF_3\overset{b}{C_6H_4}Si(\overset{c}{CH_3})_2Si(\overset{d}{CH_3})_3$		7.45–7.65	0.36	0.06	
p-$CF_3C_6H_4Si(CH_3)_2Si(CH_3)_3$		7.52	0.35	0.05	
$\overset{a}{C_6H_4}\overset{b}{CH}[Si(\overset{c}{CH_3})_2Si(\overset{d}{CH_3})_3]OC(\overset{e}{CH_3})_3$	7.19	2.68	0.14	0.04	1.17

That organosilyl radicals are of nucleophilic nature is therefore further supported by the ρ value for silylation ($\rho = +1.4$) which is relatively large as compared with that for cyclohexylation or for arylation.

Substantial ortho deactivation is evident in cyclohexylation and silylation reactions with toluene and benzotrifluoride. The steric effect may explain in part the data for toluene; however, it cannot account in full for the extreme ortho deactivation of benzotrifluoride toward the silyl radicals, since trifluoromethyl is of the same size as methyl and the inductive effect is favorable due to the electron-withdrawing nature of the trifluoromethyl group. The present data may be interpreted by fluorine hyperconjugation[24,25] in a similar manner as cyclohexylation.[12] Fluorine hyperconjugation results in a partial negative charge on fluorine as well as partial positive charges in the ortho and para position to the trifluoromethyl group. The electronegative fluorine may exert a repulsive force to an incoming nucleophilic silyl radical to the ortho position. Consequently, such an electrostatic effect of the trifluoromethyl group combined with its steric effect should be the basis for the interpretation.

Experimental Section

Materials. Benzene, toluene, benzotrifluoride, and di-*tert*-butyl peroxide (DTBP) were commercially available materials of reagent grade, and used after distillation through a 35-cm column packed with glass helicoils. Triethylchlorosilane was prepared by desilylation of phenyltriethylsilane with hydrogen chloride in the presence of a catalytic amount of aluminum chloride in chloroform, and it was reduced with lithium aluminum hydride according to the known procedure. The boiling point was 108° (lit.[26] bp 108.7°). Pentamethyldisilane and 1*H*-heptamethyltrisilane were prepared by the reduction of the corresponding chlorosilanes which were prepared according to the known procedures[27] with lithium aluminum hydride. The boiling points were 99.5 and 61° (24 mm), respectively (lit.[28] bp 97 and 61° (22 mm)).

Organosilylbenzenes. Phenyltriethylsilane was prepared from phenyltrichlorosilane, ethyl bromide, and magnesium by the Grignard method. It had bp 109° (15 mm) (lit.[29] bp 122–125° (20 mm)). We are indebted to Mr. K. Tominaga for preparation of phenylpentamethyldisilane and 1-phenylheptamethyltrisilane from the corresponding chlorosilanes and phenylmagnesium chloride in tetrahydrofuran, Mr. M. Yamagata for preparation of *n*-decamethyltetrasilane, and Dr. M. Ishikawa for preparation of *n*-tetradecamethylhexasilane.

Substituted Phenylpentamethyldisilanes. All of the *p*- and *m*-arylpentamethyldisilanes and benzylpentamethyldisilane were prepared by the Grignard method.[30] Physical properties are listed in Table VI. Table VII shows some spectroscopic data of these compounds including some derivatives separated from the reaction mixture.

***tert*-Butoxypentamethyldisilane.** *tert*-Butoxypentamethyldisilane was prepared by the reaction of 16.7 g (0.10 mol) of chloropentamethyldisilane with 7.5 g (0.10 mol) of *tert*-butyl alcohol in the presence of 7.9 g (0.10 mol) of pyridine in dry benzene. The yield was 9.0 g (0.044 mol) (44%); bp 65° (24 mm) n^{20}D 1.4258; $d^{20}{}_4$ 0.7963; mol ratio 65.76 (65.94).

Anal. Calcd for $C_9H_{24}Si_2O$: C, 52.87; H, 11.83. Found: C, 52.76; H, 11.69.

Reaction of Hydrosilanes with DTBP in Aromatic Solvents. An equimolar mixture of a hydrosilane and DTBP was dissolved in a weighed aromatic solvent and this mixture was then placed in a glass tube of *ca.* 5-ml volume. The glass tube was sealed under nitrogen and immersed in a constant-temperature bath at 135°. After 20 hr, the reaction mixture was analyzed by glc using a column packed with Apiezon-L grease on Celite 545. The products were isolated by preparative glc and identified by their ir, uv, and nmr spectra. Some of the products were prepared by an alternative and unequivocal route for comparison as listed in Table VII. Whenever possible, amounts of the products were determined by glc with corrections of thermal conductivities.

