



12-1-1964

# Phosphorus Ylids: the Influence of Electron-Withdrawing Groups on Valence Shell Expansion of Phosphorus

Ronald A. Swor

Follow this and additional works at: <https://commons.und.edu/theses>

---

## Recommended Citation

Swor, Ronald A., "Phosphorus Ylids: the Influence of Electron-Withdrawing Groups on Valence Shell Expansion of Phosphorus" (1964). *Theses and Dissertations*. 656.  
<https://commons.und.edu/theses/656>

This Thesis is brought to you for free and open access by the Theses, Dissertations, and Senior Projects at UND Scholarly Commons. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of UND Scholarly Commons. For more information, please contact [zeinebyousif@library.und.edu](mailto:zeinebyousif@library.und.edu).

PHOSPHORUS HALIDES: THE INFLUENCE OF ELECTRON-WITHDRAWING  
GROUPS ON VALENCE SHELL EXPANSION OF PHOSPHORUS

by

Ronald A. Swor

"

B.A. in Chemistry, University of Minnesota, Duluth 1962

A Thesis

Submitted to the Faculty

of the

University of North Dakota

in partial fulfillment of the requirements

for the Degree of

Master of Science

Grand Forks, North Dakota

December

1964



PHOSPHORUS HALIDES: THE INFLUENCE OF ELECTRON-WITHDRAWING  
GROUPS ON VALENCE SHELL EXPANSION OF PHOSPHORUS

by

Ronald A. Swor

B.A. in Chemistry, University of Minnesota, Duluth 1962

A Thesis

Submitted to the Faculty

of the

University of North Dakota

in partial fulfillment of the requirements

for the Degree of

Master of Science

Grand Forks, North Dakota

December

1964

1964  
Swor 74  
~~PL~~  
cop. 2

This thesis, submitted by Ronald A. Swor in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota, is hereby approved by the Committee under whom the work has been done.

A William Johnson  
Chairman

Ronald A Swor

Edward J. O'Reilly, Jr.

Christopher J. Hamme  
Dean of the Graduate School



#### ACKNOWLEDGEMENT

The author wishes to thank Dr. A. William Johnson for suggesting the problem and for his guidance and supervision of the research. The author also wishes to thank Dr. Edward J. O'Reilly and Dr. Roland G. Severson for serving on the Advisory Committee and all others who contributed to completion of this work. In addition, the author is grateful to Research Corporation for the financial support which made this research possible. Finally, the author would like to dedicate this thesis to his parents and to Miss Charmane Young in appreciation of their encouragement during this period.

## VITA

Ronald A. Swor, the son of Mr. and Mrs. Samuel E. Swor, was born on January 11, 1939 in Duluth, Minnesota. He attended the public schools in Duluth and graduated from Duluth Central High School in June 1957. The following Fall he continued his education at the University of Minnesota under a James Wright Hunt Scholarship, where he majored in chemistry and minored in mathematics. During the last two years of college he did chemical research with Dr. G. M. Christensen under a U. S. Public Health Grant and with Dr. Moses Passer under a National Science Foundation program. After graduation from the University of Minnesota in June 1962, he continued his education in chemistry at the University of North Dakota where he received a graduate teaching assistantship. In June 1963, he started research work with Dr. A. William Johnson, supported by a grant from Research Corporation. In December of 1964 he received a Master of Science Degree from the University of North Dakota and has accepted employment with U. S. Rubber Co. in Detroit, Michigan.

## TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT . . . . .	iii
VITA. . . . .	iv
LIST OF TABLES. . . . .	vii
LIST OF CHARTS. . . . .	viii
INTRODUCTION. . . . .	1
RESULTS . . . . .	37
DISCUSSION. . . . .	45
EXPERIMENTAL. . . . .	62
9-Bromofluorene. . . . .	63
p-Iodonitrobenzene . . . . .	63
p-Bromiodobenzene . . . . .	63
p-Bromochlorobenzene . . . . .	64
(p-Bromophenyl)diphenylphosphine . . . . .	64
Tris(p-bromophenyl)phosphine . . . . .	65
Tris(p-chlorophenyl)phosphine. . . . .	66
(m-Trifluoromethylphenyl)diphenylphosphine . . . . .	67
Tris(m-trifluoromethylphenyl)phosphine . . . . .	68
Tris(p-cyanophenyl)phosphine . . . . .	69
(p-Cyanophenyl)diphenylphosphine . . . . .	70
Tripiperidylphosphine. . . . .	70
Tris(p-nitrophenyl)phosphine . . . . .	70
(p-Nitrophenyl)diphenylphosphine . . . . .	72



