1171. *Aromatic Reactivity. Part XXXI.*[1] *Effects of Phosphorus-containing Substituents in Protodesilylation*

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We have measured the rates of cleavage by acetic acid–sulphuric acid–water of the compounds $X{\cdot}C_6H_4{\cdot}SiMe_3$ in which X is a phosphorus-containing group. In this electrophilic aromatic substitution, the order of decreasing deactivation by the groups X and some more common groups is as follows: p-P(O)Ph$_2$, p-P(O)Me$_2$, p-PMe$_3{}^+$, p-NO$_2$, p-P(O)(OEt)$_2$, p-P(O)(OH)$_2$ and p-NMe$_3{}^+$, m-P(O)Ph$_2$, m-P(O)(OEt)$_2$, m-P(O)(OH)$_2$, m-CF$_3$, m-O·P(O)(OEt)$_2$, m-Cl, m-CH$_2$·P(O)(OEt)$_2$, m-CH$_2$·P(O)(OH$_2$), p-O·P(O)(OEt)$_2$, p-CH$_2$·P(O)(OEt)$_2$, p-CH$_2$·P(O)(OH)$_2$, H. In the discussion of this order, emphasis is placed on (i) the protonation of the oxygen atom of the phosphoryl bond in strongly acidic media, which is probably partly responsible for the very powerful deactivation by the p-P(O)Ph$_2$ and p-P(O)Me$_2$, group, for example, and (ii) the p_π–d_π bonding between the aryl group and an attached phosphorus atom, which is responsible for the deactivation order p-PMe$_3{}^+$ > p-NMe$_3{}^+$.

Acid cleavage of aryltrimethylsilanes, protodesilylation,[2] is an electrophilic aromatic substitution, and the rate of cleavage of the compound $X{\cdot}C_6H_4{\cdot}SiMe_3$ gives a clear indication of the effect of the substituent X on the ease of electrophilic aromatic substitution generally.[2-6] To obtain information on the effects of phosphorus-containing substituents, which have been little studied, we have prepared some appropriately substituted phenyltrimethylsilanes, and have measured their rates of cleavage by a mixture of acetic acid (4 vol.) and aqueous sulphuric acid (3 vol.) at 50°.[2] The results are shown in the Table as observed first-order rate constants, k_1, and as values of k_{rel}, rates relative to that of phenyltrimethylsilane.

Cleavage of $X{\cdot}C_6H_4{\cdot}SiMe_3$ in sulphuric acid–acetic acid–water at 50°

X	$[H_2SO_4]$* (M)	10^3k_1 (min.$^{-1}$)	k_{rel}	X	$[H_2SO_4]$* (M)	10^3k_1 (min.$^{-1}$)	k_{rel}
p-P(O)Ph$_2$	18·4	6·4	$0{\cdot}40 \times 10^{-4}$	m-P(O)(OH)$_2$	16·3	44	$1{\cdot}3 \times 10^{-3}$
p-P(O)Me$_2$	18·4	9·4	$0{\cdot}59 \times 10^{-4}$	m-CF$_3$	16·3	84	—
p-PMe$_3{}^+$†	18·4	11·0	$0{\cdot}70 \times 10^{-4}$	m-CF$_3$	11·7	1·75	$2{\cdot}55 \times 10^{-3}$
p-NO$_2$	18·4	13·8	—	m-O·P(O)(OEt)$_2$	11·7	8·0	0·012
p-P(O)(OEt)$_2$	18·4	18·4	$1{\cdot}2 \times 10^{-4}$	m-Cl	11·7	8·9	—
p-P(O)(OH)$_2$	18·4	33	$2{\cdot}1 \times 10^{-4}$	m-Cl	9·9	2·25	0·013
p-NMe$_3{}^+$†	18·4	33	$2{\cdot}1 \times 10^{-4}$	m-CH$_2$·P(O)(OEt)$_2$	9·9	37	0·21
m-P(O)Ph$_2$	18·4	44	$2{\cdot}8 \times 10^{-4}$	m-CH$_2$·P(O)(OH)$_2$	9·9	55	0·32
m-P(O)(OEt)$_2$	18·4	90	$5{\cdot}7 \times 10^{-4}$	p-O·P(O)(OEt)$_2$	9·9	61	0·35
m-P(O)(OH)$_2$	18·4	150	$9{\cdot}5 \times 10^{-4}$	p-CH$_2$·P(O)(OEt)$_2$	9·9	121	0·70
p-NO$_2$	16·3	2·88	$0{\cdot}87 \times 10^{-4}$	p-CH$_2$·P(O)(OH)$_2$	9·9	134	0·77
m-P(O)(OEt)$_2$	16·3	33	$1{\cdot}0 \times 10^{-3}$	H	9·9	173	1·00

