room temperature under reduced pressure. The unreacted dimethyl fumarate was removed by filtration and the residue placed under vacuum for 12 h to remove the unreacted enamine, leaving 0.46 g of **3b** as yellow oil. Attempts to further purify **3b** resulted in isomerization to **3a**: NMR ($CDCl_3$) δ 0.92 (s, 3 H), 1.30 (s, 3 H), 2.7–3.2 (m, 8 H), 3.58 (s, 6 H); IR (thin film) 1737 cm^{-1}.

Acknowledgment. Support of this work by the National Science Foundation (CHE 78-01120) is gratefully acknowledged.

Registry No. **1**, 2403-57-8; **2**, 624-49-7; **3a**, 75444-57-4; **3b**, 75494-57-4; dimethyl α-pyrrolidinosuccinate, 62626-92-0.

Pyrolysis of 1-(Trimethylsilyl)-1-alkanols. New Carbene Precursors of Silylcarbene and Phenylcarbene[1]

Akira Sekiguchi and Wataru Ando*

Department of Chemistry, The University of Tsukuba, Niiharigun, Ibaraki 305, Japan

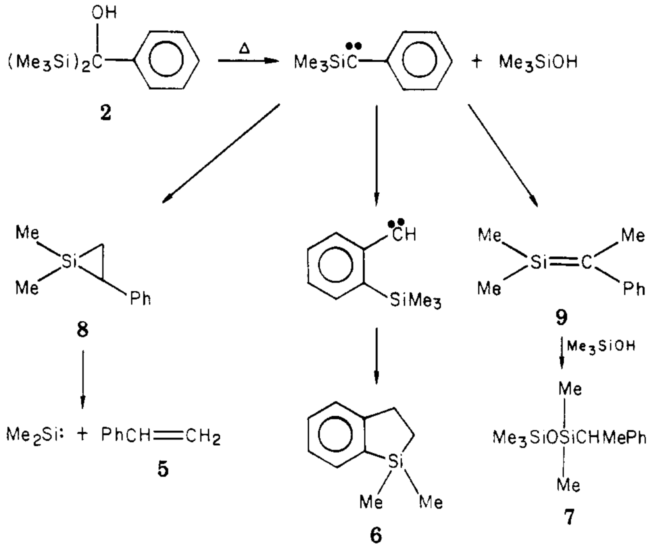
Received June 4, 1980

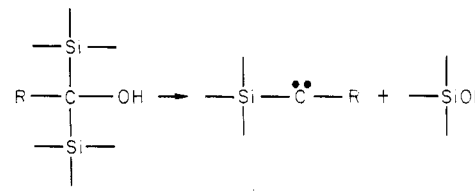
Pyrolysis of bis(trimethylsilyl)phenylmethanol gave (trimethylsilyl)phenylcarbene by the elimination of trimethylsilanol and the products were compared with those of (trimethylsilyl)phenyldiazomethane. Alkylsilylcarbenes obtained from the pyrolyses of 1,1-bis(trimethylsilyl)-1-alkanols afforded vinyltrimethylsilanes in high yields. (Trimethylsilyl)phenylmethanols were found to be excellent precursors of phenylcarbenes and their intramolecular reactions were also studied.

Introduction

In recent years, interest in the chemistry of organometallic carbenes has remarkably increased,[2] and detailed studies of silylcarbenes, (trimethylsilyl)(carboethoxy)carbene,[3-5] (trimethylsilyl)phenylcarbene,[6-9] (trimethylsilyl)carbene,[10-13] and bis(trimethylsilyl)carbene[14] have been reported. The proposed intramolecular reaction of silylcarbenes to give silicon–carbon double bonds (silenes) has also attracted interest. Silylcarbenes are generally produced by the decomposition of silyl diazo compounds, but several steps are required to synthesize silyl diazo compounds, and care must be taken to avoid the explosion of such diazo compounds. Other routes to silylcarbenes reported so far involve the decomposition of organomercury reagents such as $(Me_3SiCCl_2)_2Hg$,[15,16] base-induced α-elimination of (halomethyl)silane,[17-20] and an insertion of atomic carbon into a silicon–hydrogen bond.[21] However, some of these processes are not suitable because of several side reactions. Since silicon has a strong affinity toward oxygen, 1,1-bis(trimethylsilyl)-1-alkanols (**1**) are expected to produce silylcarbenes by the elimination of silanol.

Scheme I





1

We report here that compounds **1** are very convenient precursors of silylcarbenes and also demonstrate the intramolecular reactions of (alkylsilyl)carbenes and substi-

---

[1] Sekiguchi, A.; Ando, W. *Tetrahedron* Lett. **1979**, 4077.

[2] Sekiguchi, A.; Ando, W. *J. Synth. Org. Chem.* **1977**, *35*, 897.

[3] Ando, W.; Hagiwara, T.; Migita, T. *J. Am. Chem. Soc.* **1973**, *95*, 7518.

[4] Ando, W.; Sekiguchi, A.; Migita, T.; Kammula, S.; Green, M.; Jones, M., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 3818.

[5] Ando, W.; Sekiguchi, A.; Hagiwara, T.; Migita, T.; Chowdhry, V.; Westheimer, F. H.; Kammula, S. L.; Green, M.; Jones, M., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6393.

