

widths in the esr spectrum of $\text{RH}_2\cdot^-$ produced electrolytically are quite narrow even under conditions of incomplete reduction so that moderate amounts of unreduced RH_2 are also present.

One expects broad lines in the esr spectrum of a hydrocarbon anion radical when the parent hydrocarbon is also present due to reversible electron transfer between these species. If there is no special reason for the rate of this electron-transfer reaction to be especially slow in the case of 4,5-methylenepheneanthrene, then the narrow lines which are observed for the anion radical in the presence of the parent hydrocarbon may be attributed to irreversible radical decay caused by proton transfer from the hydrocarbon to the radical competing with the reversible electron-transfer process which causes line broadening.

Conclusions

It is evident from the results discussed above that conditions normally considered to be aprotic are not in reality so with respect to the reduction of 4,5-methylenepheneanthrene. When an ece-type mechanism involves a chemical product of a proton exchange with a higher electron affinity than the parent species, the proton-donor nature of the solvent, parent hydrocarbon itself, and possible hard-to-remove impurities are very important in studying the electrochemical parameters, half-wave potential, and diffusion-limiting current. The study of the 4,5-methylenepheneanthrene system showed that even under careful purification of sol-

vents to give aprotic conditions, evidence for a persistent ece mechanism is found. The reaction of the anion radical, $\text{RH}_2\cdot^-$, in both DMF and acetonitrile was found to be rapid enough to produce, even under aprotic conditions, an appreciable ece component to the over-all reaction mechanism. This fact is especially important when one is measuring a half-wave potential for the purpose of making correlations with the results of molecular orbital calculations. One of the objects of this study was to point out that if an ece mechanism occurs, the measured half-wave potential may be seriously different from that for the couple $\text{RH}_2 + e^- \rightleftharpoons \text{RH}_2\cdot^-$ needed for theoretical correlations (eq 5 and Figure 2 show that $E_{1/2}$ varies most significantly when the proton-donor concentration is small).

The problem is complicated even further when side reactions with $\text{RH}_2\cdot^-$ to form a different parallel ece reaction path other than sequence I occur, even in presumably inert solvent systems, such as DMF. The possibility of side reactions further serves to emphasize the fact that it is absolutely necessary to understand completely the total electrode process before using a polarographic parameter in a theoretical correlation.

Although the nature of the electrode processes taking place during the reduction of 4,5-methylenepheneanthrene in DMF (under both aprotic and high proton-donor concentrations) and the one wave in acetonitrile under aprotic conditions was elucidated by this study, the reaction of RH_2 in acetonitrile in the presence of high concentrations of phenol is not understood.

The Chemistry of Ylides. XVIII. A ^{19}F Nuclear Magnetic Resonance Study of Electronic Interactions in Phosphonium Salts, Ylides, and Oxides

A. William Johnson¹ and H. Lloyd Jones

Contribution from the Division of Natural Sciences, University of Saskatchewan, Regina, Canada, and the Department of Chemistry, University of North Dakota, Grand Forks, North Dakota. Received March 2, 1968

Abstract: Examination of the ^{19}F nmr spectra of the oxide, methyl salt, and ylide derivatives of tris(fluorophenyl)-phosphine has permitted an assessment of the inductive and conjugative electronic interactions by and with tetravalent phosphorus. Inductive interactions seem dominant in these systems. Conjugative ($p\pi-d\pi$) interactions of tetravalent phosphorus with an adjacent anionic center appear to rule out substantial conjugative interaction between the phosphorus and an attached aryl ring.

Although phosphonium ylides have been known for over 50 years and have been widely used in synthetic organic chemistry (*i.e.*, the Wittig reaction) for 15 years, only within the last 4 years have such ylides been subjected to physical studies in an effort to learn more of their molecular structure and electronic properties.² Our interest in the latter aspect was excited

(1) (a) Author to whom inquiries should be addressed at the University of North Dakota, Grand Forks, N. D. 58201. (b) The nomenclature used in this paper is contrary to that defined by the author in ref 2. The change was made to conform to current indexing practices of *Chemical Abstracts* and to ensure a consistent usage in journal practice.