* Concn. of sulphuric acid, 3 vol. of which was added to 4 vol. of an acetic acid solution of the organosilane. † The hydroxide was used.

As in earlier related studies, in order to cover a wide range of reactivities it was necessary to vary the proportion of sulphuric acid in the mixture, and to calculate values of

[1] Part XXX, C. Eaborn and D. R. M. Walton, *J. Organometallic Chem.*, 1965, **3**, 165.

[2] C. Eaborn, *J.*, 1953, 3148; 1956, 4858.

[3] F. B. Deans and C. Eaborn, *J.*, 1959, 2299.

[4] F. B. Deans and C. Eaborn, *J.*, 1959, 2303; C. Eaborn and J. A. Sperry, *J.*, 1961, 4921; R. Baker, R. W. Bott, C. Eaborn, and P. M. Greasley, *J.*, 1964, 627.

[5] R. A. Benkeser and H. Krysiak, *J. Amer. Chem. Soc.*, 1954, **76**, 6353; R. A. Benkeser, W. Schroeder, and O. H. Thomas, *ibid.*, 1958, **80**, 2283; R. A. Benkeser, R. A. Hickner, D. I. Hoke, and O. H. Thomas, *ibid.*, p. 5289; R. A. Benkeser and F. S. Clark, *ibid.*, 1960, **82**, 4881; R. A. Benkeser, Y. Nagai, and J. Hooz, *ibid.*, 1964, **86**, 3742.

[6] C. Eaborn, " Organosilicon Compounds," Butterworths, London, 1960, pp. 146—152; R. O. C. Norman and R. Taylor, " Electrophilic Substitution in Benzenoid Compounds," Elsevier, Amsterdam, London, New York, 1965, pp. 234—241.

k_{rel} by assuming that relative rates are independent of this proportion.[2-4] The nature of the substituents involved makes this assumption less justified than usual (see below), and the values of k_{rel} must be regarded as approximate, but this does not affect the validity of comparisons of rates for any one medium.

The main factor contributing to the uncertainty of the k_{rel} values is that there are interactions between the substituents and the strongly acid media. There may be either protonation, which converts $\geqslant$P(O) groups into $\geqslant$P(OH)$^+$ groups, or hydrogen-bonding, as to the oxygen atoms of $\geqslant$P(OR) and NO_2 groupings. Both types of interaction, which raise the electron-withdrawing power of the substituents, increase with increasing acidity, and both probably contribute, the protonation more strongly, to the variation of rate ratios with acidity; for example the rate ratio for the compounds with X = *m*-P(O)(OEt)$_2$ and *p*-NO_2 is 11·5 in the medium containing 16·3M (added) sulphuric acid but only 6·5 in that containing 18·4M (added) acid, while, the rate ratio even for the closely related compounds with X = *m*-P(O)(OEt)$_2$ and *m*-P(O)(OH)$_2$, respectively, changes from 0·75 to 0·60 with the same change of medium. Again, the value of k_{rel} obtained for X = *p*-NO_2 in 16·3M (added) acid, *viz.*, $0{\cdot}87 \times 10^{-4}$, differs by more than experimental error from an earlier value, *viz.*, $1{\cdot}22 \times 10^{-4}$, obtained in a more acidic medium,[2] possibly because the carboxyl which was used for overlap purposes in the earlier study is affected by hydrogen-bonding or protonation (cf. ref. 7). Such variations in k_{rel} are, of course, too small to affect the conclusions reached in this or related Papers in this Series. (There are also disagreements between values of k_1 for some compounds measured in apparently similar media in this and the earlier study,[2] but these disagreements, which arise from use of different burettes calibrated for water to deliver the required volume of the viscous sulphuric acid, are not serious, since only relative rates are discussed in this series of Papers, and it is the constancy of the medium for any one set of measurements which matters, not the exact reproducibility of any medium from worker to worker.)

