

Electrophilic Aromatic Reactivities *via* Pyrolysis of 1-Arylethyl Acetates. Part IX.¹ The Effect of the Trimethylsilyl Substituent

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The three isomeric 1-(trimethylsilylphenyl)ethyl acetates have been prepared and their rates of pyrolysis together with that of 1-phenylethyl acetate measured between 340.6 and 392.9°. The trimethylsilyl substituent activates in all positions according to the sequence $o > m > p$ as theoretically predicted and found in protodesilylation, but contrary to the activation order observed in nitration, and the deactivation order found in solvolysis of 1-aryl-1-methylethyl chlorides. The variability of the substituent effect in these and some other reactions is attributed mainly to varying demands for resonance stabilisation of the transition states together with some solvent-substituent interactions. The variation in the *meta*-substituent effect coupled with the high activation by the *ortho*-substituent indicates that the trimethylsilyl group supplies electrons inductomerically. In the light of the present results the reactivity pattern in nitration of phenyltrimethylsilane is seen to be affected by steric hindrance. Values of σ^+ are -0.16 (*m*-SiMe₃) and -0.09 (*p*-SiMe₃).

ALTHOUGH the electrical effects of most simple substituents in electrophilic aromatic substitution are now well evaluated, the effect of the trimethylsilyl substituent is not. Data have hitherto been available in proto- and bromo-desilylation,²⁻⁵ nitration,⁶ and proto-⁷ and iodo-destannylation,⁸ but only in a few of these reactions has the reactivity of all positions been measured, and the data disagree (Table 1). However, this is not too surprising as the trimethylsilyl substituent appears to be exceptionally sensitive to solvent effects, as shown by determinations of σ values (Table 2) which show that either the *meta*- or the *para*-substituent is the more electron supplying according to the conditions. In some of these reactions the *para*-substituent with-

draws electrons and this is apparent also from measurements of acidity constants of anilinium ions and ioniza-

TABLE I
Partial rate factors for substitution in PhSiMe₃

Reaction	Position of substituent			
	<i>ortho</i>	<i>meta</i>	<i>para</i>	ρ
Protodesannylation ⁷			0.93	-2.2
Iododesannylation ⁸			0.97	-2.3
Protodesilylation ²⁻⁴	8.55	1.63	1.25	-4.6
Bromodesilylation ⁵			1.52	-5.4
Nitration ⁶	1.25	2.2	2.95	-6.2

tion constants of phenols,⁹ where conjugation between the reaction site and the *d* orbitals of silicon is a major

¹ Part VIII, R. Taylor, M. P. David, and J. F. W. McOmie, *J.C.S. Perkin II*, 1972, 162.

² C. Eaborn, *J. Chem. Soc.*, 1956, 4858.

³ C. Eaborn, D. R. M. Walton, and D. J. Young, *J. Chem. Soc. (B)*, 1969, 15.

⁴ C. Eaborn and P. M. Jackson, *J. Chem. Soc. (B)*, 1969, 21.

⁵ C. Eaborn and D. E. Webster, *J. Chem. Soc.*, 1960, 179.

⁶ J. L. Speier, *J. Amer. Chem. Soc.*, 1953, **75**, 2930.

⁷ M. A. Cook, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1969, **18**, 285.

⁸ O. Buckman, M. Grosjean, and J. Nasielski, *Bull. Soc. chem. belges*, 1963, **72**, 286.

⁹ R. A. Benkeser and H. R. Krysiak, *J. Amer. Chem. Soc.*, 1953, **75**, 2423.

factor. The majority of the more reliable data indicates that the *para*- and *meta*-substituents should supply electrons, the latter being most effective in this respect,

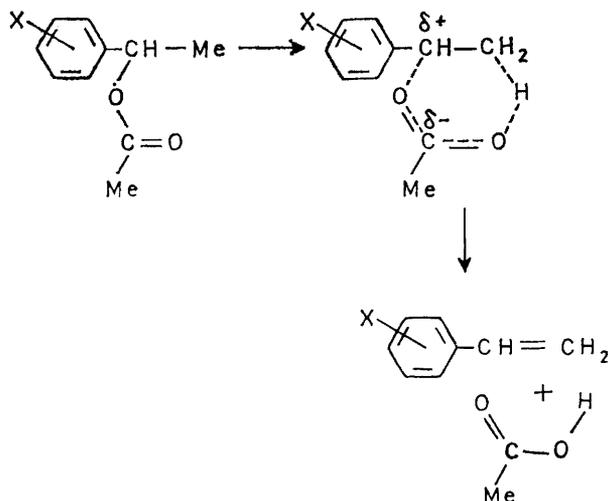
TABLE 2
Values of σ for the SiMe₃ substituent

