

Deuteroethanol and Phenylacetamide.—One-half gram of phenylacetamide was dissolved in deuteroethanol (4 ml.) and the mixture was refluxed for two hours, then diluted with ligroin. The crystalline product was filtered, rinsed with ligroin and dried *in vacuo* over phosphoric anhydride. It was found to contain 1.3 D atoms per molecule (combustion water, 16.1% D₂O). This product was next recrystallized from ordinary ethanol, heating for 15 minutes prior to crystallization. The infrared spectrum of the product was now identical with that of stock phenylacetamide, indicating the removal of N-bound deuterium.

Deuterized Raney Nickel on Methyl Benzyl Ketone.—Deuterized nickel (preparation 2, *ca.* 7 g.), methyl benzyl

ketone (2.5 ml.) and deuteroethanol (25 ml.) were mixed and the mixture was refluxed for 13 hours. The crude product was isolated as usual, then purified by distillation. The purified product was found to contain 2.35 D atoms per molecule (combustion water, 21.2% D₂O). Its infrared spectrum contained no carbonyl band, and showed only minor differences from the spectrum of methylbenzylcarbinol. A portion of the product was oxidized as usual with alkaline permanganate. The benzoic acid obtained had an infrared spectrum identical with that of stock benzoic acid, suggesting no significant amount of ring-bound deuterium.

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Electrophilic Substitution by Hydrogen in the Xylenes. The Kinetics of Acid Cleavage of the Trimethylsilylxylenes

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Pseudo first-order rate constants for the cleavage of the six isomeric trimethylsilylxylenes by *p*-toluenesulfonic acid in acetic acid have been determined at 25°. The reactions were followed by a dilatometric method. Although the cleavage reactions parallel usual electrophilic substitutions, they are considerably influenced by buttressing and steric strain effects. The order of increase in the rate of acid cleavage for the trimethylsilylxylenes is (R = trimethylsilyl): 5-R-*m*-xylene < 4-R-*o*-xylene < 2-R-*p*-xylene < 3-R-*o*-xylene < 4-R-*m*-xylene < 2-R-*m*-xylene. A plot of the logarithms of the rate constants for each of the cleavage reactions *vs.* the logarithms of the partial relative rate factors for the corresponding positions in the xylenes derived from halogenation and nitration data yields a good linear relationship. This general cleavage technique is thus indicated to be a reliable method for determining the relative rates of electrophilic substitution by hydrogen at a particular position in an aromatic ring.

A direct determination of the rate of electrophilic substitution in benzene at positions *meta* to powerful electron-releasing groups is difficult because of the preponderance of *ortho*- and *para*-substitution. The usual approach in such cases involves either a laborious separation of isomers to determine the *o-m-p* ratios, or the useful procedures of Ingold, *et al.*,^{1a,b,c} in which the rate of substitution for each position in a monosubstituted¹ or polymethylsubstituted² benzene relative to that for any position in benzene can be calculated.

Another approach to this problem of determining relative rates of substitution at different positions in substituted benzenes has been utilized by Corwin and Naylor³ who studied the kinetics of the acid cleavage of diphenylmercury. These authors reversed the usual electrophilic process and essentially carried out an *electrophilic substitution by hydrogen*. They pointed out that it was thus possible to isolate a particular position in a substituted benzene nucleus for the determination of its susceptibility toward electrophilic attack by "tagging" that position with the mercury moiety.^{3a} Since electrophilic substitution in the xylenes was of considerable interest in the present study, an approach analogous to that employed by Corwin and Naylor was sought. It was hoped thereby to obtain useful quantitative data which might possibly be correlated with the presently accepted concepts of aromatic electro-

philic substitution, and with existing data on the xylenes and their derivatives.

