two spectra showed that no PO had formed in view of the absence of the expected strong absorption at 1240 cm^{-1}. Both reactants were subsequently recovered in nearly a quantitative amount.

B. **Triethyl Phosphite and Ethyl Diphenylphosphinate.**—In a similar manner, 41.5 g (0.25 mole) of technical grade triethyl phosphite and 6.6 g (0.027 mole) of ethyl diphenylphosphinate were mixed, sampled for infrared examination, and heated to gentle reflux over an 8.5-hr period. Distillation of the reaction mixture resulted in a 92% recovery of triethyl phosphite. The distillation residue was impure ethyl diphenylphosphinate, $n^{20}D$ 1.5302.

C. **Triethyl Phosphite and Phenyl Tosylate.**—Equimolar quantities of triethyl phosphite (33.2 g, 0.2 mole) and phenyl tosylate (49.2 g, 0.2 mole) were heated to 173° over a 5-hr period, cooled, and distilled to yield 30.7 g (92.5% recovery) of triethylphosphite, bp 27° (0.75 mm). Recrystallization of the distillation residue yielded 45 g of white, crystalline phenyl tosylate (90% recovery).

4,4'-Biphenylenebis(methylphosphinic acid) (XV).—The 4,4'-biphenylenedilithium prepared in tetrahydrofuran by the interaction at −60° or lower of 0.2 mole of *n*-butyllithium and 31.2 g (0.10 mole) of 4,4'-dibromobiphenyl was immediately added to a second tetrahydrofuran solution also at −60° or lower containing 40.8 g (0.20 mole) of N,N-dimethylmethylphosphonamidic chloride (XIII). After the reaction mixture had warmed to ambient temperature, the solvents were removed at reduced pressure. The residue was digested in hot, concentrated hydrochloric acid for 4.5 hr. The mixture was next cooled, neutralized, filtered, and reacidified to precipitate crude XV. The acid obtained after two recrystallizations, 3.5 g (0.011 mole, 11%), melted at 307–310°.

Anal. Calcd for $C_{14}H_{16}O_4P_2$: C, 54.20; H, 5.20; neut equiv, 155. Found: C, 55.77; H, 5.31; neut equiv, 153.

N,N-Dimethylmethylphosphonamidic chloride (XIII), used above to prepare XV and obtained in 74% yield by the interaction of methylphosphonic dichloride and dimethylamine in ether at 0°, boiled at 72–75° (1.5 mm) [lit.[14] bp 74–75° (1.5 mm)]. The methylphosphonic dichloride was obtained in 33% yield as previously described[15] by treating dimethyl methylphosphonate with phosphorus pentachloride. Although the yield of methylphosphonic dichloride was low, its purity was high as it solidified to a beautiful, crystalline mass melting at about 30°.

***p*-Phenylenebis(methylphosphinic acid) (IV).**—A 3.0-g (0.0114 mole) quantity of dimethyl *p*-phenylenebis(methylphosphinate) (XII) and 25 ml of concentrated hydrochloric acid were heated at the reflux temperature for 4 hr and then allowed to stir overnight at ambient temperature. Excess acid and water were removed at reduced pressure to yield an off-white solid which on recrystallization from ethanol and Norit A yielded 1.4 g (0.006 mole, 52%) of beautiful, crystalline *p*-phenylenebis(methylphosphinic acid) (IV) melting at 233–235° (lit.[4] mp 231–236°). The neutralization equivalent was determined to be 117.4 (theory, 117.1). From the mother liquor there was obtained an additional 0.3 g of IV melting at 232–234°. The total yield was 63.6%.

Registry No.—I, 4583-37-3; II, 10561-78-1; VI, 10498-56-3; IX, 10498-57-4; X, 10498-58-5; XI, 10498-59-6; XII, 10580-44-6; XV, 10498-60-9; dimethyl methylphosphonate, 756-79-6; diethyl ethylphosphonate, 78-38-6; ethyl diphenylphosphinate, 1733-55-7; triethyl phosphite, 122-52-1.

Acknowledgments.—We wish to thank Messrs. K. A. Sterner, W. Birch, and K. A. Smitheman for their analytical assistance and Messrs. M. T. Cheng, G. D. Homer, and R. J. Mitchell for laboratory assistance. Finally, we wish to thank Mr. H. G. Weiss of West Coast Technical Service of San Gabriel, Calif., for obtaining the mass spectrum of P-methyl-P-phenyl-N-triphenylphosphoranylidinephosphonic amide.