Reaction	σ_m	σ_p	Ref.
Ionisation of benzoic acids in water	-0.04	-0.07	9
Ionisation of benzoic acids in 50% ethanol	-0.155	-0.020	e
Ionisation of benzoic acids in 60% ethanol		+0.024	f
Alkaline hydrolysis of ethyl benzoate in 80% ethanol	-0.04	+0.027	e
Alkaline hydrolysis of ethyl benzoate in 50% acetone	-0.15	-0.04	e
Benzoic acids with diphenyldiazomethane ^a	-0.018	-0.022	g
Benzoic acids with diphenyldiazomethane ^a	+0.025	+0.002	e
Benzoic acids with diphenyldiazomethane ^b	+0.024	0.000	h
Benzoic acids with diphenyldiazomethane ^c	+0.017	-0.029	h
Benzoic acids with diphenyldiazomethane ^d	-0.016	-0.034	h
Potentiometric titration of benzoic acids in dimethylformamide	-0.02	-0.04	h

^a In absolute ethanol. ^b In toluene. ^c In dioxan. ^d In dimethylformamide. ^e J. D. Roberts and C. M. Regan, *J. Amer. Chem. Soc.*, 1953, **75**, 4102. ^f J. Chatt and A. A. Williams, *J. Chem. Soc.*, 1954, 4403. ^g J. D. Roberts, E. A. MacElhill, and R. Armstrong, *J. Amer. Chem. Soc.*, 1949, **71**, 2923. ^h Z. Plzak, F. Mares, J. Hetflejš, J. Schraml, Z. Papoušková, V. Bazant, E. G. Rochow, and V. Chvalovsky, *Coll. Czech. Chem. Comm.*, 1971, **36**, 3115.

and the average values of σ , viz -0.121 (*meta*), -0.072 (*para*)¹⁰ show this to be so.

It seemed appropriate therefore to measure the effect of the trimethylsilyl substituent in a reaction in which solvent effects are absent and in which there is



no possibility of acid cleavage of the substituent, or of more than one reaction mechanism, as for example in nitration. The reaction chosen was pyrolysis of 1-arylethyl acetates (Scheme) which is known to pro-

ceed *via* the partial formation of a carbonium ion at the side-chain α -carbon atom and is an excellent model for electrophilic aromatic substitution.¹

RESULTS AND DISCUSSION

The kinetics of pyrolysis of the 1-arylethyl acetates were strictly first order for at least 95% of reaction and rates were reproducible to better than $\pm 2\%$. Rate coefficients are given in Table 3 together with the log k_{rel} values and the energies and the entropies of activation, the latter being calculated at 600 K for consistency with previous data in this series. The kinetic data produced excellent Arrhenius plots from which the log k_{rel} values given in Table 3 were interpolated at 625 K (the temperature at which $\rho = -0.63$); the quality of the plots is indicated by the statistical parameters in this Table. The log k_{rel} values yield the σ^+ values given in Table 3 and we stress that the value for the *ortho*-position may have only qualitative significance as an index of electrophilic aromatic reactivity.¹¹

TABLE 3
Pyrolysis of compounds RC₆H₄·CH(OAc)CH₃

T/°C	10 ³ k/s ⁻¹			
	R = <i>o</i> -SiMe ₃	<i>m</i> -SiMe ₃	<i>p</i> -SiMe ₃	H
340.6	3.74	2.17	1.96	1.74
355.0	8.1	4.92	4.47	3.91
369.1	17.25	10.65	9.32	8.25
392.9	59.5	36.15	31.8	28.8
Standard deviation	0.011	0.001	0.005	0.007
Correlation coefficient	0.99985	1.00000	0.99996	0.99993
log (A/s ⁻¹)	12.89	12.90	12.67	12.75
E/kcal mol ⁻¹	43.0	43.7	43.1	43.6
E/cal mol ⁻¹ K ⁻¹	-0.95	-0.90	-1.95	-1.55
log k/k ₀ (at 625 K)	0.33	0.105	0.058	0
σ^+	(-0.52) ^a	-0.165	-0.09	0

^a See text.

