

However, the lack of agreement between the observed and computed polarization of the B band in *trans*-azobenzene is disturbing. Implicit in the computation scheme is, in addition to the assumptions that the mathematical model is adequate and the semiempirical parameters well chosen, the assumption that configuration interaction has been included to a sufficient extent. In choosing as sufficient all configurations mono-excited with respect to the ground-state configuration, it has been pointed out by Hoyland and Goodman<sup>24</sup> that electron correlation effects are introduced to a different degree in the resulting total wave functions for ground and excited states. In unfavorable cases this may result in considerable inaccuracy in the computed transition energies, and is quite probably the

(24) L. Goodman and J. R. Hoyland, *J. Chem. Phys.*, **39**, 1068 (1965).

cause of the inordinately low value for the lowest excited triplet state of *trans*-azobenzene. The influence of such effects in the singlet states is less clear, and the extent to which this may influence the composition of excited states involved in transitions assigned to the B and C bands and their computed polarizations is currently under consideration and will be the subject of a forthcoming paper.

**Acknowledgments.** The authors are pleased to acknowledge discussions with Dr. M. B. Robin, Dr. S. Bratož, and Professor Lionel Goodman. Computer facilities were provided by the University of Cincinnati Computer Center under National Science Foundation Grant No. G 19281 and the Institute Blaise Pascal of the Centre Nationale de la Recherche Scientifique, Paris.

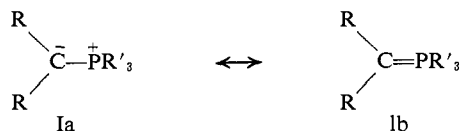
## Chemistry of Ylids. XIII. Electronic Effects in Phosponium Ylids<sup>1a</sup>

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**Abstract:** A series of substituted 9-fluorenyltriphenylphosphonium bromides (II) and another of 9-fluorenyltriphenylphosphonium bromides (IV) substituted on the phenyl group have been prepared and converted to the corresponding fluorenylidene phosphoranes. The acidities of the two series of phosphonium salts followed a linear correlation with Taft's  $\sigma^0$  and Hammett's  $\sigma$  constants with  $\rho$  values of +5.0 and +4.8, respectively. The basicity of the corresponding phosphonium ylids apparently was decreased by electron-withdrawing substituents on the carbanion or phosphonium portions of the molecule. The basicity of an ylid appears inversely proportional to the amount of  $\rho\pi$ - $d\pi$  double bonding between the phosphorus and the carbanion. Substituents other than the carbanion appear to interact with the phosphorus atom by both  $\sigma$ - and  $\pi$ -inductive mechanisms but not by a resonance mechanism.

Phosponium ylids (I) are of considerable importance in synthetic chemistry, mainly due to their use in the Wittig synthesis of olefins.<sup>2</sup> However, little quantitative data on the physical and chemical properties of phosphonium ylids has been obtained to date. We are especially interested in the nature of the ylid bond between the phosphonium atom and the carbanion and the transmission of electronic effects to and through this bond. We report herein a quantitative study of the effect of substituents at the carbanion end



(1) (a) Paper XII: A. W. Johnson and V. L. Kyllingstad, *J. Org. Chem.*, **31**, 334 (1966); (b) author to whom inquiries should be addressed at Division of Natural Sciences, University of Saskatchewan, Regina, Saskatchewan, Canada; (c) Postdoctoral Research Associate 1964-1965; (d) taken in part from the theses of R. A. S. and L. D. R. presented to the graduate school of the University of North Dakota in partial fulfillment of the requirements for the degree of Master of Science in Jan 1965 and Aug 1962, respectively.

(2) U. Schollkopf in "Newer Methods of Preparative Organic Chemistry," Vol. 3, W. Foerst, Ed., Academic Press Inc., New York, N. Y., 1964, pp 111-150; A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966, pp 132-192.

and the phosphorus end on the nature of this bond. Our physical probe for this study was a determination of the acidity of the ylid conjugate acids (II and IV).

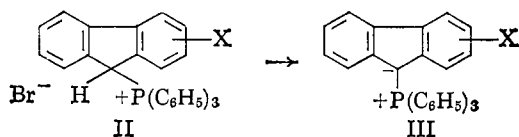
There has been only one quantitative correlation of ylid basicity with carbanion substituents although many qualitative observations have been reported. For example, fluorenylidene triphenylphosphorane (IIIa) was stable in aqueous media while methylenetriphenylphosphorane (I, R = H, R' = C<sub>6</sub>H<sub>5</sub>) reacted rapidly with water,<sup>3</sup> the difference presumably due to the decreased basicity of the fluorenyl carbanion in the former. Bestmann<sup>4</sup> studied the acid-base equilibria between phosphonium ylids and their conjugate acids and found that the ylid with the more powerful electron-attracting groups on the carbanion portion dominated the equilibrium mixture. Fliszar, *et al.*,<sup>5</sup> and Speziale and Ratts<sup>6</sup> reported the  $pK_a$ 's of the conjugate acids of acylphosphonium ylids, RCOCH=C(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>. In the work of the latter group any exact

(3) A. Wm. Johnson, *J. Org. Chem.*, **24**, 282 (1959).