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(14) P. Malatesta and A. Ciaramella, *Ann. Chim.* (Rome), **50**, 1819 (1960); *Chem. Abstr.*, **55**, 19767a (1961).

(15) P. C. Crofts and G. M. Kosolapoff, *J. Am. Chem. Soc.*, **75**, 3379 (1953).

Application of the Hammett Equation to Organophosphorus-Substituted Phosphinic and Benzoic Acids[1]

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Organophosphorus-substituted benzoic and phosphinic acids have been readily obtained from (4-bromophenyl)diphenylphosphine. From correlations with the Hammett equation, it has been possible to compute Hammett σ and Taft σ^0 values for the p-$(C_6H_5)_2P$, p-$(C_6H_5)_2P(S)$, and p-$(C_6H_5)_2P(O)$ groups. In the systems studied, the p-$(C_6H_5)_2P$ group is found to be almost neutral in its electrical effects, the p-$(C_6H_5)_2P(S)$ group is found to be a moderate electron acceptor, and the p-$(C_6H_5)_2P(O)$ group is a moderately strong electron acceptor.

The effect of structure on acidities of a variety of phosphorus acids has been recently extensively reported[2] and the Hammett equation has been applied to both substituted arylphosphonic[3] and arylphosphinic acids.[4] From these studies it was then possible, using arylphosphonic and phosphinic acids containing phenolic and carboxylic groups, to determine Hammett substituent (σ) constants for the PO_3H^-, $PO_3{}^{2-}$, and the PO_2H_2 groups[3,4] as well as the diethoxyphosphono group.[5] More recently polar-substituent constants (σ^*) have been determined for several phosphonium, dialkoxyphosphono, and diphenylphosphono groups.[6] From the analysis of C^{13} nmr spectra of organophosphorus compounds, tentative assignments of both σ and σ^+ values for ten phosphorus groups, including the $(C_6H_5)_2P$ and $(C_6H_5)_2P(O)$ groups, have been made recently.[7] We wish to report in this paper the syntheses of several organophosphorus-substituted diarylphosphinic acids as well as the evaluation of both Hammett σ and Taft σ^0 constants for the p-$(C_6H_5)_2P$, p-$(C_6H_5)_2P(S)$, and p-$(C_6H_5)_2P(O)$ groups. These new substituent constants were then successfully applied

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(1) (a) This work was supported by the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433, under Contract AF 33(615)-3570; (b) presented before the Division of Organic Chemistry at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

(2) (a) M. I. Kabachnik, T. A. Mastrukova, A. E. Shipov, and T. A. Melentyeva, *Tetrahedron*, **9**, 10 (1960); (b) D. F. Peppard, G. W. Mason, and C. M. Andrejasich, *J. Inorg. Nucl. Chem.*, **27**, 697 (1965).

(3) H. H. Jaffé, L. D. Freedman, and G. O. Doak, *J. Am. Chem. Soc.*, **75**, 2209 (1953).

(4) L. D. Quin and M. R. Dysart, *J. Org. Chem.*, **27**, 1012 (1962).

(5) L. D. Freedman and H. H. Jaffé, *J. Am. Chem. Soc.*, **77**, 920 (1955).

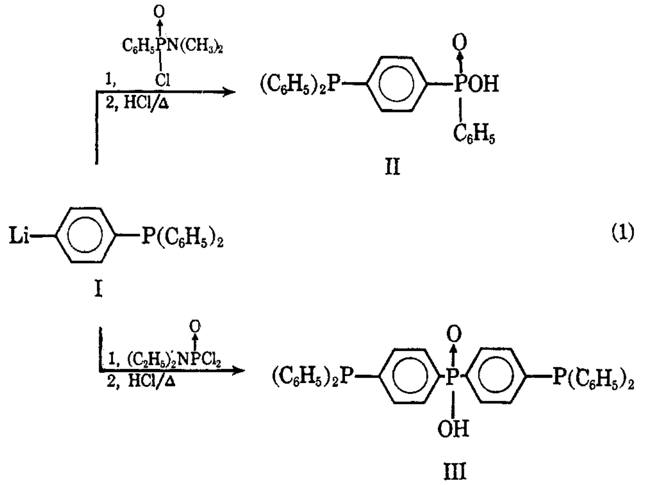
(6) D. J. Martin and C. E. Griffin, *J. Org. Chem.*, **30**, 4034 (1965).

