

919. Organosilicon Compounds. Part XXXV.¹ Effects of Some Phosphorus-containing Substituents on the Rates of Cleavage of Benzyltrimethylsilanes

By R. W. BOTT, B. F. DOWDEN, and C. EABORN

We have measured the rates of cleavage of the compounds $X \cdot C_6H_4 \cdot CH_2 \cdot SiMe_3$ where $X = m$ - and p - PMe_3^+ , $-P(O)Ph_2$, and $-P(O)Me_2$, or p - $P(O)(OEt)_2$, and from the results we have derived values of the σ - or σ^- -constants of the X groups. The effects of the substituents are discussed, and the importance of $p_\pi-d_\pi$ bonding between the aromatic ring and the phosphorus atom is emphasised.

THE cleavage of substituted benzyltrimethylsilanes, $X \cdot C_6H_4 \cdot CH_2 \cdot SiMe_3$, by aqueous-methanolic sodium hydroxide is markedly facilitated by electron-withdrawal in the substituent X, and the effects of substituents correlate well with their σ -constants, or in the case of substituents having $-T$ effects, with their σ^- -constants.^{2,3} The ease of measuring the rates spectrophotometrically, and their large sensitivity to the influence of substituents (*i.e.*, the large ρ factor), make these reactions particularly suitable to quantitative investigations of substituent effects, and to obtain information about some phosphorus-containing substituents we have studied the cleavages of $X \cdot C_6H_4 \cdot CH_2 \cdot SiMe_3$ compounds in which $X = m$ - or p - PMe_3^+ , $-P(O)Ph_2$ or $-P(O)Me_2$ and p - $P(O)(OEt)_2$.

TABLE 1

Cleavage of $X \cdot C_6H_4 \cdot CH_2 \cdot SiMe_3$ compounds by alkali in 39% w/w water-methanol at 50.3°

X	λ (μ)	[NaOH] (M)	$10^3 k_1$ (min.^{-1})	$10^2 k_s$ ($\text{min.}^{-1} \text{ mole}^{-1} \text{ l.}$)	σ	σ^-
p -NO ₂	—	—	—	5260 ^a		
p - PMe_3^+ ^b	266	0.0049	60.5	1230		1.14
p - $P(O)Ph_2$	266	0.100	43.4	43.4		0.845
p - $P(O)(OEt)_2$	266	0.100	36.3	36.3		0.83
m - PMe_3^+ ^b	285	0.199	26.8	13.4	0.74	
p - $P(O)Me_2$	266	0.100	11.2	11.2		0.725
m - $P(O)Ph_2$	285	1.00	7.55	0.755	0.485	
m - $P(O)Me_2$	278	1.00	4.03	0.403	0.43	
m -CF ₃	279	1.00	3.27	0.327		
m -Cl	280	1.00	1.93	0.193		

^a From ref. 2. ^b The phosphonium iodide was used.

The results are shown in Table 1, which lists the wavelengths used in the rate studies, the observed first-order rate constants, k_1 , at the alkali concentrations, [NaOH], specified, and the specific rate constants $k_s (= k_1/[NaOH])$. For comparison with earlier work, the compounds m -trifluoromethyl- and m -chloro-benzyltrimethylsilane were included, and the values of k_s agreed with those previously observed.³ It is known that values of k_s are effectively independent of the alkali concentration, except for charged substituents (see below).^{2,3}

Values of the substituent constants, derived by use of the relation ^{2,3} $\log k_s = 4.88\sigma - 4.49$ are also shown in Table 1. For the *para*-substituents, the values are those of the exalted constants, σ^- -constants,⁴ which are required for these substituents because the conjugative ($-T$) withdrawal of electrons, resulting from $p_\pi-d_\pi$ bonding between the ring and the phosphorus atom, can operate particularly effectively in the forming benzyl carbanion. [See, for example, structures (I)—(III), and (IV)—(V).] (Analogous $p_\pi-d_\pi$ bonding effects cause the $SiMe_2^+$ group to need a σ^- -constant, in contrast to the p - NMe_3^+ group.⁵) For the one case in which a σ - or σ^- -constant has previously been measured for the substituents

¹ Part XXXIV, R. W. Bott, C. Eaborn, and B. M. Rushton, *J. Organometallic Chem.*, 1965, **3**, 455.

² C. Eaborn and S. H. Parker, *J.*, 1955, 126.