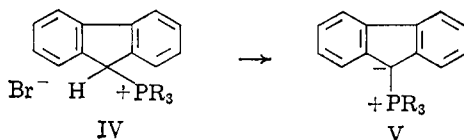
(4) H. J. Bestmann, *Chem. Ber.*, **95**, 58 (1962).

(5) S. Fliszar, R. F. Hudson, and G. Salvadori, *Helv. Chim. Acta*, **46**, 1580 (1963).

(6) A. J. Speziale and K. W. Ratts, *J. Am. Chem. Soc.*, **85**, 2790 (1963).

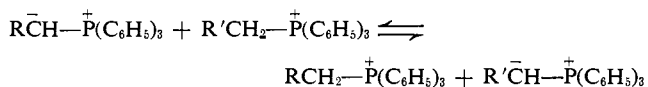


- a, X = 2-H  
 b, X = 2-CH<sub>3</sub>O  
 c, X = 2-NO<sub>2</sub>  
 d, X = 2-Br  
 e, X = 3-Br  
 f, X = 2-NHAc  
 g, X = 2-CN  
 h, X = 2-CH<sub>3</sub>



- a, R = C<sub>4</sub>H<sub>9</sub>  
 b, R = *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>  
 c, R = *m*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>  
 d, R = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>  
 e, R = *m*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>  
 f, R = *p*-ClC<sub>6</sub>H<sub>4</sub>  
 g, R = *p*-BrC<sub>6</sub>H<sub>4</sub>

interpretations were clouded by the mixing of steric and electronic effects, but it was clear again that electron-attracting substituents (R) lowered the basicity of the ylid. From the acidity data of Fliszar, *et al.*,<sup>5</sup> on three acyl ylids where R = *p*-XC<sub>6</sub>H<sub>4</sub> a  $\rho$  value can be



calculated to be +2.3. However, this is not a direct measure of the stabilizing effect of carbanion substituents since X is not in direct conjugation with the carbanion.

The most interesting and least studied feature of ylid structure is the effect of the phosphorus substituents (R' in I) on the nature of the ylid bond and carbanion basicity. In 1960 we<sup>7</sup> observed that in the fluorenylidene phosphorane series the tri-*n*-butyl derivative (Va) was more basic than the triphenyl derivative (IIIa) and proposed that in such situations the phosphorus substituents interacted with the phosphorus atom only by inductive mechanisms. In agreement with the qualitative observation Trippett and Walker,<sup>8</sup> Heitman, *et al.*,<sup>9</sup> and Bestmann and Kratzer<sup>10</sup> all subsequently claimed trialkylphosphonium ylids to be more nucleophilic than the triphenyl analogs. There have been no quantitative studies or correlations of ylid basicity with structure of the phosphonium group. This perhaps is the most interesting feature of ylid chemistry since although the favored electronic interaction should be electron donation from substituent to phosphorus, the latter has all but the 3d orbitals filled. Accordingly, a study of phosphonium ylid basicity is one of the few ways to quantitatively examine electronic interactions with d orbitals in an organic framework, specifically the

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

(8) S. Trippett and D. M. Walker, *J. Chem. Soc.*, 1266 (1961).

(9) H. Heitman, J. H. S. Wieland, and H. O. Huisman, *Chem. Abstr.*, **55**, 17562 (1961).

(10) H. J. Bestmann and O. Kratzer, *Chem. Ber.*, **95**, 1894 (1962).

importance of structure Ib to the resonance hybrid ylid structure.

## Results

The hydrobromides (II and IV) of two series of phosphoniumfluorenylides (III and V) were prepared. Those of general structure II were prepared by alkylation of triphenylphosphine with the appropriate substituted 9-bromofluorene. Those hydrobromides (IV) derived from ylids of general structure V were prepared by alkylation of the appropriate tertiary phosphine with 9-bromofluorene. The properties of the phosphonium salts and the corresponding ylids are listed in Tables I and II.