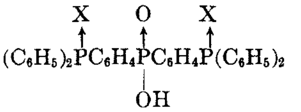
(7) H. L. Retcofsky and C. E. Griffin, *Tetrahedron Letters*, 1974 (1966).

to a series of similarly organophosphorus-substituted benzoic acids to give good agreement with the Hammett equation.

Results

In the work reported in a different paper,[8] we found that (4-bromophenyl)diphenylphosphine readily reacted with *n*-butyllithium in tetrahydrofuran at or below −65° to give a high conversion to (4-lithiophenyl)diphenylphosphine (I). Subsequent reaction of I with N,N-dimethylphenylphosphonamidic chloride and with N,N-diethylphosphoramidic dichloride in tetrahydrofuran at the same low temperature gave good yields of the mixed tertiary phosphine–phosphinic acid II and the bis(tertiary phosphine)phosphinic acid III (eq 1). No attempt was made to isolate the intermediate phosphinic amides. The acids II and III were both oxidized by means of hydrogen peroxide in glacial acetic acid to their corresponding oxide IV (eq 2) and dioxide V. Additionally, treatment of II or III with sulfur in refluxing toluene gave the sulfide VI and disulfide VII, respectively. The relationship of the tertiary phosphine–phosphinic acid II, the oxide IV, and the sulfide VI to one another was demonstrated during the attempted thionyl chloride conversion of II to the corresponding phosphinic chloride. Instead of recovering the acid II after hydrolysis of the crude phosphinic chloride VIII, the oxide IV was recovered (eq 2). A similar oxidation of VI occurred on reaction with thionyl chloride and again IV was the isolated product. The analogous thionyl chloride oxidation of triphenylphosphine sulfide to triphenylphosphine oxide has also been described.[9]





$$(C_6H_5)_2\overset{\overset{X}{\uparrow}}{P}C_6H_4\underset{OH}{\overset{\overset{O}{\uparrow}}{P}}C_6H_4\overset{\overset{X}{\uparrow}}{P}(C_6H_5)_2$$

V, X = O
VII, X = S

It was possible to determine the equivalent weights of the new acids of this study in 60:40% tetrahydrofuran–water even though the bis(tertiary phosphine)phosphinic acids III, V, and VII had limited solubilities in this solvent system. As a result of these low solubilities, the determination of the corresponding pK_a data was successful only for the mono series of II, IV, and VI. In order to develop the necessary data for determining σ constants for the p-$(C_6H_5)_2P$, p-$(C_6H_5)_2P(S)$, and p-$(C_6H_5)_2P(O)$ groups, a series of ten mono- and disubstituted diarylphosphinic acid were prepared or otherwise obtained.[10] The pK_a values in Table I were obtained as an average value of three separate determinations using the method described by Glasstone.[11]

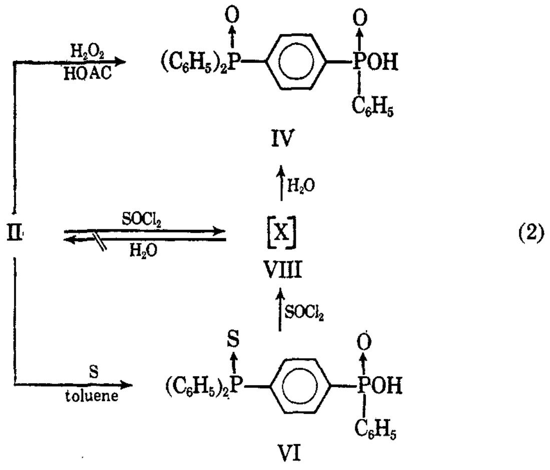
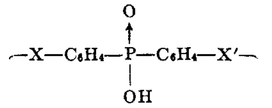


TABLE I

DISSOCIATION CONSTANTS OF SUBSTITUTED DIARYLPHOSPHINIC ACIDS IN 60:40% TETRAHYDROFURAN–WATER AT 23 ± 1°



$$-X-C_6H_4-\underset{OH}{\overset{\overset{O}{\uparrow}}{P}}-C_6H_4-X'-$$

Acid	Registry No.	X	X′	pK_a
1	1084-11-3	p-CH_3	p-CH_3	4.32
2	13118-95-1	p-CH_3O	H	4.23
3	13118-96-2	p-CH_3	H	4.08
4	1707-03-5	H	H	3.90
5	13118-97-3	p-Cl	H	3.59
6	13118-98-4	p-Br	H	3.51
7	13118-99-5	m-Br	H	3.47
8	5435-76-7	m-Cl	H	3.41
9	13119-01-2	p-Cl	p-Cl	3.18
10	5435-78-9	p-NO_2	H	2.97
II		p-$(C_6H_5)_2P$	H	3.89
VI		p-$(C_6H_5)_2P(S)$	H	3.52
IV		p-$(C_6H_5)_2P(O)$	H	3.32

