Nucleophilic Activity of the Phosphoryl Group. II. Resonance of the Phosphoryl Group with Aromatic Systems

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Ultraviolet spectra of arylphosphine oxides containing electron-donating *para* substituents show progressive shifts to longer wavelengths with increasing electron-donating ability. A linear relationship was found between λ_{max} for the first primary bond of the benzene ring and $\delta\lambda_0$, the shift constant for each substituent. These results provide additional evidence for d_π–p_π bonding between the phosphoryl group and the aromatic ring. A quantitative measure of the resonance-electron-withdrawing power of the diphenylphosphono group was sought by determination of the acidities in 50% ethanol of benzoic acids and phenols containing this substituent. To obtain consistent results for the two series of compounds, ρ values for ionization of substituted acids and phenols in 50% ethanol were redetermined. Results of a Hammett correlation of acidities indicated that the diphenylphosphono group is approximately equivalent to the carbethoxy group in resonance-electron-withdrawing power.

In connection with an investigation of factors affecting the nucleophilic activity of the phosphoryl group,[2] some measure of the extent of resonance interaction of the phosphoryl group with conjugated systems (phenyl, vinyl, etc.) is required.

Recent studies of ultraviolet spectra of tri-2-pyrryl-, tri-2-(1-methylpyrryl)-, and tri-2-furylphosphine oxides[3] and substituted arylphosphonium halides and arylphosphine oxides[4-6] have provided evidence for d_π–p_π bonding in such systems. Using a somewhat different approach, we have obtained additional evidence for resonance of this type from ultraviolet spectral studies of a series of substituted triarylphosphine oxides. In addition, a quantitative measure of the strength of this interaction for the diphenylphosphoryl group was obtained from a determination of Hammett σ constants for the diphenylphosphoryl group in benzoic acids and phenols.

Experimental Section

Materials.[7]—Inorganic reagents were Baker AR grade. Benzoic acid (Baker Primary Standard) and phenol (Mallinckrodt AR) were used as received. *m*-Toluic acid, *m*-chlorobenzoic acid, *m*-bromobenzoic acid, *m*-iodobenzoic acid, *m*-nitrobenzoic acid, *p*-nitrobenzoic acid, *p*-methoxyphenol, *m*-methoxyphenol, *p*-bromophenol, *m*-nitrophenol, and *p*-nitrophenol were all Eastman products, recrystallized or redistilled before use. *m*-Cyanophenol (Aldrich) was recrystallized before use, mp 81–82°; *m*-bromophenol[8] was fractionated with the fraction boiling at 115–116° (9 mm) used for determinations. All phosphines except *m*-methylphenyldiphenylphosphine and *m*-methoxyphenyldiphenylphosphine have been reported previously. Phosphines were prepared by a modified procedure of Senear, Valient, and Wirth.[9] It was found that the yield was significantly increased in most cases by a 16–24-hr reflux period after addition of chlorodiphenylphosphine. The following compounds (yields, recrystallization solvents, and melting points) were prepared in this way: ***m*-Methylphenyldiphenylphosphine**, 82%, methanol followed by sublimation, mp 48.8–50.2° [the phosphine was converted to the phosphine oxide for analysis (see below)]; ***p*-methylphenyldiphenylphosphine**, 79%, methanol, mp 65.5–66.2°, lit.[10] mp 68°; ***m*-methoxyphenyldiphenylphosphine**, 82% (crude) oil; ***p*-methoxyphenyldiphenylphosphine**, 82%, ligroin, mp 62–64°, lit.[9] mp 78–79° (from methanol). *m*-Methylphenyldiphenylphosphine oxide, *p*-methylphenyldiphenylphosphine oxide, and *m*- and *p*-methoxyphenyldiphenylphosphine oxides were prepared by oxidation of the corresponding phosphines by the method of Shriner and Wolf.[11] *p*-Carboxyphenyldiphenylphosphine oxide has not been reported previously. Yields, recrystallization solvents, melting points, and analyses where made were as follows: ***m*-methylphenyldiphenylphosphine oxide**, 97%, sublimed, mp 126.6–127.5°, lit.[12] mp 123–124° (*Anal.* Calcd for $C_{10}H_{17}OP$: 78.06; H, 5.86. Found: C, 77.89; H, 5.66.); ***p*-methylphenyldiphenylphosphine oxide**, 84%, benzene–ligroin, mp 131.5–133°, lit.[12] mp 129–130°; ***m*-methoxyphenyldiphenylphosphine oxide**, 84%, benzene–ligroin followed by sublimation, mp 107.9–108.5°, lit.[12] mp 112–113° (*Anal.* Calcd for $C_{19}H_{16}O_2P$: C, 74.01; H, 5.56. Found: C, 73.99; H, 5.46.); ***p*-methoxyphenyldiphenylphosphine oxide**, 79%, benzene–ligroin followed by sublimation, mp 115.0–116.0°, lit.[9] mp 117–118°;[9] ***p*-dimethylaminophenyldiphenylphosphine oxide**,[14] . . .; toluene, mp 181–183°, lit. mp 186–189°,[13] 183.5°.[14]