Preparation of Ylid Salts . . . . .	73
(p-Bromophenyl)diphenylfluorenylphosponium bromide . . . . .	73
Tris(p-bromophenyl)fluorenylphosponium bromide . . . . .	74
Tris(p-chlorophenyl)fluorenylphosponium bromide. . . . .	74
Tripiperidylfluorenylphosponium bromide. . . . .	74
Preparation of Ylids. . . . .	74
(p-Bromophenyl)diphenylphosponiumfluorenylide. . . . .	75
Tris(p-chlorophenyl)phosponiumfluorenylide . . . . .	75
Tris(p-bromophenyl)phosponiumfluorenylide. . . . .	75
(p-Cyanophenyl)diphenylphosponiumfluorenylide. . . . .	76
Preparation of Phosphine Oxides . . . . .	76
Tris(p-bromophenyl)phosphine Oxide. . . . .	76
Tris(p-chlorophenyl)phosphine Oxide . . . . .	76
(p-Bromophenyl)diphenylphosphine Oxide. . . . .	76
Reaction of Ylids IIIa, IIIb and IIIc with Carbonyls. . . . .	77
pKa Determination . . . . .	78
Attempted Syntheses . . . . .	86
Suggested Syntheses . . . . .	88
SUMMARY. . . . .	89
LITERATURE CITED . . . . .	91

## LIST OF TABLES

Table	Page
1. Tertiary Aryl Derivatives of Phosphorus Trichloride . . . . .	35
2. Reaction of Ylids With Carbonyls. . . . . (Yields based on total ylid added)	40
3. Reaction of Ylids With Carbonyls. . . . . Yields based on amount of ylid reacted)	41
4. Percent Ylid Reacted in the Wittig Reaction . . . . .	41
5. Melting Points of Olefins Obtained From the Wittig Reaction . .	42
6. pKa of Ylid Conjugate Acids (Buffers at pH of 9.20 and 8.20). .	42
7. pKa of Ylid Conjugate Acids by Royer. . . . .	43
8. pKa of Ylid Conjugate Acids by Johnson. . . . .	44
9. Wittig Reaction of p-anisaldehyde With Triphenylphosphonium fluorenylide. . . . .	48
10. pKa Spectra Data for IIIa . . . . .	80
11. pKa Spectra Data for IIIb . . . . .	81
12. pKa Spectra Data for IIIc . . . . .	82
13. pKa Spectra Data for IIIe . . . . .	83
14. pKa Spectra Data for IIIg . . . . .	84
15. pKa Spectra Data for IIIj . . . . .	85

LIST OF CHARTS

Chart	Page
1. List of Ylids Cited in Text . . . . .	5,46
2. Olefins Found in Wittig Reaction. . . . .	40

PHOSPHORUS YLIDS:  
THE INFLUENCE OF ELECTRON-WITHDRAWING GROUPS ON  
VALENCE SHELL EXPANSION OF PHOSPHORUS

Ronald A. Swor, Master of Science

The thesis here abstracted was written under the direction of A. William Johnson and approved by R. G. Severson and E. J. O'Reilly as members of the examining committee, of which Dr. A. William Johnson was Chairman.

The influence of electron-withdrawing substituents attached to phosphorus on the valence shell expansion of phosphorus was studied using para-substituted tri-phenylphosphoniumfluorenylides. The ylids, resonance hybrids of an ylene form (Ia) and an ylid form (Ib) were used to investigate the effect electron-withdrawing groups have on the relative contribution of the two forms to the hybrid and thus on valence shell expansion of phosphorus. With increased positive character, the valence shell expansion of phosphorus (by (p-d)pi overlap) would increase the importance of the contributing form Ia and vice versa.

Mono-para-bromo-(IIa), tri-para-bromo-(IIb), tri-para-chloro-(IIc) and mono-para-cyano-(IIId) derivatives of triphenylphosphonium-fluorenylides (IIe) were prepared and their relative reactivity, except IIId, determined by the Wittig reaction with substituted benzaldehydes. The results revealed the order of reactivity was  $IIe > IIa > IIb = IIc$ .

The ylids were less reactive than the tri-para-methoxy-(IIIf) and tri-para-N, N-dimethylamino-(IIg) derivatives of IIe used in earlier studies.

An ultraviolet spectrophotometric determination of the pKa of the ylid conjugate acids confirmed the proposal that the most reactive ylid was also the most basic. The order of increasing basicity was  $\text{IIc} < \text{IIb} < \text{IId} < \text{IIa} < \text{IIe} < \text{IIf}$ .