The  $pK_a$ 's of the phosphonium salts were determined in 95% ethanol solution by the spectrophotometric method of Hammett, *et al.*,<sup>11</sup> using a Beckmann DU spectrophotometer. The values were checked by using more than one buffer solution. The average deviation was  $\pm 0.03$   $pK_a$  unit. The  $pK_a$ 's also are listed in Tables I and II.

The acidities of the conjugate acids of structure II were correlated by a plot of  $\log K/K_0$  vs.  $\sigma^0$  where  $K_0$  was the dissociation constant of IIa and  $\sigma^0$  was the "normal substituent constant".<sup>12</sup> The  $\rho$  value for this plot was +5.0 (Figure 1). The acidities of the conjugate acids of structure IV were correlated by a plot of  $\log K/K_0$  vs.  $\sigma$  giving a  $\rho$  value of +4.8 (Figure 2). Attempts to effect correlations with  $\sigma^+$  or  $\sigma^-$  led to serious deviations in both instances.

The series of buffers of apparent pH 4.86 to 9.64 were prepared in 95% ethanol solution but according to the directions pertaining to aqueous media. As a result, the pH values determined by the pH meter differed from those expected for aqueous solution, undoubtedly due to the effect of the nonaqueous solvent on the glass electrode. Accordingly, the  $pK_a$  values determined for the phosphonium salts are only relative and cannot be compared to values in aqueous media. However, these values do appear internally consistent since they were checked with more than one buffer.

## Discussion

The use of 2- and 3-substituted fluorenyl groups and *meta*- and *para*-substituted phenyl groups for the examination of substituent effects should have precluded the interference of steric effects. The observed substituent effects should be purely electronic effects.

**Effect of Carbanion Substituents.** As indicated in Figure 1 the acidities of the substituted fluorenyltriphenylphosphonium salts (II) correlated reasonably well with  $\sigma^0$ , the "normal substituent constant".<sup>12</sup> This is equivalent to saying that the ylid basicities also correlated. The fact that the  $\rho$  value was positive indicated that the ylids were stabilized by electron-withdrawing groups on the fluorenyl portion, presumably by delocalization of the carbanion electrons through the fluorenyl ring to the substituents.

The magnitude of the  $\rho$  value (+5.0) deserves comment. In the phosphonium salt series (II) replacement of a 2-methoxy group by a 2-nitro group resulted in a  $pK_a$  change of 3.73 units. In the phenol series, a

(11) L. A. Flexser, L. P. Hammett, and A. Dingwall, *J. Am. Chem. Soc.*, **57**, 2103 (1935).

(12) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

**Table I.** Properties of X-Fluorenyltriphenylphosphonium Bromides (II) and the Corresponding Ylids (III)

Substituent	Phosphonium salt (II)								Phosphonium ylid (III)							pK <sub>a</sub>	
	Mp, °C	% obsd				% calcd				Mp, °C	% obsd			% calcd			
		C	H	P	Br	C	H	P	Br		C	H	P	C	H	P	
2-H	289-291	...	...	...	...	...	...	...	...	258-260	87.68	5.39	7.30	87.28	5.44	7.26	8.99
2-OCH <sub>3</sub>	265-266	...	...	...	...	...	...	...	...	253-255	84.10	5.61	6.61	84.19	5.52	6.79	9.09
2-NO <sub>2</sub>	281-282 dec	...	...	...	...	...	...	...	...	276-277	78.85	4.79	3.09	78.97	4.70	2.97	5.36
2-Br	264-265	...	...	...	...	...	...	...	...	262-263	73.46	4.47	6.00	73.67	4.39	6.13	7.33
3-Br	261-262	63.81	4.02	5.34	26.93	63.50	3.95	5.29	27.26	243-244	...	...	...	...	...	...	7.53
2-HNac	264-266	69.55	5.44	5.34	13.94	70.21	4.82	5.49	14.16	283-285	...	...	...	...	...	...	9.25
2-CN	279-280d	71.98	4.74	5.79	14.84	72.19	4.35	5.82	15.01	280 dec	...	...	...	...	...	...	5.81
2-CH <sub>3</sub>	254-256d	73.63	5.07	5.91	15.52	73.70	5.03	5.94	15.33	251-253	...	...	...	...	...	...	9.38