***p*-Carboxyphenyldiphenylphosphine oxide** was prepared from *p*-methylphenyldiphenylphosphine oxide according to the procedure of Morgan and Herr.[15] To 14.8 g (0.05 mole) of phosphine oxide were added 100 ml of pyridine and 75 ml of distilled water. The solution was heated to boiling and 31.6 g (0.2 mole) of potassium permanganate was added over a 3-hr period. The mixture was refluxed for 2 hr after the addition was complete and then stirred overnight. The reaction mixture was filtered and the manganese dioxide cake added to a pyridine–water mixture, heated, and refiltered. The filtrates were combined and cooled by the addition of ice. The product was precipitated by addition of concentrated hydrochloric acid (to pH 1). After filtration, the product was washed with distilled water and redissolved in a solution of 25 g of sodium bicarbonate in 500 ml of water. The solution was heated and filtered to remove unreacted starting material. The acid was reprecipitated with concentrated hydrochloric acid, yielding 13.9 g (86.3%) of white crystals, mp 263–265°. *Anal.* Calcd for $C_{19}H_{15}O_3P$: C, 70.80; H, 4.69. Found: C, 70.92; H, 4.67.

***m*-Carboxyphenyldiphenylphosphine oxide** was synthesized from 3-methylphenyldiphenylphosphine oxide according to the above procedure, yielding 13.5 g (84%) of crude acid. Recrystallization from 75% ethanol gave pure acid, mp 234-236°, lit.[16] mp 232°.

***m*-Hydroxyphenyldiphenylphosphine Oxide.**—*m*-Methoxyphenyldiphenylphosphine oxide, 4.6 g (0.012 mole), was dissolved in a mixture of glacial acetic acid (45 ml) and 47% hydriodic acid (30 ml) and heated under reflux for 40 hr. The solution was poured into ice water, the light tan solid was collected by filtration, dried in air (3.6 g, 82%), and recrystallized from 50% ethanol, mp 185–186°, lit.[12] mp 158–160°. *Anal.* Calcd for

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(1) (a) To whom all correspondence should be addressed at the Department of Chemistry, University of Alabama, University, Ala. 35486. (b) Taken from portions of theses submitted by J. V. M. and D. A. J. in partial fulfillment of requirements for the M.S. degree, 1964.

(2) J. J. Monagle and J. V. Mengenhauser, *J. Org. Chem.*, **31**, 2321 (1966), and references cited therein.

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(7) Boiling points and melting points are uncorrected. Analyses were by Galbraith Laboratories, Knoxville, Tenn.

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(15) P. W. Morgan and B. C. Herr, *J. Am. Chem. Soc.*, **74**, 4256 (1952).

