Substitutent Effects of Phosphorus- and Arsenic-containing Groups in Aromatic Substitution. Part 7.[1] Comparison of Carboxy and Phosphonic Groups

By **Tomasz A. Modro** * and **William F. Reynolds**, Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada
Eugenia Skorupowa, Institute of Chemistry, University of Gdansk, Gdansk, Poland

Partial rate factors for the nitration of carboxylic and phosphonic acids $PhCH_2X$ and PhCH=CHX (X = CO_2H or PO_3H_2) have been determined in acetic anhydride and in strongly acidic media. For β-styrylphosphonic acid the rate of bromine addition has been measured and compared with that for cinnamic acid. ^{13}C N.m.r. spectra of the PhX, $PhCH_2X$, and PhCH=CHX systems have been recorded. Substituent effects of the carboxy and phosphonic groups upon the reactivity and upon the shielding of ring carbon atoms are compared and discussed. Close similarity of substituent effects of CO_2H and PO_3H_2 has been demonstrated. Good correlation between the partial rate factors and ^{13}C chemical shifts has been found for the systems PhX and $PhCH_2X$; in β-styryl derivatives this parallel breaks down owing to the versatile nature of the vinyl group.

PHOSPHINYL substituents directly attached to a benzene ring have been found dominantly *meta,ortho*-directing with rigorous discrimination against *para*-substitution.[2] To account for this orientation, a specific '*ortho*' mechanism has been postulated, involving prior interactions of the electrophile with the phosphinyl group, followed by selective transfer of the electrophile to the *ortho*-position.[3] It is however well recognized[4] that orientation alone is not a useful guide in quantitative studies of substituent effects in aromatic reactivity. To obtain meaningful results, it is necessary to compare the changes in the free energy of the substitution due to different substituents at a given position of the ring.

The phosphonic and carboxy groups (or their ester derivatives) frequently demonstrate similar effects on the properties of an adjacent aromatic system.† Their inductive and resonance substituent constants are similar [for $P(O)(OEt)_2$ $\sigma_I = 0.34$, $\sigma_R = 0.18$;[6] for CO_2Et $\sigma_I = 0.32$, $\sigma_R = 0.13$[7]] and they show similar effects on the benzene *B* band in the electronic spectrum of the PhX derivative [for X = PO_3H_2, $\lambda_{max.}$ 270 nm (log ε 2.76);[8] for X = CO_2H, $\lambda_{max.}$ 273 nm (log ε = 2.87)[9]]. The available data also allow a comparison of the substituent effects of phosphonic and carboxy groups in aromatic nitration, both in acidic and in aprotic media. Such a comparison, expressed in terms of the relative changes (with respect to benzene) of the free energy of substitution at *ortho*- and *meta*-positions, is presented in Table 1. The data show that the two substituents produce almost identical selectivity with respect to the *ortho*- and *meta*-positions of the ring. This observation rules out immediately any specific '*ortho*' effect in nitration of phenylphosphonic acid, since no decrease in the relative change of the free energy for *ortho*-substitution is observed [in acetic anhydride the PO_3H_2 group discriminates in favour of the *meta*-position (with respect to the *ortho*-) even more than does the carboxy group]. Data in Table 1 also indicate the remarkable similarity of the substituent effects of these two functional groups. To test how far this similarity might be fortuitous, we decided to extend such comparison over systems where the discussed substituents are separated from the ring by a methylene or a vinylene bridge ($PhCH_2X$ and PhCH=CHX, where X = CO_2H or PO_3H_2).

TABLE 1

Substituent effects of carboxy and phosphonic groups on intramolecular selectivity in nitration (25 °C)

Substrate	Nitrating system	$\delta\Delta G^{\ddagger}_{ortho}/\delta\Delta G^{\ddagger}_{meta}$
$PhCO_2Et$	$AcONO_2$ in Ac_2O	1.23 [a]
$PhCO_2H$	HNO_3 in aq. H_2SO_4	1.15 [b]
$PhPO_3H_2$	$AcONO_2$ in Ac_2O	1.31 [c]
$PhPO_3H_2$	HNO_3 in aq. H_2SO_4	1.14 [c]

[a] Ref. 4, p. 83. [b] Ref. 4, p. 179. [c] T. A. Modro and A. Piekos, *Tetrahedron*, 1972, **28**, 3867.

