606. *Aromatic Reactivity. Part V.* Desilylations of Trimethylsilyldiphenyls.*

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The influence of a phenyl substituent on the reactivity of a benzene ring towards electrophilic substitution has been studied for desilylations of *o*-, *m*-, and *p*-trimethylsilyldiphenyl. The results show that an *o*- or *p*-Ph substituent has an activating and a *m*-Ph substituent a deactivating effect, and considered along with data for electrophilic substitutions in diphenyl itself they indicate that the polar effect of either the *m*- or the *p*-phenyl group is too variable to be represented satisfactorily by a single substituent constant.

DESILYLATION of substituted phenyltrimethylsilanes provides a measure of the effects of nuclear substituents on the reactivity of a benzene ring towards electrophilic reagents.[1] This paper is concerned with the influence of *o*-, *m*-, and *p*-Ph substituents as revealed in the ease of cleavage of *o*-, *m*-, and *p*-trimethylsilyldiphenyl by (i) sulphuric acid–acetic acid–water at 50·18° (in which the attacking electrophile is an oxonium ion or related positive species),[1c] (ii) bromine in 1·5 wt.-% water–acetic acid at 25° (in which the electrophile is the bromine molecule or related neutral species),[1d] and (iii) mercuric acetate in 20 wt.-% water–acetic acid at 25° in which the electrophile is probably the AcO·Hg$^+$ ion or similar species (cf. ref. 1*h*).

The results are expressed in the Table as rate factors, *f*, for the rate of desilylation relative to that of the parent compound, phenyltrimethylsilane. The corresponding partial rate factors for some substitutions in diphenyl are given for comparison, namely: (i) nitration by nitric acid in acetic anhydride;[2] (ii) deuteration in the system $CH_3{\cdot}CO_2D$–D_2SO_4–CCl_4;[3] (iii) acid-catalysed bromination by hypobromous acid in aqueous dioxan (involving a positive bromine species, Br$^+$ or $BrOH_2^+$);[2a] (iv) chlorination in acetic acid (involving molecular chlorine).[4] Corresponding figures for methyl substituents are listed for comparison.

It will be seen that in all cases the phenyl group activates *ortho*- and *para*-positions and, for all the cases in which the figures are available, deactivates the *meta*-position.

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* Part IV, *J.*, 1959, 2303.

[1] (*a*) Eaborn, *J.*, 1953, 3148; (*b*) Eaborn, *J.*, 1956, 4588; (*c*) Deans and Eaborn, *J.*, 1959, 2299; (*d*) Eaborn and Webster, *J.*, 1957, 4449; (*e*) Benkeser and Krysiak, *J. Amer. Chem. Soc.*, 1954, **76**, 6353; (*f*) Benkeser, Hickner, and Hoke, *ibid.*, 1958, **80**, 2279; (*g*) Benkeser, Hickner, Hoke, and Thomas, *ibid.*, p. 528; (*h*) Benkeser, Hoke, and Hickner, *ibid.*, p. 5294.

[2] (*a*) de la Mare and Hassan, *J.*, 1957, 3004; (*b*) Dewar, Mole, and Warford, *J.*, 1956, 3576, 3581.

[3] Dallinga, Verrijn Stuart, Smit, and Mackor, *Z. Elektrochem.*, 1957, **61**, 1019.

[4] de la Mare, Hall, Harris, and Hassan, *Chem. and Ind.*, 1958, 1086.

These facts are in accord with representation [2a] of the phenyl group as withdrawing electrons by an inductive effect but returning electrons directly to *ortho-* and *para-*positions by an electromeric effect at the demand of the reagent (and possibly, though much less effectively, to the *meta*-position by secondary relay). Calculations of the free-valence number [5] and atom localisation energy [6] (which are more applicable to free-radical substitutions) indicate that *ortho-* and *para-*positions in diphenyl should be activated and the *meta*-position slightly deactivated. Using the Wheland model [7] for aromatic substitution Dewar calculates that *ortho-* and *para-*positions should be activated to about the same extent and the *meta*-position unaffected.[8] Calculation by the self-consistent field method of the energy required to convert the hydrocarbon ArH into the ion ArH_2^+ indicates that the *ortho-* and *para-*positions should be activated to about the same extent and that the *meta*-position should be slightly activated.[3]

The effect of a *p*-Ph group depends very much on the reaction concerned. This can be seen most effectively by considering the ratio ($\log f_p^{Me})/\log f_p^{Ph}$) (which is equivalent to considering the ratio of the effects of *p*-Me and *p*-Ph substituents on the free energies of activation). It will be seen (Table) that the ratio varies from 2·82 to 1·05, and it is clear that no single substituent constant of the Hammett type [10] can adequately represent the effect of the *p*-Ph substituent in electrophilic aromatic substitutions.* Similar variations are found if the corresponding ratios for *m*-Me and *m*-Ph or *m*-Ph and *p*-Ph substituents are taken, and it seems that the effect of the *m*-Ph group also cannot be represented by a single substituent constant.

Rate factors for phenyl and methyl substituents.

