placed 5935 g. (33.3 moles) of triethoxymethylsilane and 1525 g. of ethyl alcohol, formula 2B. To this was slowly added, over a period of two hours, a solution of 13.3 g. (0.33 mole) of sodium hydroxide in 300 g. (16.7 moles) of water. During the addition, heat was evolved. After the addition was completed the mass was allowed to stand overnight. Then the reflux condenser was replaced with a downward condenser, heat was applied and volatiles (principally alcohol) were removed to a pot temperature of 100°. The distillate amounted to 2754 g. (theory, 3055 g.). The residue was blown with carbon dioxide as it cooled to room temperature. The mass was filtered to yield 4160 g. of fluid (theory, 4400 g.).

The filtrate was distilled in a fractionating still with a four-foot by one-inch column packed with 0.25-inch single-turn glass helices. This gave some unreacted triethoxymethylsilane and a series of progressively higher boiling plateaus which were characterized as shown in Table I.

Summary

1. Open-chain ethoxymethylsiloxane polymers with diethoxymethylsiloxy end-groups containing from 2 to 5 silicon atoms have been isolated and characterized.

MIDLAND, MICHIGAN RECEIVED FEBRUARY 9, 1949

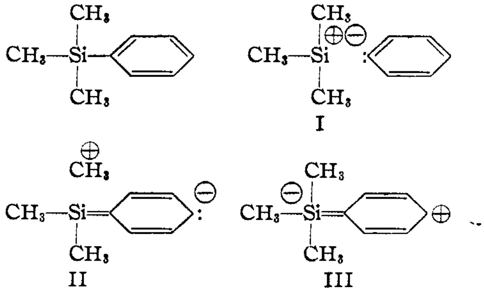
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Electrical Effect of the Trimethylsilyl Group

BY JOHN D. ROBERTS, ELIZABETH A. MCELHILL AND ROSE ARMSTRONG

The magnitude and direction of the electrical effect of tetravalent silicon atoms in organosilicon compounds has not been definitely established. The difference in electronegativity between carbon and silicon on the Pauling scale[1] (+0.7 unit) suggests that silicon should be fairly strongly electron-releasing with respect to carbon. Nonetheless, the low reactivity of trimethylsilylmethyl chloride toward ionizing reagents has been interpreted as indicating that tetravalent silicon atoms are "electronically unsaturated" relative to tetravalent carbon.[2] The possibility exists that silicon atoms may tend to be more electron-attracting than otherwise anticipated since resonance forms involving more than four pairs of electrons in the outer atomic valence shells should be energetically more favorable for silicon than carbon. Actually, strong evidence has been obtained for important contributions of resonance forms involving pentacovalent silicon in the transition states of the displacement reactions of organosilicon halides.[3]

For trimethylsilylbenzene, three possible electrical effects due to the trimethylsilyl group can be represented by resonance forms I, II and III.



I II III

The electropositive nature of silicon relative to carbon is reflected by I while II represents hyperconjugative resonance of the type postulated for alkylbenzenes.[4] III depicts the tendency for silicon to expand its valence shell by the interaction of the $3d$ orbitals of silicon with the unsaturation electrons of the benzene ring. It is expected that I should be somewhat more important than the corresponding resonance forms involving the Si–C bonds of the methyl groups since the phenyl group is more electron-attracting than saturated alkyl groups.[4c]

In the present work a study was made of the dipole moments and relative reactivities of substituted trimethylsilylbenzenes to allow a decision to be made regarding the relative importance of resonance of types I, II and III involving silicon atoms attached to a benzene ring. The dipole moments of trimethylsilylbenzene, *p*-fluoro- and *p*-chlorotrimethylsilylbenzenes were determined in benzene solution at 25°. The results are given in Table I.

TABLE I

MOLAR REFRACTIONS, POLARIZATIONS AND DIPOLE MOMENTS

Substance	MR_D	P_∞ (25°)[a]	μ (Debye)
Trimethylsilylbenzene	49.87	53.9	0.44
p-Fluorotrimethylsilylbenzene	49.76	108.0	1.69[b]
p-Chlorotrimethylsilylbenzene	54.87	114.0	1.70[c]

[a] The data used for the calculation of P_∞ are given in Table II. [b] The average value of the moments obtained by five investigators for fluorobenzene in benzene solution near 25° is 1.44*D*. [c] The average value of the moments obtained by eighteen investigators for chlorobenzene in benzene solution near 25° is 1.57*D*.

Our value for the moment of trimethylsilylbenzene is in reasonable agreement with that obtained by Malatesta and Pizzotti[5a] (0.7*D*) for triethylsilylbenzene in carbon tetrachloride solutions. However, the interpretation by Malatesta[4b] of

---

[1] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, pp. 58-70.