[6] Ando, W.; Sekiguchi, A.; Hagiwara, T.; Migita, T. *J. Chem. Soc., Chem. Commun.* **1974**, 372.

[7] Ando, W.; Sekiguchi, A.; Ogiwara, J.; Migita, T. *J. Chem. Soc., Chem. Commun.* **1975**, 145.

[8] Barton, T. J.; Kilgour, J. A.; Gallucci, R. R.; Rothschild, A. J.; Slutsky, J.; Wolf, A. D.; Jones, M., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 657.

[9] Ando, W.; Sekiguchi, A.; Rothschild, A. J.; Gallucci, R. R.; Jones, M., Jr.; Barton, T. J.; Kilgour, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 6995.

[10] Ando, W.; Sekiguchi, A.; Migita, T. *Chem. Lett.* **1976**, 779.

[11] Kreeger, R. L.; Schechter, H. *Tetrahedron Lett.* **1975**, 2061.

[12] Chapman, O. L.; Chang, C.-C.; Jung, J.; Kolc, M. E.; Lowe, J. A.; Barton, T. J.; Tumey, M. L. *J. Am. Chem. Soc.* **1976**, *98*, 7844.

[13] Chedekel, M. R.; Skoglund, M.; Kreeger, R. L.; Schechter, H.; *J. Am. Chem. Soc.* **1976**, *98*, 7846.

[14] Barton, T. J.; Hoekman, S. K. *J. Am. Chem. Soc.* **1980**, *102*, 1584.

[15] Seyferth, D.; Hanson, E. M. *J. Am. Chem. Soc.* **1968**, *90*, 2439.

[16] Seyferth, D.; Hanson, E. M. *J. Organomet. Chem.* **1971**, *27*, 19.

[17] Skell, P. S.; Goldstein, E. J. *J. Am. Chem. Soc.* **1964**, *86*, 1442.

[18] Connoly, J. W.; Urruy, G. *J. Org. Chem.* **1964**, *29*, 619.

[19] Connoly, J. W. *J. Organomet. Chem.* **1968**, *11*, 429.

[20] Olofson, R. A.; Hoskin, D. H.; Lotts, K. D. *Tetrahedron Lett.* **1978**, 1677.

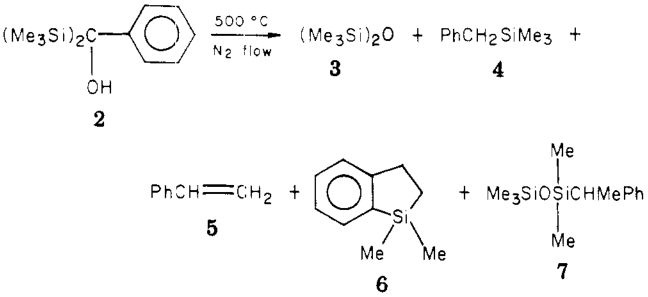
[21] Skell, P. S.; Owen, P. W. *J. Am. Chem. Soc.* **1972**, *94*, 1578.

0022-3263/80/1945-5286$01.00/0

tuted phenylcarbenes generated by the pyrolyses of (trimethylsilyl)phenylmethanols.

Results and Discussion

The pyrolyses were carried out by passing bis(trimethylsilyl)-1-alkanols through a vertical Pyrex tube heated at ca. 500 °C (nitrogen flow; ca. 11 mL/min) and then the pyrolysates were trapped in a receiver cooled by dry ice–acetone. Pyrolysis of bis(trimethylsilyl)phenylmethanol (**2**) at ca. 500 °C gave five products which were identified as hexamethyldisiloxane (**3**), benzyltrimethylsilane (**4**, 2%), styrene (**5**, 10%), 1,1-dimethyl-1-silaindan (**6**, 27%), and siloxane (**7**, 29%) by gas chromatographic analyses. The structures of the products were confirmed by NMR, IR, and mass spectra and comparisons with authentic samples.



2 **3** **4** **5** **6** **7**

Next, we studied the pyrolysis of (trimethylsilyl)phenyldiazomethane [$Me_3SiC(N_2)Ph$] (ca. 500 °C, nitrogen flow system) which gave bis(trimethylsilyl)stilbene (13%), benzyltrimethylsilane (2%), styrene (2%), and the silaindan **6** (15%).[9] Copyrolysis with methanol produced methoxysilane $MeOSi(Me_2)CHMePh$ (16%) together with the above products.[9] The similarity in products suggests that the bis(trimethylsilyl)methanol (**2**) produced (trimethylsilyl)phenylcarbene by the elimination of trimethylsilanol under the reaction conditions (Scheme I).

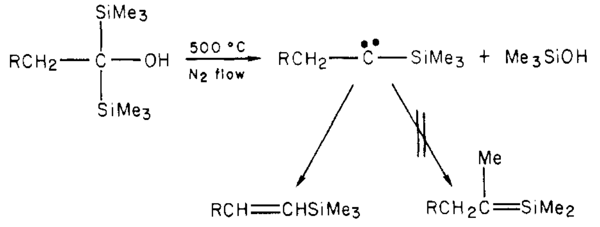
Benzyltrimethylsilane (**4**) is a hydrogen-abstraction product of (trimethylsilyl)phenylcarbene and is a typical minor product of carbene reactions. The silaindan (**6**) arises from [*o*-(trimethylsilyl)phenyl]carbene via a carbene–carbene rearrangement of the (trimethylsilyl)phenylcarbene.[8,9,22] The styrene **5** is probably formed by the thermal decomposition of 1,1-dimethyl-2-phenylsilirane (**8**) produced by the intramolecular C–H insertion of the (trimethylsilyl)phenylcarbene. The siloxane (**7**) is the addition product of trimethylsilanol to 1,2,2-trimethyl-1-phenylsilene (**9**) and hexamethyldisiloxane (**3**) is produced by dehydration of trimethylsilanols. It appears that 1,1-bis(trimethylsilyl)-1-alkanols are convenient sources of silylcarbenes.