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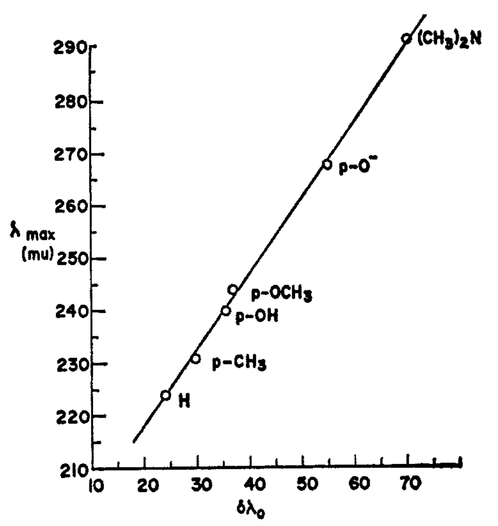


Figure 1.—Correlation of λ_{max} for $XC_6H_4P(=O)(C_6H_5)_2$ with $\delta\lambda_0$.

$C_{18}H_{15}OP$: C, 73.46; H, 5.13; P, 10.52. Found: C, 73.33; H, 5.31; P, 10.61.

p-**Hydroxyphenyldiphenylphosphine oxide** was prepared by the above procedure in 83% yield, mp 241.5–242.5° from 50% ethanol, lit.[9] mp 243–244°.

50% Ethanol Solution.—Commercial absolute ethanol was purified by distillation from magnesium ethoxide.[17] Equal volumes of purified ethanol and distilled water were mixed to form a solution containing 50% ethanol by volume.

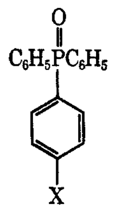
Carbonate-free Potassium Hydroxide Solution.—An ion-exchange method was used to prepare this reagent.[18] A 20-cm column was filled with 10 g of Permutit S-2 strong base resin in the chloride form. The resin was converted to the hydroxide form by passing 50-ml portions of 5% sodium hydroxide solution through the column until the effluent gave a negative chloride ion test. The column was rinsed with three 50-ml portions of 0.2 *N* potassium hydroxide. The carbonate-free solution was prepared by passing 850 ml of 0.2 *N* potassium hydroxide twice through the column into a polyethylene container for storage. Potassium hydroxide solution prepared by this method gave no turbidity upon addition of barium ion and the methyl orange and phenolphthalein end points were identical when titrated with sulfuric acid.

Procedure for Ultraviolet Spectra.—Spectra were determined using a Bausch and Lomb Spectronic 505 recording spectrophotometer equipped with 1-cm cells. Spectra were recorded over the range 200–350 mμ using 50% ethanol (by volume) as the solvent. The solvent was transparent above 210 mμ. Concentrations were chosen to give a maximum optical density of 0.30–0.95 for the first primary band. Band positions were calibrated against lines from a mercury lamp at 253.7 mμ.

Determination of Dissociation Constants and ρ Values.—Dissociation constants were determined by the method of Albert and Serjeant.[19] Solutions of acids and phenols were prepared by dissolving 0.001 mole of compound in 100 ml of solvent. From a 10-ml buret, 0.2 *M* carbonate-free potassium hydroxide was added in 0.5-ml increments in the region between 25 and 75% neutralization. When 50% (by volume) ethanol was the solvent, an equal increment of absolute ethanol was added for each increment of potassium hydroxide to maintain the percentage of ethanol constant. A Beckman Model 76 expanded scale pH meter equipped with glass and saturated calomel electrodes was used to measure the pH after each addition of base. Dissociation constants reported are the average of five values obtained from the 25–75% neutralization range. Dissociation constants determined in water were corrected for activity. The correction was +0.03 p*K* units using 0.005 as the ionic strength at the half-neutral point. The apparent dissociation constants determined in 50% ethanol were not corrected for activity or liquid junction potentials. A value of 1.2×10^{-15} was used as the ion product of 50% ethanol.[20] The dissociation constants of four compounds were determined in water as a check on the accuracy of the method used. The following values were obtained: benzoic acid, 4.18 (4.17);[21] phenol, 10.02 (10.00);[22] *m*-nitrophenol 8.36 (8.38);[23] *p*-nitrophenol, 7.14 (7.15.)[22] Values of σ were obtained by the method of least squares. Values of the correlation coefficient *r* and the standard deviation *s* were calculated by the standard statistical methods used by Jaffé.[23] Values of σ were obtained by dividing the experimentally determined values of $pK_0 - pK$ by ρ.