We also decided to compare the reactivity data with the corresponding substituent effects on the phenyl carbon atoms' ^{13}C chemical shifts in the same compounds. We have recently pointed out[10] a close parallel between ^{13}C chemical shifts and partial rate factors in electrophilic substitution for benzene derivatives substituted with positive poles. In this case the substituent effects are primarily due to the field effect of the pole. It seemed worthwhile to investigate the possibility of correlating the ^{13}C chemical shift values with reactivities for systems with more complex patterns of substituent effects as well as to use ^{13}C n.m.r. spectroscopy as a probe for further

---

† The similarity of the electron-acceptor abilities of $P(O)(OR)_2$ and CO_2R, expressed in terms of Taft's σ* constants, has been pointed out.[5]

[1] Part 6, T. A. Modro and J. Pioch, *Canad. J. Chem.*, 1976, **54**, 560.

[2] E. Malinski, A. Piekos, and T. A. Modro, *Canad. J. Chem.*, 1975, **53**, 1468.

[3] E. Malinski, A. Piekos, and T. A. Modro, *Phosphorus*, 1976, **6**, 99.

[4] J. G. Hoggett, R. B. Moodie, J. R. Penton, and K. Schofield, 'Nitration and Aromatic Reactivity,' Cambridge University Press, 1971, p. 172.

[5] D. J. Martin and C. E. Griffin, *J. Org. Chem.*, 1965, **30**, 4034.

[6] E. N. Tsvetkov, D. I. Lobanov, L. A. Izosenkova, and M. I. Kabachnik, *Zhur. obshchei Khim.*, 1969, **39**, 2177.

[7] C. D. Johnson, 'The Hammett Equation,' Cambridge University Press, 1973, p. 84.

[8] 'Organic Electronic Spectral Data,' vol. II, Interscience, New York, 1960, p. 67.

[9] C. N. R. Rao, 'UV and Visible Spectroscopy,' Butterworths, London, 1967, p. 60.

[10] W. F. Reynolds, T. A. Modro, and P. G. Mezey, *J.C.S. Perkin II*, in the press.

comparison of the substituent effects of the phosphonic and carboxy groups upon the properties of an aromatic ring.

RESULTS AND DISCUSSION

We have determined partial rate factors for the nitration of benzyl- and β-styryl-phosphonic and phenylacetic and cinnamic acids (or their ethyl esters) in acetic anhydride and in strongly acidic medium. The isomer distribution was determined by oxidation of the nitration product (oxidation of a side-chain to a carboxy group) and estimation of the proportions of isomeric nitrobenzoic acids formed.[11] The relative rates were determined by the competition method,[12] with benzene as reference. The individual values of k_{rel} showed some scatter and the accuracy of the mean values is not high ($\leqslant \pm 15\%$). However, the scatter was of random nature and no trend in change of k_{rel} values with changes of experimental conditions (proportions of substrates, extent of reaction, *etc.*) was observed. At the concentrations used (10^{-2}M in aromatic compounds) the nitration is slow and the final results are unlikely to be influenced by the rate of mixing.* Nevertheless, the calculated values of the partial rate factors have to be considered as approximate (to *ca.* ±20%). Since we were interested in general comparison of the substituent effects in these systems, any small changes in the values of f_i would not influence the final conclusions. The reactivity data for nitration obtained in this work and taken from the literature are collected in Table 2.