[2] Whitmore and Sommer, THIS JOURNAL, **68**, 483 (1946)

[3] Swain, Esteve and Jones, *ibid.*, **71**, 965 (1949).

[4] (a) Mulliken, Rieke and Brown, *ibid.*, **63**, 41 (1941); (b) Berliner and Bondhus, *ibid.*, **68**, 2355 (1946); **70**, 854 (1948); (c) Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944.

[5] (a) Malatesta and Pizzotti, *Gazz. chim. ital.*, **72**, 491 (1942); (b) **73**, 143 (1943).

the moment as being due to resonance of type III appears to be decisively negated by the moments of the *p*-halogen–substituted trimethylsilylbenzenes which are in each case higher than those of the corresponding halobenzenes. The trimethylsilyl group actually appears to release electrons to the benzene ring although the effect is small since the net vector component of the dipole moment in the direction of the ring due to the trimethylsilyl group is only 0.1–0.25*D*.[6]

Evidence regarding the relative importance of electron-releasing resonance of types I and II was obtained from the relative ionization constants and reactivities toward diphenyldiazomethane of *m*- and *p*-trimethylsilylbenzoic acids. The relative ionization constants of the acids were determined in 50% water–50% ethyl alcohol (by volume) solutions at 25.0°. The values of the logarithms of the apparent ionization constants for several substituted benzoic acids are plotted against the corresponding σ-values of Hammett[7] in Fig. 1. The value of ρ for the ionization of the acids in 50% water–50% alcohol is +1.464 at 25.0°. The median deviation, *r*, is 0.025 which is considerably less than the mean value (0.060) of *r* for the 52 reactions cited by Hammett.[7] The σ constants for *p*- and *m*-trimethylsilyl groups obtained from the plot of Fig. 1 are −0.060 and −0.208, respectively.

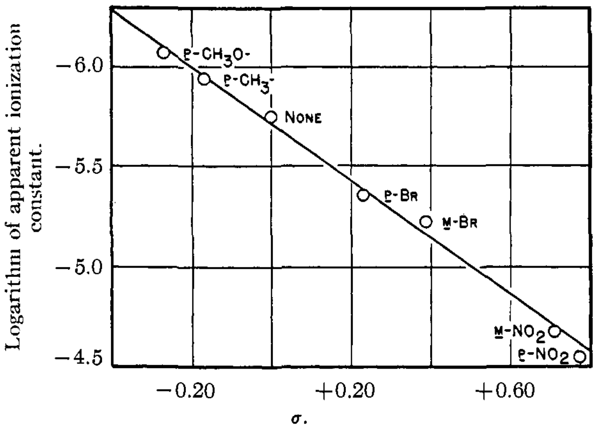


Fig. 1.—Relationship between apparent ionization constants of substituted benzoic acids in 50% (by volume) ethyl alcohol–water at 25° and σ.

The reactivities of a number of *m*- and *p*-substituted benzoic acids toward diphenyldiazomethane were measured in absolute alcohol at 30.0°.[8] Similar studies with di-*p*-tolyldiazomethane have been reported by Norris and Strain[9] for toluene and ethyl acetate solutions. Norris and Strain employed a gasometric method of analysis while in the present work the reactions were followed colorimetrically. In Fig. 2 the logarithms of the rate constants of the reactions of several benzoic acids are plotted against the corresponding σ-values. The value of ρ for the reaction is 0.937 and *r* was 0.010. The σ-constants of the *p*- and *m*-trimethylsilyl groups obtained from the rate data are −0.022 and −0.018, respectively. The agreement between the σ-values from the ionization constant and rate data for the *p*-position is good but rather less satisfactory for the *m*-position. The average values of the σ-constants indicate that the trimethylsilyl group slightly decreases the acid strength of benzoic acids when substituted in the *p*-position and has a rather stronger repressive effect in the *m*-position. The results do not seem to be consistent with important resonance contributions of type II since such resonance should lead to a greater repressive effect when the trimethylsilyl group is substituted in the *p*- rather than the *m*-position. In fact, the pattern of influence of the trimethylsilyl group is apparently opposite to that of alkyl substituents where resonance forms analogous to II are considered to be quite important.[4] The present results seem to indicate that the principal influence of the silicon atom on a benzene ring is due largely to the electropositive or electron-releasing properties of