Results

Ultraviolet Spectral Study.—Since electronic excitations are highly sensitive to resonance effects, evidence was sought for this effect in a study of the ultraviolet spectra of triarylphosphine oxides according to the procedure of Doub and Vandenbelt.[24] In this procedure, for a given electron-withdrawing group (by resonance), the first primary band of the benzene absorption showed a progressive shift to longer wavelengths as substituents of increasing electron-donating-activity were substituted in the *para* position. Accordingly, the ultraviolet spectra of a series of phosphoryl compounds (I) containing electron donors in the *para* position were used to determine the extent of first primary band displacement. Results are shown in Table I. The spectral data are in good agreement with those obtained by Griffin and Hsieh.[6] As an additional test for resonance, the λ_{max} values were plotted *vs.* $\delta\lambda_0$, the empirical value for the displacing effect of the electron-donating substituent in the *para*-disubstituted compound.[24,25] Results are shown in Figure 1.



I, X = H, CH_3, OH, OCH_3, O^-, $N(CH_3)_2$

TABLE I

WAVELENGTHS OF MAXIMUM ABSORPTION FOR *p*-$XC_6H_5P(=O)(C_6H_5)_2$

X	λ_{max},[a] mμ
H	224
CH_3	231
OH	240[b]
OCH_3	244
O^-	268[c]
$N(CH_3)_2$	282

[a] Solvent 50% ethanol. [b] Solvent was made 1 *M* in HCl. [c] Solvent was made 1 *M* in NaOH.

Application of the Hammett Equation.—The enhancement of σ values for substituents has been used frequently as a test for, and measure of, resonance

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(17) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, Heath and Co., Boston, Mass., 1957, p 286.

(18) C. W. Davies and G. H. Naucolles, *Nature*, **165**, 237 (1950).

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(20) L. A. Cohen and W. M. Jones, *J. Am. Chem. Soc.*, **85**, 3397 (1963).

(21) I. M. Kolthoff and W. Bosch, *J. Phys. Chem.*, **36**, 1695 (1932).

(22) A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 388 (1961).

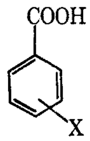
(23) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

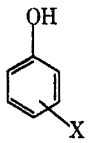
(24) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947).

(25) Using value of $\Delta\lambda$ (40.5) for dimethylaniline obtained by H. E. Ungnade, *ibid.*, **75**, 432 (1953).

interactions.[26] For phosphorus compounds, the Hammett relationship has been applied to dissociation constants of arylphosphonic acids[27a] and arylphosphinic acids.[27b] σ values for phosphoryl substituents in arylphosphonic acids[27a] and their esters[27c] and arylphosphinic acids[27b] have been determined by measurement of dissociation constants of derivatives containing the carboxyl and phenol groups. In addition, approximate σ_p and σ_{p^+} values for several phosphoryl substituents, including the diphenylphosphono [$-P(O)(C_6H_5)_2$] group, were determined from C^{13} nmr spectra.[28] In the latter case, the diphenylphosphono group was found to be approximately equal to the carboethoxy group in electron-withdrawing power, while, from a Taft treatment of acetic acids containing phosphoryl substituents,[29] the diphenylphosphono group was found to be approximately equivalent to the carbomethoxy group in this respect.