TABLE 2

Nitration of carboxy and phosphonic derivatives (25 °C) [a]

Compound	Nitrating system	Relative rate (benzene = 1)	Isomer proportions (%)			Partial rate factors		
			ortho	*meta*	*para*	f_o	f_m	f_p
$PhCH_2{\cdot}CO_2Et$ [b]	$AcONO_2$ in Ac_2O	3.66	42.0	10.6	47.4	4.62	1.10	10.41
$PhCH_2{\cdot}CO_2H$	HNO_3 in $CF_3{\cdot}CO_2H$	1.1	59.0	<2	41.0	1.9		2.7
	HNO_3 in 70% H_2SO_4	0.57	60.0	<2	40.0	1.0		1.4
$PhCH_2{\cdot}P(O)(OEt)_2$	$AcONO_2$ in Ac_2O	2.6 [c]	30.0		70.0	2.3		10.9
$PhCH_2{\cdot}PO_3H_2$	HNO_3 in aq. H_2SO_4 [c]	0.18	26.0		74.0	0.14		0.80
	HNO_3 in $CF_3{\cdot}CO_2H$	0.20	25.0		75.0	0.15		0.90
$PhCH{:}CH{\cdot}CO_2H$	$AcONO_2$ in Ac_2O	1.6 [d]	70.5	[e]	29.5	3.4		2.8
	HNO_3 in $CF_3{\cdot}CO_2H$	0.64	54		46	1.0		1.8
$PhCH{:}CH{\cdot}PO_3H_2$	$AcONO_2$ in Ac_2O	3.1	68.5		31.5	6.4		5.8
	HNO_3 in $CF_3{\cdot}CO_2H$	0.4	74		26	0.9		0.6

[a] Each result is the average of at least five independent determinations. Relative rates are accurate to within ±15%; isomer proportions are accurate to within ±5%. [b] C. K. Ingold and F. R. Shaw, *J. Chem. Soc.*, 1949, 575. [c] T. A. Modro and A. Piekos, *Tetrahedron*, 1973, **29**, 2561. [d] F. G. Bordwell and K. Rhode (*J. Amer. Chem. Soc.*, 1948, **70**, 1191) report $k_{rel} = 0.11$ for the nitration of cinnamic acid in Ac_2O. We found in all competitive nitrations, varying the extent of reaction from 10 to 60%, the value of $k_{rel} > 1$. The molar extinction coefficient for the mixture of nitrocinnamic acids formed varies slightly with experimental conditions; the determinations based on two extreme values of ε_{mixt} (10^4 and 8×10^3) gave less than 10% difference in the estimated value of k_{rel}. [e] In agreement with the observation of H. W. Underwood and E. L. Kochman (*J. Amer. Chem. Soc.*, 1926, **48**, 264), who found no *meta*-nitro-product in nitration of cinnamic acid.

It can be seen that the similarity between the substituent effects of phosphonic and carboxy groups extends over the corresponding benzylic and β-styryl systems. For nitration in acetic anhydride the partial rate factors for the carboxylic acid (or ester) parallel closely those for the corresponding phosphorus derivatives. In strongly acidic media, although the general behaviour is similar, the situation is partly complicated by the different involvement of substituents in protonation equilibria. Carboxy derivatives, by analogy with benzoic acid,[13] are most likely nitrated as free bases, whereas the phosphonic compounds probably react as protonated species. For carboxy compounds, the decrease in relative reactivity (resulting from a hydrogen-bonding effect) with change of reaction medium from Ac_2O to $CF_3{\cdot}CO_2H$ is 3.3 for phenylacetic acid and 2.5 for cinnamic acid. The corresponding changes in relative reactivity of phosphonic acids are 13.0 and 7.7; more consistent with full protonation of the substituent. As expected, all compounds in Table 2 are *para,ortho*-directing, with negligible *meta*-orientation. It is surprising that we were unable to detect any *meta*-substitution product in nitration of benzylphosphonic acid (or its ester); other benzylic derivatives of similar reactivity, although *para,ortho*-directing, do not shown such a rigorous discrimination against the *meta*-position.[14] The observed high *para,-ortho*-selectivity in the benzylphosphonic system can perhaps be interpreted in terms of hyperconjugative electron release by the C–P bond, as suggested[15] for benzylphosphonium ion.