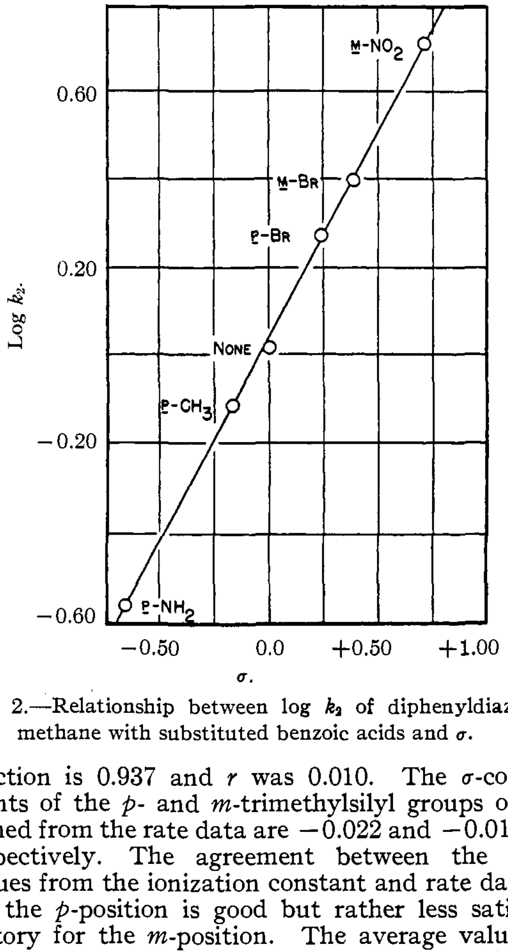


Fig. 2.—Relationship between log k_2 of diphenyldiazomethane with substituted benzoic acids and σ.

---

(6) The value of the vector component of the moment of the trimethylsilyl group calculated from the moments of the *p*-halogen derivatives is considered to be more accurate than that obtained from the moment of trimethylsilylbenzene since, in the calculation of μ from P_∞ of the latter compound, the atomic polarization P_A was not taken into account. If P_A amounts to 5% of P_E then the calculated value of μ would be 0.25*D*.

(7) Hammett "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, Chapter VII.

(8) The mechanism of these reactions will be the subject of a forthcoming paper.

(9) Norris and Strain, THIS JOURNAL, **57**, 187 (1935).

silicon relative to carbon. This conclusion is not considered to be incompatible with the previously postulated[3] formation of reaction intermediates or transition states in which silicon tends to be pentacovalent for under such circumstances activated silicon atoms are undoubtedly involved. The situation with silicon in organic compounds appears to be the reverse of that which obtains with the halogens which are predominantly electron-attracting in the ground state but may be electron-releasing in activated states.

Experimental

Trimethylsilylbenzene and ***p*-chlorotrimethylsilylbenzene** were prepared by the method of Burkhard.[10] Trimethylsilylbenzene had b. p. 98–99° (80 mm.), $n^{25}D$ 1.4880, d^{25}_4 0.8680. *p*-Chlorotrimethylsilylbenzene had b. p. 98–100° (20 mm.), $n^{25}D$ 1.5079, d^{25}_4 1.0034.

***p*-Fluorotrimethylsilylbenzene.**—To a stirred solution of *p*-fluorophenylmagnesium bromide prepared from 46.5 g. (0.22 mole) of *p*-fluorobromobenzene 8.0 g. (0.33 gram atom) of magnesium and 10.0 ml. of anhydrous ether was added 28.7 g. (0.27 mole) of chlorotrimethylsilane. The reaction mixture was refluxed for twenty-four hours and then poured into iced ammonium chloride solution. The ethereal layer was separated and dried over calcium chloride. Distillation gave 33.5 g. (91%) of *p*-fluorotrimethylsilylbenzene; b. p. 92–93° (60 mm.), $n^{25}D$ 1.4711, d^{25}_4 0.9452.

Anal. Calcd. for $C_9H_{13}FSi$: Si, 16.67. Found: Si, 16.67.

***p*-Trimethylsilylbenzoic Acid.**—A solution of *p*-trimethylsilylphenylmagnesium bromide prepared from 39.6 g. (0.173 mole) of *p*-bromotrimethylsilylbenzene,[10] 5.6 g. (0.23 gram atom) of magnesium and 100 ml. of ether was poured with stirring onto a large excess of crushed Dry Ice. After the excess carbon dioxide had evaporated the residue was acidified and extracted with ether. The ether was evaporated and the residue treated with sodium bicarbonate solution. The bicarbonate solution was filtered, acidified and the resulting solid filtered. After successive crystallizations from acetic acid–water and low-boiling petroleum ether the yield of pure *p*-trimethylsilylbenzoic acid was 11.1 g. (38%); m. p. 117–118°.