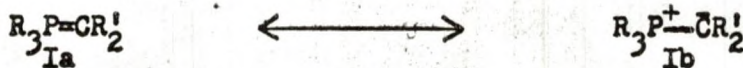
The synthesis of tris(m-trifluoromethylphenyl)phosphine, tris(p-nitrophenyl)phosphine, (p-nitrophenyl)diphenylphosphine and tris(p-cyanophenyl)phosphine were attempted, but either the phosphines could not be obtained or they were obtained only as their oxides.

## INTRODUCTION

To study the valence shell expansion of phosphorus, a system had to be employed which permitted control of the availability and distribution of electrons to the phosphorus atom. The system selected for this study employed pentavalent organophosphorus compounds known as alkylidene-trialkyl-(or triaryl)phosphoranes, commonly called phosphorus ylids. This system was unique in that various physical and chemical measurements (Wittig reaction rates,  $P^{31}$  NMR spectral data and pKa determinations on the conjugate acids of the ylids) could be made in order to reveal information concerning the valence shell expansion of phosphorus.

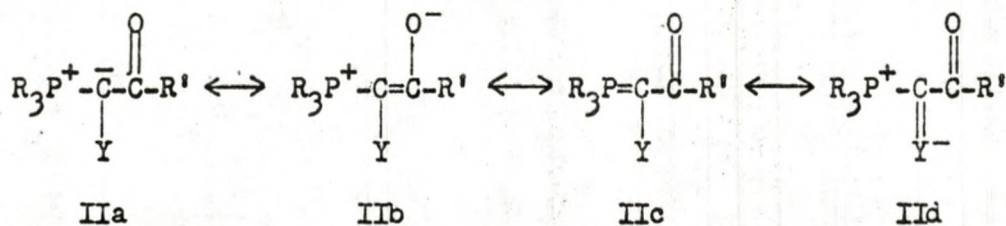
In a tetra-substituted phosphonium system, the vacant 3d orbitals of the phosphorus atom could overlap with the filled p-orbital of an adjacent carbanion resulting in a valence shell expansion to create a pentavalent system having (p-d) $\pi$  overlap.<sup>1,2</sup> Quantitative evidence for this "d-orbital resonance" was provided by Doering and Hoffmann when they found the heat of activation for the deuterioxide-catalyzed exchange of deuterium in tetramethyl-phosphonium iodide to be much lower than the calculated value.<sup>3,4</sup> They attributed this lowering of the heat of activation to the valence shell expansion by the phosphorus atom stabilizing the intermediate ylid.

The phosphorus ylids(I), whether R is an aryl or an alkyl group,



should be written as a resonance hybrid of an ylene form(Ia) and an ylid form(Ib).<sup>5</sup> The extent of the contribution of forms Ia and Ib to the hybrid has not yet been fully determined, but the contribution is known to depend somewhat upon the effect of the substituents R and R'. However, it should be mentioned that Speziale and Ratts,<sup>6</sup> in their P<sup>31</sup> NMR studies of phosphorus ylids of the type Ph<sub>3</sub>P:C(X)COR(where R = Ph<sub>2</sub>N, OEt, CN or Ph and X = H, halogen or COOEt), concluded that the contribution of Ia to the hybrid was very small. Contrary to the findings of Speziale and Ratts, Mark<sup>7</sup> concluded, again from an NMR investigation, that ylids of the type (Et<sub>2</sub>N)<sub>3</sub>P:CF<sub>2</sub> exhibited a large contribution of Ia to the resonance hybrid of the ylid.

G. Aksnes<sup>8</sup> assigned C-O absorption bands to spectra of various ylids of the type Ph<sub>3</sub>P:CHCOR. He observed very strong displacements to low frequencies of the C=O bands upon formation of the ylids from the phosphonium salts. This indicated that the ionic structure Ph<sub>3</sub>P<sup>+</sup>-CH=C(O<sup>-</sup>)R contributed very strongly to the resonance hybrid of the ylids. In accordance with this observation, the dipole moments for Ph<sub>3</sub>P:CHCOPh and Ph<sub>3</sub>P:CHCOMe were found to be 5.54 D. and 5.45D., respectively, indicating the existence of highly polar species.<sup>5</sup> Speziale and Ratts<sup>6</sup> investigated a series of stable ylids(Ph<sub>3</sub>P:C(Y)COR, where Y = halogen or H and R = Ph, MeO, EtO or Ph<sub>2</sub>N) to study the influence of adjacent halogen and phosphorus d-orbitals upon carbanion stabilization(IIa, IIb, IIc and IIId).<sup>6,9</sup> The shift in the  $\nu_{C=O}$  from the normal  $\nu_{C=O}$  was attributed to the contri-