(2) A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966, pp 7-189.

by the observation³ that triphenylphosphonium ylides ($\text{Ph}_3\text{P}=\text{CR}_2'$) were less basic and less nucleophilic than the corresponding trialkylphosphonium ylides ($\text{R}_3\text{P}=\text{CR}_2'$). It seemed to follow that there was more $p\pi-d\pi$ overlap between the carbanion and phosphorus in the former ylides, indicating that the phenyl groups on phosphorus were electron-withdrawing relative to the alkyl groups.

As a follow up to that observation, recently we have explored the effect of aryl substituents on the basicity of fluorenylidetriaryphosphoranes (I, $\text{R} = \text{C}_6\text{H}_4\text{-X}$).

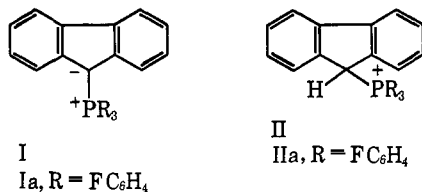
(3) A. W. Johnson and R. B. LaCount, *Tetrahedron*, **9**, 130 (1960).

Table I. Chemical Shift Parameters of Substituted Fluorobenzenes (F-C₆H₄-X) in Parts per Million

Compound	X	Solvent	\int_{H}^{m-X}	\int_{H}^{p-X}	\int_{m-X}^{p-X}
V	P(C ₆ H ₄ F) ₂	C ₆ H ₁₂	-1.24	-0.85	+0.39
IIIc	P(C ₆ H ₄ F) ₂ O	CCl ₄	-2.58	-6.04	-3.46
IIIa	+P(C ₆ H ₄ F) ₂ CH ₃	CH ₂ Cl ₂	-2.47	-6.78	-4.31
		DMSO	-3.97	-10.52	-6.55
		TFA	-8.40	-16.05	-7.65
IIIId (IIa)	+P(C ₆ H ₄ F) ₂ C ₁₃ H ₉	DMSO	-4.0 ^a	-10.5 ^a	-6.5 ^a
		TFA	-8.40	-15.97	-7.57
IIIb	+P(C ₆ H ₄ F) ₂ CH ₂ ⁻	DMSO	-1.47	-4.86	-3.39
IIIe (Ia)	+P(C ₆ H ₄ F) ₂ C ₁₃ H ₉ ⁻	DMSO	-3.40	-7.72	-4.32
IVc ^b	P(C ₆ H ₅) ₂ O	CCl ₄	-1.56	-5.01	-3.45
		DMSO	-1.76	-5.13	-3.37
IVa ^b	+P(C ₆ H ₅) ₂ CH ₃	DMSO	-3.63	-10.32	-6.69
		TFA	-7.49	-14.97	-7.48
		DMSO	-2.46	-8.46	-6.00
VI ^b	+P(CH ₃) ₃	DMSO	-2.46	-8.46	-6.00
		TFA	-7.12	-14.21	-7.09
IVb ^b	+P(C ₆ H ₅) ₂ CH ₂ ⁻	DMSO	-1.95	-5.35	-3.40

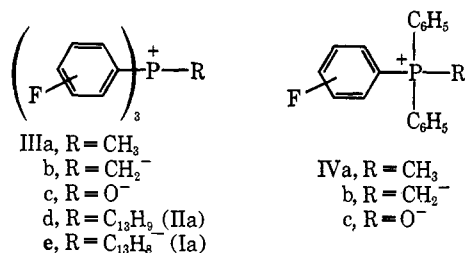
^a By extrapolation from the data observed for IIIa (*i.e.*, the TFA values are almost identical). ^b Compounds and data kindly provided by Professor Taft.^{7,9}