Pyrolysis of 1,1-bis(trimethylsilyl)-1-decanol (**10**) at ca. 500 °C gave 1-(trimethylsilyl)-1-decene in 93% yield along with hexamethyldisiloxane and at ca. 400 °C the vinylsilane was obtained in 71% yield together with 27% yield of the recovered **10**. The vinylsilane was collected by bulb-to-bulb distillation, and then the cis and trans isomers were separated by preparative gas chromatography. The cis to trans ratio of the vinylsilanes was almost unity by gas chromatographic analysis. The coupling constant of olefinic hydrogens was 19 Hz for the trans isomer and 14 Hz for the cis isomer. The vinylsilane may be formed by a hydrogen migration to a carbenic carbon in nonyl(trimethylsilyl)carbene produced by the pyrolysis of the silylated alcohol (**10**). The nonstereospecific mixture of the vinylsilane was obtained because of the high temperature of the reaction. No product from a silene reaction could be found.

Table I. Pyrolysis of 1,1-Bis(trimethylsilyl)-1-alkanols[a]

alkanol	product[b]	% yield[c]	cis/ trans[d]
$Me(CH_2)_8$-$C(SiMe_3)_2OH$ (**10**)	$Me(CH_2)_7CH=CHSiMe_3$	93	1.0
$Me(CH_2)_6$-$C(SiMe_3)_2OH$ (**11**)	$Me(CH_2)_5CH=CHSiMe_3$	98	1.0
$PhCH_2CH_2$-$C(SiMe_3)_2OH$ (**12**)	$PhCH_2CH=CHSiMe_3$	94	1.3

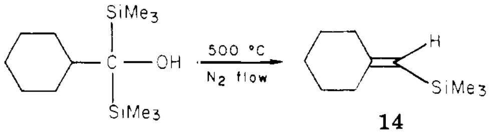
[a] Pyrolysis at ca. 500 °C. [b] Products were collected by bulb-to-bulb distillation. [c] Isolated yields. [c] Determined by gas chromatographic analysis.



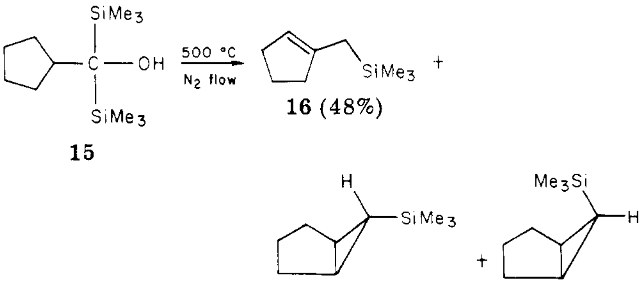
It is observed that (alkylsilyl)carbene prefers hydrogen migration to give vinylsilane rather than silyl methyl migration to give a silene intermediate. Pyrolyses of bis(trimethylsilyl)alkanols **11** and **12** also produced vinylsilanes in high yields and their isomer ratios were almost unity (Table I).

These results provide a new method for the synthesis of vinylsilanes via silylcarbene intermediates. Although the reaction conditions are relatively drastic, it seems to be a very convenient method for the preparation of vinylsilanes because 1,1-bis(trimethylsilyl)-1-alkanols are easily prepared from the corresponding ester and trimethylchlorosilane in the presence of sodium.[23]

Pyrolysis of bis(trimethylsilyl)cyclohexylmethanol (**13**) afforded cyclohexylidene trimethylsilane (**14**) in 90% yield together with hexamethyldisiloxane. However, the reaction of bis(trimethylsilyl)cyclopentylmethanol (**15**) was quite different from that of the cyclohexylmethanol **13** and gave allylsilane **16** along with *exo*- and *endo*-(trimethylsilyl)cyclopropanes **17** and **18**.



13 **14**



15 **16** (48%) **17** (26%) **18** (9%)

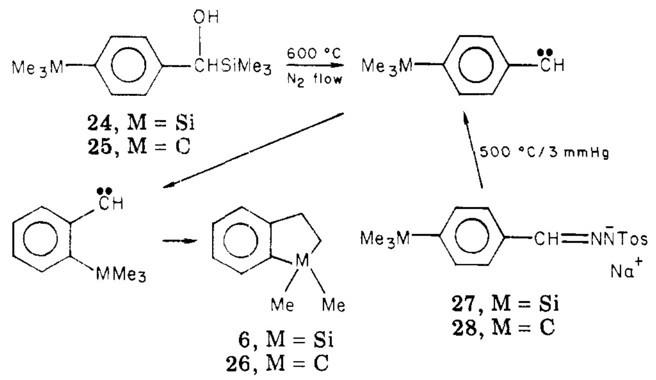
The identifications of *exo*- and *endo*-(trimethylsilyl)cyclopropanes **17** and **18** were based on their NMR spectra.