**Table II.** Properties of Fluorenyl(tri-R)phosphonium Bromides (IV) and the Corresponding Ylids (V)

R	Mp, °C		Compd	Anal, %				pK <sub>a</sub>
	IV	V		% obsd		% calcd		
				C	H	C	H	
C <sub>6</sub> H <sub>9</sub>	194-195	123-124	IV	67.19	8.18	67.11	8.11	10.53
C <sub>6</sub> H <sub>5</sub>	289-291	258-260	V	87.68	5.39	87.28	5.44	8.99
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	232-233	255-256	V	79.16	5.53	79.04	5.67	10.11
<i>m</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	116-118	158-161	...	...	...	...	...	9.20
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	266-268	...	...	...	...	...	...	9.64
<i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	255-257	...	...	...	...	...	...	9.55
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	273-274	226-227	V	70.51	4.09	70.27	3.80	7.87
<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	261-263	266-268	V	56.10	3.29	56.14	3.04	7.86
Mono- <i>p</i> -BrC <sub>6</sub> H <sub>4</sub> - di-C <sub>6</sub> H <sub>5</sub>	201-203	110-112	V	73.65	4.51	73.67	4.39	8.67
Di- <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> - mono-C <sub>6</sub> H <sub>5</sub>	238-239	220-221	V	84.00	5.37	84.19	5.52	9.80

case where there also is the possibility of direct conjugation between substituents and the reaction site,

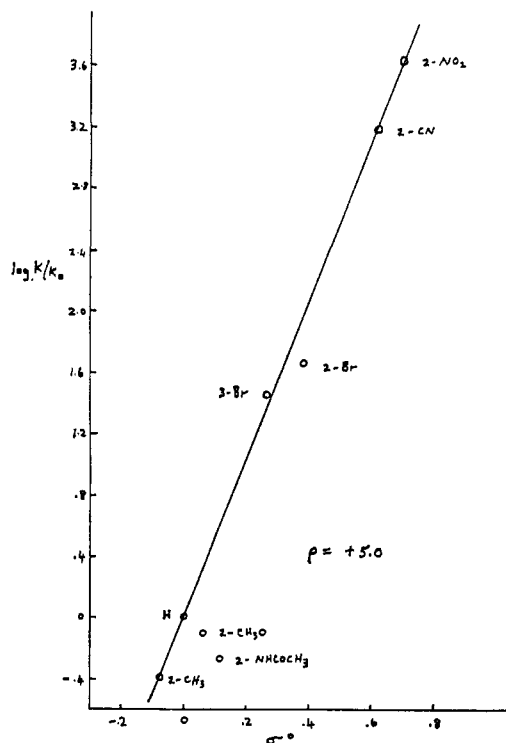


Figure 1. Acidities of X-fluorenyltriphenylphosphonium bromides vs.  $\sigma$ .

replacement of a *m*-methoxy group by a *m*-nitro group resulted in a pK<sub>a</sub> change of only 1.30 units.<sup>13</sup> The

greater sensitivity of a carbanion (e.g., III) over an oxyanion (e.g., phenoxide) to the nature of the substituents is not unexpected in view of its lower electro-negativity.

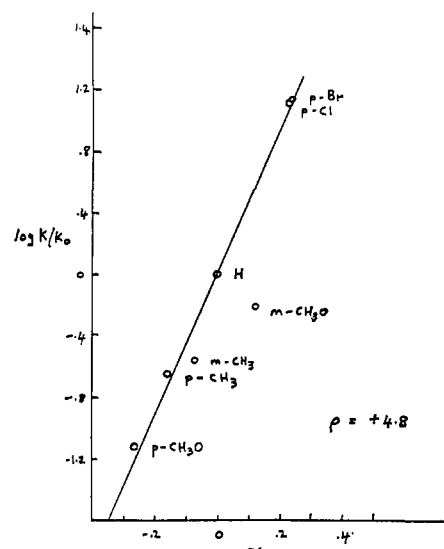


Figure 2. Acidities of fluorenyltri(*p*-X-phenyl)phosphonium bromides vs.  $\sigma$ .

The  $\rho$  value in the fluorenyl series (+5.0) was more than twice as large as the  $\rho$  value for the acyl ylids (+2.3) reported by Fliszar, *et al.*<sup>5</sup> This reflects the

(13) H. C. Brown, D. H. McDaniel, and O. Hafiger in "Determination of Organic Structures by Physical Methods," Vol. I, E. A. Braude and F. C. Nachod, Ed., Academic Press Inc., New York, N. Y., 1955, p 589.