In this work it was found that linear correlations of ylide basicity with substituent constants for the groups X were obtained without the use of "exalted" sub-



stituent constants.⁴ On this basis we concluded that the P-phenyl groups were interacting with the phosphorus atom mainly by an inductive mechanism. In other words, in the phosphonium ylides there appeared to be relatively little conjugative ($p\pi-d\pi$) interaction between the aryl group and the quaternary phosphorus. This in spite of the fact that there must be substantial $p\pi-d\pi$ overlap between the carbanion and phosphorus.² The same conclusions were reached as a result of our studies on the reactions and physical properties of the analogous iminophosphoranes ($\text{Ar}_3\text{P}=\text{N}-\text{Ar}$)⁵ and studies of the basicities of a wider series of "onium ylides."⁶

We wish to report the use of ¹⁹F nmr spectroscopy as a probe for further study of the electronic interactions between a phenyl ring and a tetravalent phosphorus atom in compounds of type III. In a companion publication, Rakshys, Taft, and Sheppard have reported a similar study of compounds of type IV.⁷



(4) A. W. Johnson, S. Y. Lee, R. A. Swor, and L. D. Royer, *J. Amer. Chem. Soc.*, **88**, 1953 (1966).

(5) A. W. Johnson and S. C. K. Wong, *Can. J. Chem.*, **44**, 2793 (1966).

(6) A. W. Johnson and R. T. Amel, *ibid.*, **46**, 461 (1968).

(7) J. W. Rakshys, R. W. Taft, and W. A. Sheppard, *J. Amer. Chem. Soc.*, **90**, 5236 (1968).

Taft and his coworkers⁸ have demonstrated the extreme sensitivity of ¹⁹F shielding to intramolecular perturbations by ring substituents in fluorobenzenes. In addition, they have developed precise linear relationships from the ¹⁹F shielding parameters which permit the isolation of inductive (σ_I) and conjugative (σ_R) effects based on eq 1 and 2, where \int_{H}^{m-X} and \int_{H}^{p-X} are the ¹⁹F chemical shifts in parts per million of the *meta*- and *para*-substituted fluorobenzenes (F-C₆H₄-X) relative to fluorobenzene and \int_{m-X}^{p-X} is the difference between the two.

$$\int_{\text{H}}^{m-X} = -7.10\sigma_I + 0.60 \quad (1)$$

$$\int_{m-X}^{p-X} = -29.5\sigma_R \quad (2)$$

Results

We have prepared the *meta* and *para* isomers of the following compounds: tris(fluorophenyl)phosphine (V), tris(fluorophenyl)phosphine oxide (IIIc), tris(fluorophenyl)methylphosphonium iodide (IIIa), tris(fluorophenyl)-9-fluorenylphosphonium bromide (IIIId), methylenetris(fluorophenyl)phosphorane (IIIb), 9-fluorenylidene-tris(fluorophenyl)phosphorane (IIIe). We were able to isolate, purify, and characterize all compounds except the methylenephosphorane (IIIb). The latter was generated in solution from IIIa using dimethylsodium. The ¹⁹F measurements were performed by Taft and Rakshys at the University of California, Irvine, Calif., using techniques they have previously developed and published.⁷ In Table I are presented the chemical shift results for the above compounds. Included are data on the related derivatives of *p*-fluorophenyldiphenylphosphine [the methyl salt (IVa), the methylene (IVb), and the oxide (IVc)] as

(8) (a) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 709 (1963); (b) *ibid.*, **85**, 3146 (1963); (c) R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960); (d) F. Prosser and L. Goodman, *J. Chem. Phys.*, **38**, 373 (1963); (e) R. W. Taft, F. Prosser, and L. Goodman, *ibid.*, **38**, 380 (1963).

well as for trimethyl(*p*-fluorophenyl)phosphonium tetrafluoroborate (VI).⁹

In Table II are reported the σ values for the substituents X on F-C₆H₄-X. These values were calculated from the data in Table I using eq 1 and 2.