---

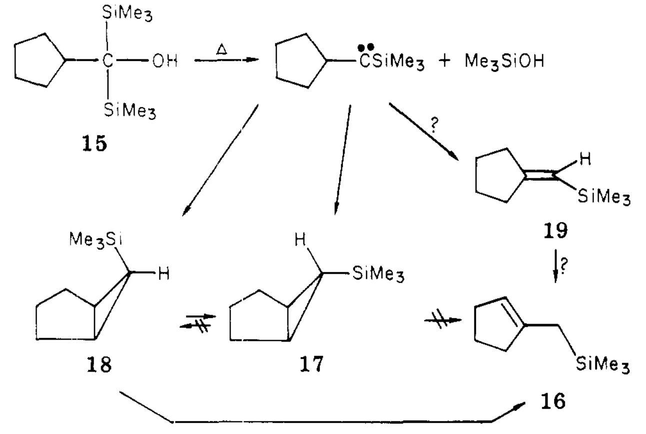
(22) Jones, M., Jr. *Acc. Chem. Res.* **1974**, *7*, 415.

(23) Kuwajima, I.; Minami, N.; Abe, T.; Sato, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2391.

Scheme II



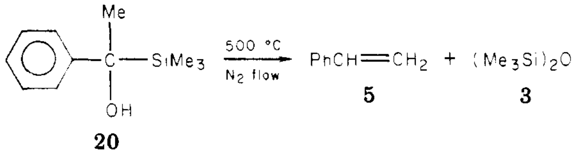
The NMR spectrum of **17** showed the trimethylsilyl group at δ −0.10 as singlet and the cyclopropyl methine proton attached to the trimethylsilyl group at δ −0.65 as triplet (J = 5 Hz). In the compound **18**, these resonances were observed at δ 0.07 (s) and −0.60 (t, J = 9 Hz). It is well-known that the magnitude of the cis coupling constant between vicinal protons in cyclopropanes is greater than that of the trans coupling constant.[24-26] *exo*- and *endo*-(trimethylsilyl)cyclopropanes **17** and **18** are evidently direct intramolecular C–H insertion products in cyclopentyl(trimethylsilyl)carbene. The formation of the cyclopropanes provides strong support for the generation of the free silylcarbenes.

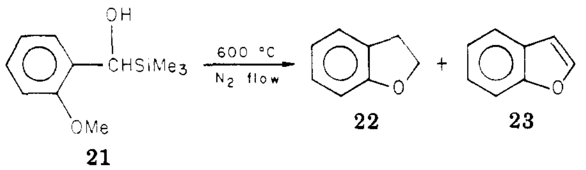


Allylsilane **16** may be formed from either thermal decomposition of the silylcyclopropanes or 1,3-shift of a hydrogen in cyclopentylidene trimethylsilane **19**. Although the pyrolysis of *exo*-cyclopropane **17** did not give the allylsilane **16**, *endo*-cyclopropane **18** produced the allylsilane **16** (22%) together with *exo*-cylopropane **17** (32%) and unchanged cyclopropane **18** (46%) under the same conditions.

The ring-size effect observed is quite similar to that observed in the reaction of cyclopentyl- and cyclohexylcarbenes.[27] As a Newman projection shows, the divalent carbon, the ring carbon to which it is attached, and the adjacent C–H bond are nearly coplanar, and the conformation required for insertion can be achieved.

Our reactions were extended to the generation of phenylcarbenes by intramolecular elimination of trimethylsilanol from (trimethylsilyl)phenylmethanol. Phenylcarbenes are generally produced by the decomposition of either phenyldiazomethane or benzaldehyde tosylhydrazone salt. However, they are often unsuitable phenylcarbene precursors because of their instability or low solubility. (Trimethylsilyl)phenylmethanols would be convenient sources of phenylcarbenes since they are readily available and can be easily handled. Pyrolysis of 1-(trimethylsilyl)-1-phenylethanol (**20**) at 500 °C afforded styrene (**5**, 91%) and hexamethyldisiloxane (**3**). Similar pyrolysis of **21** produced 2,3-dihydrobenzofuran (**22**, 28%) and 2,3-benzofuran (**23**, 16%).





These results seem to involve the formation of phenylcarbenes by the elimination of trimethylsilanol. The styrene may be produced by a hydrogen migration in methylphenylcarbene, and dihydrobenzofuran **22** by a direct intramolecular insertion of (*o*-methoxyphenyl)carbene into the C–H bonds of the methoxy group. Dehydrogenation of the dihydrobenzofuran **22** gives the benzofuran **23**.

Pyrolyses of (trimethylsilyl)[*p*-(trimethylsilyl)phenyl]methanol (**24**) and (trimethylsilyl)(*p*-*tert*-butylphenyl)methanol (**25**) gave 1,1-dimethyl-1-silaindan (**6**) and 1,1-dimethylindan (**26**) in 44 and 22% yields, respectively. These products arise from intramolecular insertion of *o*-(trimethylsilyl)- and (*o*-*tert*-butylphenyl)carbenes into the C-H bonds of the *o*-trimethylsilyl and *tert*-butyl groups via carbene-carbene rearrangement of *p*-(trimethylsilyl)- and (*p*-*tert*-butylphenyl)carbenes[28,29] (Scheme II).