bution of IIb, although IIc would decrease the amount of contribution of IIb if Y was a halogen. Both reactivity of the ylid in the Wittig reactions,<sup>10</sup> as mentioned for Royer's<sup>11</sup> work, and C=O stretching frequencies<sup>6</sup> then were used as indicators of the extent of charge delocalization in the ylid. It was observed that where R' was EtO or MeO, the C=O stretching frequency increased (more double bond character in the carbonyl due to greater contribution of IIc) for cases where Y was a halogen more than when Y was hydrogen. Where R' was Ph<sub>2</sub>N or Ph and Y was halogen, the opposite effect, a decrease in  $\nu_{\text{C=O}}$ , was observed. This was attributed to steric requirements causing the oxygen of the carbonyl to become trans to the halogen, producing an opposite field effect, which cancelled the delocalization by halogens in IIc.

On the other hand, most stable phosphoranes, such as Ph<sub>3</sub>P:CHCOOR, are known to react either slowly or not at all with ketones.<sup>12</sup> Ramirez and Levy,<sup>13,14</sup> working with triphenylphosphoniumcyclopentadienylide, found it to be a stable, unreactive ylid. They attributed the stability to delocalization of the negative charge into the cyclopentadienyl ring forming a pseudo-aromatic system of (4n+2)pi electrons. Evidence for resonance in ylids through a non-benzenoid system was supplied by Bestmann.<sup>15</sup> He found that treatment of tricyclohexylalkylphosphonium halides with tritium-labeled alcohol-alcoholate gave tritium-labeled phosphinealkylenes on the basis of the equilibrium: phosphonium alcoholate  $\rightleftharpoons$  phosphinealkylene. Bestmann found that tritium was also introduced into the gamma position of the ylid of the type RCH:CHCH:PR'<sub>3</sub>, proving that there was delocalization of the carbanion electrons through the carbon substituents of phosphinealkylenes. Closely related to this evidence for delocalization of the electrons of the ylid carbon, were the physical and chemical properties, such as color,



stability, melting point and reactivity towards carbonyl compounds.<sup>5,16</sup>

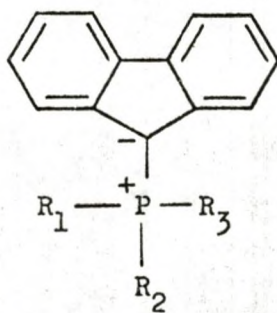
In previous work Royer<sup>11</sup> made the R group in I an electron-donating substituent (to increase the distribution of electrons around the phosphorus atom and decrease the amount of positive charge associated with the phosphorus atom) in an attempt to affect the relative contributions of Ia and Ib to the resonance hybrid. Where  $R_1$ ,  $R_2$  and  $R_3$  were electron-donating groups (IIIh-m and f), the electron density around the phosphorus atom should be increased. This would decrease the positive character of the phosphorus atom and decrease the attraction for available electrons from the ylid carbanion. In such cases, Ib would be expected to contribute more to the resonance hybrid. Indeed, this is indirectly what Royer observed.

On the other hand, just the opposite effect, producing a greater contribution of Ia, would be expected if  $R_1$ ,  $R_2$  and  $R_3$  were electron-withdrawing groups (IIIa-g).<sup>17</sup> Electron-withdrawing groups would lower the energy of the 3d orbitals of phosphorus (contract the d-orbitals)<sup>18</sup> to create more suitable conditions for overlap of the 3d orbitals with the p-orbital of the adjacent carbanion. Craig and Magnusson<sup>19</sup> suggested that phosphorus could accept and hold this increase in positive character, for increased positive character would cause contraction of the d-orbitals and facilitate bonding by increasing the orbital overlap. Thus phosphorus should find it easier to expand its valence shell and permit a higher contribution of form Ia under these conditions. Therefore, theory predicts that the amount of positive charge on the phosphorus should affect the degree of valence shell expansion.<sup>20</sup>

Evidence for this proposal that the amount of positive character of phosphorus influenced the degree of valence shell expansion was provided by the observation that in the cis isomer of  $(R_3P)_2PtCl_2$ , the ligand containing phosphorus was more tightly bound to the central atom than in the