Table II. Substituent Constants of Organophosphorus Groups (X) in X-Fluorobenzene (R = C₆H₄F and R' = C₆H₅)

X	Compd	Solvent	σ_I	σ_R	σ_p^a
PR ₂	V	C ₆ H ₁₂	+0.26	-0.01	+0.25
PR ₂ '	...	C ₆ H ₁₂	+0.17	-0.01	+0.16
PR ₂ O	IIIc	CCl ₄	+0.45	+0.12	+0.57
PR ₂ 'O	IVc	CCl ₄	+0.30	+0.12	+0.42
		DMSO	+0.33	+0.17	+0.50
+PR ₂ CH ₃	IIIa	DMSO	+0.65	+0.22	+0.87
		TFA	+1.27	+0.26	+1.53
+PR ₂ 'CH ₃	IVa	DMSO	+0.60	+0.23	+0.83
		TFA	+1.14	+0.25	+1.39
+P(CH ₃) ₃	VI	DMSO	+0.43	+0.20	+0.63
		TFA	+1.09	+0.24	+1.33
+PR ₂ C ₁₈ H ₉	IIIId (IIa)	DMSO	+0.65	+0.22	+0.87
		TFA	+1.27	+0.26	+1.53
+PR ₂ CH ₂ ⁻	IIIb	DMSO	+0.29	+0.12	+0.41
+PR ₂ 'CH ₂ ⁻	IVb	DMSO	+0.36	+0.18	+0.54
+PR ₂ C ₁₈ H ₉ ⁻	IIIe (Ia)	DMSO	+0.56	+0.15	+0.71

$$^a \sigma_p = \sigma_R + \sigma_I.$$

Discussion

As expected, in all instances where tetravalent phosphorus was attached to the fluorobenzene ring the fluorine was strongly deshielded as reflected by the

negative \int_H^{m-X} values. In other words, the phosphorus-containing groups in phosphine oxides, phosphonium salts, and phosphonium ylides all are highly electronegative as represented by their positive σ_I values. The phosphonium salts exhibited significantly larger inductive effects than did the oxides or ylides, undoubtedly due to the larger net positive charge on phosphorus in the salts. In the oxides and ylides both coulombic effects and conjugative effects ($p\pi-d\pi$ overlap from the adjacent oxyanion or carbanion; see below) contributed to a lowering of the net positive charge on phosphorus.

In a molecular system such as F-C₆H₄P⁺ the nature of the remaining substituents on phosphorus has considerable influence on the total electronic effect exerted by the phosphonium group on the fluorobenzene ring. For example, comparison of the σ_I values of the salts IIIa, IVa, and VI reveals that replacement of methyl by phenyl and of phenyl by fluorophenyl leads to an increase in the electron-withdrawing power of the entire group. Similarly, in the phosphine oxides (*i.e.* a case where there is competitive back-bonding) replacement of phenyl groups by fluorophenyl groups (*i.e.*, IVc to IIIc) also leads to an increase in the σ_I value. The fact that the σ_I values of the entire groups were increased implies that the net positive charge on phosphorus was increased by the structural change in each instance. This evidence provides yet an additional example of an aryl group attached to a cationic phosphorus atom exerting a stronger net withdrawal effect than a methyl group, presumably the result of a dominant inductive interaction and a diminished conjugative

(9) These data were kindly provided by R. W. Taft, private communication.

interaction between the aryl ring and tetravalent phosphorus.

A substantial solvent effect was present in the shielding parameters of the phosphonium salts. The lower inductive effect (σ_I) of the phosphonium group in dimethyl sulfoxide solution may be due to a complexation between the oxygen anionic site of the solvent and the phosphorus cationic site of the solute decreasing the net positive charge on phosphorus. The direction of the solvent effect on σ_R was the same as for σ_I but the magnitude and ratio of the effect was much smaller. The explanation for this decrease is not apparent.