In the present study, the cleavage of mercury-carbon bonds was not considered suitable because of the probability of too rapid rates of cleavage, limited choice of cleaving acid³ and the possibility of complications due to unusually large steric effects. Instead, the cleavage of the silicon-carbon bond appeared to be the reaction of choice. The silicon atom has smaller steric requirements than mercury, and steric effects should therefore be lessened. The silicon atom, having the characteristics of a metalloid, is cleaved by acids from aromatic nuclei with varying ease, depending upon the electron-releasing ability of the substituent present on the ring.^{4a,b} For example, *p*-methoxyphenyltrimethylsilane is cleaved by hydrogen chloride in refluxing acetic acid much more readily than *p*-chlorophenyltrimethylsilane. Anisole and chlorobenzene, respectively, are the products of such cleavages, the silicon fragment being released as trimethylchlorosilane.^{4a,b}

Experimental

Trimethylsilylxylenes.—All the trimethylsilylxylenes were prepared by the reaction of the appropriate xylyllithium compound and trimethylchlorosilane in the usual manner.⁵ Color Test I⁶ was used to indicate completion of reaction. In most cases, the xylyllithium intermediates were quite insoluble, and it was necessary to add a fairly large volume of ether in order to obtain efficient stirring.

Upon completion of the coupling, the reaction mixture was filtered through a glass wool plug. The filtrate was

(1) (a) M. L. Bird and C. K. Ingold, *J. Chem. Soc.*, 918 (1938); (b) C. K. Ingold and M. S. Smith, *ibid.*, 905 (1938); (c) C. K. Ingold, A. Lapworth, E. Rothstein and D. Ward, *ibid.*, 1959 (1931).

(2) F. E. Condon, *THIS JOURNAL*, **70**, 1963 (1948).

(3) A. H. Corwin and M. A. Naylor, *ibid.*, **69**, 1004 (1947).

(3a) ADDED IN PROOF.—W. M. Schubert and co-workers also have measured the rate of electrophilic substitution by hydrogen in some highly hindered aldehydes, ketones, and acids; see *THIS JOURNAL*, **76**, 9 (1954), for pertinent references.

(4) (a) R. A. Benkeser and H. R. Krysiak, *ibid.*, **75**, 4528 (1953); (b) H. Gilman and F. J. Marshall, *ibid.*, **71**, 2066 (1949).

(5) For the preparation of organolithium compounds, see R. G. Jones and H. Gilman, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 352.

(6) H. Gilman and F. Shultz, *THIS JOURNAL*, **47**, 2002 (1925).

TABLE I
 ISOMERIC TRIMETHYLSILYLXYLENES

Product ^a (R = Me, Si-)	n_D^{20}	d_4^{20}	B.p., ^b °C.	M_R^d (found) ^c	Yield, %	Analyses ^e %	
						Carbon	Hydrogen
1 4-R- <i>m</i> -Xylene	1.5040	0.885	97-98	59.65	41 ^d	74.37	10.37
2 2-R- <i>p</i> -Xylene	1.5048	.889	96	59.49	77	74.38	10.15
3 4-R- <i>o</i> -Xylene	1.5010	.880	93-94	59.71	74	73.95	10.19
4 3-R- <i>o</i> -Xylene	1.5080	.894	96-97	59.48	66	73.84	10.29
5 5-R- <i>m</i> -Xylene	1.4948	.869	91	59.80	65	74.48	10.39
6 2-R- <i>m</i> -Xylene	1.5190	.912	61 (1 mm.)	59.35	75	73.93	10.06

^a Compounds 2 and 3 were made from RLi types derived from the corresponding bromo compound. The rest were prepared from the iodo compounds. ^b Unless otherwise indicated the pressure was 14 mm. ^c M_R^d (calcd.) 59.47. ^d Reaction run only once, therefore lower yield probably not significant. ^e Anal. Calcd. for C₁₁H₁₃Si: C, 74.09; H, 10.17.

cooled in an ice-bath and then hydrolyzed with cold water. The layers were separated, and the ethereal layer was washed twice with water and dried over Drierite. In the case of the trimethylsilylxylenes prepared *via* the corresponding iodoxylenes, it was necessary to wash the ethereal layers with a 10% solution of sodium thiosulfate preliminary to drying in order to remove iodine formed by oxidation of lithium iodide. The ethereal solutions were allowed to stand over Drierite for about three hours. These suspensions were then filtered, the ether was stripped off and the residues were distilled under reduced pressure through a Todd continuous wire spiral column.