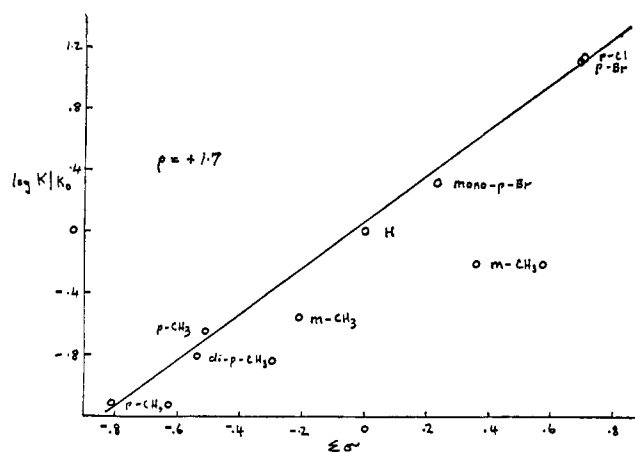


Figure 3. Acidities of fluorenyltri(X-phenyl)phosphonium bromides vs.  $\Sigma\sigma^0$ .

direct conjugation of the substituents with the carbanion in the former and the cross conjugation in the latter. The large magnitude of the  $\rho$  value in the fluorenylides is a striking reflection of the delocalization demanded by the carbanion.

The use of 2-substituted fluorenyltriphenylphosphonium salts avoided the necessity of using  $\sigma^-$  values as may have been the case for 3 substituents. The satisfactory correlation using  $\sigma^0$  values testifies to the normal *meta*-type interaction of the 2 substituents with the ylid carbanion. However, the points for the 2-methoxy and 2-acetamido groups did not fall on the line. There is some precedent for this observation in Smith and Bayer's study of the reduction of fluorenones with sodium borohydride.<sup>14</sup> They found that the 2-methoxy and 2-amino substituents should have more negative  $\sigma$  values in order to fall on the line with the other 2 substituents. The former should have been  $-0.02$  rather than  $+0.06$ . Dickinson and Eaborn<sup>15</sup> also found that the 2-methoxy group should have a more negative  $\sigma$  value to follow the correlation for the  $S_N2$  displacement of substituted 9-bromofluorenes with iodide ion in acetone. Both groups concluded that these electron-donating substituents, when in the 2 position, were exerting resonance effects through the unsubstituted ring to the 9 position, thereby canceling the inductive withdrawal normally expected for the 2 position, effectively a *meta* position.

We suggest as an alternate possibility that the total effect of the substituents is mainly a combination of a  $\sigma$ -inductive effect and a  $\pi$ -inductive effect exerted through only one ring. In the case of the 2-methoxy, 2-acetamido, and 2-bromo substituents of III these effects are opposed. The normally positive  $\sigma^0$  values, mainly due to  $\sigma$ -inductive effects, would have to be assigned less positive values due to any  $\pi$ -inductive (electron-donating) contribution. For these three substituents the changes should be  $-0.07$ ,  $-0.15$ , and  $-0.06$   $\sigma^0$  unit, respectively. From our data we suggest that the value for the 2-methoxy group in the fluorene series should be  $-0.01$ , very close to the  $-0.02$  value suggested by Smith and Bayer.<sup>14</sup> The fact that these negative shifts of  $\sigma^0$  are necessary is but

a further indication of the sensitivity of ylid basicity to the electronic effect of the carbanion substituents.

**Effect of Phosphorus Substituents.** As indicated in the introduction, there have been no previous quantitative determinations of how a substituent interacts with a positively charged phosphorus atom in any molecular environment. Using ylid basicity as a probe we have been able to provide evidence on the nature of the interaction between a phenyl group and a phosphonium atom, thereby testing the proposal made earlier.<sup>7</sup>

As indicated in Figure 2 the acidities of the fluorenyltriphenylphosphonium bromides (IV) substituted on the phenyl group correlated reasonably well with  $\sigma$ . The positive sign of the  $\rho$  value indicated that electron-withdrawing substituents on the P-phenyl groups stabilized the carbanion (V), making it less basic (its conjugate acid (IV) more acidic). In this series (V) differences in the stabilization of the ylid carbanions must result from changes in the ability of the phosphonium group to delocalize the carbanion electrons. This conjugative delocalization must be by overlap of the filled carbon 2p orbital with a vacant phosphorus 3d orbital. In other words, the less basic ylids (*e.g.*, Vg) appeared to have more  $p\pi-d\pi$  overlap, *i.e.*, a larger contribution of the double bonded structure (1b) to the resonance hybrid.