The main features of the substituent effects are as follows.

(1) The *p*-PMe_3^+ deactivates three times as strongly as the *p*-NMe_3^+ group, and slightly more strongly than the *p*-NO_2 group. The PMe_3^+ group should have a smaller $-I$ effect than the NMe_3^+ group, since phosphorus bears a positive charge more easily than nitrogen, but the electron-withdrawal by the former group is enhanced by a $-T$ effect involving p_π-d_π bonding between the aromatic ring and the phosphorus atom.[8] In nitration in 98% sulphuric acid, the PMe_3^+ group deactivates the *para*-position slightly less than the NMe_3^+ group;[8] in view of the importance of solvation, the extent of which varies from medium to medium and differs for the two groups, in determining the electronic effects of positive-poles, this small reversal of the relative deactivating effects need not be surprising. It is noteworthy that in alkali cleavage of $X{\cdot}C_6H_4{\cdot}CH_2{\cdot}SiMe_3$ compounds, in which the electromeric component of the $-T$ effect is called strongly into play, the *p*-NO_2 group behaves as more strongly electron-withdrawing than the *p*-PMe_3^+ group.[9]

(2) The *p*-P(O)Ph$_2$ and *p*-P(O)Me$_2$ groups deactivate even more strongly than the *p*-PMe_3^+ group, whereas in the alkali cleavage of $X{\cdot}C_6H_4{\cdot}CH_2{\cdot}SiMe_3$ compounds the *p*-PMe_3^+ group is the most strongly electron-withdrawing.[9] An ultraviolet spectroscopic study indicates that triphenylphosphine oxide is completely protonated in the medium containing 18·4M (added) acid, and thus it is very likely that the *m*- and *p*-$Me_3Si{\cdot}C_6H_4{\cdot}P(O)R_2$ compounds are also effectively fully protonated. The $Ph_2(HO)P^+$ group would be expected to withdraw electrons more strongly (by $-I$ and $-T$ effects) than the $Me_2(HO)P^+$ group, because of the $-I$ effect of the phenyl groups, and also because of their steric hindrance to solvation of the positive centre. The greater deactivation by both $R_2(OH)P^+$ groups than

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[7] C. Eaborn and K. C. Pande, *J.*, 1961, 5082.

[8] J. H. Ridd and J. H. P. Utley, *Proc. Chem. Soc.*, 1964, 24; J. H. Ridd, "Nitro Compounds, Proc. of the International Symposium held at the Polish Academy of Sciences, Warsaw, 1963," Pergamon Press, Oxford, 1964, pp. 43—51.

[9] R. W. Bott, B. F. Dowden, and C. Eaborn, *J.*, 1965, 4994.

by the Me_3P^+ group can be understood in terms of the $-I$ effect of the hydroxyl group. However, it is likely that the compounds with X = p-$P(O)(OEt)_2$ and p-$P(O)(OH)_2$ are also effectively fully protonated, and yet these compounds are more reactive than that with X = p-PMe_3^+; possibly p_π–d_π bonding between the oxygen and phosphorus atoms in $(EtO)_2(HO)P^+$ and $(HO)_3P^+$ groups outweighs the $-I$ effect of the oxygen atoms, but the efficiency of solvation may also be a major factor.

Since the phosphorus atom of $\geqslant$P(O) groups bears a large fractional positive charge, protonation would not be expected to raise the electron-withdrawing power by a very great factor. In agreement with this, since the p-$P(O)Ph_2$ group activates (as a result of electron-withdrawal) only 30 times less than the p-PMe_3^+ groups in the alkali-cleavage in which there is no protonation,[9] and deactivates less than twice as effectively as the p-PMe_3^+ group in the acid-cleavage, it seems that protonation probably lowers the reactivity of the p-$Ph_2(O)P{\cdot}C_6H_4{\cdot}SiMe_3$ compound less than 100-fold. (The numerical values of the Hammett ρ constant are not very different in the acid and alkali cleavages.) By the same over-simplified reasoning, protonation appears to affect the electron-withdrawing power of the p-$P(O)Me_2$ more and that of the p-$P(O)(OEt)_2$ group and less than that of the p-$P(O)Ph_2$ group.