Plots of log K/K_0 *vs.* both Hammett σ values as given by Jaffé[12] and Taft[13] σ^0 values were then made. Since the resulting plots were linear with little scatter of data (see Figure 1), the slopes (ρ), the standard deviations (s), and the correlation coefficients (r) were calculated according to the method described previously by Jaffé.[12] From these data it was subsequently possible to calculate[12] both Hammett σ and Taft σ^0 constants for the p-$(C_6H_5)_2P$, p-$(C_6H_5)_2P(S)$, and p-$(C_6H_5)_2P(O)$ groups. The data obtained for these groups from this study as well as related substituent constants are given in Table II.

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[8] R. A. Baldwin and M. T. Cheng, *J. Org. Chem.*, **32**, 1572 (1966).

[9] K. A. Pollard and H. J. Harwood, *ibid.*, **27**, 4444 (1962); **28**, 3430 (1963).

[10] We wish to thank Dr. L. D. Quin of Duke University, and Dr. G. O. Doak of North Carolina State University, for samples of compounds 5 and 10 (Table I), respectively.

[11] S. Glasstone, "Textbook of Physical Chemistry," 2nd ed, D. Van Nostrand Co., Inc., New York, N. Y., 1946, p 1003.

[12] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

[13] R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

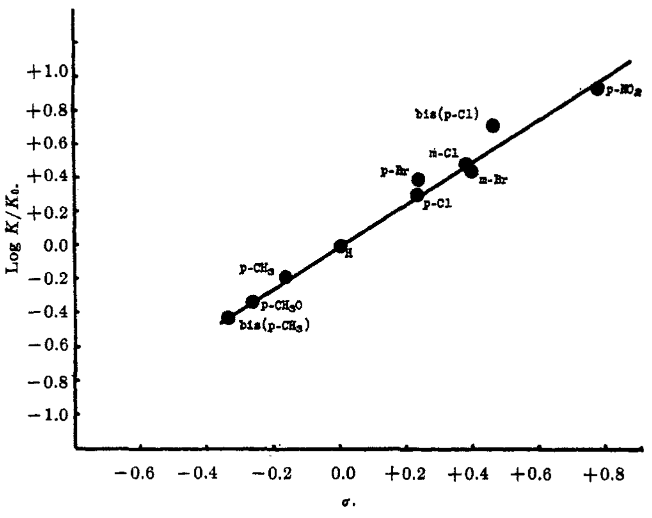

Figure 1.—Plot of log K/K_0 for substituted diarylphosphinic acids *vs.* Hammett's σ constants.

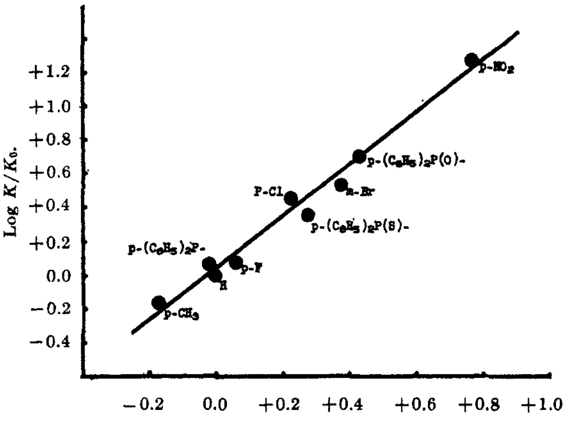

Figure 2.—Plot of log K/K_0 for substituted benzoic acids *vs.* Hammett σ constants.

TABLE II

SUBSTITUENT CONSTANTS

Substituent	σ	σ^0	$\sigma^{*\,a}$	σ^b	$\sigma^{+\,b}$
p-$(C_6H_5)_2P$	−0.01	+0.03	...	+0.68	0.70
p-$(C_6H_5)_2P(O)$	+0.44	+0.47	+1.68	+0.53	+0.52
p-$(C_6H_5)_2P(S)$	+0.28	+0.32	...	...	...

[a] Reference 6. [b] Reference 7.