Chart I

	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
IIIa	p-Br-C <sub>6</sub> H <sub>4</sub> -	C <sub>6</sub> H <sub>5</sub> -	C <sub>6</sub> H <sub>5</sub> -
b	p-Br-C <sub>6</sub> H <sub>4</sub> -	p-Br-C <sub>6</sub> H <sub>4</sub> -	p-Br-C <sub>6</sub> H <sub>4</sub> -
c	p-Cl-C <sub>6</sub> H <sub>4</sub> -	p-Cl-C <sub>6</sub> H <sub>4</sub> -	p-Cl-C <sub>6</sub> H <sub>4</sub> -
d	m-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -	C <sub>6</sub> H <sub>5</sub> -	C <sub>6</sub> H <sub>5</sub> -
e	p-CN-C <sub>6</sub> H <sub>4</sub> -	C <sub>6</sub> H <sub>5</sub> -	C <sub>6</sub> H <sub>5</sub> -
f	C <sub>5</sub> H <sub>10</sub> N-	C <sub>5</sub> H <sub>10</sub> N-	C <sub>5</sub> H <sub>10</sub> N-
g	C <sub>6</sub> H <sub>5</sub> -	C <sub>6</sub> H <sub>5</sub> -	C <sub>6</sub> H <sub>5</sub> -
h	p-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -	C <sub>6</sub> H <sub>5</sub> -	C <sub>6</sub> H <sub>5</sub> -
i	p-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -	p-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -	C <sub>6</sub> H <sub>5</sub> -
j	p-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -	p-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -	p-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -
k	p-(CH <sub>3</sub> ) <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> -	p-(CH <sub>3</sub> ) <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> -	p-(CH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -
l	n-C <sub>4</sub> H <sub>9</sub> -	n-C <sub>4</sub> H <sub>9</sub> -	n-C <sub>4</sub> H <sub>9</sub> -
m	CH <sub>3</sub> -	CH <sub>3</sub> -	CH <sub>3</sub> -
n	C <sub>6</sub> H <sub>5</sub> -	C <sub>2</sub> H <sub>5</sub> -	CH <sub>3</sub> -

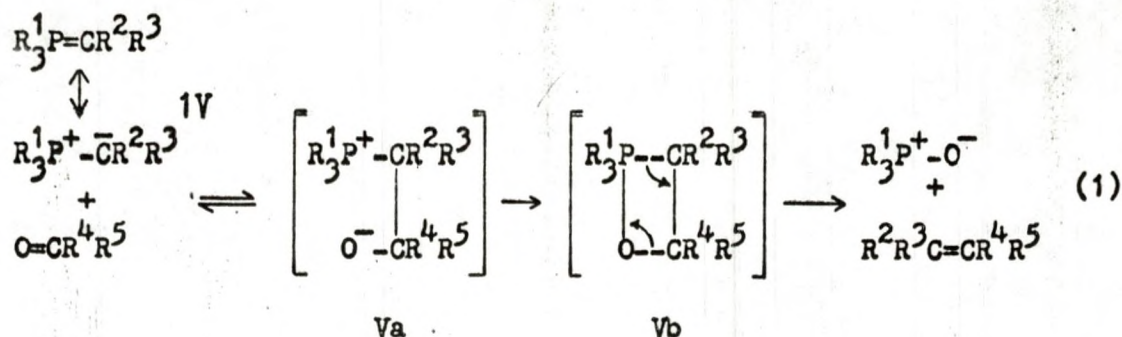


III

trans molecule.<sup>21</sup> In the trans form the same d-orbitals of the platinum atom should be acted upon by both phosphorus atoms, weakening the bonding. This should not occur in the cis complex. As R was varied from alkyl (-I effect) to halogen (-I effect) the bonding strength increased. This increase in Pt-P bonding strength was attributed to increased (d-d)pi overlap between platinum and phosphorus. The overlap was believed to have been further induced by the effect of larger -I properties of substituents attached to the phosphorus atom. In addition, in cis complexes of  $L_3Mo(CO)_3$ , where L was either  $Ph_3P$ ,  $Ph_2PCl$  or  $PhPCl_2$ , the C-O stretching frequency increased in the order indicated.<sup>22</sup> This was taken to imply that backbonding to the carbonyl group by molybdenum was decreased as the formal positive charge on phosphorus was increased by increased substitution of chlorine for a phenyl group. This decrease in backbonding would cause the triple bond character of the carbonyl group to increase over that of the hexacarbonyl.<sup>23</sup>