(3) The deactivation order $P(O)Ph_2 > P(O)(OEt)_2 > P(O)(OH)_2$ applies to both *meta*- and *para*-positions. The ratios of *para*- to *meta*-deactivation, *viz.*, 6·9 for the $P(O)Ph_2$, 4·9 for the $P(O)(OEt)_2$, and 4·5 for the $P(O)(OH)_2$ group, would be consistent with greatly predominant *meta*-substitution of the compounds Ph_3PO, $PhP(O)(OEt)_2$, and $PhP(O)(OH)_2$ in ordinary electrophilic aromatic substitutions, but detectable amounts of *para*-substitution would also be expected in reactions such as nitration, not too different in selectivity from the protodesilylation, the results for which (if *ortho*-substitution is neglected) correspond to ~7% of *para*-substitution for triphenylphosphine oxide, and ~10% for diethyl phenylphosphonate and phenylphosphonic acid. No *para*-substitution has, in fact, yet been observed in nitration of these compounds.[10] (The phosphonate and phosphonic acid do, however, give some *ortho*-products.) It is noteworthy that since we pointed out, on the basis of protodegermylation results, that the reported absence of *para*-substitution in nitration of the trimethylanilinium ion was anomalous,[7] Ridd and Utley have shown that, in fact, 11% of *para*-nitration occurs (representing a *m*/*p* ratio of only 4/1).[8]

(4) In the $O{\cdot}P(O)(OEt)_2$ group, which may be protonated to some extent in the medium used, the electron-withdrawing ($-I$ and $-T$) effect of the phosphorus atom must both increase the $-I$ and lower the $+T$ effect of the oxygen atom attached to the ring. The m-$O{\cdot}P(O)(OEt)_2$ group deactivates much more than the m-OMe group,[3] and slightly more than the m-Cl group, and even the p-$O{\cdot}P(O)(OEt)_2$ group causes a 3-fold deactivation. The results indicate that the substitution of diethyl phenyl phosphate should give markedly less *meta*- than *para*-product, but a few per cent of *meta*-nitration would be expected. No *meta*-product has been detected with this or with other phenyl phosphates.[11]

(5) The $CH_2{\cdot}P(O)(OEt)_2$ and $CH_2{\cdot}P(O)(OH)_2$ groups deactivate *meta*- and *para*-positions by fairly small factors. If possible effects of differing degrees of protonation in the different reaction media are neglected, the results indicate that a substantial amount of *meta*-nitration would be expected for diethyl benzylphosphonate and benzylphosphonic acid, but in sulphuric acid the ester is said[12] to give 95%, and di-n-butyl benzylphosphonate at least 91%,[13] of *para*-nitration. These nitration results are somewhat puzzling in view of the fact that the protonated species $PhCH_2{\cdot}P(OH)(OEt)_2^+$ is presumably involved in the nitrating media, since it is known that nitration of the related ion $PhCH_2{\cdot}PMe_3^+$ in nitromethane

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[10] F. Challenger and J. F. Wilkinson, *J.*, 1924, **125**, 2675 (cf. D. C. Morrison, *J. Amer. Chem. Soc.*, 1950, **72**, 4820); G. M. Kosolapoff, *ibid.*, 1949, **71**, 4021; L. D. Freedman and G. O. Doak, *ibid.*, 1955, **77**, 6221.

[11] B.I.O.S. Final Report, 714 (1949); J. M. A. Hoeflake, *Rec. Trav. chim.*, 1916, **36**, 24.

[12] G. M. Kosolapoff, *J. Amer. Chem. Soc.*, 1949, **71**, 1876.