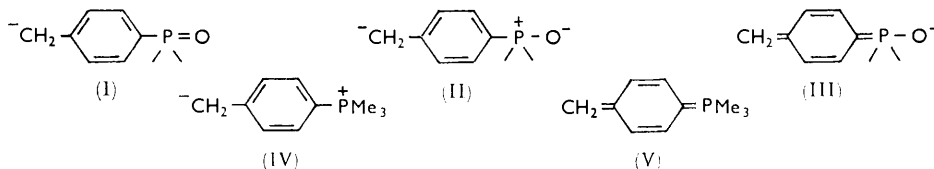
³ R. W. Bott, C. Eaborn, and B. M. Rushton, *J. Organometallic Chem.*, 1965, **3**, 448.

⁴ H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191; P. R. Wells, *ibid.*, 1963, **63**, 171.

⁵ F. G. Bordwell and P. J. Boutan, *J. Amer. Chem. Soc.*, 1956, **78**, 87.

studied, *viz.*, for the P(O)(OEt)₂ group, the calculated value of σ^- in Table 1 (0.83) is in excellent agreement with that (0.84) derived from the dissociation of the ion $p\text{-(EtO)}_2\text{(O)P}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_3^+$ but is rather larger than that (0.73) derived from dissociation of the phenol $p\text{-(EtO)}_2\text{(O)P}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$.⁶

It is presumably the effect of the $p_\pi\text{-}d_\pi$ bonding which makes the substituents much more effective from the *para*- than the *meta*-position. Probably this bonding is more important with the Me₃P⁺ group than with the groups containing the phosphoryl linkage



because with the latter the $p_\pi\text{-}d_\pi$ bonding between the oxygen and phosphorus atoms [compare structure (I)] reduces to some extent the ease of π -bonding with the ring; in agreement with this, the difference between the effects of a group from the *meta*- and from the *para*-position is greatest for the Me₃P⁺ group. The Me₃P⁺ group also has, of course, a strong $-I$ effect; the $-I$ effect of the P(O)R₂ groups is smaller because the formal positive charge in the phosphorus atom in structures such as (II) is partly neutralised by electrostatic interaction with the negative charge on oxygen and by the contribution of $p_\pi\text{-}d_\pi$ bonding as in structure (I). The combined $-I$ and $-T$ effects of the $p\text{-Me}_3\text{P}^+$ group cause it to be almost as activating as the $p\text{-NO}_2$ group. It is noteworthy that, in acid cleavage of X·C₆H₄·SiMe₃ compounds, an electrophilic aromatic substitution, the $p\text{-Me}_3\text{P}^+$ group is more deactivating (electron-withdrawing) than the $p\text{-Me}_3\text{N}^+$ or the $p\text{-NO}_2$ group,^{7*} but in the cleavage under study the somewhat more powerful electromeric ($-E$) effect of the $p\text{-NO}_2$ group, corresponding to the large difference between the σ -constant (0.78) and the σ^- -constant (1.26), enables it to withdraw electrons rather more effectively overall than the $p\text{-Me}_3\text{P}^+$ group.

The P(O)Ph₂ group is more strongly electron-withdrawing than the P(O)Me₂ group; presumably this is because of the $-I$ effect of the Ph groups, though this effect might have been expected to be outweighed by the $+T$ effect of the Ph groups arising from the $p_\pi\text{-}d_\pi$ bonding.[†] The larger $+T$ effect of the OEt groups seems to compensate for their stronger $-I$ effects to make the P(O)OEt₂ group slightly less activating overall than the P(O)Ph₂ group.

We have neglected above the influence of ionic strength on the effect of the Me₃P⁺ group. The value of k_s for the reaction between the oppositely charged Me₃Si·CH₂·C₆H₄·PMe₃⁺ and HO⁻ (and MeO⁻) ions should decrease with increasing ionic strength,¹⁰ and study of the *meta*-compound shows that there is in fact a small decrease with increasing alkali concentration (Table 2). (A larger effect, in the opposite direction—that of increasing k_s with increasing [NaOH]—was noted for the reaction involving the negatively-charged Me₃Si·CH₂·C₆H₄·CO₂⁻ ions.¹¹) Because of this effect, the activating influence of the $p\text{-Me}_3\text{P}^+$ group will be closer to that of the $p\text{-NO}_2$ group the lower the alkali concentration, but it seems clear that it will still be the smaller even at zero ionic strength.