Phosphorus ylids, in which R' in I is an alkyl or other electron-donating substituents, have been shown to be highly reactive towards air oxidation and hydrolysis.<sup>24</sup> Consequently, such compounds have been difficult to isolate and study. Their stability varies directly with the extent of the delocalization of the electrons on the ylid carbanion.<sup>10</sup> However, where R' was an electron-withdrawing substituent (COOR, COR, Ph, etc.) the ylids were usually stable. The contribution of R to the stability of the ylid appeared to be less critical. In ylids having the same R', the ylid was usually more stable where R was an aryl group, as opposed to an alkyl group.<sup>17</sup> To permit isolation and characterization of the ylids, the fluorenylidene group was substituted for the  $CR'_2$  in structure I as in earlier work in this laboratory.<sup>11,17</sup>

Perhaps the most important function of phosphorus ylids has remained in their ability to react with carbonyl systems to yield an olefin and a phosphine oxide. Trippett<sup>12</sup> summarized this reaction, the Wittig reaction, as being a two stage process involving an intermediate betaine(Va), where the rate determining step could be either the formation of the betaine or its decomposition.



If we assume, as seems likely, that the formation of the betaine from stable ylids involves a nucleophilic attack of the carbanion of the phosphorane on the carbonyl group, the rate could depend on the nucleophilicity of the carbanion (which is dependent upon the extent of (p-d)pi overlap) and on the susceptibility of the carbonyl group to nucleophilic attack.<sup>10,12,17</sup> If this statement is true, the Wittig reaction could be used to measure the nucleophilicity of an ylid and, consequently, infer the extent of delocalization of the electrons on the ylid carbon. Using isolable fluorenylides only, one should be able to obtain a relative measurement of the extent of delocalization of the electrons of the ylid carbon towards phosphorus, with a change in substituents attached to phosphorus, by reacting the ylids with the same aldehyde under identical reaction conditions. Using para-substituted phenyl groups in the ylids, as opposed to ortho-substituted phenyl groups, should keep any problems of steric interference at a minimum. Reviews of the Wittig reaction have been listed in references 25-28 and 12.

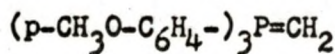
Substituents on phosphorus which tend to decrease the positive character of the phosphorus atom (electron-donating groups) should increase the reactivity of the ylid by stabilizing the contributing dipolar form Ib. Stable ylids having delocalization of the negative charge of the carbanion by substituents  $R^2$  and  $R^3$  in IV (in our case the fluorene nucleus)<sup>29</sup> should reduce the reactivity as should electron-withdrawing substituents attached to phosphorus. Consistent with this view, it was found that IIIg, which had the negative charge delocalized through the fluorene nucleus, reacted in varying yields with aldehydes and not at all with ketones,<sup>30</sup> but IIIl and IIIm reacted readily with aldehydes and with the more reactive ketones (4-nitroacetophenone).<sup>17</sup> This information is consistent with the view that phenyl groups, having carbons of  $sp^2$  hybridization, could exert an electron-withdrawing inductive effect<sup>31</sup> (due to the increased s character in bonding)<sup>32</sup> increasing the positive character of phosphorus and thus causing a greater contribution of form Ia relative to the effect of the alkyl groups.<sup>33</sup> If the phenyl groups exhibited a resonance effect (an electron donation to decrease the positive character of phosphorus and consequently localize the electrons on the ylid carbon), the reactivity of the ylids would be just the opposite. This effect of a phenyl group being electron-withdrawing was substantiated in work by Wagner.<sup>34</sup> Calculating the electronegativity of groups attached to phosphorus in phosphine oxides, the phenyl, chlorophenyl and methyl groups had values of 2.4, 2.2 and 2.0 respectively. Therefore, greater contribution of Ia should mean the first step (nucleophilic attack of ylid carbon on the carbonyl carbon) would be retarded where R = phenyl. The alkyl groups of IIIl and IIIm exerted an opposite effect and thus increased the rate of the slow step of the Wittig reaction.<sup>35,36</sup>

Cook and Allen<sup>37</sup> found that in complexes of platinum, which contained substituted arylphosphines and arylacetylenes as ligands, the electron donation by the methyl group in tris(p-methylphenyl) phosphine and the methoxy group of tris(p-methoxyphenyl)phosphine reduced the electron accepting properties of the phosphorus atom compared to the phosphorus atom in triphenylphosphine. This was observed by the increase in the degree of double bonding to the metal atom by the acetylene. The authors also observed that an opposite affect occurred with tris(p-fluorophenyl)- and tris(p-chlorophenyl)phosphine, that is, the electron-withdrawing substituent increased the electron-accepting properties of phosphorus above that of triphenylphosphine.