Although the coupling of 2,6-dimethylphenyllithium and trimethylchlorosilane proceeded readily, the resulting 2-trimethylsilyl-*m*-xylene was very easily cleaved if the subsequent hydrolysis was not carried out carefully. Similarly, a large excess of trimethylchlorosilane was to be avoided, since upon hydrolysis of the reaction mixture, the hydrochloric acid present caused extensive cleavage. It was also important to have a sufficiently large excess of lithium metal so that the iodo compound was completely converted to the organometallic. If this precaution was not observed, the unreacted iodo compound was extremely difficult to separate from the silane by distillation. The hydrolysis of the filtered reaction mixture was carried out by *thoroughly cooling* the filtrate in an ice-bath and then slowly adding cold water to it dropwise. The remainder of the procedure for working up this silane was similar to that described above. The residue was distilled under reduced pressure through a 22-inch modified Widmer column.

The data for the preparation of the trimethylsilylxylenes is summarized in Table I.

Purification of Materials.—Dioxane was purified as described by Fieser.⁷ *p*-Toluenesulfonic acid was crystallized from concd. hydrochloric acid followed by treatment with Norite and crystallization from hydrochloric acid. The crystalline material was dried at 100-110° at 0.5-1.0 mm. for 4 hours and the fused product was then powdered. *p*-Toluenesulfonic acid monohydrate and C.P. toluenesulfonic acid were obtained from Eastern Chemical Corporation and the Fisher Scientific Co., respectively. These were used without further purification, but each batch was tested for the absence of chloride ion (silver nitrate) and sulfate ion (barium chloride). Each batch was also checked by titration of samples with standard sodium hydroxide, and the amount of water present was calculated by difference. In comparable runs with recrystallized and commercial toluenesulfonic acid, there was no appreciable difference in the rates of cleavage of 4-trimethylsilyl-*o*-xylene. Toluene for the thermoregulator was purified as described by Beal and Souther.⁸ Glacial acetic acid was purified by the addition of the calculated amount of acetic anhydride and fractional distillation over a small amount of potassium permanganate.

Thermostat.—The thermostat employed consisted of a Sargent model S-84805 constant temperature-bath, surrounded by three inches of granulated mica insulation. A port through the insulation was provided for viewing the interior of the bath. The mercury thermoregulator furnished with the bath was replaced by a mercury-toluene thermoregulator in order to obtain higher sensitivity. The thermoregulator was of approximately the same size and shape as the commercial model. The modified portion con-

sisted of a six mm. diameter concentric tube, whose top periphery was sealed to the inner wall of the thermoregulator about one cm. below the standard taper joint, and which extended to within one cm. of the bottom of the thermoregulator.⁹

With these modifications, the temperature could be maintained at 25° to within $\pm 0.002^\circ$ or better.

Dilatometers.—The tapless dilatometers¹⁰ had a capacity of about 35 ml. and the bulbs were made long and of thin-walled glass tubing so that rapid temperature equilibrium with the bath could be attained. The capillary tubing had a bore of about one mm. and was tested for uniformity by measuring a thread of mercury at different positions of the tubing. During a run, the ends of the capillaries were protected from the atmosphere by connecting a short loop of rubber tubing to them.

Effect of Water and of Added Salts on Cleavage Rate.—A series of runs were carried out to determine the effect of water and of added salts upon the rates of cleavage of 4-trimethylsilyl-*o*-xylene.

p-Toluenesulfonic acid monohydrate, whose water content had been checked by titration, and water were weighed into a 50-ml. glass stoppered erlenmeyer flask and about 35 ml. of glacial acetic acid was then added. The silane was weighed into a 50-ml. volumetric flask and then thermostated. At zero time, the thermostated acid solution was quickly poured into the volumetric flask, the erlenmeyer flask was rinsed out with several ml. of acetic acid and the rinsings were added to the reaction solution. The solution was then made up to the proper volume. This solution was shaken vigorously and then transferred rapidly by suction to the thermostated dilatometer. Readings of meniscus height were recorded with the aid of a cathetometer, which could be read to 0.01 cm. All these runs exhibited an expansion in volume upon cleavage, the change in meniscus height amounting to 2-5 cm.