The \int_{m-X}^{p-X} shielding parameter was negative for all of the tetravalent phosphorus derivatives, oxides, salts, and ylides, indicating that the phosphorus-containing groups also were electron withdrawing by a conjugative mechanism. Accordingly, the resonance parameter (σ_R) was positive. The conjugative electron acceptance by tetravalent phosphorus necessitates the use of vacant, low-energy 3d orbitals of phosphorus in $p\pi-d\pi$ overlap.^{7,10} In this instance, such overlap is from the fluorobenzene ring to phosphorus, a kind of overlap previously claimed to be relatively insignificant.¹¹ Indeed, the inductive effect of the phosphorus group was severalfold more powerful than the conjugative effect. In most instances, the larger the σ_I value the larger was the σ_R value. This observation is consistent with our previous observations⁴ and with the theory of Craig and Magnusson¹² claiming that phosphorus should be a better π acceptor when it carries a larger net positive charge (*i.e.*, substituents with larger σ_I values).

Comparison of the σ_I and σ_R values for the phosphonium salts (IIIa, IIIId, IVa, VI) in TFA with the values for the *p*-fluorophenyldiphenylcarbonium ion in TFA⁹ indicates clearly that while the inductive effect (σ_I) of a phosphonium group is greater than that of a carbonium group, the π effect (σ_R) of the phosphonium group is significantly smaller. This observation clearly

FC ₆ H ₄ +P(Ar) ₂ CH ₃	+1.09	-1.27	+0.24	-0.26	+1.33	-1.53
FC ₆ H ₄ +C(Ar) ₂	+1.04		+0.88		+1.92	

indicates that there is a diminished conjugative interaction between an aryl ring and a tetravalent phosphorus. This conclusion is consistent with our prior observations that "exalted" σ constants do not provide satisfactory correlations in studies of P⁺-C₆H₄-X systems,⁴ indicating thereby that an inductive interaction dominates.

The σ_p values are in general accord with the few values already reported. The value for P(O)(C₆H₄F)₂ has been reported to be +0.64¹³ compared to our value of +0.57. That for P(O)(C₆H₅)₂ has been reported to range from +0.44 to +0.59¹⁴ while the data calculated from the data of Rakshys and Taft^{7,9} ranges from

(10) R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 59-85.

(11) H. H. Jaffé, *J. Chem. Phys.*, **22**, 1430 (1954).

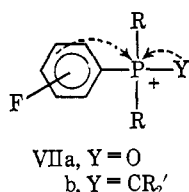
(12) D. P. Craig and E. A. Magnusson, *J. Chem. Soc.*, 4895 (1956).

(13) H. Schindlbaur, *Chem. Ber.*, **100**, 3432 (1967).

(14) (a) G. P. Schiemenz, *Tetrahedron Lett.*, 3023 (1964), *Angew. Chem. Intern. Ed. Engl.*, **5**, 595 (1966); (b) H. L. Retcofsky and C. E. Griffin, *Tetrahedron Lett.*, 1975 (1966); (c) J. J. Monagle, J. V. Mengenhauser, and D. A. Jones, Jr., *J. Org. Chem.*, **32**, 2477 (1967); (d) R. A. Baldwin, M. T. Cheng, and G. D. Homer, *ibid.*, **32**, 2176 (1967).

+0.42 to +0.50. Bott, *et al.*,¹⁵ reported a σ^- value of +1.14 for $^+P(CH_3)_3$ and Schiemenz^{14a} reported a σ value of +1.01 for $^+P(C_6H_5)_2CH_3$. The two values calculated from ^{19}F nmr data^{7,9} bracket the reported values.

Comparison of the effect of replacing a phenyl group by a fluorophenyl group in phosphonium salts, ylides, and oxides indicates the role of $p\pi-d\pi$ bonding between the phosphorus atom and an oxyanion or carbanion. In both the oxides (IVc to IIIc) and the salts (IVa to IIIa) such a replacement led to an increase in σ_I and little or no change in σ_R . In the ylide series (IVb to IIb), however, the same structural change led to a decrease in both σ_I and σ_R . These observations can be accounted for on the basis of a model such as VII. It would appear that an increase in the electro-