In order to define the contribution of resonance to the over-all electron-withdrawing power of the diphenylphosphono group, evaluations of σ_m and σ_p values for the group were made using compounds II and III. Because of the limited solubility of the phosphoryl compounds II and III in water, their dissociation constants were determined in 50% ethanol. Two values of ρ for the dissociation of benzoic acids in this solvent were listed in the literature[30,31] but did not agree. For consistency in this work, the ρ value was redetermined. Also, while a value of ρ for the dissociation of phenols in 50% ethanol was available, only *para*-substituted phenols were used in its determination.[32] Therefore, the value of ρ for phenols was also redetermined. In both cases the ρ values were determined by the procedure of Van Bekkum, Verkade, and Wepster.[30] Each ρ value was determined from the dissociation constants of seven substituted compounds chosen so that in no case was direct resonance possible. To check on the accuracy of the experimental method used, ionization constants for benzoic acids and several phenols were also determined in water and compared with literature values (see Experimental Section). In each case agreement with the literature value was good.


IIa, X = m-$(C_6H_5)_2PO$
b, X = p-$(C_6H_5)_2PO$


IIIa, X = m-$(C_6H_5)_2PO$
b, X = p-$(C_6H_5)_2PO$

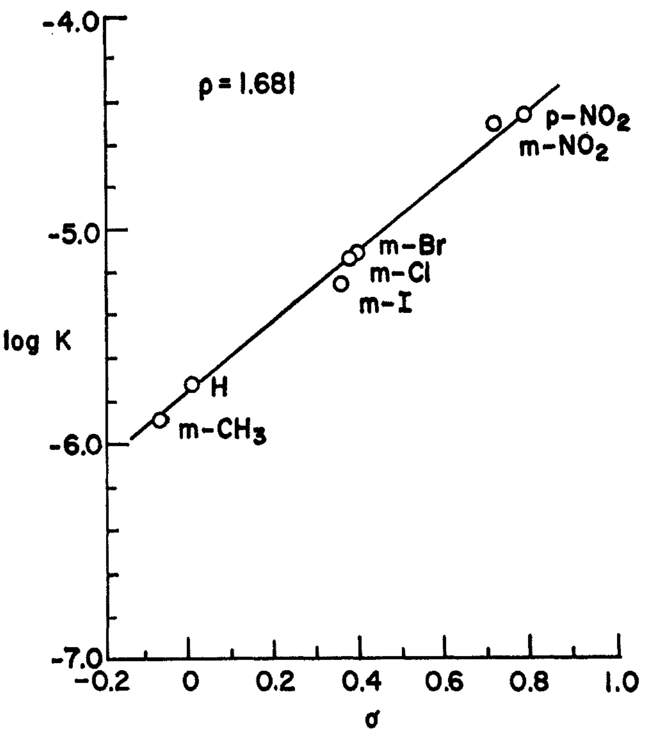


Figure 2.—Dissociation constants of XC_6H_4COOH in 50% ethanol at 25° *vs.* σ constants.

TABLE II

DISSOCIATION CONSTANTS OF BENZOIC ACIDS AND PHENOLS IN 50% ETHANOL AT 25°

Substituent	pK_a Present work	pK_a Lit. value
	Benzoic Acids	
m-CH_3	5.88	5.72[a]
H	5.72	5.71[b]
m-I	5.26	. . .
m-Cl	5.14	5.11[a]
m-Br	5.11	5.22[c]
m-NO_2	4.51	4.66[c]
p-NO_2	4.47	4.53[c]
	Phenols	
p-OCH_3	11.72	11.52[d,e]
H	11.47	11.28[f,e]
m-OCH_3	11.10	10.99[d,e]
p-Br	10.60	10.57[a]
m-Br	10.36	10.21[d,e]
m-CN	9.54	. . .
m-NO_2	9.35	9.25[f,g]
p-NO_2[h]	7.95	7.89[a]

[a] W. L. Bright and H. T. Briscoe, *J. Phys. Chem.*, **37**, 787 (1933). [b] J. P. Schaefer and T. J. Miraglia, *J. Am. Chem. Soc.*, **86**, 64 (1964). [c] J. D. Roberts, E. A. McElhill, and R. Armstrong, *ibid.*, **71**, 2923 (1949). [d] 48.9% ethanol, 20–22°. [e] G. Schwarzenbach and E. Rudin, *Helv. Chim. Acta*, **22**, 360 (1939). [f] 48% ethanol. [g] K. C. Schreiber and M. C. Kennedy, *J. Am. Chem. Soc.*, **78**, 153 (1956). [h] Not used in determination of ρ value.