The above results were compared with those of the pyrolyses of *p*-(trimethylsilyl)benzaldehyde tosylhydrazone sodium salt (**27**) and *p*-*tert*-butylbenzaldehyde tosylhydrazone sodium salt (**28**). Silaindan **6** was obtained in 15% yield when the sodium salt **27** was pyrolyzed at 500 °C in vacuo. Indan **26** was also produced in 23% yield by the pyrolysis of the sodium salt **28** under the above reaction conditions. It is now clear that free phenylcarbenes are involved in the pyrolysis of (trimethylsilyl)phenylmethanols.

Experimental Section

The NMR and IR spectra were recorded on Varian EM 360A and Hitachi 260-50 spectrometers. Mass spectra were obtained by a Hitachi RMU-6M mass spectrometer at 20 eV. Gas chromatographic analyses were done by a Hitachi gas chromatograph with a 5 mm × 3 m glass column of 10% SF-96 on Celite 545. Preparative gas chromatographic separations were carried out on an Ohkura gas chromatograph with a 7 mm × 2 m stainless steel column of 10% SF-96 on Celite 545 or with 7 mm × 3 m stainless steel column of 10% polyethylene glycol 20M on Celite 545. All boiling points and melting points were uncorrected.

---

(24) Graham, J. D.; Rogers, M. T. *J. Am. Chem. Soc.* **1962**, *84*, 2249.

(25) Patel, D. J.; Howden, M. E. H.; Roberts, J. D. *J. Am. Chem. Soc.* **1963**, *85*, 3218.

(26) Schöllkopf, U.; Pitterof, W. *Chem. Ber.* **1964**, *97*, 636.

(27) Richey, H. G., Jr.; Hill, E. A. *J. Org. Chem.* **1964**, *29*, 421.

(28) Sekiguchi, A.; Ando, W. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3067.

(29) Chambers, G. R.; Jones, M., Jr. *Tetrahedron Lett.* **1978**, 5193. Chambers and Jones observed several very minor products together with indan derivatives in the reactions of (*p*-*tert*-butylphenyl)carbene and [*p*-(trimethylsilyl)phenyl]carbene, but we did not observe these very minor products.

Table II. Spectroscopic Data of New 1,1-Bis(trimethylsilyl)-1-alkanols

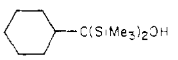
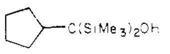
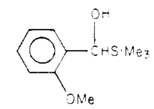
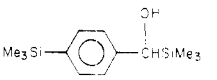
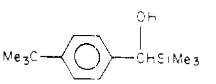
alkanol	bp, °C (mmHg)	% yield	NMR (CCl_4), δ	IR (neat), ν(OH), cm^{-1}	anal. found	anal. calcd
$Me(CH_2)_8C(SiMe_3)_2OH$	165-169 (13)	43	0.06 (s, 18 H, $SiCH_3$), 0.40 (br s, 1 H, OH), 0.68-1.90 (m, 19 H, aliphatic CH)	3450	C, 63.76 H, 12.59	63.49 12.65
	111-116 (3)	52	0.17 (s, 18 H, $SiCH_3$), 0.63 (br s, 1 H, OH), 0.87-2.00 (m, 11 H, aliphatic CH)	3470	C, 60.73 H, 11.81	60.39 11.69
	83-86 (2)	37	0.67 (s, 18 H, $SiCH_3$), 0.78 (br s, 1 H, OH), 1.07-2.33 (m, 9 H, aliphatic CH)	3480	C, 59.92 H, 11.43	58.94 11.54

Table III. Spectroscopic Data of (Trimethylsilyl)phenylmethanols

alkanol	mp, °C	NMR (CCl_4), δ	IR (KBr), ν(OH), cm^{-1}	anal. found	anal. calcd
	63-64	−0.05 (s, 9 H, $SiCH_3$), 1.62 (s, 1 H, OH), 3.80 (s, 3 H, OCH_3), 4.85 (s, 1 H, CHSi), 6.60-7.53 (m, 4 H, Ar H)	3325	C, 62.90 H, 8.57	62.81 8.62
	77-78	−0.03 (s, 9 H, $SiCH_3$), 0.30 (s, 9 H, $SiCH_3$), 1.95 (br s, 1 H, OH), 4.33 (s, 1 H, CHSi), 7.05 and 7.37 (a pair of d, AA'BB', J = 8 Hz, aromatic, 4 H)	3525	C, 61.95 H, 9.59	61.83 9.58
	82-83	−0.05 (s, 9 H, $SiCH_3$), 1.37 (s, 9 H, CMe_3), 1.92 (s, 1 H, OH), 4.33 (s, 1 H, CHSi), 7.07 and 7.33 (a pair of d, AA'BB', J = 8 Hz, aromatic, 4 H)	3525	C, 71.28 H, 10.27	71.12 10.23

Preparation of 1,1-Bis(trimethylsilyl)-1-alkanols.[23,30] Bis(trimethylsilyl)phenylmethanol (**2**),[30] 1,1-bis(trimethylsilyl)-1-octanol (**11**),[23] and 1,1-bis(trimethylsilyl)-3-phenyl-1-propanol (**12**)[23] were prepared by known procedures as referenced. 1,1-Bis(trimethylsilyl)-1-decanol (**10**), bis(trimethylsilyl)cyclohexylmethanol (**13**), and bis(trimethylsilyl)cyclopentylmethanol (**15**) were also prepared by similar methods. Spectroscopic data are given in Table II.