Substituent effects upon the ^{13}C n.m.r. chemical shifts of the individual carbon atoms of the benzene ring have been determined for the systems PhX, $PhCH_2X$, and PhCH=CHX. These values could be compared directly with the corresponding chemical shifts of the parent hydrocarbon (benzene, toluene, or styrene) only in acetic anhydride solution and with benzene and toluene in trifluoroacetic acid. Styrene could not be studied in any acidic medium and solubility problems (as well as sulphonation) prevented measurements of chemical shift values for benzene and toluene in aqueous sulphuric

---

* *Cf.* ref. 4, ch. 4.4.2.

[11] W. E. Truce and J. A. Simms, *J. Org. Chem.*, 1957, **22**, 762.

[12] C. K. Ingold and F. R. Shaw, *J. Chem. Soc.*, 1927, 2918.

[13] R. B. Moodie, J. R. Penton, and K. Schofield, *J. Chem. Soc.* (*B*), 1969, 578.

[14] Ref. 4, ch. 9.1.1.

[15] M. C. R. Symons, *Tetrahedron Letters*, 1971, 4919.

acid. In Table 3 are collected the reactivity data (partial rate factors) for nitration together with ^{13}C n.m.r. chemical shifts in acetic anhydride for three structural types of carboxylic and phosphonic derivatives. The partial rate factors and ^{13}C chemical shifts obtained in strongly acidic media are presented in Table 4.

For the system PhX, benzoic and phenylphosphonic acids show very similar patterns of reactivity in both solvent systems. This reactivity pattern is paralleled by the *meta*- and *para*-^{13}C chemical shifts for both derivatives, which indicate much greater electron withdrawal from the *para*-position. The *meta*- and *para*-^{13}C chemical shifts should reflect changes in ground state electron density.[16] Although the same parallel may not hold between *ortho* (and *ipso*) ^{13}C chemical shifts and carbon electron densities,[16] the *ortho*-^{13}C chemical shifts are consistent with the reactivity order $f_m > f_o \gg f_p$.]

TABLE 3

Partial rate factors for nitration (25 °C) and phenyl carbon atom chemical shifts (solvent acetic anhydride)

System	X	Partial rate factors (relative to benzene) f_o	f_m	f_p	Chemical shifts (in p.p.m.; low field positive) relative to benzene and (in parentheses) relative to the parent hydrocarbon C-1	C-2, -6	C-3, -5	C-4
PhX	CO_2Et [a]	2.6×10^{-3}	7.9×10^{-3}	0.9×10^{-3}	+0.54	+1.91	+0.68	+6.25 [b]
	PO_3H_2 [c]	1.5×10^{-3}	7.1×10^{-3}		−1.91	+3.62	+0.49	+5.55
$PhCH_2X$	CO_2Et	4.62	1.10	10.41	+6.45 (−2.97)	+0.89 (+0.32)	+0.05 (+0.20)	−1.51 (+1.57)
	$P(O)(OEt)_2$	2.3		10.9	+2.69 (−6.73)	+1.67 (+1.10)	+0.07 (+0.22)	−1.62 (+1.46)
PhCH⁚CHX	CO_2H	3.4		2.9	+5.57 (−3.75)	+0.78 (+2.97)	+0.34 (+0.13)	+2.94 (+3.44)
	PO_3H_2	6.4		5.8	*d*	+0.77 (+2.96)	−0.04 (−0.25)	+2.89 (+3.39)

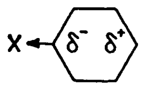
[a] Partial rate factors taken from ref. 4, p. 83. [b] Chemical shifts for benzoic acid. [c] Partial rate factors taken from T. A. Modro and A. Piekos, *Tetrahedron*, 1972, **28**, 3867. [d] No peak observed owing to solubility limitations.