Dissociation constants of benzoic acids and phenols in 50% ethanol are shown in Table II along with literature values, where available. Agreement with literature values is good in some cases, while significant differences occur in others. Since activity corrections and liquid junction potentials are usually neglected in mixed solvents, some of the disagreement may be due to these factors. Values of ρ for the dissociation of benzoic acids and phenols in 50% ethanol were calculated by the method of least squares from the dissociation constants in Table II and the σ values listed by Wells[31] and are shown in Figures 2 and 3 and in

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(26) (a) L. P. Hammett, *J. Am. Chem. Soc.*, **59**, 96 (1937); (b) H. Zollinger, *Nature*, **172**, 257 (1953); (c) F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **74**, 1058 (1952); (d) H. Kloosterziel and H. J. Backer, *ibid.*, **74**, 5806 (1952); (e) R. A. Benkeser and H. R. Krysiak, *ibid.*, **75**, 2421 (1953).

(27) (a) H. H. Jaffé, L. D. Freedman, and G. O. Doak, *ibid.*, **75**, 2209 (1953); (b) L. D. Quin and M. R. Dysart, *J. Org. Chem.*, **27**, 1012 (1962); (c) L. D. Freedman and H. H. Jaffé, *J. Am. Chem. Soc.*, **77**, 920 (1955).

(28) H. L. Retcofsky and C. E. Griffin, *Tetrahedron Letters*, 1975 (1966).

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(30) H. Van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. Chem.*, **78**, 815 (1959).

(31) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

(32) L. A. Cohen and W. M. Jones, *J. Am. Chem. Soc.*, **85**, 3397 (1963).

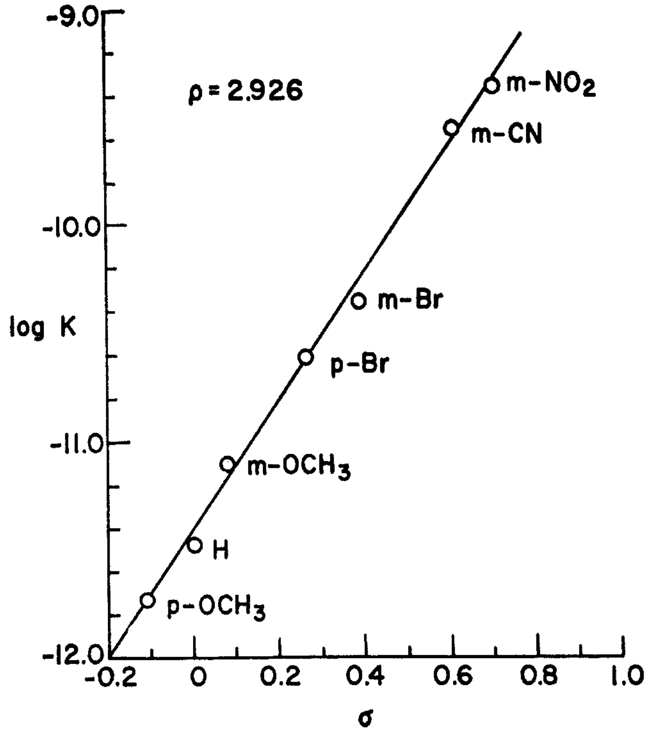


Figure 3.—Dissociation constants of XC_6H_4OH in 50% ethanol at 25° *vs.* σ constants.

TABLE III

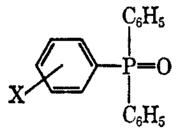
VALUES OF ρ IN 50% ETHANOL AT 25°

	Present work			Literature		
Dissociation of	ρ	r	s	ρ	r	s
Benzoic acids	1.681	0.996	0.052	1.570[a]	0.997	0.049
				1.851[b]	0.993	0.099
Phenols	2.926	0.997	0.074	2.687[a,c]	0.984	0.116
				2.67[d]		

[a] See ref 30. [b] See ref 31. [c] 48.9% ethanol, 20–22°. [d] See ref 32.