negativity of the groups R in the phosphonium salts (IVa to IIIa) increases the net positive charge on phosphorus, thereby increasing the inductive effect (σ_I) exerted by the entire phosphorus group on the phenyl ring. In the phosphine oxides (VIIa) the analogous structural change (R = phenyl to R = fluorophenyl) also leads to an increase in the positive charge on phosphorus. However, in the oxides the net charge is lower than for the salts due to the coulombic or back-bonding effect of the oxyanion. This observation is consistent with available ^{31}P nmr data.^{16,17} Since σ_R is lower for the oxides than for the salts it would appear that P-O multiple bonding competes with and decreases the extent of P-phenyl multiple bonding. The fact that σ_R is not affected by the change of R = phenyl to R = fluorophenyl in VIIa seems to imply that the extent of P-O multiple bonding remains approximately constant (*i.e.*, the multiple bond is not too polarizable).

The case of the two ylides (VIIb), however, seems quite different. First of all, from the small σ_I values it is clear that there is a relatively low net positive charge on phosphorus in the methyldes (IVb, IIb). Most significantly, however, it appears that an increase in the electronegativity of R (VIIb), and thereby an increase in the effective net positive charge on phosphorus, leads to an increase in the $p\pi-d\pi$ overlap between the carbanion and phosphorus rather than an increase in the σ_I or σ_R values. An increase in such overlap would be expected to lower the net positive charge on phosphorus, thereby leading to a decrease in both the σ_I and σ_R values for the entire phosphorus-containing group. Such a state of affairs implies that the $p\pi-d\pi$ overlap in the ylide bond (P^+-C^-) is considerably more susceptible to the effect (mainly inductive) of the substituents on phosphorus than is the P-phenyl bond. This seems a not unreasonable conclusion and is sub-

stantiated by the very large ρ values obtained from correlations of ylide basicity.⁴

Comparison of the σ values for the ylides IIIb and IIIc (Ia) also reveals the sensitivity of the ylide bond to structural changes. That there is considerable $p\pi-d\pi$ overlap between the carbanion and phosphorus atom in the methyldes (IIIb) is evident by the small σ_I and σ_R values which reflect a low net positive charge on phosphorus. Replacement of the methyldes group by the fluorenylide group would be expected to result in less $p\pi-d\pi$ overlap between phosphorus and the carbanion since there should be extensive delocalization of electron density through the fluorenyl ring.⁴ The result should be a higher net positive charge on phosphorus. This appears to be the case in view of the increased σ_I and σ_R values of the entire phosphorus-containing group.

In summary, the results of this work seem to suggest the following conclusions: (a) R_3P^+ groups exert both inductive and conjugative withdrawal effects on aryl rings; (b) in the general relationship $\sigma_p = a\sigma_I + b\sigma_R$ as applied to an $X-C_6H_4P^+$ system, a is larger than b (*i.e.*, there is relatively little conjugative interaction between phenyl and tetravalent phosphorus); (c) substantial changes in the σ_I values of tetravalent phosphorus-containing groups create only minor changes in the σ_R values of the same groups; (d) the extent of $p\pi-d\pi$ overlap in the ylide bond is very sensitive to the influence of substituents and, in turn, markedly affects the substituent effect (σ value) of the phosphorus; (e) substantial conjugative interaction of tetravalent phosphorus with an adjacent carbanion or oxyanion rules out simultaneous substantial conjugative interaction between the phosphorus and an attached aryl group (*i.e.*, the 3d orbital geometry in tetravalent phosphorus is such that only one strong conjugative interaction is possible).

Experimental Section

General. Melting points are uncorrected. Analyses were by Alfred Bernhardt Microanalytical Laboratory, Mulheim (Ruhr), Germany. ^{19}F nmr spectra were recorded in the solvents indicated in Table I and according to the procedure outlined in ref 7. The isomeric bromofluorobenzenes were obtained from Pierce Chemical Co.