The results show the trimethylsilyl substituent to activate in all positions and according to the sequence *o* > *m* > *p*. This is the expected order for a substituent which has predominantly a +I effect, and it is the order that was obtained previously in protodesilylation. There are some quantitative differences between these reactions however. The σ^+ values required to correlate the data for protodesilylation would be -0.20 (*ortho*), -0.05 (*meta*), and -0.02 (*para*), and for bromodesilylation -0.035 (*para*). Since these reactions have lower demands for resonance than the pyrolysis the differences (at the *para*-position at least) can be rationalised on this basis. Thus in the reaction of higher electron demand the withdrawal of electrons by the substituent (in this case by conjugation into the empty *d* orbitals) is successfully opposed by the demand of the reagent to the extent that a nett electron supply occurs. Consistent with this explanation is the small deactivation observed in proto- and iodo-destannylation and the former reaction at least is known to have a smaller

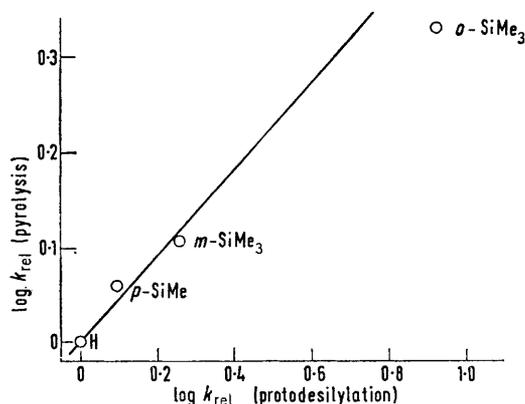
¹⁰ H. H. Jaffe, *Chem. Rev.*, 1953, **53**, 191.

¹¹ R. Taylor, *J. Chem. Soc. (B)*, 1971, 622, 1450.

demand for resonance than does protodesilylation.¹² Indeed the data in Table I show a good correlation between $f_p^{\text{SiMe}_3}$ and ρ .

Our results show that in the reaction of highest electron demand, the pyrolysis, the *ortho*-position is in particular highly activated so that it seems possible that this arises from the importance of the inductomeric effect. It is difficult to distinguish this effect from a combination of a constant $+I$ effect and a variable $-M$ effect (which would of course preferentially deactivate the *para*-position). However a clue is given by the reactivity of the *meta*-positions (which should not be affected by the $-M$ effect) and the larger σ^+ value required for this position in the pyrolysis indicates that the inductomeric effect is operating.

It might appear that in comparison to protodesilylation, in the pyrolysis the *ortho*-position is exceptionally activated relative to the other positions. However the Figure shows a plot of the $\log k_{\text{rel}}$ values in this



Plot of $\log k_{\text{rel}}$ for protodesilylation of $\text{XC}_6\text{H}_4\text{SiMe}_3$ vs. $\log k_{\text{rel}}$ for pyrolysis of $\text{XC}_6\text{H}_4\cdot\text{CH}(\text{OAc})\text{CH}_3$

reaction *vs.* those in protodesilylation from which it is seen that the *ortho*-position is relatively more strongly activated in the *latter* reaction. This probably arises through steric acceleration for which indeed there was evidence from earlier work.³ Because of the high σ^+ values required to correlate the reactivity of the *ortho*-position in both reactions it would be valuable to measure the effect of the SiMe_3 substituent in a reaction of high demand for resonance but there is little prospect of this because of the problem of C-Si cleavage.

Clearly for the SiMe_3 substituent there is a close balance between electron supply and withdrawal and this is also indicated by the value of $\sigma^+_{p\text{-SiMe}_3}$ of 0 ± 0.04 obtained from measurements of carbonyl stretching frequencies of substituted acetophenones,¹³ by the small deactivation by this substituent in protodesilylation

¹² C. Eaborn and J. A. Waters, *J. Chem. Soc.*, 1961, 542.

¹³ H. Sakurai, S. Deguchi, M. Yamagata, S. Morimoto, M. Kira, and M. Kimada, *J. Organometallic Chem.*, 1969, **18**, 285.

¹⁴ R. Baker, R. W. Bott, C. Eaborn, and P. M. Greasley, *J. Chem. Soc.*, 1964, 627.