Anal. Calcd. for $C_{10}H_{14}O_2Si$: C, 61.81; H, 7.26. Found: C, 61.64; H, 7.25.

***m*-Trimethylsilylbenzoic Acid.**—*m*-Chloroiodobenzene was converted to *m*-chlorotrimethylsilylbenzene by a procedure similar to that used for the preparation of *p*-fluorotrimethylsilylbenzene. The yield of crude *m*-chlorotrimethylsilylbenzene was 53%, b. p. 97–102.5° (23 mm.), $n^{25}D$ 1.5070. A solution of *m*-trimethylsilylphenyllithium was prepared in a helium atmosphere using vigorous stirring from 35 g. (0.19 mole) of *m*-chlorotrimethylsilylbenzene, 1.6 g. (0.23 gram atom) of lithium metal cut into thin strips and 200 ml. of ether. The reaction appeared to be complete after about two hours. The lithium compound was carbonated by pouring the mixture onto crushed Dry Ice with stirring. After the excess carbon dioxide evaporated, water was added and the mixture extracted with ether. The aqueous residue was acidified and the precipitate filtered and dried. The crude material was recrystallized from pentane. The yield of *m*-trimethylsilylbenzoic acid was 17.1 g. (47%); m. p. 113.7–114.2°.

Anal. Calcd. for $C_{10}H_{14}O_2Si$: C, 61.81; H, 7.26. Found: C, 62.15, 61.79; H, 7.28, 7.12.

Dipole Moments.—The dipole moments were determined by the method described previously.[11] The data are given in Tables I and II.

TABLE II

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS IN BENZENE AT 25°

f_2	ϵ	d	P_2
Trimethylsilylbenzene			
0.00000	2.2729	0.87259	(P_1 = 26.666)
.00906	2.2730	.87211	53.1
.02295	2.2781	.87204	55.4
.03515	2.2754	.87185	53.0
.04295	2.2776	.87151	53.8
.06129	2.2806	.87109	54.0
p-Fluorotrimethylsilylbenzene			
0.00000	2.2717	0.87253	(P_1 = 26.650)
.00518	2.2918	.87306	111.6
.00881	2.3038	.87358	107.4
.01752	2.3359	.87482	107.4
.03042	2.3821	.87638	107.1
.03736	2.4057	.87727	106.5
.05674	2.4713	.87946	105.8
p-Chlorotrimethylsilylbenzene			
0.00000	2.2725	0.87267	(P_1 = 26.666)
.00889	2.3073	.87494	112.0
.02015	2.3561	.87768	116.1
.02997	2.4016	.88005	118.5
.03919	2.4552	.88200	123.8
.06493	2.5426	.88785	116.9

Ionization Constants.—Samples (about 0.07 g.) of the substituted benzoic acids were titrated in 100 ml. of 50% water–50% ethyl alcohol (by volume) solutions using carbonate-free sodium hydroxide solution. The titrations were carried out under a nitrogen atmosphere at 25.0 ± 0.1° and the change in water content of the solutions resulting from the addition of the sodium hydroxide solution was compensated by addition of ethyl alcohol. The change in acidity of the solutions during the titrations was followed using a glass electrode and a Beckman Model G *p*H meter. The reference electrode was a saturated potassium chloride calomel electrode. The electrode system was standardized several times each day against aqueous buffer solutions. The half-point acidities were obtained graphically. The results are summarized in Table III.

TABLE III

DETERMINATION OF ACID STRENGTHS OF SUBSTITUTED BENZOIC ACIDS IN 50% WATER–50% ETHYL ALCOHOL (BY VOLUME) SOLUTIONS AT 25°

R	Half-point[a]	$k^b \times 10^{-6}$	R	Half-point[a]	$k^b \times 10^{-6}$
None	5.75	1.78	*p*-CH_3O–	6.07	0.85
p-Br–	5.35	4.47	*p*-CH_3–	5.94	1.15
m-Br–	5.22	6.03	*m*-$(CH_3)_3Si$–	6.01	0.96
m-NO_2–	4.66	21.9	*p*-$(CH_3)_3Si$–	5.85	1.41
p-NO_2–	4.53	29.5			

[a] Reading on *p*H scale of *p*H meter calibrated for aqueous buffer solutions at half-neutralization point using glass and saturated calomel electrodes without correction for liquid junction potentials. [b] Calculated assuming unit activities and readings of *p*H meter scale equal to logarithm of reciprocal of hydrogen-ion concentration.

Rate Runs.—The rates of the reactions of the substituted benzoic acids with diphenyldiazomethane were determined colorimetrically using a Beckman Model DU Spectrophotometer with a

---

[10] Burkhard, THIS JOURNAL, 68, 2103 (1946).