To further substantiate the newly computed values of the substituent constants for the above three organophosphorus groups, a series of substituted benzoic acids was treated in a similar manner. The necessary organophosphorus-substituted benzoic acids were obtained *via* the carbonation of (4-lithiophenyl)diphenylphosphine (I) and subsequent oxidation or sulfurization of the 4-diphenylphosphinobenzoic acid. The dissociation constants obtained for these substituted benzoic acids are given in Table III.[14] Again plots of log K/K_0 *vs.* Hammett σ (see Figure 2) and Taft σ^0 constants were linear and the necessary reaction parameters were calculated as before. These reaction parameters for both the phosphinic and benzoic acids are presented in Table IV.

TABLE III

DISSOCIATION CONSTANTS OF SUBSTITUTED BENZOIC ACIDS IN 60:40% TETRAHYDROFURAN–WATER AT 23 ± 1°

Acid	Registry No.	X in X-C_6H_4COOH	pK_a
1	99-94-5	p-CH_3	6.64
2	65-85-0	H	6.42
3	2129-31-4	p-$(C_6H_5)_2P$	6.38
4	456-22-4	p-F	6.25
5	5068-24-6	p-$(C_6H_5)_2P(S)$	6.03
6	74-11-3	p-Cl	5.93
7	585-76-2	m-Br	5.90
8	2272-04-0	p-$(C_6H_5)_2P(O)$	5.72
9	62-27-7	p-NO_2	5.16

TABLE IV

REACTION PARAMETERS

	ρ^a	r^b	s^c
Diarylphosphinic acids			
Hammett (σ)	1.25	0.990	0.066
Taft (σ^0)	1.27	0.991	0.064
Benzoic acids			
Hammett (σ)	1.52	0.989	0.069
Taft (σ^0)	1.52	0.992	0.059

[a] Slope. [b] Correlation constant. [c] Standard deviations.

Discussion

From the pK_a values obtained for 13 mono- and disubstituted diarylphosphinic acids and the linear plots of log K/K_0 of ten nonphosphorus-substituted phosphinic acids *vs.* Hammett σ and Taft σ^0 constants, it was possible to calculate Hammett and Taft substituent constants for the p-$(C_6H_5)_2P$, p-$(C_6H_5)_2P(S)$, and p-$(C_6H_5)_2P(O)$ groups. The correlation constant and standard deviation data in Table IV for the phosphinic acids indicate a very good fit of the data to the Hammett equation. However, since the solvent system employed was somewhat different from the water or water–alcohol mixtures frequently employed in such studies, interpretation of the significance of the ρ values was tenuous without additional data, particularly since a change in ρ was expected with a change of the dielectric constant of the solvent.[15]

The calculated values for the new Hammett σ constants follow the relative order that one would expect. The fact that the p-$(C_6H_5)_2P$ group is found to be very slightly electron releasing was somewhat surprising. The computed σ value indicates only a slight effect resulting from the resonance of the nonbonding electron pair on the phosphine phosphorus with the benzene ring. This seems reasonable, however, since one might intuitively expect the group to be only weakly donating owing to the negative inductive effect of the two phenyl groups on the phosphine phosphorus atom. The Hammett σ value of +0.68 recently obtained *via* carbon-shielding data from the analyses of the C^{13} nmr spectra for selected organophosphorus compounds[7] appears much too large and does not fit the log K/K_0 plots of this study (compare Figures 1 and 2). When the tertiary phosphine group was converted to the corresponding oxide IV and sulfide VI, nonbonded electron release is no longer possible and these groups become moderately strong electron-attracting groups as expected. Agreement with the carbon-shielding σ value[7] (+0.53) for the $(C_6H_5)_2P(O)$ group is now much better.

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(14) We wish to thank Dr. M. F. Hawthorne, University of California at Riverside, Riverside, Calif., for samples of several substituted benzoic acids.

(15) Reference 12, p 219.

A similar good fit of the data was obtained when Taft σ^0 values were utilized in the computations. It appears that the phosphorus atom in phosphinic acid is behaving like a center of saturation[16] and that the transmission of electronic effects is primarily due to induction and resonance–induction. The computed Taft σ^0 values for the three organophosphorus substituents follow the same relative order as obtained above for the Hammett σ values. The only difference is the fact that the p-$(C_6H_5)_2P$ group now shows apparently a very slight electron-attacting ability with σ^0 as opposed to the slight electron-releasing capacity as indicated by σ.

The additive nature of polar substituents has been discussed in some detail by Jaffé. The fact that both the disubstituted compounds 1 and 9 of Table I fit the plots of $\log K/K_0$ *vs.* σ further points out this additive property of the substituents. It further indicates that the σ values basically reflect polar effects.