TABLE 4

Partial rate factors for nitration (25 °C) and phenyl carbon atom chemical shifts; acidic medium

System	X	Medium	Partial rate factors (relative to benzene) f_o	f_m	f_p	Chemical shifts (in p.p.m.; low field positive); relative to benzene and (in parentheses) relative to parent hydrocarbon Medium	C-1	C-2, -6	C-3, -5	C-4
PhX	CO_2H	aq. H_2SO_4 [a]	2.2×10^{-5}	5.4×10^{-5}	0.3×10^{-5}	$CF_3{\cdot}CO_2H$	−0.51	+2.11	+0.36	+6.66
	PO_3H_2	aq. H_2SO_4 [b]	0.6×10^{-5}	2.7×10^{-5}		$CF_3{\cdot}CO_2H$	*c*	+2.77	+0.66	+5.79
$PhCH_2X$	CO_2H	$CF_3{\cdot}CO_2H$	1.9		2.7	$CF_3{\cdot}CO_2H$	*c*	−0.66 (−0.08)	+1.03 (+1.07)	−0.33 (+2.78)
	PO_3H_2	$CF_3{\cdot}CO_2H$	0.15		0.90	$CF_3{\cdot}CO_2H$	*c*	+1.59 (+0.85)	+0.80 (+0.84)	−0.23 (+2.88)
PhCH⁚CHX	CO_2H	$CF_3{\cdot}CO_2H$	1.04		1.77	$CF_3{\cdot}CO_2H$	+5.26	+0.74	+0.32	+3.48
	PO_3H_2	$CF_3{\cdot}CO_2H$	0.89		0.62	$CF_3{\cdot}CO_2H$	*c*	+0.73	−0.30	+3.13

[a] Ref. 4, p. 179. [b] T. A. Modro and A. Piekos, *Tetrahedron*, 1972, **28**, 3867. [c] No peak observed owing to solubility limitations.



(1)

The close parallel between the ^{13}C chemical shifts and the partial rate factors indicates a parallelism between substituent effects upon the ground state and upon the transition state in nitration. The *meta*-directing and deactivating effects of the phosphonic and carboxy groups presumably mainly reflect the field effects of these polar groups.[17] However, an additional polar effect may also be operative. One of us has previously shown that polar groups can polarize the entire π electron system of a benzene derivative [diagram (1)].[16,18,19] The large low-field shifts for the *para*-carbon atoms (and the relatively small shifts for the *ipso*-carbon atoms) suggest that this effect is operative in benzoic acid and phenylphosphonic acid. This π polarization should deactivate the *para*-carbon atom towards electrophilic attack by NO_2^+,[20] thus accounting for the rigorous discrimination against *para*-substitution. π-Polarization could also be at least partly responsible for the relatively high proportion of *ortho*-isomers in nitration of benzoic acid and phenylphosphonic acid. *Ab initio* (STO-3G) calculations for benzoic acid indicate that the *ipso*-carbon atom has the largest π electron density (1.04 [21]) of the phenyl carbon atoms, consistent with the situation in diagram (1). *ipso*-Attack in aromatic nitration is well known,[22] and

---

[16] W. F. Reynolds, I. R. Peat, M. H. Freedman, and J. R. Lyerla, *Canad. J. Chem.*, 1973, **51**, 1857.

[17] J. H. Rees, J. H. Ridd, and A. Ricci, *J.C.S. Perkin II*, 1976, 294.

[18] W. F. Reynolds and G. K. Hamer, *J. Amer. Chem. Soc.*, 1976, **98**, 7296.

[19] W. F. Reynolds, G. K. Hamer, and P. G. Mezey, *Canad. J. Chem.*, 1977, **55**, 522.

[20] D. M. Bishop and D. P. Craig, *Mol. Phys.*, 1963, **6**, 139.

[21] W. J. Hehre, L. Rodom, and J. A. Pople, *J. Amer. Chem. Soc.*, 1972, **94**, 1496.

[22] For a recent review see R. B. Moodie and K. Schofield, *Accounts Chem. Res.*, 1976, **9**, 287.

has been observed for derivatives with phosphorus-containing substituents.[23] *ipso*-Substitution products were not observed in either of the systems discussed above. However, according to Moodie and Schofield,[22] one possible fate of an *ipso*-intermediate in aromatic nitration is 1,2-migration of the *nitro*-group followed by loss of a proton, *i.e.* formation of a 'normal' *ortho*-nitro-product. Thus, it seems attractive to postulate that *ipso*-substitution followed by 1,2-rearrangement is at least partially responsible for the *ortho*-nitro-product.