The cleavage of the compound $m\text{-(EtO)}_2\text{(O)P}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{SiMe}_3$ was not studied because

* It seems that in nitration, however, the Me₃P⁺ deactivates the *para*-position slightly less than the Me₃N⁺ group.⁸

† But see ref. 9.

⁶ L. D. Freedman and H. H. Jaffé, *J. Amer. Chem. Soc.*, 1955, **77**, 920.

⁷ R. W. Bott, B. F. Dowden, and C. Eaborn, *J.*, 1965, in the press.

⁸ J. H. Ridd and J. H. P. Utley, *Proc. Chem. Soc.*, 1964, 24.

⁹ D. J. Martin and C. E. Griffin, *J. Organometallic Chem.*, 1964, **1**, 292.

¹⁰ A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons Inc., New York, 2nd edn., 1961, pp. 145—146.

¹¹ C. Eaborn and S. H. Parker, *J.*, 1957, 955.

TABLE 2
Dependence on alkali concentration of the specific rate constant for cleavage of
 $m\text{-Me}_3\text{Si}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{PMe}_3^+$

[NaOH] (M)	0.199	0.399	0.522	0.756	1.000
10^2k_1 (min. ⁻¹)	2.68	5.18	6.65	9.55	12.4
$10k_2$ (min. ⁻¹ mole ⁻¹ l.)	1.35	1.30	1.27	1.26	1.24

it was thought that hydrolysis of the ester groups would occur concurrently. A brief examination showed that both *m*- and *p*- $\text{Me}_3\text{Si}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{PO}_3^{2-}$ compounds are cleaved more slowly than benzyltrimethylsilane, as expected from the values¹² of the σ -constants for *m*- and *p*- PO_3^{2-} groups.

EXPERIMENTAL

Diethyl m- and p-(Trimethylsilylmethyl)phenylphosphonate.—The Grignard reagent prepared from *p*-chlorobenzyltrimethylsilane (99 g., 0.50 mole) and magnesium turnings (12.2 g., 0.50 g.-atom) under nitrogen in refluxing tetrahydrofuran was added dropwise to diethyl phosphorochloridate (77.4 g., 0.45 mole) in ether (200 ml.), the temperature of the mixture being kept below 0°. The mixture was subsequently allowed to warm to room temperature, an excess of dilute sulphuric acid added, and the ethereal layer, combined with ether extracts of the aqueous layer, was separated, washed, dried (Na_2SO_4), and fractionated to give *diethyl p-(trimethylsilylmethyl)phenylphosphonate* (49 g., 36%), b. p. 134°/0.2 mm., n_D^{25} 1.4955 (Found: C, 55.4; H, 8.4. $\text{C}_{14}\text{H}_{25}\text{O}_3\text{PSi}$ requires C, 55.9; H, 8.3%).

The *meta-isomer*, b. p. 160—161°/3.0 mm., n_D^{25} 1.4942, was prepared similarly in 56% yield from *m*-chlorobenzyltrimethylsilane (Found: C, 55.7; H, 8.2%).

m- and p-Trimethylsilylmethylphenylphosphonic Dichloride.—Phosphorus pentachloride (64.2 g., 0.30 mole) and diethyl *p*-trimethylsilylmethylphenylphosphonate (49.5 g., 0.15 mole) were refluxed together for 4 hr. Fractionation gave phosphorus oxychloride followed by *p*-trimethylsilylmethylphenylphosphonic dichloride (34 g., 81%), b. p. 136—138°/0.5 mm., which was used in subsequent preparations without analysis or further purification.

The *meta-isomer*, b. p. 119—122°/0.7 mm., was similarly prepared in 86% yield.

p-Trimethylsilylmethylphenylphosphonic Acid.—To *p*-trimethylsilylmethylphenylphosphonic dichloride (5 g.) in acetone was added 2*N*-aqueous sodium hydroxide until a clear solution was formed. The mixture was then acidified with dilute hydrochloric acid; ether extraction, washing, and evaporation left a solid which was recrystallised to give the *acid* (3.9 g., 90%), m. p. 178° (Found: C, 48.9; H, 7.0. $\text{C}_{10}\text{H}_{17}\text{O}_3\text{PSi}$ requires C, 49.1; H, 7.0%).