These observations are in accord with the theoretical deductions of Craig and Magnusson<sup>16</sup> who concluded that the 3d orbitals of phosphorus would be contracted and therefore capable of better overlap when the phosphorus atom carried more electronegative substituents. In effect, the substituents would be raising the electronegativity of phosphorus to approach that of carbon, thereby raising the C-P bond order from 1.0 toward 2.0. The correlations presented in this paper verify the speculations resulting from our earlier work<sup>7</sup> that in a series of ylids with a constant carbanion moiety (*e.g.*, V), ylid basicity was a useful reflection of  $p\pi-d\pi$  overlap. Conversely, ylid properties (*e.g.*, basicity, nucleophilicity, rate of betaine formation in the Wittig reaction, etc.) could be predicted on the basis of the relative contributions of structures Ia and Ib in that the more electronegative were the phosphorus substituents, the more P-C double bonding existed and the less carbanionic was the ylid. Gillespie and Robinson<sup>17</sup> observed the same general behavior for the S-O bond in sulfoxides and sulfones. In this instance also the more electronegative were the sulfur substituents the greater was the S-O bond order (approaching a maximum of 2.0). These increases in bond order were attributed to the electronegativity of the substituent increasing the extent of  $p\pi-d\pi$  overlap.

The large magnitude of the  $\rho$  value ( $+4.8$ ) for the relation between phosphorus substituent and ylid basicity also deserves comment. In this instance it may be due to the fact that three substituents were introduced into the phenyl rings of the triphenylphosphonium group. However, the large magnitude indicates again that an ylid carbanion makes stringent demands on attached groups for delocalization of the high electron density.

Many examples of additivity in the  $\sigma$  values upon multiple substitution are known.<sup>18</sup> In the case of the

(14) G. G. Smith and R. P. Bayer, *Tetrahedron*, **18**, 323 (1962).

(15) J. D. Dickinson and C. Eaborn, *J. Chem. Soc.*, 3574 (1959).

(16) D. P. Craig and E. A. Magnusson, *ibid.*, 4895 (1956).

(17) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **41**, 2074 (1965).

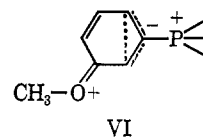
acidities of the phosphonium salts (IV) a plot of  $\log K/K_0$  vs.  $\Sigma\sigma$  afforded a straight line with a  $\rho$  value of +1.7 (Figure 3), about one-third of the slope of the original curve as expected. Significantly, however, the  $\log K/K_0$  value for *p*-bromophenyldiphenylfluorenylphosphonium bromide, a monosubstituted derivative of IIa, also fell on that line. Therefore, one bromine atom exerted one-third the effect of the three bromine atoms in Vg, the substituent effects being additive. The  $\log K/K_0$  value for di(*p*-methoxyphenyl)phenylfluorenylphosphonium bromide also fit the correlation in Figure 3.

Some insight to the mode of interaction of the groups R with the phosphorus atom in V is available from this work. When a substituent interacts through a benzenoid ring with an electron-deficient center attached directly to the ring, linear free energy correlations usually are best obtained by using  $\sigma^+$  values.<sup>19</sup> In spite of the fact that the electron-deficient phosphorus atom was attached directly to the phenyl ring in V, the  $\log K/K_0$  values for V did not correlate with  $\sigma^+$ . This probably indicates that there was no direct resonance interaction between the substituents and the phosphorus atom. On the other hand, a somewhat better correlation of the acidities of V was obtained with  $\sigma$  values than with  $\sigma^0$  values. Together these observations point to the conclusion that the substituents on the P-phenyl groups of V were exerting mainly inductive effects on phosphorus but with a significant contribution of a  $\pi$ -inductive effect along with the normal  $\sigma$ -inductive effect.

A further and more convincing indication of the relative unimportance of direct resonance interaction between the phenyl rings and the phosphorus atom in IIIa resulted from a comparison of the  $\log K/K_0$  value for IIIa with the value for Va. The value for the former was 0.00 by definition whereas that for the latter was -1.54. In a relative sense this implied that the three *n*-butyl groups in Va together had an "effective"  $\sigma$  value 0.34 unit more negative than the three phenyl groups in IIIa.<sup>20</sup> In other words, the phenyl groups were electron withdrawing with respect to the *n*-butyl groups. This conclusion implied that there could be little if any resonance interaction between the phenyl groups and the phosphorus atom of IIIa in spite of the possibility of  $p\pi-d\pi$  overlap. At the very least it could be concluded that since the *n*-butyl groups surely were electron donating by an inductive mechanism, any conjugative electron donation by the phenyl groups must have been more than counterbalanced by inductive electron withdrawal. Wepster<sup>21</sup> also has cited evidence for the powerful inductive electron-withdrawal effect of the phenyl group. Therefore, we conclude that the major electronic interaction between the phosphorus substituents (except the carbanion) and the phosphorus atom in phosphoniumfluorenylides (V) is of an inductive nature.