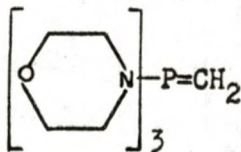
Royer<sup>11</sup> with his work on the fluorenylides derived from the mono-, di- and tri-p-methoxy derivatives of triphenylphosphine and tris(p-N, N-dimethylaminophenyl)phosphine(IIIh-k), observed that the reactivity of the ylids with aldehydes increased as one would expect in the order listed. Apparently, the methoxy- and dimethylamino-substituted benzene ring would withdraw less electron density than an unsubstituted phenyl ring, resulting in less (p-d)pi overlap in the ylid. It could also be that the tri-p-methoxy and tri-p-dimethylamino derivatives contributed greater electron density towards phosphorus, which diminished the amount of (p-d)pi overlap with the ylid carbon.<sup>11</sup> Royer<sup>11</sup> interpreted this experimental data as indicating that resonance interaction existed between the methoxy group and the benzene ring, as expected, but that there was little or no resonance interaction between the rings and the phosphonium atom. This left only inductive interactions to operate. Therefore, the electron-donating groups decreased the electron-withdrawing effect of the phenyl groups,<sup>31</sup> consequently reducing the delocalization of the electrons on the ylid carbon towards

phosphorus. This increased localization of the electrons on the ylid carbon caused the nucleophilicity of the ylid to increase as reflected by the Wittig reaction.

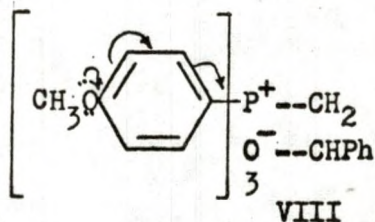
Decomposition of the betaine intermediate in the Wittig reaction is believed to involve a four-membered cyclic transition state. This process would be retarded by electron-donating substituents ( $R^1$  in Vb) which decreased the positive character and thus the oxygen-affinity of the phosphorus atom (P-O bond formation is believed to be the driving force of the reaction)<sup>38,39</sup> and accelerated by substituents ( $R^2-R^5$  in Vb) which could conjugate with the incipient double bond in the transition state.<sup>40</sup> Wittig et al.<sup>41</sup> varied the ligands on phosphorus of ylids (VI, VII and VIII) to obtain insight into the mechanism of the carbonyl-olefination reaction. They observed that substitution of a phenyl group by a p-methylphenyl, p-methoxyphenyl, piperidino and morpholino groups (electron-donating groups) favored the betaine formation with a carbonyl compound, but made the decomposition of the betaine more difficult. Consequently, factors which helped to form the betaine retarded the process of decomposition, and vice versa.



VI



VII

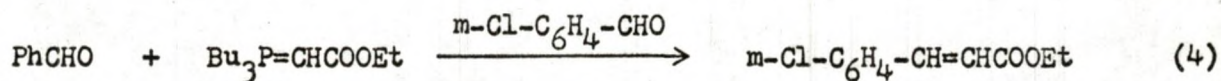
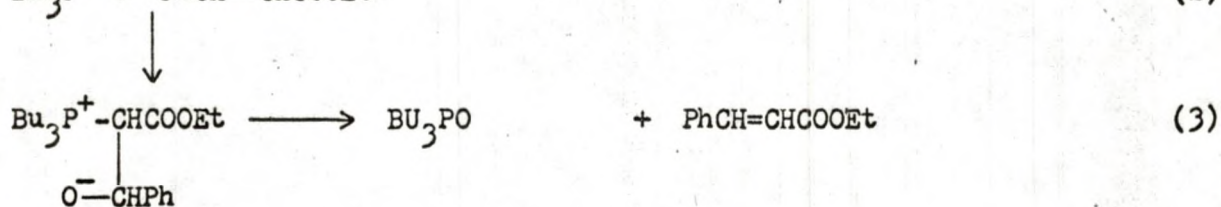


VIII

Trippett<sup>42</sup> and Johnson<sup>17,43</sup> have shown that whether R in I is a phenyl or an alkyl group, the Wittig reaction would still produce olefins. However, unstable ylids VI and VII were very reactive towards benzaldehyde to form stable betaines (VIII), but do not form the subsequent olefin and

phosphine oxide.<sup>12</sup> The lack of olefin formation was attributed to the electron-releasing effect of the substituents on phosphorus decreasing the positive character of phosphorus, which hindered the attack by the negatively charged oxygen. On the other extreme, betaines of stable phosphoranes have never been isolated,<sup>17</sup> because betaine formation was followed by rapid elimination in which the double bond being formed was stabilized by conjugation with the stabilizing group.