In order to substantiate the validity of the computed substituent values and to gain insight in the interpretation of the significance of ρ for these reaction systems in tetrahydrofuran–water, a series of nine substituted benzoic acids was similarly studied. Included among the substituents were the same three organophosphorus groups for which we have now computed new σ values. The ρ values (Table IV) for the benzoic acid series were found to be somewhat larger than those obtained for the phosphinic acids. Thus, it seems that the substituent electrical effects are transmitted to the phosphinic acid group to a somewhat lesser extent than to the carboxy group of benzoic acid. Interestingly, the ratios of ρ_{PO_2H}/ρ_{COOH} and $\rho_{PO_2H}{}^0/\rho_{COOH}{}^0$ for 60:40% tetrahydrofuran–water (0.82 and 0.84) are very close to the similar ratios obtained in water and previously noted for phosphinic acids [Ar(H)P(O)OH, 0.83][4] and for the primary ionization constant of phosphonic acids[3] (0.76). Again the correlation constants (r) and standard deviations (s) obtained for the benzoic acid series indicate a good fit of the data with the Hammett equation.

The correlation with σ^0 values merits additional comment. The σ^0 constants reflect all polar effects (inductive and mesomeric) exerted by a substituent which are transmitted by induction to the reaction center. They exclude polar effects arising from direct resonance interactions between the substituents and the reaction center. The excellent correlation with σ^0, particularly for the phosphinic and benzoic acids with strongly electron-withdrawing groups, argues against a direct resonance effect. It further supports our earlier hypothesis that the resonance contribution of the nonbonding electron pair on the phosphorus atom of the p-$(C_6H_5)_2P$ group must be small. This also agrees with the small resonance effect recently proposed for the p-$(C_6H_5)_2P$ group as a result of the small value obtained for the π-electron effect parameter $\mathcal{J}_{m\text{-}X}^{p\text{-}X}$.[17]

Martin and Griffin[6] have previously suggested that the correlation of the approximate polar substituent constant (σ^*) of +1.68 obtained for the p-$(C_6H_5)_2P(O)$ group with the Hammett σ value for the p-carbomethoxy group indicated an equivalent electron-acceptor capacity. Continuing this analogy *via* the correlation of the σ of 0.46 for the p-carbomethoxy group with the computed σ of +0.44 for the p-$(C_6H_5)_2P(O)$ group further indicates an equivalence of the electron-acceptor characteristics of the two groups. Additionally, similar comparison of the σ^+ value of 0.70 suggested[7] for the p-$(C_6H_5)_2P$ group indicates an equivalence to the p-NO_2 group. Since, as shown above, the p-$(C_6H_5)_2P$ group is nearly neutral in its electrical effects and since the p-$(C_6H_5)_2P(O)$ group is only comparable to the p-carbomethoxy group, this suggested[7] σ^+ value also appears much too large.

Thus, σ and σ^0 constants which indicate increasing electron-acceptor capabilities have been chemically determined for the p-$(C_6H_5)_2P$, p-$(C_6H_5)_2P(O)$, and p-$(C_6H_5)_2P(S)$ groups. In the systems studied, the p-$(C_6H_5)_2P$ group is found to be almost neutral in its electrical effects, the p-$(C_6H_5)_2P(S)$ group is found to be a moderate electron acceptor, and the p-$(C_6H_5)_2P(O)$ group is found to be a moderately strong electron acceptor. Additional studies are in progress to further expand these data.

Experimental Section

Determination of pK_a Data.—The diarylphosphinic or benzoic acid (approximately 2 mmoles, weighed accurately) was dissolved in 100 ml of 60–40% tetrahydrofuran–water solution. This solution was then titrated with standard 0.1035 N sodium hydroxide. The temperature during all the titrations was maintained at 23.0 ± 1°. Determination of the pH during the titration was made with a Beckman Zeromatic pH meter using calomel and glass electrodes. The pK_a values were then calculated according to standard methods.[11] Several values were obtained for each acid; agreement was within ±0.05 pK_a unit. The average values appear in Tables I and III. The ionic strength was not constant during a determination and liquid junction potentials were neglected; therefore, the values are nonthermodynamic. Plots of $\log K/K_0$ against Hammett σ constants (see Figures 1 and 2) and Taft σ^0 constants were made. The slope (ρ), standard deviation (s), and the correlation coefficient (r) were calculated according to Jaffé[12] for both plots (Table II).