For the benzylic and β-styryl systems, the reactivities of carboxy derivatives again resemble those of the corresponding phosphonic acids. For the compounds $PhCH_2X$, $\delta\Delta G_p^{\ddagger}/\delta\Delta G_o^{\ddagger}$, a measure of the relative changes in free energy of activation for substitution at the *para*- and *ortho*-carbon atoms resulting from the replacement of one hydrogen atom in benzene by CH_2X, has values of 1.53 for the $CH_2{\cdot}CO_2Et$ group and 2.86 for the $CH_2P(O)(OEt)_2$ group (in acetic anhydride). The analogous values for the system PhCH=CHX are (in acetic anhydride) 0.87 for $X = CO_2H$ and 0.94 for $X = PO_3H_2$.

In acetic anhydride, the f values for the benzyl derivatives indicate that both CH_2X groups activate the ring, particularly towards *para*-attack.[*] However, both CH_2X groups are deactivating relative to a CH_3 group [$f_p = 0.17$ for the $CH_2{\cdot}CO_2Et$ derivative and 0.18 for the $CH_2P(O)(OEt)_2$ derivative, both expressed relative to toluene]. The ^{13}C chemical shifts for $PhCH_2X$ derivatives again closely parallel the reactivity patterns. In particular, the *para*-carbon atoms are the most shielded. Furthermore, the chemical shifts of the *para*-carbon atoms are almost half-way between those for toluene and benzene, exactly paralleling the partial rate factors at this position. Finally, the ^{13}C chemical shifts predict decreased shielding of the *para*-carbon atoms on going from acetic anhydride to trifluoroacetic acid as solvent, paralleling the decrease in the partial rate factors (Tables 3 and 4).

By contrast, the parallel between chemical shifts and reactivity breaks down entirely in the styryl stystems. The CH=CHX group acts as an activating and *ortho,para*-directing group in nitration, while the ^{13}C chemical shifts reveal marked deshielding at the *ortho*- and *para*-carbon atoms. It is apparent that different factors must influence the stability of the Wheland intermediate and the ground state electron distribution in these systems. The vinyl group can act as a π donor in stabilizing a positively charged transition state, or as a π acceptor in stabilizing a negatively charged transition state in nucleophilic aromatic substitution,[26] or as a link to transmit electron density from one group to another in the ground state.[27,28] In the system PhCH=CHX the greater electron demand of X must predominate, resulting in net electron transfer from the phenyl π electron system in the ground state.

The close resemblance of the substituent effects of the carboxy and phosphonic groups upon the properties of the neighbouring π electron system seems to be of a general nature. For example, we have measured the rates of bromine addition to β-styrylphosphonic acid and compared the results with the available data for the addition of bromine to cinnamic acid and styrene (see Table 5). Both carboxy and phosphonic groups enormously deactivate the double bond towards the addition, but the difference in deactivating effects is very small. In the presence of hydrochloric acid, where the possible participation of substrate conjugate base in reaction is minimized, the phosphonic derivative reacts less than three times as fast as cinnamic acid. In methanol (where direct comparison with styrene is possible) $\delta\Delta G^{\ddagger}(PO_3H_2)/\delta\Delta G^{\ddagger}(CO_2H)$ is only 0.85. From available kinetic data for electrophilic addition to β-alkylstyrenes, $\delta\Delta G_{Et}^{\ddagger}/\delta\Delta G_{Me}^{\ddagger}$ is 1.36 for bromination in methanol at 25 °C[29] and 1.37 for the addition of arenesulphenyl chloride in acetic acid at 25 °C.[30] Thus for addition reactions of styrene, there is less difference between substituent effects of β-carboxy and phosphonic groups than between β-methyl and ethyl groups.