[11] Roberts, Armstrong, Trimble and Burg, *ibid.*, 71, 843 (1949); Rogers and Roberts, *ibid.*, 68, 843 (1946).

thermostated cell holder. The temperature was maintained at 30.0 ± 0.05°.

Solutions of diphenyldiazomethane and benzoic acids (about 0.1 *M*) in absolute alcohol were thermostated for at least an hour, then pipeted into a small flask, mixed and transferred to a spectrophotometer cell. Optical density readings were taken at 525 mμ using ethyl alcohol as a standard at two-minute intervals over a period equivalent to at least two half-lives. Zero-time was taken as the time of mixing of the solutions. The optical density readings were plotted on semi-logarithmatic paper and the pseudo-unimolecular rate constants of the reactions obtained from the slopes of the best straight line through the experimental points. A plot of the data for a typical run using benzoic acid is shown in Fig. 3. Since the acid concentrations were several times those of the diphenyldiazomethane the reactions appeared to be unimolecular. However, the slopes of the curves were strictly dependent on the concentration of acid and the final rate constants (k_2) were calculated by dividing the pseudo-unimolecular constants by the corresponding acid concentrations. The reaction rates were shown to be insensitive to the intensity of the light used in the spectrophotometer. The rate data for the various benzoic acids are summarized in Table IV.

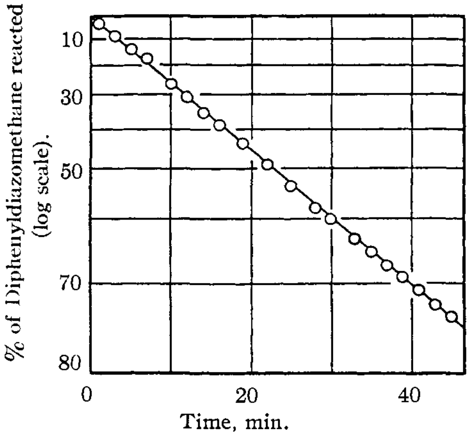


Fig. 3.—Rate of reaction of diphenyldiazomethane with benzoic acid in ethyl alcohol at 30°.

Table IV

Rate Constants for the Reaction of Substituted Benzoic Acids with Diphenyldiazomethane in Absolute Alcohol at 30°

Substituent	Concn. of acid, mole/l.	Half-life, min.	k_2, l./mole-min.
p-NH_2–	0.0289	89.7	0.268
p-CH_3–	.0289	31.2	0.770
None	.0284	23.5	1.04
p-$(CH_3)_3Si$–	.0287	23.0	1.05
m-$(CH_3)_3Si$–	.0293	22.1	1.07
p-Br–	.0284	13.0	1.88
m-Br–	.0286	9.65	2.51
m-NO_2–	.0287	4.70	5.15
p-OH–	.0284	45.9	0.533[a]

[a] The σ-constant calculated for the *p*-OH group from this rate constant is −0.341.

Summary

Trimethylsilyl groups attached to benzene rings have been shown by dipole moment studies to be slightly electron-releasing. The relative reactivities of the carboxyl groups in *m*- and *p*-trimethylsilylbenzoic acids indicate that the electrical influence of the trimethylsilyl group is different in kind from that of alkyl groups.

Cambridge 39, Massachusetts
Received March 1, 1949

NOTES

Formation of the Chloroiodate(I) Ion from the Reaction of Iodide and Thionyl Chloride

By William B. Brownell and L. Carroll King

During the course of an investigation of the reactions of certain quaternary pyridinium iodides it was noted that thionyl chloride acting directly on the salts converted the iodide ion to chloroiodate(I) with appearance of free sulfur. The reaction may be formulated as

$$2SOCl_2 + 2I^- \longrightarrow 2ICl_2^- + SO_2 + S$$

The identity of the anion was established by analysis and in two cases by direct comparison with known cycloammonium quaternary salts containing the chloroiodate(I) anion.

The reaction of thionyl chloride with potassium iodide was reported by Rao.[1] The reaction of dry hydrogen iodide with thionyl chloride was reported by Besson[2]; neither author observed the chloroiodate(I) ion in the reaction products.

Compounds containing the chloroiodate(I) ion have been prepared by the reaction of iodine monochloride with a quaternary ammonium

---

[1] Rao, *Proc. Indian Acad. Sci.*, **11A**, 185 (1940); *C. A.*, **34**, 7200 (1940).

[2] Besson, *Compt. rend.*, **123**, 884 (1896); *Chem. Zentr.*, **68**, I, 12 (1897).