Reaction	*o*-Ph	*m*-Ph	*p*-Ph	*o*-Me	*m*-Me	*p*-Me	$\frac{\log f_p^{Me}}{\log f_p^{Ph}}$	Notes
Protodesiln.	6·0	0·33	2·8	15	2·2	18	2·82	(*a*)
Bromodesiln.	1·18	0·41	12·5	82	2·9	49	1·54	(*b*)
Mercuridesiln.	2·5	0·58	3·3	~11	2·5	17·5	2·40	—
Nitration	18·5	—	11·0	42	2·5	58	1·70	(*c*)
Bromination (Br^+)	10·7	0·28	15·6	76	2·5	59	1·48	(*d*)
Deuteration	37	(>0·3)	37	350	—	350	1·62	(*e*)
Chlorination	338	—	595	617	4·95	820	1·05	(*f*)

(*a*) The figure for *p*-Me is from ref. 1*c*, and those for *m*-Me and *p*-Me are deduced from data for $HClO_4$–MeOH–H_2O in ref. 1*b*. (*b*) Data for the tolyl compounds are from ref. 1*d*. (*c*) Figures for diphenyl are derived in ref. 2*a* from data in ref. 2*b*. Values of 41, <0·6, and 38 have also been given for *o*-, *m*-, and *p*-positions of diphenyl in nitration in acetic anhydride (Simamura and Mizuno, *Bull. Chem. Soc. Japan*, 1957, **30**, 196). (*d*) Data from ref. 2*a*. (*e*) Data for diphenyl are from ref. 3. Data for toluene are from Mackor, Smit, and van der Waals (*Trans. Faraday Soc.*, 1957, **53**, 1309), and actually refer to de-deuteration in $CF_3\cdot CO_2H$–H_2SO_4. (*f*) Data for diphenyl are from ref. 4 and for toluene from Brown and Stock (*J. Amer. Chem. Soc.*, 1957, **79**, 5175).

The ratio ($\log f_p^{Me})/(\log f_p^{Ph}$) is markedly smaller for bromodesilylation than for proto- and mercuri-desilylation, probably because electromeric release of electrons by the phenyl group is called forth more strongly by a neutral reagent (with its greater electron-demand) than by a positive one.[2a,10] It is of interest that in the Table the highest values of the ratio are associated with the lowest values of f_p^{Me}, *i.e.*, with the smallest electron-demand as roughly indicated by the activating effect of the *p*-Me group. The lowest value of the

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* The ratio of the (σ^+) substituent constants proposed for the *p*-Me and *p*-Ph groups in electrophilic reactions,[9] which should agree with observed ($\log f_p^{Me}/\log f_p^{Ph}$) ratios, is 1·74.

[5] Burkitt, Coulson, and Longuet-Higgins, *Trans. Faraday Soc.*, 1951, **47**, 553.

[6] Seel, *Z. Elekrochem.*, 1948, **52**, 191.

[7] Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900.

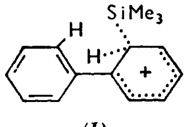
[8] Dewar, *ibid.*, 1952, **74**, 3341 *et seq.*; Dewar, *J.*, 1952, 3544; Dewar, Mole, and Warford, *J.*, 1956, 3581.

[9] Brown and Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

[10] de la Mare and Harvey, *J.*, 1956, 36; 1957, 131.

ratio, that for molecular chlorination, is correspondingly associated with the highest value of f_p^{Me}. Intermediate figures show an appropriate general trend, though with obvious deviations.

Satisfactory interpretation of the effects of *o*-Ph substituents is not yet possible. The simplest explanation of the large activation by an *o*-Ph group compared with that by *p*-Ph group in protodesilylation is that in *o*-trimethylsilyldiphenyl steric interaction between the Me_3Si group of one ring and the *o*-hydrogen atoms of the other ring prevents co-planarity of the rings, and thus hinders conjugation between the activating phenyl group and other ring to a greater extent than it is hindered in diphenyl itself. In a transition state approximating to the intermediate (I), the tetrahedral disposition of bonds around the carbon atom participating in the aryl–$SiMe_3$ bond may allow the two rings to become coplanar (as presumably they do during reaction of the *p*-Ph isomer). (Substitutions in diphenyl itself involve the same initial state whatever the position attacked, and different considerations apply.) The high reactivity of the *ortho*-isomer may thus be attributed mainly to destabilization of the initial state (by as little as 0·5 kcal. mole^{-1}). Trapping of the *o*-hydrogen atom of the activating phenyl group between the hydrogen atom and Me_3Si group at the attacked carbon may in addition somewhat stabilize the transition state by enforcing (as distinct from permitting) coplanarity of the rings.*



(I)

Such an explanation neglects the effects of entropy changes, which may be considerable. A structure such as (I), in which a hydrogen atom of the activating phenyl group is constrained between the entering and the leaving group, would be very rigid, and there would be an unfavourable entropy change on going from the initial state to a transition state similar to the intermediate. It is possible that the abnormally low reactivity of *o*-trimethylsilyldiphenyl in bromodesilylation arises from an entropy change more unfavourable than that in protodesilylation, the difference originating in the differing sizes and shapes of the entering group and in a differing balance of bond-making and bond-breaking processes.

EXPERIMENTAL

The preparations of the trimethylsilyldiphenyls have been described.[1c]

The procedure for measuring the substituent effects in bromodesilylation was identical with that previously employed.[1d]

An account of studies of mercuridesilylation reactions will be presented later. The conditions are such that reaction is of first order with respect to both the aromatic compound and the mercuric acetate. The results for this reaction are less accurate that those for the other desilylations.

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* Trapping of the activating phenyl group between the entering nitronium ion and the leaving hydrogen atom was postulated to explain the high reactivity of the *ortho*-position relative to that of the *para*-position in nitration of diphenyl in acetic acid (see Table).[2a] The difficulty of generalizing this explanation is seen when it is realized that towards nitration by mixed acid at 35—40° the *ortho*-position is less reactive than the *para*.[11]

[11] Jenkins, McCullough, and Booth, *Ind. Eng. Chem.*, 1930, **22**, 31; de la Mare and Hassan, *J.*, 1958, 1519.