TABLE 5

Second-order rate coefficients for bromine addition at 25 °C

Substrate	Medium	k_2/l mol^{-1} s^{-1}
PhCH:CH$_2$	MeOH	1 160 [a]
PhCH:CH·CO$_2$H	MeOH	0.024 [b]
	0.075M-HCl in MeOH	0.108 [b]
PhCH:CH·PO$_3$H$_2$	MeOH	0.121 [c]
	0.075M-HCl in MeOH	0.300 [c]

[a] M. F. Ruasse and J. E. Dubois, *J. Amer. Chem. Soc.*, 1975, **97**, 1977. [b] G. H. Schmid, A. Modro, and K. Yates, unpublished results. [c] This work.

In conclusion we believe that the carboxy and phosphonic functions (and their ester derivatives) can be classified as very closely related with respect to their substituent effects. When they are directly attached to the aromatic ring, their influence is most consistent with a field effect, with minor contributions from a π polarization effect; any conjugative effects (π–π conjugation, *d* orbital participation) being probably of lesser importance. There are no indications of any kind of substituent–electrophile interactions in the case of the phosphinyl substituent and the high proportion of the *ortho*-isomer observed in nitration (and other electrophilic

---

[*] In the $Ph[CH_2]_nNMe_3^+$ system,[24] owing to the greater field effect of the NMe_3^+ group ($\sigma_I = +0.92$ [25]), the effect of the polymethylene link only becomes dominant when the positive pole is one bond further removed from the ring.

[23] T. A. Modro and A. Piekos, *Phosphorus*, 1974, **3**, 195.

[24] R. Danieli, A. Ricci, H. M. Gilow, and J. H. Ridd, *J.C.S. Perkin II*, 1974, 1477.

[25] J. Hine, 'Structural Effects on Equilibria in Organic Chemistry,' Wiley–Interscience, New York, 1975, p. 98.

[26] J. Miller, 'Aromatic Nucleophilic Substitution,' Elsevier, Amsterdam, 1968, ch. 4.5.6.

[27] S. K. Dayal, S. Ehrenson, and R. W. Taft, *J. Amer. Chem. Soc.*, 1972, **94**, 9113.

[28] I. R. Ager and L. Phillips, *J.C.S. Perkin II*, 1972, 1975.

[29] E. Bienvenue-Goetz and J. E. Dubois, *J. Org. Chem.*, 1975, **40**, 221.

[30] G. H. Schmid, A. Modro, and K. Yates, *J. Org. Chem.*, 1977, **42**, 871.

substitutions) of phenylphosphonic acid, as well as the rigorous discrimination against *para*-substitution, is paralleled by the shielding pattern of the phenyl carbon atoms. The similarity of substituent effects appears to extend both to other systems ($PhCH_2X$ and PhCH=CHX) and to other reactions (electrophilic bromine addition).

The close parallel between ^{13}C chemical shift patterns and reactivity patterns in PhX and $PhCH_2X$ and in $Ph[CH_2]_nNR_3^+$ [10] suggests that ^{13}C chemical shifts might be useful for predicting substitution patterns (and planning synthetic pathways) for aromatic derivatives (including more complex derivatives such as substituted naphthalenes). However, it would be first necessary for each system to establish whether the parallel between ground-state substituent effects and reactivities held in that particular case.

EXPERIMENTAL

Solvents were purified by conventional methods. AnalaR nitric acid (*d* 1.42) was distilled from an equal volume of concentrated H_2SO_4 immediately before use. U.v. spectra were determined with a Perkin-Elmer 402 spectrophotometer. ^1H N.m.r. spectra were obtained with a Tesla BS-487 (80 MHz) spectrometer with Me_4Si as internal standard.

Substrates.—Benzoic acid, phenylphosphonic acid, phenylacetic acid, ethyl phenylacetate, diethyl benzylphosphonate, and cinnamic acid were obtained commercially and were used without further purification. Benzylphosphonic acid was prepared by acidic hydrolysis of the diethyl ester; [31] m.p. (from H_2O) 169.5—170° (lit., 166°). β-Styrylphosphonic acid was prepared according to Bergmann;[32] m.p. (from H_2O) 149—150° (lit., 146°).