¹⁵ H. C. Brown, Y. Okamoto, and T. Inukai, *J. Amer. Chem. Soc.*, 1958, **80**, 4964.

¹⁶ R. Taylor and G. G. Smith, *Tetrahedron*, 1963, **19**, 937.

of biphenyls,¹⁴ and by the σ^+ values obtained from solvolysis of 1-aryl-1-methylethyl chlorides, *viz.* 0.01 (*meta*), 0.02 (*para*).¹⁵ These latter results are however somewhat surprising because first they predict deactivation at the *meta*-position contrary to theoretical predictions of a value more negative than -0.066 for $\sigma_{m\text{-Me}}$ (and as indeed observed in pyrolysis), and secondly, correlation between the pyrolysis and solvolysis reactions is usually good. Discrepancies have however been detected previously and these were for the *m*-Ph¹⁶ and *m*-CF₃¹¹ substituents for which in both cases the solvolysis data were shown to be in error; the latter is also incorrect in predicting the effect of the *m*-NMe₃⁺ substituent in other electrophilic substitutions and solvent effects in the solvolysis reaction were responsible.¹⁷ Two other factors may be relevant. First the 1-aryl-1-methylethyl chlorides containing the trimethylsilyl substituent were prepared from the bromo-analogues¹⁵ which are extremely difficult to separate from the trimethylsilyl derivatives¹⁸ and any bromo-substituted 1-methyl-1-phenylethyl chloride in the product could produce a reduced rate; some indication of this possibility is revealed by the fact that the trimethylsilyl derivatives were assessed at only 95% purity.¹⁵ Secondly the high instability of the 1-aryl-1-methylethyl chlorides required their *in situ* preparation from the corresponding alcohol and hydrogen chloride; the possibility of C-Si cleavage by the latter could also have effected the kinetics.

Finally the reactivity pattern in nitration is anomalous though the reactivity of the *para*-position is normal (and requires a σ^+ value of -0.08 to correlate, in excellent agreement with our prediction): both the *ortho*:*para* ratio and (to a lesser extent) the *meta*:*para* ratio are low. Now the former phenomenon has recently come to be associated with nitration *via* nitrosation,¹⁹ but this is not a factor in the present case since nitration of phenyltrimethylsilane in the presence of either urea or sodium nitrite produces little effect on the ratio.²⁰ (Indeed in view of the fairly small electrical effect of the substituent any change in the ratio would have been very surprising.) It seems clear therefore that the ratio is affected by steric hindrance. Speier drew attention to the fact that the *ortho*:*para* ratio (0.42) seemed very high in nitration (bearing in mind that the ratio for nitration of *t*-butylbenzene under the same conditions²¹ is 0.06), and the reason for this may now be reasonably attributed to a combination of the high *ortho*-activation by this substituent and steric hindrance to substitution. The *meta*:*para* ratio may also be influenced by steric hindrance but to a much smaller extent as indeed the results suggest.

¹⁷ R. O. C. Norman and R. Taylor, 'Electrophilic Substitution in Benzenoid Compounds,' Elsevier, Amsterdam, 1965, p. 289.

¹⁸ C. Eaborn, *J. Chem. Soc.*, 1956, 4858.

¹⁹ J. G. Hoggett, R. B. Moodie, and K. Schofield, *Chem. Comm.*, 1969, 605; R. Taylor, *Tetrahedron Letters*, 1972, 1735.

²⁰ C. Eaborn, Z. S. Salih, and D. R. M. Walton, *J.C.S. Perkin II*, 1972, 172.

²¹ J. R. Knowles, R. O. C. Norman, and G. K. Radda, *J. Chem. Soc.*, 1960, 4885.

EXPERIMENTAL

The apparatus and general experimental technique for pyrolysis has been described.¹ The nature and purity (99%+) of the 1-(trimethylsilylphenyl)ethyl acetates was confirmed by elemental analysis, n.m.r. spectroscopy, and g.l.c.