Rate constants (pseudo first-order) were determined graphically from a large scale plot of $\log(l_\infty - l_t)$ against time t in minutes, or more conveniently, $\log(l_\infty - l_t)$ against t , where l_∞ is the length of travel in cm. of the meniscus at the completion of the reaction (7-8 half-lives), and l_t is the length of meniscus travel in cm. after time t . The slope of this plot is equal to $-k/2.303$ where k is the pseudo first-order rate constant.

The rate constants and corresponding half-lives for the cleavage of 4-trimethylsilyl-*o*-xylene by 0.8000 *M* *p*-toluenesulfonic acid in acetic acid with varying concentrations of water and of added salts at 25° are summarized in Table II. The corresponding slopes of the plots of $\log(l_\infty - l_t)$ vs. t are compared graphically in Fig. 1.

General Kinetic Procedure.—The kinetic procedure which was used for determining the rates of cleavage of all the trimethylsilylxylylene isomers under comparable conditions was carried out as follows. Samples of the silane ranging from 0.5 to 0.7 g. were weighed into 50-ml. volumetric flasks. Twenty-five ml. of glacial acetic acid was added to the flask which was then thermostated. A stock solution 2.000 molar in *p*-toluenesulfonic acid and 8.000 molar in water was made up in glacial acetic acid at exactly 25°. Twenty ml. of the thermostated stock solution was with-

(7) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 368.

(8) C. D. Beal and B. L. Souther, *This Journal*, **49**, 1094 (1927).

(9) A practical discussion of thermostats and thermoregulators can be found in J. Reilly and W. N. Rae, "Physico-Chemical Methods," 3rd ed., Vol. I, D. Van Nostrand and Co., Inc., New York, N. Y., 1939, p. 185; and A. Findlay, "Practical Physical Chemistry," 7th ed., Longmans, Green and Co., New York, N. Y., 1949, p. 29.

(10) G. A. Benford and C. K. Ingold, *J. Chem. Soc.*, 929 (1938).

TABLE II
EFFECT OF WATER AND OF ADDED SALTS ON THE RATE OF
CLEAVAGE OF 4-TRIMETHYLSILYL-*o*-XYLENE BY 0.8000 *M*
p-TOLUENESULFONIC ACID IN ACETIC ACID AT 25°

Run	Water, molarity, <i>M</i>	4-Tri-methyl-silyl- <i>o</i> -xylene, <i>M</i>	$k \times 10^3$, min. ⁻¹	Ave.	Half-life, min.	Ave.
10	6.000	0.05608	1.16		597	
7	6.000	.05608	1.21	1.19	573	585
44 ^a	6.000	.05638	1.63	1.63	424	424
43 ^b	6.000	.05608	1.88	1.88	369	369
12	4.000	.05608	2.15		322	
11	4.000	.05608	2.16	2.16	321	321
33 ^c	6.000	.05608	2.35	2.35	295	295
15	3.000	.03264	3.60		192	
13	3.000	.05608	3.64		190	
14	3.000	.05608	3.65		190	
16	3.000	.06808	3.66	3.64	189	190
17 ^d	6.000	.05608	25.0	25.0	28	28

^a 0.3000 molar in lithium perchlorate. ^b 0.3000 molar in potassium chloride. ^c 0.3000 molar in lithium chloride. ^d 1.000 molar in lithium chloride.