Phosphinic Acids.—The following general procedure was utilized to prepare the new organophosphorus-substituted diarylphosphinic acids of this study. The apparatus consisted of two reaction flasks, one atop the other, connected through a wide-bore stopcock. Both flasks were jacketed to hold a Dry Ice–acetone cooling bath and the upper flask was stirred by a mechanical stirrer while the lower was stirred by means of a magnet. The system was further pressure equalized and held under dry nitrogen. Each flask also contained a low-temperature thermometer.

The (4-lithiophenyl)diphenylphosphine (I) was formed by the controlled addition of a tetrahydrofuran solution of (4-bromophenyl)diphenylphosphine to a cold hexane solution of n-butyllithium (1:1 mole) to maintain the reaction temperature at or below −65°. After the addition was complete and a brief period at −65° (~15 min), the lithio derivative was then dropped into a tetrahydrofuran solution of the necessary amine-blocked phosphorus chloride, again at −65 to −70°. The reaction mixture was allowed to warm to ambient temperature before the solvents were removed at reduced pressure and the residue was digested with hot, concentrated hydrochloric acid (~18 hr). The oxides were prepared by hydrogen peroxide oxidation in glacial acetic. The sulfides were obtained after a brief reflux of the phosphine in toluene with 1 equiv of sulfur. Pertinent data for these acids are presented in Table V.

Organophosphorus-Substituted Benzoic Acids.—The (4-lithiophenyl)diphenylphosphine (I) was prepared as above, and carbon dioxide, either solid or gas, was introduced. The yield of 4-diphenylphosphinobenzoic acid melting at 156–157° (lit.[18] mp 156–158°) was nearly quantitative. Subsequent oxidation or sulfurization of 4-diphenylphosphinobenzoic acid, as described

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[16] R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958).

[17] R. W. Taft and J. W. Rakshys, Jr., *ibid.*, **87**, 4387 (1965).

[18] P. Schiemenz, *Ber.*, **99**, 504 (1966).

TABLE V

ORGANOPHOSPHORUS-SUBSTITUTED DIARYLPHOSPHINIC ACIDS

Compd	Yield, %	Mp, °C	Formula	Carbon, %		Hydrogen, %		Phosphorus, %		Equiv wt	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
II[a]	53	192.5–193.5	$C_{24}H_{20}O_2P_2$	71.63	71.68	5.02	4.86	15.4	15.4	402	406
III	66	258–261	$C_{36}H_{29}P_3O_2$	73.72	73.50	4.98	4.97	15.8	15.5	586.5	575
IV	54	231–232[b]	$C_{24}H_{22}O_4P_2$[b]	66.20	65.57	5.07	4.97	14.2	14.6	436	438
V	82.5	192–196	$C_{36}H_{29}O_4P_3$	69.90	69.26	4.72	4.45	15.0	14.2	619	613
VI	86	268–270	$C_{24}H_{20}O_2P_2S$	66.40	67.15	4.64	4.91	14.3	14.6	434	436
VII[c]	93	>300	$C_{36}H_{29}O_2P_3S_2$	66.45	65.88	4.49	4.40	14.3	14.4	651	636

[a] Molecular weight by vapor pressure osmometry in chloroform, 848. [b] As the monohydrate, IV changed form at 144° and melted, resolidified at 155°, and then melted sharply at 231–232°. [c] *Anal.* Calcd: S, 9.86. Found: S, 9.63.

above, gave the corresponding 4-diphenylphosphinylbenzoic acid melting at 270–272° (lit.[18] mp 273–274°) and 4-diphenylthiophosphinylbenzoic acid melting at 180–182° (lit.[18] mp 181–182°), respectively.

Reaction of (4-Diphenylphosphinophenyl)phenylphosphinic Acid (II) and Thionyl Chloride.—A mixture of 25 ml of thionyl chloride and 2.0 g (0.0050 mole) of (4-diphenylphosphinophenyl)-phenylphosphinic acid (II) was stirred overnight at ambient temperature and then at reflux for 2 hr. The reaction mixture was cooled and the excess thionyl chloride was removed *in vacuo* by means of a water aspirator to yield a yellow oil which gradually formed a hard glass. The glass was hydrolyzed with excess water to give 1.8 g of a white solid which was recrystallized from isopropyl alcohol and water. The solid melted at 145°, resolidified at 155°, and remelted at 231–233° which is characteristic of the phosphine oxide–acid, (4-diphenylphosphinylphenyl)-phenylphosphinic acid (IV), not the tertiary phosphine–acid II starting material. The phosphine II melts sharply at 192.5–193.5°. The identity of the material as the oxide was confirmed by comparison of the infrared spectra of II and IV which showed it to be the oxide IV.