Product Studies.—Substrate (*ca.* 10^{-2} M) was dissolved in acetic anhydride, trifluoroacetic acid, or aqueous sulphuric acid and the solution of nitric acid (slight excess) in the same solvent was added slowly at 0 °C with stirring. The mixture was then left at room temperature for 1—24 h, until t.l.c. showed that the reaction was complete. The product was then isolated by evaporation of the solvent (Ac_2O or $CF_3{\cdot}CO_2H$) or extraction. In all cases the yield was practically quantitative and the elemental analysis of the product agreed with the composition of a mononitro-derivative. The nitration product was examined chromatographically (t.l.c.) to determine the number of isomers and then oxidized with alkaline permanganate [11] to a mixture of nitrobenzoic acids (*ortho*- and *para*-isomers); the yields in oxidation were greater than 95%. The proportions of isomers were determined by quantitative separation of individual compounds and by comparison of the u.v. spectrum of the oxidation product with the spectra of model mixtures of known composition. For benzyl derivatives the product composition was also determined by analysis of the ^1H n.m.r. spectrum (methylene proton signals) of the nitration product before oxidation. All determinations gave good internal agreement. Both chromatographic and spectroscopic analysis showed that the *meta*-nitro-product was in all cases either absent or present in negligible amount.

Relative Rates.—To a solution of a substrate and benzene (molar ratio varied from 2 : 1 to 1 : 2) in an appropriate solvent (total concentration of both substrates did not exceed 10^{-2}M) a solution of nitric acid in the same solvent ($[HNO_3] <$ [aromatic derivative]) was added at 25 °C. Samples were taken at intervals (corresponding to 10—60% of reaction) and made alkaline (pH *ca.* 9.5) by quenching in a large volume of aqueous sodium hydroxide. The solution was then extracted several times with ether. After required dilution, concentrations of nitrobenzene and nitro-derivatives of carboxy or phosphonic substrate were determined spectrophotometrically (u.v.) in the ethereal and aqueous solutions, respectively. Relative rates were then calculated in the usual way.[12]

Addition of Bromine to β*-Styrylphosphonic Acid.*—Rates of bromination were measured conventionally by using a Cary 16 spectrophotometer (thermostatted at 25 °C), by following the disappearance of bromine absorption at 490 nm, under pseudo-unimolecular conditions. Excellent plots ($r > 0.999$) of ln $(A_t - A_\infty)$ *vs.* time *t* were obtained. Each reported value of k_2 is the average of two determinations and is accurate to within ±5%.

^{13}C *Chemical Shift Measurements.*—^{13}C Chemical shifts were determined with a Varian CFT-20 spectrometer operating in pulsed Fourier transform mode at a probe temperature of 35—40 °C. A capillary containing 4 : 1 D_2O–dioxan was used as lock and to provide the ^{13}C external reference signal in each case. 0.5M-Solutions were used, solubility permitting. ^{13}C Chemical shift assignments were based upon relative intensities, off-resonance decoupling experiments and, in the case of the phosphonic acid derivatives, values of $^{13}C,^{31}P$-coupling constants in related systems.[33] Assignment of *ortho* and *meta* chemical shifts was also aided by the observation that *meta* chemical shifts (relative to benzene) are generally very small.[34]

[6/2350 *Received, 30th December,* 1976]

---

[31] G. M. Kosolapoff, *J. Amer. Chem. Soc.*, 1945, **67**, 2259.

[32] E. Bergmann and A. Bondi, *Ber.*, 1930, **63**, 1158.

[33] T. A. Albright, W. J. Freeman, and E. E. Schweizer, *J. Org. Chem.*, 1975, **40**, 3437; H. J. Jakobsen and O. Manscher, *Acta Chem. Scand.*, 1971, **25**, 680.

[34] G. C. Levy and G. L. Nelson, ' Carbon-13 NMR for Organic Chemists,' Wiley–Interscience, New York, 1972, ch. 4.