TABLE IV

VALUES OF σ IN 50% ETHANOL AT 25°
FROM DISSOCIATION CONSTANTS OF



X	pK	Log K/K_0[a]	σ_m	σ_p
m-COOH	5.01	0.71	0.422	. . .
m-OH	10.20	1.27	0.434	. . .
p-COOH	4.79	0.93	. . .	0.553
p-OH	9.48	1.99	. . .	0.680

[a] Experimentally determined value of K_0 used.

Table III along with literature values. The ρ value of benzoic acids from this work is intermediate between the two literature values. The ρ value for phenols is higher than the literature value but the correlation coefficient r is better and the standard deviation s is smaller.

σ constants for the ionization constants for benzoic acids and phenols containing the diphenylphosphoryl group were calculated using the redetermined ρ values and are shown in Table IV. Evaluation of the electron-withdrawing power of the diphenylphosphoryl group in terms of the "*para* resonance energy" ($\Delta\Delta F_p$) of Van Bekkum, Verkade, and Wepster[30] gave a value of −0.51 kcal. As a check on the agreement between our data and those of Verkade, we determined a value of $\Delta\Delta F_p$ for the *para* nitro groups using our new ρ values. The value for this term (−1.83 kcal) was in good agreement with that previously determined (−1.87 kcal).[30]

Alternatively, evaluation of the resonance effect using σ_R[33] gave the value 0.25 and by σ_R'[34] the value 0.39.

Discussion of Results

Results of both the ultraviolet and dissociation constant studies are consistent with a moderate resonance effect of the phosphoryl groups with conjugated systems, in agreement with other results.[4,5]

The linear plot of the λ_{max} *vs.* $\delta\lambda_0$ for the ultraviolet spectrum is typical for systems containing groups which interact by resonance through the benzene ring.[23] The dissociation constants of benzoic acids and phenols containing the diphenylphosphoryl groups (see Table IV) show that for both types of compounds the *para* isomers are more acidic than the *meta* isomers. Consequently, for both the benzoic acids and phenols, σ_p is greater than σ_m, the difference being greater in the case of the phenols. Values of σ_m, which reflect inductive effects, are approximately equal for the benzoic acid and the phenol. This relationship of σ values therefore corroborates the ultraviolet data indicating the presence of a resonance effect.

The σ_p value for the diphenylphosphono group in benzoic acid, where no direct resonance is possible, is in good agreement with the value obtained by analysis of the C^{13} nmr spectrum of triphenylphosphine oxide.[28] From the dissociation constant studies, the value of the "*para* resonance energy" (−0.51 kcal) indicates that the group withdraws electrons somewhat less effectively than the carbethoxy group (−0.82 kcal).[26] Alternatively, however, the values for σ_R (0.25) and σ_R' (0.39) show the diphenylphosphoryl group to be about as effective as the carbethoxy group ($\sigma_R = 0.27$,[34] $\sigma_R' = 0.39$)[35] in agreement with the conclusions of Griffin.[28,29] The difference in these two comparisons may be a result of the fact that "*para* resonance energies" are based on the differences between σ_p values for benzoic acids and phenols, while σ_R and σ_R' are based on the difference between σ_p and σ_m for phenols only. The results do not differentiate between resonance of the conjugated system which involves only the phosphorus atom or resonance which may extend to the phosphoryl oxygen.

Also, conclusions drawn from the data concerning the resonance effect of the phosphoryl group are complicated by the presence of the two unsubstituted phenyl rings which may themselves be involved in resonance with the phosphoryl group or which may be causing steric inhibition of resonance.[35] Further

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(33) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13.

(34) L. A. Cohen and W. M. Jones, *J. Am. Chem. Soc.*, **85**, 3402 (1963).

(35) M. I. Kabachnik, T. A. Mastryukova, and T. A. Melent' Eva, *J. Gen. Chem. USSR*, **33**, 375 (1963).

work to examine these possibilities using less sterically hindered compounds is in progress.