The *meta-isomer*, m. p. 133°, was similarly prepared in 80% yield (Found: C, 49.1; H, 7.0%).

m- and p-Trimethylsilylmethylphenyl(diphenyl)phosphine Oxide.—A solution of *p*-trimethylsilylmethylphenylphosphonic dichloride (6.5 g., 0.022 mole) in ether (25 ml.) was added to phenylmagnesium bromide (*ca.* 0.05 mole) in ether (50 ml.), and the mixture was refluxed for 5 hr. The usual working-up left, after removal of the ether, a yellow solid, which was recrystallised from ethanol—light petroleum to give *p-trimethylsilylmethylphenyl(diphenyl)phosphine oxide* (5.0 g., 62%), m. p. 151—152° (Found: C, 72.9; H, 6.8. $\text{C}_{22}\text{H}_{25}\text{OPSi}$ requires C, 72.7; H, 6.6%).

The *meta-isomer*, b. p. 215—218°/0.1 mm., was similarly prepared, but with fractionation in place of crystallisation, in 80% yield (Found: C, 72.5; H, 6.7%).

Dimethyl-m- and -p-trimethylsilylmethylphenylphosphine Oxides.—By the method described above for the diphenyl analogues, but with use of methylmagnesium iodide, were prepared *dimethyl-p-trimethylsilylmethylphenylphosphine oxide* (55%), m. p. 134° (from light petroleum) (Found: C, 60.1; H, 8.6. $\text{C}_{12}\text{H}_{21}\text{OPSi}$ requires C, 60.15; H, 8.75%) and its *meta-isomer* (75%), b. p. 132°/0.07 mm., m. p. 36—38° (Found: C, 60.0; H, 8.5%).

Trimethyl-m and -p-trimethylsilylmethylphenylphosphonium Iodide.—A solution of *dimethyl-p-trimethylsilylmethylphenylphosphine oxide* (7.2 g., 0.03 mole) in benzene (40 ml.) was added to lithium aluminium hydride (2.3 g., 0.06 mole) in di-*n*-butyl ether (40 ml.), and the mixture was refluxed for 3 hr., with stirring. The excess of lithium aluminium hydride was destroyed with ethyl acetate, and the mixture was added to a mixture of ice and dilute hydrochloric acid. The ethereal layer was quickly separated, washed, and dried (Na_2SO_4), and the solvents were removed on a rotary evaporator. The residual oil, assumed to be *dimethyl-p-trimethylsilylmethylphenylphosphine*, was dissolved in benzene (40 ml.), and methyl iodide (10 ml.) in

¹² H. H. Jaffé, L. D. Freedman, and G. O. Doak, *J. Amer. Chem. Soc.*, 1953, **75**, 2209.

benzene (20 ml.) was added. The precipitate was recrystallised from ethyl acetate to give *trimethyl-p-trimethylsilylmethylphenylphosphonium iodide* (8.0 g., 73%), m. p. 186° (Found: C, 42.6; H, 6.7. $C_{13}H_{24}IPSi$ requires C, 42.5; H, 6.6%).

The *meta-isomer*, m. p. 160—162°, was prepared in 80% yield (Found: C, 42.7; H, 6.5%).

Rate Studies.—The methods previously described^{2,3} were used, except that in all cases the “infinity” values of the optical density were measured on reaction samples left for 10 half-lives. Runs were followed to at least 80% completion. The reaction mixture was contained in a thermostat-controlled absorption cell, but if the half-life exceeded 10 hr. the “infinity” value was obtained from samples kept in sealed tubes in a thermostat-controlled bath. In most cases rate constants from duplicate runs agreed to within 0.5%, and in all cases to within 1.5%.

The alkali concentration shown in Table 1 has been corrected (by a factor of 0.976) to allow for the expansion of the solution at 50.3° (the concentration was measured at room temperature by titration).

The cleavage of the compound *m*-(EtO)₂(O)P·C₆H₄·CH₂·SiMe₃ was not studied because, in a medium suitable for cleavage, containing 1.00M-sodium hydroxide, the ultraviolet absorption of the compound Ph(EtO)₂P(O) changed markedly, as expected for hydrolysis of the ester groups, during 10 hr. No cleavage was detected during 96 hr. with 1.00M-sodium hydroxide with the ions *m*- and *p*-Me₃Si·CH₂·C₆H₄·PO₃²⁻.

We thank Messrs. Joseph Crosfield and Sons Ltd., for support of this work, and the Royal Society for the loan of apparatus.

UNIVERSITY OF LEICESTER.

[Present address (R. W. B. and C. E.): UNIVERSITY OF SUSSEX,
BRIGHTON.]

[Received, March 12th, 1965.]