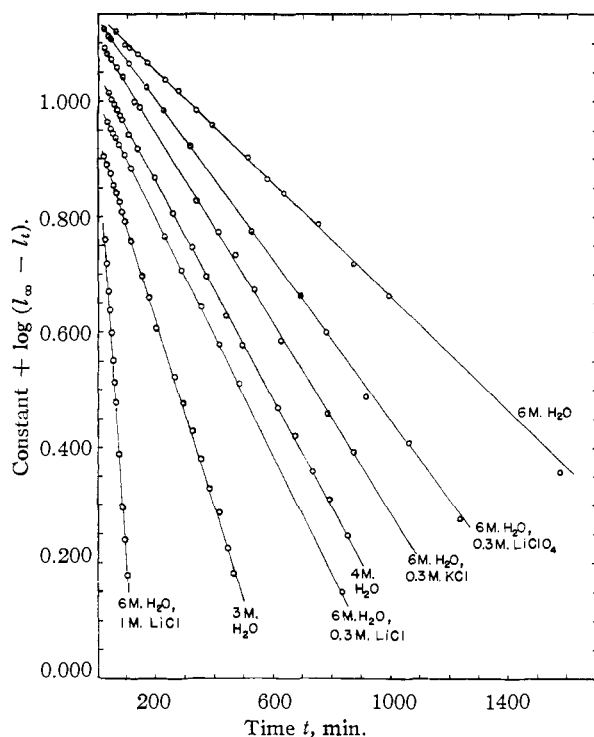


Fig. 1.—Effect of water and of added salts on the rate of cleavage of 4-trimethylsilyl-*o*-xylene by 0.8000 *M* *p*-toluenesulfonic acid in acetic acid at 25°.

drawn into a fast-flowing pipet, and at zero time was added to the silane solution. Acetic acid was added to the mark on the flask, and the flask was then shaken vigorously. The remainder of the procedure was similar to that described above.

The cleavage of 2-trimethylsilyl-*m*-xylene occurred too rapidly for measurement in acetic acid solutions containing 0.8000 *M* toluenesulfonic acid and 3.200 *M* water. A stock solution containing 2.000 *M* *p*-toluenesulfonic acid and 15.00 *M* water was therefore made up in glacial acetic acid at 25°, and 20-ml. aliquots of this solution were made up to 50 ml. with the silane in acetic acid in the same manner as described above. Cleavage runs with 4-trimethylsilyl-*m*-xylene also were made using these concentrations.

The rate constants and half-lives are presented in Table III, and the slopes are compared graphically in Fig. 2.

TABLE III
RATE CONSTANTS AND HALF-LIVES FOR CLEAVAGE OF TRI-METHYLSILYLXYLENES BY 0.8000 *M* *p*-TOLUENESULFONIC ACID IN ACETIC ACID CONTAINING 3.200 *M* WATER AT 25°

Run	Tri-methyl-silyl-xylene, R =	Molar-ity, <i>M</i>	$k \times 10^3$, min. ⁻¹	Ave.	Half-life, min.	Ave.
26	5-R- <i>m</i> .	0.06741	0.303		2290	
27	5-R- <i>m</i> .	.06399	.308	0.306	2250	2270
21	4-R- <i>o</i> .	.05608	2.97		233	
34	4-R- <i>o</i> .	.07047	2.99	2.98	232	233
32	2-R- <i>p</i> .	.06991	3.08		225	
28	2-R- <i>p</i> .	.06064	3.09	3.09	225	225
25	3-R- <i>o</i> .	.07038	4.15		167	
45	3-R- <i>o</i> .	.06794	4.19	4.17	165	166
42 ^a	4-R- <i>m</i> .	.06770	6.30		110	
40 ^a	4-R- <i>m</i> .	.06845	6.34	6.32	109	110
30	4-R- <i>m</i> .	.06862	24.5		28	
29	4-R- <i>m</i> .	.06841	24.6	24.6	28	28
39 ^a	2-R- <i>m</i> .	.06906	73.3		9.46	
41 ^a	2-R- <i>m</i> .	.06909	73.6	73.5	9.42	9.44

^a This run 6,000 molar in water.