Tris(fluorophenyl)phosphines (V). To a stirred slurry of 1.68 g (69.1 g-atoms) of magnesium in 10 ml of THF (tetrahydrofuran) held at 25° under nitrogen was added a solution of 12.0 g (68.5 mmol) of *p*-bromofluorobenzene in 100 ml of THF. After stirring at room temperature for 2 hr the solution was cooled to -80° then a solution of 2.35 g (17.1 mmol) of PCl_3 in 50 ml of THF was added slowly. After stirring at room temperature for 3 hr the solution was quenched with 50 ml of 20% ammonium chloride solution then with 50 ml of water. The THF was removed by evaporation after which the aqueous solution was extracted with ether. The ether extracts were dried and the solvent removed to afford 3.3 g (61%) of crude tris(*p*-fluorophenyl)phosphine which was recrystallized from methanol as colorless needles, mp 80-81°.

Anal. Calcd for $C_{18}H_{12}F_3P$: C, 68.34; H, 3.83; F, 18.03; P, 9.80. Found: C, 68.35; H, 3.93; F, 18.21; P, 9.91.

Tris(*m*-fluorophenyl)phosphine was prepared in an identical manner from *m*-bromofluorobenzene. It crystallized from methanol as colorless prisms, mp 63-64°.

Anal. Calcd for $C_{18}H_{12}F_3P$: C, 68.34; H, 3.83; F, 18.03; P, 9.80. Found: C, 68.52; H, 3.84; F, 17.82; P, 10.50.

Tris(fluorophenyl)phosphine Oxides (IIIc). To a solution of 0.5 g of phosphine (V) in 20 ml of acetone was added 1 ml of 30% hydrogen peroxide. After heating under reflux for 1 hr 50 ml of water was added and the solution extracted with benzene. After washing with ferrous ammonium sulfate solution and drying the

(15) R. W. Bott, B. F. Dowden, and C. Eaborn, *J. Chem. Soc.*, 4994 (1965).

(16) M. Grayson and P. T. Keough, *J. Amer. Chem. Soc.*, **82**, 3919 (1960).

(17) S. O. Grim, W. McFarlane, and T. J. Marks, *Chem. Commun.*, 1191 (1967).

benzene layer, the solvent was evaporated to afford the crude oxide. The oxides crystallized from hexane, the *para* isomer as colorless needles, mp 122–123°, and the *meta* isomer as colorless needles, mp 101.5–103°.

Tris(fluorophenyl)methylphosphonium Iodide (IIIa). A sample of the phosphine in acetonitrile was heated under reflux overnight with excess methyl iodide. Removal of the solvent and methyl iodide left the crude salt which crystallized from ethanol-ether as colorless microcrystals, mp 306–307° (*para* isomer) and mp 212–213° (*meta* isomer).

Tris(fluorophenyl)-9-fluorenylphosphonium Bromide (IIIc). Equimolar quantities of the phosphine and 9-bromofluorene in acetonitrile solution were heated under reflux overnight. Removal of the solvent and crystallization of the solid residue from ethanol-ether afforded the pure colorless salts, mp 276–277° (*para* isomer) and mp 249–251° (*meta* isomer).

9-Fluorenylidene-tris(fluorophenyl)phosphoranes (IIIe). The salts (IIIc) were dissolved in ethanol then a few milliliters of 5% aqueous sodium hydroxide were added slowly. An immediate yellow pre-

cipitate formed which was filtered, washed with water then dried. The *para* isomer was recrystallized from benzene-hexane as fine yellow needles, mp 254–255°.

Anal. Calcd for $C_{31}H_{20}F_3P$: C, 77.48; H, 4.20; P, 6.45. Found: C, 77.90; H, 4.24; P, 6.40.

The *meta* isomer was recrystallized from benzene-hexane as thick yellow-orange needles, mp 194–195°.

Anal. Calcd for $C_{31}H_{20}F_3P$: C, 77.48; H, 4.20; P, 6.45. Found: C, 78.35; H, 4.52; P, 6.22.