[13] F. Kagan, R. D. Birkenmeyer, and R. E. Strube, *J. Amer. Chem. Soc.*, 1959, **81**, 3026.

gives 19% of *meta*- as well as 67% of *para*-product.[14] (Nitration of the ion in sulphuric acid gives >70% of *para*-product.[8])

It is noteworthy that, with the substituents *m*- and *p*-$\mathrm{P(O)(OEt)_2}$, -$\mathrm{P(O)(OH)_2}$, -$\mathrm{CH_2{\cdot}P(O)(OEt)_2}$, and -$\mathrm{CH_2{\cdot}P(O)(OH)_2}$, those containing the ethoxyl groups are more strongly electron-withdrawing than those containing hydroxyl groups, contrary to what would be expected from inductive effects alone, possibly because of the greater hindrance to solvation of the positive centre in the ethoxy-compounds.

EXPERIMENTAL

Aryltrimethylsilanes.—The preparations of the phosphorus-containing aryltrimethylsilanes are described elsewhere.[15]

Rate Studies.—The method used has been described.[2-4] The wavelengths (in mμ) used were as follows: (X =) *p*-$\mathrm{P(O)Ph_2}$, *p*-$\mathrm{P(O)Me_2}$, *p*-$\mathrm{P(O)(OEt)_2}$, *p*-$\mathrm{P(O)(OH)_2}$, 276·5; *p*-$\mathrm{PMe_3^+}$, 277·5; *m*-$\mathrm{P(O)Ph_2}$, 283; *m*-$\mathrm{P(O)(OEt)_2}$, *m*-$\mathrm{O{\cdot}P(O)(OEt)_2}$, 276; *m*-$\mathrm{P(O)(OH)_2}$, 275·5; *m*-$\mathrm{CH_2{\cdot}P(O)(OEt)_2}$, *m*-$\mathrm{CH_2{\cdot}P(O)(OH)_2}$, 264; *p*-$\mathrm{O{\cdot}P(O)(OEt)_2}$, 273; *p*-$\mathrm{P(O)(OEt)_2}$, *p*-$\mathrm{P(O)(OH)_2}$, *p*-$\mathrm{NMe_3^+}$, 269; *p*-$\mathrm{NO_2}$, 335; *m*-$\mathrm{CF_3}$, 272; *m*-Cl, 280; H, 271·5.

Protonation of Triphenylphosphine Oxide.—The extinction coefficient, ε, of triphenylphosphine oxide was measured at 268 and 274 mμ in aqueous sulphuric acid of various concentrations, with the following results:

[H_2SO_4] (wt. %)	19·71	30·35	42·2	46·0	49·25	51·2	53·1	57·25	62·5	68·7	81·4
ε, 268	2273	2360	2590	2740	2899	3016	3137	3479	3732	3873	3907
ε, 274	2067	2120	2258	2365	2470	2560	2650	2916	3142	3278	3332

Plots of ε against the Hammett acidity function H_0[16] are sigmoid curves with an inflexion at $H_0 = 3{\cdot}65$, indicating that the oxide is half-protonated in 53 wt. % acid if the rise in absorption is due to protonation, as is assumed. These results correspond very roughly to pK_a of $-3{\cdot}65$ for the oxide; however, the derivation of the pK_a value involves the assumption that the oxide behaves as a Hammett base, which is not strictly true; plots of log ([B]/[BH^+]) against H_0 are linear but have slopes of 0·68 and 0·67 at 268 and 274 mμ, respectively.

Examination of the ultraviolet spectrum of triphenylphosphine oxide in acetic acid containing various weights of 18·4M-sulphuric acid indicated that protonation was effectively complete in a medium containing ~ 29 wt. % sulphuric acid. It will be seen that the sulphuric acid–acetic acid–water medium has a much higher acidity than aqueous sulphuric acid containing the same wt. % of sulphuric acid (cf. ref. 17). The medium used for kinetics involving 18·4M (added) acid contains about 60 wt. % of sulphuric acid.

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[14] F. L. Riley and E. Rothstein, *J.*, 1964, 3872.
[15] R. W. Bott, B. F. Dowden, and C. Eaborn, *J. Organometallic Chem.*, 1965, in the press.
[16] M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, 1.
[17] N. F. Hall and W. F. Spengeman, *J. Amer. Chem. Soc.*, 1940, **62**, 2487.