General Preparation of (Trimethylsilyl)phenylmethanols. 1-(Trimethylsilyl)-1-phenylethanol (**20**) was prepared by the reaction of benzoyltrimethylsilane with methylmagnesium iodide.[30] (Trimethylsilyl)(o-methoxyphenyl)methanol (**21**), (trimethylsilyl)[*p*-(trimethylsilyl)phenyl]methanol (**24**), and (trimethylsilyl)(*p-tert*-butylphenyl)methanol (**25**) were prepared by the hydrolysis of the corresponding α-bromobenzyltrimethylsilanes. For example, (trimethylsilyl)(*p-tert*-butylphenyl)methanol (**25**) was prepared as follows. α-Bromo(*p-tert*-butylbenzyl)trimethylsilane (29.9 g, 0.1 mol) was dissolved in 100 mL of water and 500 mL of acetone. Silver acetate (16.7 g, 0.1 mol) was added to the mixture which was stirred overnight in a flask. Precipitated silver bromide was filtered off and the filtrate was concentrated. The residue was extracted with ether and dried over anhydrous magnesium sulfate. Evaporation of the ether afforded the crude product which was recrystallyzed from hexane to give a white solid (11.4 g, 48%). Spectroscopic data are given in Table III.

General Pyrolysis Procedure. The pyrolysis apparatus consisted of a 28 × 1 cm Pyrex glass tube packed with Pyrex chips. The upper end of the tube was equipped with a rubber cap for a syringe introduction of the sample and a nitrogen gas inlet. The pyrolysis tube was maintained at ca. 500 °C and the nitrogen flow was ca. 11 mL/min. The sample was introduced drop by drop by using a 1-mL syringe. The pyrolysates were trapped in a receiver cooled by dry ice-acetone.

Pyrolysis of Bis(trimethylsilyl)phenylmethanol (2). Bis(trimethylsilyl)phenylmethanol (0.485 g) was pyrolyzed at 500 °C. An additional 1 mL of benzene was slowly passed through the pyrolysis tube as a wash. Separation of the product mixture by preparative gas chromatography gave hexamethyldisiloxane, benzyltrimethylsilane (2%), styrene (10%), 1,1-dimethyl-1-silaindan (27%), and the siloxane **7** (29%). Hexamethyldisiloxane, benzyltrimethylsilane, styrene, and 1,1-dimethyl-1-silaindan[9] were identified by comparison of their NMR and IR spectra with those of authentic samples. The siloxane **7** was identified by its NMR, IR, and mass spectra and elemental analysis: NMR (CCl_4) δ 0.03 (s, 15, H, $Me_3SiOSiMe_2$), 1.38 (d, J = 7 Hz, 3 H, SiCMe), 2.17 (q, J = 7 Hz, 1 H, SiCH), 6.80-7.37 (m, 5 H, Ar H); IR (neat) 1250 (SiMe), 1060 cm^{-1} (Si-O-C); mass spectrum, *m/e* 252 (M^+). Anal. Calcd. for $C_{13}H_{24}OSi_2$: C, 61.83; H, 9.58. Found: C, 61.53; H, 9.42.

Pyrolysis of 1,1-Bis(trimethylsilyl)-1-decanol (10). 1,1-Bis(trimethylsilyl)-1-decanol (1.02 g) was pyrolyzed at 500 °C. 1-(Trimethylsilyl)-1-decene (93%) was obtained by bulb-to-bulb distillation [150-160 °C (150 mmHg)]. The *trans*- and *cis*-vinylsilanes were separated by preparative gas chromatography and identified by their NMR, IR, and mass spectra and elemental analysis.

trans-1-(Trimethylsilyl)-1-decene: NMR (CCl_4) δ 0.03 (s, 9 H, $SiCH_3$), 0.67-1.63 (m, 15 H, aliphatic CH), 1.78-2.28 (m, 2 H, $C{=}CCH_2$), 5.50 (d, J = 19 Hz, 1 H, SiCH=C), 6.00 (d of t, J_1 = 19 Hz, J_2 = 6 Hz, 1 H, SiC=CH); IR (neat) 1605 (C=C), 1240 (SiMe), 980 cm^{-1} (trans CH=CH); mass spectrum, *m/e* 212 (M^+).

cis-1-(Trimethylsilyl)-1-decene: NMR (CCl_4) δ 0.10 (s, 9 H, $SiCH_3$), 0.60-1.60 (m, 15 H, aliphatic CH), 1.77-2.33 (m, 2 H, $C{=}CCH_2$), 5.40 (d, J = 14 Hz, 1 H, SiCH=C), 6.27 (d of t, J_1 = 14 Hz, J_2 = 7 Hz, 1 H, SiC=CH); IR (neat) 1600 (C=C), 1240 (SiMe), 750 cm^{-1} (cis CH=CH); mass spectrum, *m/e* 212 (M^+). Anal. Calcd. for $C_{13}H_{28}Si$ (mixture of trans and cis): C, 73.49; H, 13.28. Found: C, 73.31; H, 13.30.