Finally, it should be possible to determine if resonance involving the phosphoryl oxygen is occurring, by the reaction of arylphosphine oxides containing electron-donating substituents with phenyl isocyanate.[2] Resonance of this type which places an increased negative charge on the oxygen atom should enhance the nucleophilic activity of the phosphoryl group. This work is also in progress.

Registry No.—I ($X = H$), 791-28-6; I ($X = CH_3$), 6840-28-4; I ($X = OH$), 793-43-1; I ($X = OCH_3$), 795-44-8; I ($X = O^-$), 13145-79-4; I [$X = N(CH_3)_2$], 797-72-8; IIa, 2129-29-5; IIb, 2272-04-0; IIIa, 13145-82-9; *m*-methylphenyldiphenylphosphine, 7579-70-6; *m*-methoxyphenyldiphenylphosphine, 13145-84-1.

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The Chemistry of Carbanions. XIII. The Nuclear Magnetic Resonance Spectra of Various Methylmagnesium Derivatives and Related Substances[1a,b]

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The nmr spectra of solutions of dimethylmagnesium and methylmagnesium bromide have been studied in the presence of added magnesium alkoxides, methyllithium, magnesium bromide, and manganese(II) salts. Of particular interest were the nmr spectra of the unsymmetrical magnesium reagents, methylcyclopentadienylmagnesium (**4**), phenylcyclopentadienylmagnesium (**7**), methylphenylmagnesium (**2**), and 3,3-dimethylbutylcyclopentadienylmagnesium (**10**). From studies of these spectra at several temperatures, it was possible to determine the rates of exchange of alkyl groups from one magnesium atom to another and to study the effect of various additives on the rate of this exchange. These exchanges are retarded by the good solvating agents 1,2-dimethoxyethane and, especially, N,N,N′,N′-tetramethylethylenediamine and are catalyzed by magnesium bromide. The exchange of methyl groups between dimethylmagnesium and methylcyclopentadienylmagnesium (**2**) appears to be a bimolecular reaction which is first order in each reagent. A study of the exchange of alkyl groups between the mixed reagent 3,3-dimethylbutylcyclopentadienylmagnesium (**10**) and bis(3,3-dimethylbutyl)magnesium (**9**) indicates that the rate of exchange is substantially faster than the rate of configurational inversion at the CH_2–Mg bond. Consequently, the exchange reaction occurs primarily with retention of configuration.

In an effort to learn more about the structures of the organometallic reactants involved in the addition reactions of organomagnesium compounds,[2,3] we have studied the nmr spectra of solutions containing various methylmagnesium derivatives and related compounds.[4]

Mixtures of Magnesium and Lithium Reagents.—Our initial measurements of ethereal solutions of methyllithium (containing lithium bromide), methylmagnesium bromide, dimethylmagnesium, and dimethylmercury are presented in Table I. In agreement with earlier observations for alkylmagnesium bromides and the corresponding dialkylmagnesiums,[2b,4a–c,n] the spectra of methylmagnesium bromide and of dimethylmagnesium are very similar both in position of chemical shift and in ^{13}C–H coupling constants. The position of the methyl signal for dimethylmagnesium was dependent on concentration[4a,b] and moved to higher field as the concentration was lowered, suggesting that the extent of solvation or the degree of association of dimethylmagnesium varied with concentration. From a study of its crystal structure,[5] solvent-free dimethylmagnesium is known to exist in polymeric chains with four methyl groups arranged in a tetrahedral fashion around each magnesium atom. We have determined the apparent degree of association of a 0.13 *M* solution of dimethylmagnesium in ether solution by isothermal distillation and find it to be approximately monomeric (apparent mol wt 1.20–1.28 × monomer) at this concentration level. This observation is in agreement with the results previously obtained for dilute ethereal solutions of diethylmagnesium and diphenylmagnesium.[6]

We examined the nmr methyl signals of ether solutions containing the various mixtures of magnesium

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