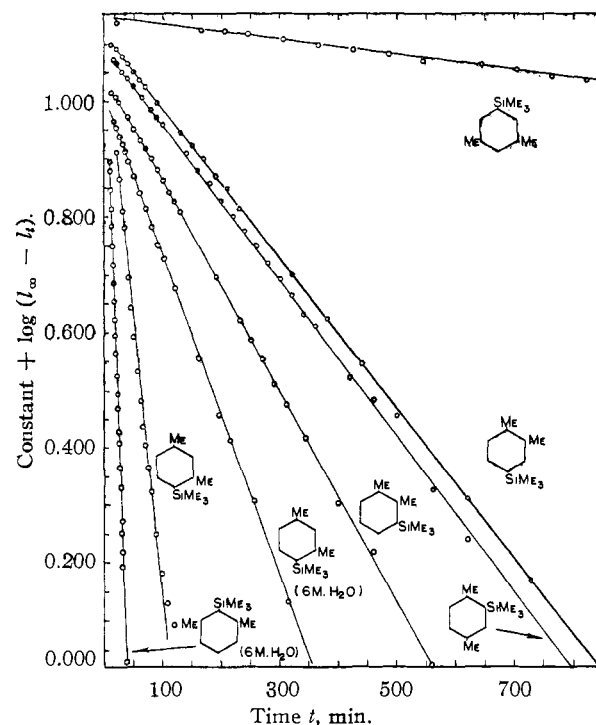


Fig. 2.—Comparison of the rates of cleavage of the trimethylsilylxylenes by 0.8000 *M* *p*-toluenesulfonic acid in acetic acid containing 3.200 and 6.000 *M* water at 25°.

Isolation of Cleavage Products.—To a solution of 38 g. (0.2 mole) of *p*-toluene-sulfonic acid monohydrate, 18 ml. of water and 125 ml. of glacial acetic acid was added 15 g. (0.084 mole) of 2-trimethylsilyl-*p*-xylene. This mixture was refluxed gently for four hours, after which it was cooled and diluted with a sufficiently large volume of water so that no further increase in turbidity was evidenced. This mixture was then extracted repeatedly with small portions of 35–37° petroleum ether. The ether extracts were combined and washed once with water, after which the ether solution was dried over Drierite. This was filtered, and the ether was stripped off carefully. Fractional distillation of the residue at 750 mm. yielded 4.62 g. (68%) of hexamethyldi-

siloxane boiling at 99°, n_D^{20} 1.3774; and 6.92 g. (78%) of *p*-xylene, b.p. 137–138°, n_D^{20} 1.4930, m.p. 13–14°.

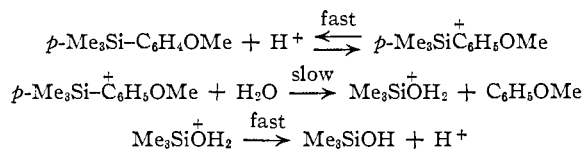
The acetic acid solutions containing the cleavage products of 4-trimethylsilyl-*o*-xylene resulting from all the rate runs were combined, omitting, however, the runs containing the added salts. To this solution was added a large volume of distilled water and the cleavage products were extracted and worked up as described for 2-trimethylsilyl-*p*-xylene. There was obtained upon distillation, hexamethyldisiloxane, b.p. 99–100°, n_D^{20} 1.3775, and *o*-xylene, b.p. 143–144°.

Results and Discussion

All the cleavage reactions were accompanied by an increase in volume, and the meniscus height change was of the order of two to five cm. The first-order plot remained linear for at least four or five half-lives for all the cleavage reactions except in the case of 4-trimethylsilyl-*m*-xylene. In solutions containing 3.200 *M* water, the curve for this compound began curving upward after about two half-lives. In this case there is a possibility that a consecutive reaction¹¹ is occurring, in which the rate of the cleavage reaction may be of the same magnitude as the rate of condensation of trimethylsilanol to hexamethyldisiloxane. This effect was not observed, however, in the case of 2-trimethylsilyl-*m*-xylene. In a few cases, Guggenheim plots¹² were employed and good checks with the other plots were obtained.

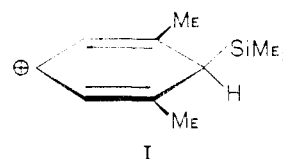
All the salt effects were positive and, of the three salts tested, lithium chloride was most effective in increasing the rate of cleavage. Possibly the high solvation of the lithium ion was effective in reducing the water concentration, thus influencing the cleavage rate.

The only kinetic study of the acid cleavage of the aryl carbon-silicon bond has been made by Eaborn,¹³ who determined the rates of cleavage of *p*-methoxyphenyltrimethylsilane in aqueous methanol and aqueous dioxane solutions of hydrochloric and perchloric acids by a spectrophotometric method. On the basis of the dependence of the rate of cleavage of the silane on the acidity function¹⁴ and the water concentration, Eaborn postulated the mechanism



The first step in this mechanism consists of a fast and reversible proton transfer from the solvent to the substrate, and the trimethylsilanol in the last step rapidly condenses to form hexamethyldisiloxane. The effect of electron-releasing substituents on the benzene nucleus is thus to increase the concentration of the protonated intermediate in the first step, and the acid-catalyzed cleavage should therefore parallel the usual electrophilic aromatic substitutions.