Pyrolysis of 1,1-Bis(trimethylsilyl)-1-octanol (11). 1,1-Bis(trimethylsilyl)-1-octanol (0.977 g) was pyrolyzed at 500 °C. 1-(Trimethyl)-1-octene (98%) was obtained by bulb-to-bulb distillation [105-110 °C (170 mmHg)]. The *trans*- and *cis*-vinylsilanes were separated by gas chromatography and identified by comparison with the reported spectral data.[31]

Pyrolysis of 1,1-Bis(trimethylsilyl)-3-phenyl-1-propanol (12). 1,1-Bis(trimethylsilyl)-3-phenyl-1-propanol (1.11 g) was pyrolyzed at 500 °C. 1-(Trimethylsilyl)-3-phenyl-1-propene (94%) was obtainbed by bulb-to-bulb distillation [140-150 °C (115 mmHg)]. The *trans*- and *cis*-vinylsilanes were separated by preparative gas chromatography and identified by comparison with the reported spectral data.[31]

Pyrolysis of Bis(trimethylsilyl)cyclohexylmethanol (13). Bis(trimethylsilyl)cyclohexylmethanol (1.08 g) was pyrolyzed at

---

[30] Picard, J. P.; Calas, R.; Dunoguès, J.; Duffaut, N. *J. Organomet. Chem.* **1971**, *26*, 183.

[31] Carey, F. A.; Toler, J. R. *J. Org. Chem.* **1976**, *41*, 1966.

500 °C. Cyclohexylidene(trimethylsilyl)methane (90%) was obtained by bulb-to-bulb distillation [120–125 °C (75 mmHg)] and identified by comparison with the reported spectral data.[32]

Pyrolysis of Bis(trimethylsilyl)cyclopentylmethanol (15). Bis(trimethylsilyl)cyclopentylmethanol (0.720 g) was pyrolyzed at 500 °C. Separation of the product mixture by preparative gas chromatography gave allylsilane **16** (48%), *exo*-(trimethylsilyl)cyclopropane **17** (26%), and *endo*-(trimethylsilyl)cyclopropane **18** (9%). Allylsilane **16** was identified by its NMR, IR, and mass spectra: NMR (CCl_4) δ 0.07 (s, 9 H, $SiCH_3$), 1.33–2.00 (m, 4 H), 2.00–2.57 (m, 4 H), 5.37 (t, J = 2 Hz, 1 H, C=CH); IR (neat) 1615 (C=C), 1240 cm^{-1} (SiMe); mass spectrum, m/e 154 (M^+). The allylsilane **16** was desilylated by *p*-toluenesulfonic acid to give 1-methylcyclopentene. *exo*- and *endo*-(Trimethylsilyl)cyclopropanes **17** and **18** were identified by their NMR, IR, and mass spectra and elemental analyses.

exo-(Trimethylsilyl)cyclopropane **17**: NMR (CCl_4) δ −0.65 (t, J = 5 Hz, 1 H, SiCH), −0.10 (s, 9 H, $SiCH_3$), 0.85–1.92 (m, 8 H, aliphatic CH); IR (neat) 1240 cm^{-1} (SiMe); mass spectrum, m/e 154 (M^+). Anal. Calcd for $C_9H_{18}Si$: C, 70.04; H, 11.75. Found: C, 69.91; H, 11.68.

endo-(Trimethylsilyl)cyclopropane **18**: NMR (CCl_4) δ −0.60 (t, J = 9 Hz, SiCH), 0.07 (s, 9 H, $SiCH_3$), 1.13–1.90 (m, 8 H, aliphatic CH); IR (neat) 1245 cm^{-1} (SiMe); mass spectrum, m/e 154 (M^+). Anal. Calcd for $C_9H_{18}Si$: C, 70.04; H, 11.75. Found: C, 70.30; H, 11.91.

Pyrolysis of 1-(Trimethylsilyl)-1-phenylethanol (20). 1-(Trimethylsilyl)-1-phenylethanol (1.20 g) was pyrolyzed at 500 °C. To the pyrolysates was added 0.102 g of *p-tert*-butylphenol and distillation [95–105 °C (160 mmHg)] gave styrene (91%).

Pyrolysis of (Trimethylsilyl)(*o*-methoxyphenyl)methanol (21). A benzene solution of (trimethylsilyl)(*o*-methoxyphenyl)methanol (0.333 g) was pyrolyzed at 600 °C. Separation of the product mixture by preparative gas chromatography gave 2,3-dihydrobenzofuran (28%) and 2,3-benzofuran (16%). Products were identified by comparison with the reported spectral data.[28,33]

Pyrolysis of (Trimethylsilyl)[*p*-(trimethylsilyl)phenyl]methanol (24). A benzene solution of (trimethylsilyl)[*p*-(trimethylsilyl)phenyl]methanol (0.296 g) was pyrolyzed at 600 °C. Separation of the product mixture by preparative gas chromatography gave 1,1-dimethyl-1-silaindan (44%).[9,28]

Pyrolysis of (Trimethylsilyl)(*p-tert*-butylphenyl)methanol (25). A benzene solution of (trimethylsilyl)(*p-tert*-butylphenyl)methanol (0.729 g) was pyrolyzed at 600 °C. Separation of the product mixture by preparative gas chromatography gave 1,1-dimethylindan (22%). 1,1-Dimethylindan was identified by comparison of its NMR and IR spectra with those of authentic sample.[28]

Acknowledgment. We are indebted to the Ministry of Education for financial support of this work through a Grant for Scientific Research (No. 447019). We are pleased to acknowledge a gift of trimethylchlorosilane from the Shinetsu Chemical Co.