The interactions of the phenyl substituents with the phosphorus atom in Vb-Vg undoubtedly contained both a  $\sigma$ - and a  $\pi$ -inductive component. The fact that

the *m*-methoxy and *m*-methyl groups would have required more negative  $\sigma$  values to fit an otherwise satisfactory correlation indicated that these groups were more electron donating than expected from the *meta* position. Such a result probably was due to the operation of a significant  $\pi$ -inductive effect such as represented by VI. The magnitude of such effects



exerted by various substituents probably is closely related to the nature of the reaction center. In the case of the fluorenylidetri(X-phenyl)phosphoranes (V) such effects may be especially important due to the electrostatic attraction exerted on the phenyl rings by the positively charged phosphorus atom.

We have no evidence indicating why there is little resonance interaction between the phenyl rings and the phosphorus atom in IIIa or Vb-g. However, this seems to be a consistent feature of quaternary phosphonium chemistry. It may be due to the crowded environment about the phosphorus atom resulting in hindrance to the phenyl rings becoming perpendicular to the axis of the 3d orbitals of phosphorus, thereby precluding effective  $p\pi-d\pi$  overlap. The recent X-ray results of Wheatley<sup>22</sup> have indicated that the three phenyl rings in *p*-tosylmethylenetriphenylphosphorane were twisted about the phosphorus atom in a "paddle wheel" or "propeller" confirmation.

We are pursuing further studies on the effect of the phosphorus substituents on ylid characteristics, and we expect to find linear correlations of ylid basicity with the rates of various ylid reactions. Already we have found qualitative agreement with this data for a series of Wittig reactions.

## Experimental Section

**General.** Melting points are uncorrected. Analyses were by Alfred Bernhardt Microanalytical Laboratory, Mulheim (Ruhr), Germany. Optical density measurements for the  $pK_a$  determinations were carried out on a Beckman DU spectrophotometer. All pH determinations were carried out with a Beckman Model 76 expanded scale pH meter equipped with glass and saturated calomel electrodes and standardized with a standard buffer to pH 7.02 at 25° in aqueous medium.

**$pK_a$  Determinations.** The solvent for all solutions of acids, bases, buffers, and phosphonium salts was 95% ethanol. This choice was dictated by the solubility characteristics of the phosphonium salts, the ylids, and the buffer components.

The acid solution was 0.1 M HCl prepared by adding 9.3 ml of concentrated hydrochloric acid to 40.7 ml of water and 950 ml of absolute ethanol. The base solution was 0.1 M KOH prepared by dissolving 5.61 g of potassium hydroxide in 50 ml of water and 950 ml of absolute ethanol.

Seven buffer solutions were prepared as previously described in the literature<sup>23</sup> except that the final solvent composition was 95% ethanol-water. These buffers were shown to actually effect a buffering action. The apparent pH of the buffers used were 9.64 (10.0), 8.63 (9.0), 8.72 (9.0), 7.79 (8.0), 6.89 (7.2), 6.05 (3.6), and 4.86 (2.6). The values in parentheses are the pH values of the same buffers when prepared in aqueous media. The first two were Ammediol-HCl buffers (Ammediol = 2-amino-2-methyl-1,3-

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

(19) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p 203.

(20) The "effective"  $\sigma$  value for the *n*-butyl groups was obtained by extrapolating to the  $\sigma$  axis from the point on the line of Figure 2 corresponding to a  $\log K/K_0$  of -1.54.

(21) B. M. Wepster, *Rec. Trav. Chim.*, **71**, 1159, 1171 (1952).

(22) P. J. Wheatley, *J. Chem. Soc.*, 5785 (1965).

(23) (a) "Methods in Enzymology," Vol. I, S. P. Colowick and N. O. Kaplan, Ed., Academic Press Inc., New York, N. Y., 1955; (b) C. Long, "Biochemists Handbook," D. Van Nostrand Co., Inc., Princeton, N. J., 1961.

propanediol), the next three were Tris-HCl buffers (Tris = tris-(hydroxymethyl)aminomethane), and the last two were formic acid-potassium hydroxide buffers.

Stock solutions of each phosphonium salt (II and IV) were prepared by dissolving about 4 mg of salt in 10 ml of 95% ethanol. Aliquots (0.5 ml) of each stock solution were diluted to 5 ml separately with the basic solution, the acidic solution, and the appropriate buffer solution. The absorbancy of the three solutions was recorded at five wavelengths in the area (320-400 m $\mu$ ) where the phosphonium ylids absorbed strongly but where the phosphonium salts were nearly transparent. The  $pK_a$  values were calculated as follows.<sup>11</sup>

$$pK_a = \text{pH} - \log \frac{B - b}{b - A}$$

where  $B$  = absorbancy of the stock aliquot in basic solution,  $b$  = absorbancy of the stock aliquot in buffered solution,  $A$  = absorbancy of the stock aliquot in acid solution, and  $\text{pH}$  = pH of the buffer solution used.