Competitive Reactions. 1. Substituted Aromatics–Benzene. An appropriate mixture of benzene and substituted benzene was prepared and allowed to react with pentamethyldisilane and DTBP under the same conditions described in the previous section. Then the reaction mixture was analyzed directly by glc and the ratio of arylsilane to silylbenzene was determined. In this manner the relative reactivity (k_X/k_H) of each monosubstituted benzene relative to benzene was obtained, and the partial rate factors (f_X) for the ortho, meta, and para substitution were calculated. The values in Table V are accurate to a few per cent. In the case of *o*- and *m*-anisylpentamethyldisilane, which were not separated by glc, differ-

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ences of chemical shifts of methoxy methyl protons and methyl protons on silicon were utilized in the determination, and amounts of each isomers were calculated from the peak area of protons.

2. Benzene–Hexadeuteriobenzene. A mixture of carefully weighed benzene and hexadeuteriobenzene was made and an aliquot was saved. The remainder was added to the hydrosilane, followed by introduction of DTBP. In this manner, each of five solutions was prepared for pentamethyldisilane and *n*-propyldimethylsilane of varying concentration. Each mixture was allowed to react in the same way described above. From the reaction mixtures, phenylsilanes were separated by glc.

Mass spectra of phenylsilanes were obtained with a Hitachi RMU-6D mass spectrometer, the ionizing energy being maintained at 70 eV. The analyses of phenylpentamethyldisilane–pentadeuteriophenylpentamethyldisilane mixtures were carried out by comparing the relative intensity of the molecular ions, $(C_6H_5Si_2Me_5)^+$ at *m/e* 208 and $(C_6D_5Si_2Me_5)^+$ at *m/e* 213. The fragment ions at *m/e* 193 and 135 were also compared to the corresponding ions at *m/e* 198 and 140. The results were in good agreement and were averaged. The molar ratio of reactants had little effect on the k_H/k_D values.

By comparing the relative intensity of ions at *m/e* 178, 163, 135, and 121 from *n*-propyldimethylsilane with the corresponding ions at *m/e* 183, 168, 140, and 126 from the deuterated compound, the k_H/k_D was calculated.

The same approach was used to determine the k_H/k_D of cyclohexylation by comparing the relative intensity of ions at *m/e* 160, 117, and 91 with the corresponding peaks at *m/e* 165, 122, and 96.

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Polylithium Compounds. IV. Polylithiation of Nitriles and the Preparations of Trisilyl Ynamines[1,2]

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Abstract: Acetonitrile reacts with excess *tert*-butyllithium in ether at −78° to form Li_2C_2HN and 2 equiv of isobutane. With aldehydes and ketones, Li_2C_2HN gives diadducts, $(LiOCR_2)_2CHCN$, in high yields. These adducts are converted to the corresponding trimethylsilyl derivatives with trimethylchlorosilane. Li_2C_2HN, in the presence of excess base, and trimethylchlorosilane in tetrahydrofuran give a mixture of tris(trimethylsilyl)ethynylamine (**9**) and tris(trimethylsilyl)ketenimine (**1**). Li_2C_2HN also reacts with *tert*-butyldimethylchlorosilane and dimethylchlorosilane to give the corresponding trisilyl ynamines and ketenimines. Trisilyl ynamines undergo a quantitative thermal rearrangement to trisilyl ketenimines. Trimethylsilylacetonitrile and bis(trimethylsilyl)acetonitrile react with *n*-butyllithium forming a dilithium derivative, $Li_2(Me_3Si)C_2N$, and a monolithium derivative, $Li(Me_3Si)_2C_2N$, respectively. The structures of the metalated nitriles were investigated by infrared spectroscopy.

An isoelectronic series of linear species containing 16 valence electrons (the carbon dioxide structure) is known in inorganic chemistry (Table I).[3] It has been shown that propyne reacts with excess *n*-butyllithium to form the perlithio compound C_3Li_4.[2,4] This compound can be regarded formally as a derivative of the linear trianion $C_3{}^{4-}$, isoelectronic with carbon dioxide. If this formalism is used, Table I shows that there is a gap at −3 charge. The trilithium derivatives of acetonitrile or methylisocyanide[5] could be considered members of this series and would serve to fill in the gap at −3 charge.

Table I. Isoelectronic Species with 16 Valence Electrons

Charge	Species
+1	$NO_2{}^+$
0	CO_2, N_2O, CS_2, FCN
−1	NCO^-, NCS^-, $N_3{}^-$, CNO^-
−2	NCN^{2-}
−3	
−4	(CCC^{4-})

Metalation of Acetonitrile. Acetonitrile readily reacts with 1 equiv of *N*-sodiohexamethyldisilazane[6] or 1 equiv of *n*-butyllithium in tetrahydrofuran (THF)[7,8] to give monometalated derivatives. The possible formation of trimetalated derivatives from the reaction of acetonitrile with 3 equiv of these bases has been reported also.[7,9] The existence of trimetalated acetonitriles was based solely on the isolation of trialkyl and trisilyl derivatives of acetonitrile from reactions of the metalated nitriles with alkyl halides and trimethylchlorosilane.

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