Registry No. 2, 31129-63-2; **3**, 107-46-0; **4**, 770-09-2; **5**, 100-42-5; **6**, 17158-48-4; **7**, 73727-41-0; **10**, 73727-43-2; **11**, 61289-37-0; **12**, 61157-30-0; **13**, 73727-42-1; **14**, 38329-94-1; **15**, 75311-59-0; **16**, 75311-60-3; **17**, 75311-61-4; **18**, 75311-62-5; **20**, 53173-00-5; **21**, 75311-63-6; **22**, 496-16-2; **23**, 271-89-6; **24**, 75311-64-7; **25**, 75311-65-8; **26**, 4912-92-9; **27**, 65609-68-9; **28**, 65609-67-8; *trans*-$Me(CH_2)_7CH{=}CHSiMe_3$, 71779-75-4; *cis*-$Me(CH_2)_7CH{=}CHSiMe_3$, 71779-78-7; *trans*-$Me(CH_2)_5CH{=}CHSiMe_3$, 57365-47-6; *cis*-$Me(CH_2)_5CH{=}CHSiMe_3$, 57365-48-7; *cis*-$PhCH_2CH{=}CHSiMe_3$, 73727-44-3; *trans*-$PhCH_2CH{=}CHSiMe_3$, 58541-15-4; α-bromo(*o*-methoxybenzyl)trimethylsilane, 75311-66-9; α-bromo(*p*-(trimethylsilyl)benzyl]trimethylsilane, 75311-67-0; α-bromo(*p-tert*-butylbenzyl)trimethylsilane, 75311-68-1.

---

[32] Martel, B.; Varache, M. *J. Organomet. Chem.* **1972**, *40*, C53.

[33] Pouchert, C. J.; Campbell, J. R. "The Aldrich Library of NMR Spectra"; Aldrich Chemical Co.; Milwaukee, WI, Vol. VIII p 80.

Separation of Polar and Resonance Substituent Effects. Comparison of Dual Substituent Parameter Equations

Paul R. Young* and Patrick E. McMahon

Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60680

Received June 26, 1980

Ionization constants for substituted pyridinium ions are analyzed by using the dual substituent parameter equation suggested by Yukawa and Tsuno [$\log k/k_0 = \rho\sigma^n + \rho^r(\sigma^+ - \sigma^n)$]. The results are compared with values obtained from analysis of the same data set by using the Taft equations ($\log k/k_0 = \rho_I\sigma_I + \rho_R\sigma_R$). Approximate free-energy changes due to direct conjugative resonance, estimated by the Yukawa method, are found to be directly proportional to the values estimated by using the Taft equations. A similar direct proportionality is observed for free-energy changes for direct conjugative resonance in the rate and equilibrium benzaldehyde cyanohydrin reactions. The Taft analysis predicts a late, product-like transition state for this reaction. This is consistent with the transition-state structure obtained from the Yukawa analysis and from secondary deuterium isotope effect studies. Assumptions inherent in the simple Yukawa treatment are discussed.

It is well recognized that the Hammett relationship, $\log k/k_0 = \sigma\rho$, is a result of the linear combination of effects arising from both polar and resonance contributions.[1,2] Several correlations have been proposed for the evaluation of these separate polar and resonance terms. The simplest of these is the modified Yukawa equation (eq 1),[3-6] and perhaps the best known is the method described by Taft.[7,8]

For the Yukawa–Tsuno equation, the Gibbs free-energy changes arising from each of the interaction mechanisms can be expressed in the general terms of eq 1,[5] where polar

$$\log k/k_0 = \sigma^n\rho + \sigma^r\rho^r \propto \Delta\Delta G_{\text{polar}} + \Delta\Delta G_{\text{reson}} \qquad (1)$$

---

[1] Leffler, J. E.; Grunwald, E. "Rates and Equilibria of Organic Reactions"; Wiley: New York, 1963; p 192.

[2] Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; Wiley: New York, Chapter 3.

[3] Tsuno, Y.; Masami, S.; Takahiro, F.; Yoshihiko, T.; Yasuhide, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3356–3366. Yukawa, Y.; Tsuno, Y.; Sawada, M. *Ibid.* **1966**, *39*, 2277–2286. Yukawa, Y.; Tsuno, Y. *Ibid.* **1959**, *32*, 965–971.

[4] Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 3288–3294; **1978**, *100*, 1228–1235; **1977**, *99*, 8238–8248.

[5] Young, P. R.; McMahon, P. E. *J. Am. Chem. Soc.* **1979**, *101*, 4678–4681.

[6] Young, P. R.; Bogseth, R. C.; Rietz, E. G. *J. Am. Chem. Soc.* **1980**, *102*, 6268–6271.

[7] Ehrenson, S.; Brownlee, R. T. C.; Taft, R. *Prog. Phys. Org. Chem.* **1973**, *10*, 1–80.

[8] Taft, R. W.; Ehrenson, S.; Lewis, I. C.; Glick, R. E. *J. Am. Chem. Soc.* **1959**, *81*, 5352–5361. Taft, R. W.; Lewis, I. C. *Ibid.* **1958**, *80*, 2436–2443; **1959**, *81*, 5343–5352.

0022-3263/80/1945-5290$01.00/0