1-Phenylethyl Acetates.—This compound was available from previous work.¹

1-(2-Trimethylsilylphenyl)ethyl Acetate.—*o*-Trimethylsilyltoluene was prepared in 64% yield from *o*-chlorotoluene by the literature method.²² By treatment with *N*-bromosuccinimide in the presence of benzoyl peroxide this was converted in 16.5% yield into α -dibromo-*o*-trimethylsilyltoluene²³ which in turn was converted in 49% yield into *o*-trimethylsilylbenzaldehyde. This aldehyde (10.0 g, 0.056 mol) was treated with excess of methylmagnesium iodide to yield, after hydrolysis and work-up 1-(2-trimethylsilylphenyl)ethyl alcohol (9.8 g, 93%), m.p. 65.5–67.0° (Found: C, 68.3; H, 8.9. C₁₁H₁₈OSi requires C, 68.0; H, 9.25%). This alcohol (5.0 g, 0.017 mol) was acetylated with acetic anhydride in pyridine at room temperature during several days to give, after work-up, 1-(2-trimethylsilylphenyl)ethyl acetate (2.9 g after mechanical loss, 51%), b.p. 88° at 1.0 mmHg, *n*_D²⁰ 1.4996 (Found: C, 65.9; H, 8.5. C₁₃H₂₀O₂Si requires C, 66.1; H, 8.5%), τ (CCl₄; no internal standard) 2.8 (4H, m, ArH), 4.05 (q, *J* 6.5 Hz, CH), 8.18 (s, COCH₃), 8.64 (d, *J* 6.5 Hz CH₃), and 9.77 (s, SiMe₃).

1-(3-Trimethylsilylphenyl)ethyl Acetate.—*m*-Bromotoluene (50 g, 0.29 mol) was converted into *m*-trimethylsilyltoluene²⁴ in 41% yield. Treatment of this with *N*-bromosuccinimide and benzoyl peroxide gave a 59% yield of α -dibromo-

²² H. Freiser, M. V. Eagle, and J. L. Speier, *J. Amer. Chem. Soc.*, 1953, **75**, 2821.

²³ R. G. Severson, R. J. Rosscup, D. M. Lindberg, and R. D. Engberg, *J. Amer. Chem. Soc.*, 1956, **79**, 6540.

m-trimethylsilyltoluene²³ which in turn gave a 57% yield of *m*-trimethylsilylbenzaldehyde on treatment with calcium carbonate in water. This aldehyde (7.4 g, 0.041 mol) was reacted with excess of methylmagnesium iodide to yield after hydrolysis and work-up, 1-(3-trimethylsilylphenyl)ethyl alcohol (6.2 g, 77%), b.p. 128° at 14 mmHg. This alcohol (5.04 g, 0.017 mol) was acetylated as above to give after work-up, 1-(3-trimethylsilylphenyl)ethyl acetate (1.9 g after mechanical loss, 33%), b.p. 89° at 1.0 mmHg, *n*_D²⁰ 1.4910 (Found: C, 66.0; H, 8.55%), τ (CCl₄; no internal standard) 2.8 (4H, m, ArH), 4.28 (q, *J* 6.5 Hz, CH), 8.11 (s, COCH₃), 8.59 (d, *J* 6.5 Hz, CH₃), and 9.79 (s, SiMe₃).

1-(4-Trimethylsilylphenyl)ethyl Acetate.—*p*-Dibromobenzene (60 g, 0.254 mol) was treated with *n*-butyl-lithium at room temperature followed by excess of chlorotrimethylsilane under reflux during 2 h to give after work-up *p*-bromophenyltrimethylsilane²⁵ in 47% yield. This compound (13.7 g, 0.06 mol) was converted into the Grignard reagent and treated with excess of acetaldehyde to give after work-up, 1-(4-trimethylsilylphenyl)ethyl alcohol (3.6 g, 33%), b.p. 98° at 1.8 mmHg, *n*_D²⁰ 1.5111 (Found: C, 67.6; H, 9.3%). This alcohol was acetylated as above to yield after work-up, 1-(4-trimethylsilylphenyl)ethyl acetate (1.6 g, 40%), b.p. 92° at 0.9 mmHg, *n*_D²⁰ 1.4931 (Found: C, 65.7; H, 8.3%), τ (CCl₄; no internal standard) 2.8 (4H, m, ArH), 4.32 (q, *J* 6.5 Hz CH), 8.13 (s, COCH₃), 8.61 (d, *J* 6.5 Hz CH₃), and 8.93 (s, SiMe₃).

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²⁴ H. A. Clark, A. F. Gordon, C. W. Young, and M. J. Hunter, *J. Amer. Chem. Soc.*, 1951, **73**, 3798.

²⁵ R. G. Jones and H. Gilman, *Org. Reactions*, 1951, **6**, 355.