Acknowledgment. We gratefully acknowledge the cooperation of Professor Taft and Dr. Rakshys in obtaining all of the ^{19}F nmr data and for continuing to communicate their results. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Research Council of Canada, for the support of this research.

The Electronic Properties of Tri-, Tetra-, and Pentacoordinate Phosphorus Substituents¹

J. W. Rakshys,² R. W. Taft, and W. A. Sheppard³

Contribution from the Department of Chemistry, University of California, Irvine, California 92664, and the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19808. Received April 5, 1968

Abstract: Fluorine nuclear magnetic resonance shifts (and derived σ values) have been obtained for the families *m*- and *p*- $FC_6H_4PX_2$, *m*- and *p*- $FC_6H_4P(C_6H_5)_2X$, and *m*- and *p*- $FC_6H_4PF_4$. The effects of substitution at phosphorus can be described by the polar and resonance substituent parameters, σ_I and σ_R^0 . The results provide evidence of π acceptor orbitals on phosphorus in all families, in accord with proposed $\pi(p-d) C_{ar}-P=X$ interactions.

Substituent effects on chemical and physical properties have been treated in a number of aromatic systems as additive blends of polar (inductive) and π delocalization (resonance) effects.^{4–6} The polar effect is considered to arise as the consequence of the net polarization of the reaction (or detection) center by an interaction mechanism which does not require delocalization (transfer) of π charge between the substituent and the aromatic nucleus. The polar effect is characterized by the substituent parameter, σ_I , which is based upon polar effects measured at saturated carbon where, presumably, little or no transfer of π charge can occur.⁴

The π delocalization effect is considered to arise as the consequence of the effective polarization of the reaction (or detection) center which results from the transfer of π charge between substituent and the aromatic nucleus. The π delocalization effect is characteristic of the substituent but may also depend upon the nature of the aromatic or conjugating system. The substituent parameter σ_R^0 measures the π delocalization effect in systems in which the reaction center is effectively insulated from the aromatic nucleus.⁷ Other scales of the π delocalization effect, which are limited by reaction type, include⁸ $\sigma_R \equiv \sigma_p - \sigma_I$; $\sigma_{R^+} \equiv \sigma_p^+ - \sigma_I$; and $\sigma_{R^-} \equiv \sigma_p^- - \sigma_I$.

These various substituent parameter scales are all based upon substitution at carbon. A critical test of the generality of the parameters and the treatment is provided by application to substitution at other atoms. In this paper the second row element phosphorus has been chosen to provide such a test. Evidence is obtained for the nature of the charge distribution which is associated with bonding at the phosphorus atom.

The effect of *meta* and *para* substituents on fluorine nuclear magnetic resonance (^{19}F nmr) shielding in

(1) This work was supported in part by the National Science Foundation. Grateful acknowledgment is made to the National Science Foundation for the support which made available the nmr spectrometer to the U.C.I. Chemistry Department.

(2) (a) Taken in part from the Ph.D. Thesis of J. W. Rakshys, University of California, Irvine, Calif., June 1967; (b) National Science Foundation Cooperative Graduate Fellow, 1965–1967.

(3) Central Research Department, Contribution No. 1442.

(4) (a) R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13; (b) R. W. Taft, *J. Amer. Chem. Soc.*, **79**, 1045 (1957); (c) R. W. Taft and I. C. Lewis, *ibid.*, **81**, 5343 (1959); (d) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 709 (1963); (e) P. R. Wells, S. Ehrenson, and R. W. Taft, *Progr. Phys. Org. Chem.*, in press.

(5) S. Ehrenson, *Tetrahedron Lett.*, **7**, 351 (1964).

(6) D. R. Eaton and W. A. Sheppard, *J. Amer. Chem. Soc.*, **85**, 1310 (1963).

(7) R. W. Taft, S. Ehrenson, I. C. Lewis, and R. E. Glick, *ibid.*, **81**, 5352 (1959).

(8) R. W. Taft, N. C. Deno, and P. S. Skell, *Ann. Rev. Phys. Chem.*, **9**, 287 (1958).