The protonated intermediate of a trimethylsilyl-xylene can be represented spatially as shown in I



(and other resonance contributions), which is similar to the protonated forms proposed by Eaborn¹³ and others.⁴ These intermediates are formally analogous to the aromatic complexes proposed by Brown and Brady¹⁵ and by McCaulay and Lien,¹⁶ and are spatially analogous to the reaction intermediate in the nitration of an aromatic ring.¹⁷

The rates of acid cleavage of the trimethylsilylxylenes are influenced measurably by the water concentration as can be seen by comparing Table I and Fig. 1. Similar observations have been made by Eaborn.¹³ This dependence is no doubt related to the acidity function of the medium, for the acidity function of sulfuric acid in acetic acid changes quite markedly with changing water concentration.¹⁸

In Fig. 3 are plotted the logarithms of the partial relative rate factors for electrophilic substitution at each of the six isomeric positions in the xylenes against the logarithms of the rate constants for the acid cleavage of the corresponding trimethylsilylxylenes. The partial relative rate factors were calculated by the method of Condon,² and the data for the other reactions were obtained and calculated from the partial rate factors for toluene listed by Brown and Nelson.¹⁹ The rate constant for 2-trimethylsilyl-*m*-xylene shown in the plot was estimated for comparison with the other trimethylsilylxylenes under similar conditions from the rate data for 4-trimethylsilyl-*o*-xylene and 4-trimethylsilyl-*m*-xylene; $k = 3 \times 10^{-1}$ min.⁻¹, half-life 2 min.

The plot in Fig. 3 shows an excellent linear relationship for halogenation and nitration, and a good to fair relationship for sulfonylation, isopropylation and chloromethylation. Mercuration with perchloric acid catalyst¹⁹ and sulfonation¹⁹ correlate rather poorly with the cleavage reaction, the center points showing considerably more scatter than that observed in the chloromethylation plot.

The cleavage reaction is influenced considerably by steric factors which are evidenced by deviational trends from linearity for certain of the points. Considering first the point for the highly hindered 2-trimethylsilyl-*m*-xylene, it is not surprising that this should exhibit a large deviation, since this compound can be considered a homomorph²⁰ of 2,6-dimethyl-*t*-butylbenzene. As such, it is expected to be a highly strained molecule, and the cleavage reaction therefore occurs readily in order to relieve this strain by forming a protonated intermediate

(15) (a) H. C. Brown and J. Brady, *THIS JOURNAL*, **71**, 3573 (1949); (b) **74**, 3570 (1952).

(16) D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951).

(17) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 281; G. W. Wheland, *THIS JOURNAL*, **64**, 900 (1942).

(18) D. S. Noyce and P. Castellfranco, *ibid.*, **73**, 4482 (1951).

(19) H. C. Brown and K. L. Nelson, *ibid.*, **75**, 6292 (1953).

(20) H. C. Brown and M. Grayson, *ibid.*, **75**, 20 (1953).

(11) S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 1075.

(12) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

(13) C. Eaborn, *J. Chem. Soc.*, 3148 (1953).

(14) (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter IX; (b) E. A. Braude, *J. Chem. Soc.*, 1971 (1949).

such as I. Molecular models of these two homomorphs show that, although the silicon analog is highly hindered, there apparently is less strain in this model than in the carbon analog.

Another point exhibiting a deviation in Fig. 3 is the one representing 2-trimethylsilyl-*p*-xylene. The rate of halogenation of *o*-xylene is greater than that for *p*-xylene,²¹ whereas 2-trimethylsilyl-*p*-xylene cleaves more rapidly than 4-trimethylsilyl-*o*-xylene (cf. Fig. 2 and Table III). This reversal can be attributed to the superimposition of two effects: an electron-releasing inductive effect of a methyl group exerting a stronger influence at the *o*-position and a more important steric effect. The cleavage reaction involves substitution of a large group by a much smaller one—the antithesis of the usual electrophilic substitution—and the relieving of the steric strain caused by a contiguous methyl group thus favors the formation of a protonated intermediate similar to I over that of 4-trimethylsilyl-*o*-xylene.