Reaction of (4-Diphenylthiophosphinylphenyl)phenylphosphinic Acid (XI) and Thionyl Chloride.—In a similar manner, 2 g (0.0046 mole) of (4-diphenylthiophosphinylphenyl)phenylphosphinic acid (VI) was allowed to react with 25 ml of thionyl chloride at reflux for 6 hr. After removal of the excess thionyl chloride, the yellow oil was hydrolyzed with water. The white solids were collected to give a nearly quantitative yield of the oxide IV and not the sulfide VI as evidenced by the melting-range characteristics of the solids. The product solids liquefied at about 145°, resolidified at 155°, and remelted at 230–232°, while sulfide VI melts at 268–270°. Comparison of the infrared spectrum of the product with those of both the corresponding sulfide VI and oxide IV further confirmed the identity of the product as the oxide IV.

Registry No.—II, 13119-04-5; III, 13135-36-9; IV, 13119-05-6; V, 13119-06-7; VI, 13119-07-8; VII, 13119-08-9.

2,5-Benzodiazocines and Intermediates[1]

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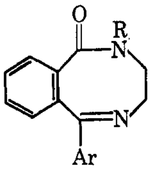
The condensation of ethylenediamines and *o*-aroylbenzoic acids has afforded a series of 9b-aryl-1,2,3,9b-tetrahydro-5H-imidazo[2,1-*a*]isoindol-5-ones (**2**). An intermediate in the condensation has been isolated and identified as an α-(2-aminoethylimino)-α-aryl-*o*-toluic acid (**5**). An acid hydrolysis product of the imidazoisoindolones, 2-(2-aminoethyl)-3-aryl-3-hydroxyphthalimidine (**6**), could not be recyclized. The lithium aluminum hydride reduction of 1-unsubstituted 9b-aryl-1,2,3,9b-tetrahydro-5H-imidazo[2,1-*a*]isoindol-5-ones in ether was shown to afford 1,2,3,4,5,6-hexahydro-2,5-benzodiazocines (**8**). One of the series, 1-(*p*-chlorophenyl)-1,2,3,4,5,6-hexahydro-2,5-benzodiazocine (**8a**), was resolved into optical isomers by means of *d*-camphorsulfonic acid.

Our interest in the pharmacological activity of medium-sized ring compounds[2] prompted us to examine the possibility of preparing some 2,5-benzodiazocines for biological evaluation. The recorded examples of this relatively unknown class of compounds are limited to several quaternary derivatives prepared from α,α'-dibromo-*o*-xylenes[3] and the tetrahydro-2,5-benzodiazocine-1,6-dione prepared from *o*-phthaloyl chloride and ethylenediamine.[4] A possible method of preparing 3,4-dihydro-2,5-benzodiazocin-1-ones (**1**) appeared to be through the condensation of an *o*-aroylbenzoic acid and ethylenediamine. This reaction of bifunctional molecules could, however, result in products other than the desired one or in a mixture of products. Other theoretically important possibilities would be the 1,2,3,9b-tetrahydro-5H-imidazo[2,1-*a*]isoindol-5-one (**2**) and the 2-(2-imidazolinyl)benzophenone (**3**).



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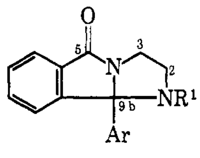

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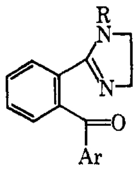

3

Reaction of *o*-(*p*-chlorobenzoyl)benzoic acid with ethylenediamine in toluene afforded a single product with the empirical formula $C_{16}H_{13}N_2ClO$, mp 165–166°. The presence of carbonyl absorption at 5.90 μ in the infrared spectrum (KBr pellet) eliminated the benzophenone (**3**, Ar = *p*-chlorophenyl; R = H) from further consideration. The nmr spectrum of the condensation product was determined in deuteriochloroform. The spectrum consisted of a broadened, single-proton peak at δ 2.18 which disappeared on deu-

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[3] (a) M. Scholtz, *Ber.*, **35**, 3047 (1902); (b) W. E. Rosen, V. P. Toohey, and A. C. Shabica, *J. Am. Chem. Soc.*, **80**, 935 (1958).

[4] H. Stetter, L. Marx-Moll, and H. Rutzen, *Ber.*, **91**, 1775 (1958).