The  $pK_a$ 's determined for the two series of phosphonium salts (II and IV) are listed in Tables I and II. The values reported are the average of the  $pK_a$ 's determined using at least two different buffers. The  $pK_a$  determined using any given buffer solution was the average of the  $pK_a$  values determined at five different wavelengths. The average deviation in the listed values was  $\pm 0.03$   $pK_a$  unit.

**Preparation of Phosphines.** Triphenylphosphine, used in the preparation of all salts of general structure II, was Eastman White Label and used directly. Tris(*p*-tolyl)phosphine and tris(*m*-tolyl)phosphine were obtained from the same source. Tri(*n*-butyl)phosphine was a gift of the Metal and Thermit Corp. Tris(*p*-anisyl)phosphine<sup>24,25</sup> di-*p*-anisylphenylphosphine,<sup>25</sup> tris(*p*-chlorophenyl)phosphine,<sup>24</sup> and *p*-bromophenyldiphenylphosphine<sup>26</sup> were prepared essentially as described in the literature.

Tris(*p*-bromophenyl)phosphine was prepared as for the *p*-chloro analog from the Grignard reagent of *p*-dibromobenzene and phosphorus trichloride in 45% yield. It crystallized from acetone-water as colorless needles, mp 118-119°.

*Anal.* Calcd for C<sub>18</sub>H<sub>12</sub>PBr<sub>3</sub>: C, 43.32; H, 2.42; Br, 48.04. Found: C, 42.95; H, 2.42; Br, 47.66.

Tris(*m*-anisyl)phosphine was prepared as for the *p*-anisyl isomer<sup>25</sup> from the Grignard reagent of *m*-bromoanisole and phosphorus tri-

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(25) A. E. Senear, W. Valient, and J. Wirth, *J. Org. Chem.*, **25**, 2001 (1960).

(26) H. Goetz, F. Nerdel, and K. H. Wiechel, *Ann.*, **665**, 1 (1963).

chloride.<sup>27</sup> It crystallized in 33% yield from methanol as colorless needles, mp 113-115° (lit.<sup>27</sup> mp 112-114°).

*Anal.* Calcd for C<sub>21</sub>H<sub>21</sub>O<sub>3</sub>P: C, 71.60; H, 6.01; P, 8.79. Found: C, 70.92; H, 5.85; P, 9.01.

**Preparation of Substituted 9-Bromofluorenes.** The following 9-bromofluorenes were prepared essentially as described in the literature: 9-bromofluorene,<sup>28</sup> 2-cyano-9-bromofluorene,<sup>29</sup> 2,9-dibromofluorene,<sup>29</sup> 2-methoxy-9-bromofluorene,<sup>29</sup> 2-nitro-9-bromofluorene,<sup>28,30</sup> and 2-methyl-9-bromofluorene.<sup>29</sup>

The known 3,9-dibromofluorene<sup>31</sup> was obtained by treatment of 3-bromo-9-fluorenone<sup>32</sup> with 48% hydrobromic acid in acetic acid. The alcohol was obtained by reduction of the commercially available 3-bromo-9-fluorenone with sodium borohydride.

2-Acetamidofluorene was oxidized with sodium dichromate to 2-acetamido-9-fluorenone<sup>32</sup> which was, in turn, reduced with sodium borohydride to the fluorenone.<sup>32</sup> The latter was converted to the known 2-acetamido-9-bromofluorene<sup>33</sup> with 48% hydrobromic acid in acetic acid.

**Preparation of Phosphonium Salts.** The phosphonium salts were prepared by treatment of an acetone solution of the appropriate substituted 9-bromofluorene with a 10% molar excess of the tertiary phosphine. The salt normally precipitated on standing overnight and was recrystallized from ethanol-benzene solution. The properties of the salts are listed in Tables I and II.

Not all of the phosphonium ylids (III, V) were characterized fully. The properties of some are listed in Tables I and II. The ylids reported therein were prepared by treatment of an ethanolic solution of the phosphonium salt with dilute aqueous ammonia as described previously.<sup>7</sup>

**Acknowledgments.** We gratefully acknowledge the support of the Research Corporation in initiating this work through a Frederick Gardner Cottrell grant. This investigation also was supported by Grant No. GM-10488 from the Public Health Service.

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