Attention can again be directed to the deviations of points for the isomeric positions represented by 3-trimethylsilyl-*o*-xylene. The rate of bromination at the 3-position in *o*-xylene must be very slow compared to bromination in the 4-position, since the 4-bromo isomer is formed almost exclusively.²² On the other hand, 3-trimethylsilyl-*o*-xylene cleaves more rapidly than 4-trimethylsilyl-*o*-xylene probably because of the greater steric strain in the former. In this regard, it is of interest to compare the marked difference in rates of cleavage of 3-trimethylsilyl-*o*-xylene and 2-trimethylsilyl-*p*-xylene. These two isomers each have a methyl group *ortho* and *meta* to the trimethylsilyl group. One would therefore expect that the purely electrical effects at the silicon-carbon bond should be approximately the same in the two isomers. The former isomer, however, has the additional influence of an extra methyl group pushing against the trimethylsilyl group. This additional buttressing^{23,24} probably favors the formation of the reaction intermediate and the subsequent cleavage to a greater extent than in the other isomer. A good correlation is thus obtained in Fig. 3 so long as steric effects are relatively minor. The fact that the point for the position represented by 4-trimethylsilyl-*m*-xylene falls in line with the other points where steric influences are absent, can be attributed to the much greater importance of the activation due to resonance contributions,^{15b} which effectively overshadows the much smaller steric effect.

It is interesting to note that the slopes for the

(21) P. B. D. De La Mare and P. W. Robinson, *J. Chem. Soc.*, 279 (1943).

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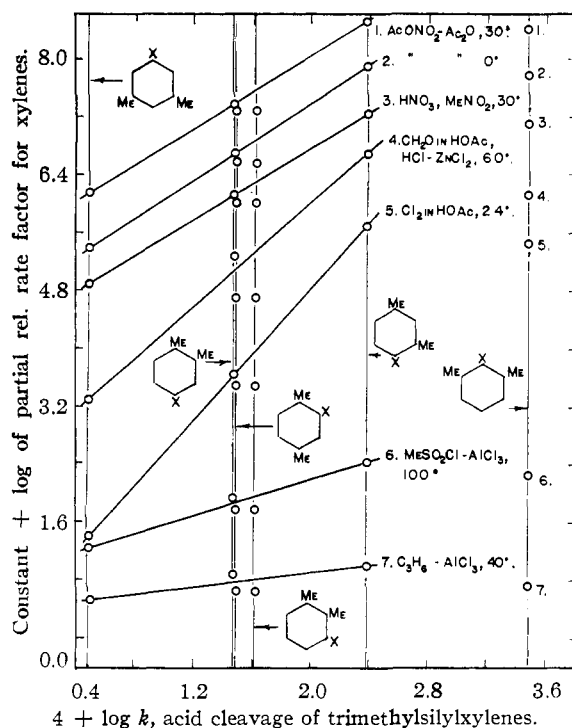


Fig. 3.—Relationship between the logarithms of the partial relative rate factors for electrophilic substitution in the xylenes and the rates of acid cleavage of the trimethylsilylxylenes.

reactions in Fig. 3 follow an order which is probably related to the "activity"¹⁹ or electrophilic character of the attacking reagent. For example, the electrophilic character of attacking reagents increases in the order $\text{Br}_2 < \text{NO}_2^+ < (\text{CH}_3)_2\text{CH}^+$.¹⁹

The fact that a linear correlation is observed in these reactions is thus good supporting evidence for the formation of σ -complexes^{15b} analogous to I.²⁵

In summary, it may be said that the type of acid cleavage herein described should prove of value in comparison with electrophilic substitutions so long as the reaction site is at a sufficient distance from groups which may cause complications due to steric influences. It would thus appear that these reactions should be limited to *m*- and *p*-positions just as they are in the side-chain reactions of benzene derivatives.²⁶

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(25) A further extension of the acid cleavage reaction of trimethylarylsilanes to other alkyl substituents is reserved for a subsequent publication.

(26) Reference 14a, Chapter VII.