When Wittig<sup>41</sup> discovered that a fairly stable betaine, formed from the reaction of benzaldehyde with methylenetriphenylphosphorane, when heated with benzophenone gave very little 1,1-diphenylethylene, he supplied evidence that the formation of the betaine was not reversible. However, Speziale<sup>10,44</sup> provided evidence for reversible betaine formation when he reacted ethyl trans-phenylglycidate with tributylphosphine in the presence of *m*-chlorobenzaldehyde and obtained both ethyl cinnamate and ethyl *m*-chlorocinnamate (see equations 2, 3 and 4). The betaine intermediate



believed to be present could either eliminate phosphine oxide to form cinnamate or dissociate to benzaldehyde and a phosphorane ester which was then free to react with the more reactive carbonyl compound, *m*-chlorobenzaldehyde.



With this evidence for reversibility of betaine formation, one could attribute the stereochemistry of the Wittig reaction, which normally resulted in a mixture of cis and trans olefins, to the ylid and the aldehyde being able to form two, diastereoisomeric betaines, according to steric requirements and dipole-dipole interactions between the phosphorus and oxygen atoms.<sup>12,45,46,47</sup> The trans form was usually favored stereochemically if betaine equilibration was of little importance. Fortunately, with fluorenylides, olefin isomers and diastereoisomeric betaines could not exist. This fact eliminated any confusion arising over differences in rates of reaction due to the formation of diastereoisomeric betaines and made the scale of relative reactivity of the ylids more reliable.

Speziale and Bissing<sup>10</sup> have performed the only detailed kinetic study of the Wittig reaction using substituted carbomethoxymethylenephosphoranes ( $\text{Ph}_3\text{P}:\text{C}(\text{Y})\text{COOMe}$ , where  $\text{Y} = \text{H}, \text{Cl}$  or  $\text{Br}$ ) with substituted benzaldehydes ( $p\text{-R-C}_6\text{H}_4\text{-CHO}$ , where  $\text{R} = \text{MeO}, \text{Me}, \text{H}, \text{Cl}$  and  $\text{NO}_2$ ). They found the reaction was second order (first order for ylid and first order for aldehyde) and the slope of the rho-sigma plot was +2.7 (electron-withdrawing substituents in the aldehyde facilitated the reaction).<sup>30</sup> Within experimental error in the reaction of carboethoxymethylenetriphenylphosphorane with p-methoxybenzaldehyde, the rate of formation of olefin was found to be the same as the rate of disappearance of the ylid. The reversibility of betaine formation was determined as before by reacting both tributyl- and triphenylphosphine with cis- and trans-ethyl phenylglycidate in the presence of m-chlorobenzaldehyde and isolating the chloro-substituted olefin (see equations 2, 3 and 4).<sup>10,44</sup>

Four distinct mechanisms for the Wittig reaction of stable ylids were discussed: (a) rapid, irreversible betaine formation and its rate-

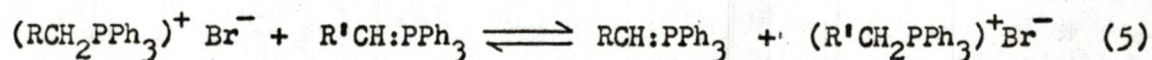
controlling decomposition to products; (b) slow, irreversible formation of betaine and rapid decomposition of betaine to products; (c) rapid, reversible betaine formation and rate determining formation of phosphine oxide and olefin; and (d) slow, reversible betaine formation with rapid decomposition of betaine to phosphine oxide and olefin. Of these four proposals, a, b and c were eliminated completely by kinetic data. Although mechanism d appeared to satisfy most of the experimental data collected, the authors felt that the generality of this reaction mechanism had yet to be proven.<sup>48</sup> Thus Speziale's<sup>6</sup> studies confirmed Johnson's<sup>17</sup> conclusion that the first step was slow and the rate was dependent upon the nucleophilic attack of the ylid carbanion on the carbonyl carbon. Therefore, with stable ylids, the Wittig reaction could be used to measure the nucleophilicity of these ylids.

It should be mentioned that Bergelson and Shemyakin<sup>45,46,49</sup> in their work on controlling the stereochemical course of the Wittig reaction with solvents and Lewis bases, have suggested an alternate mechanism for the Wittig reaction. The Russian authors believed that the Wittig reaction also could take place by a nucleophilic attack on phosphorus by the carbonyl oxygen, because in stable ylids the electrons of the carbanion were too delocalized for a nucleophilic attack on the carbonyl and with a Lewis base interaction with the phosphorus atom present, the phosphorus became less electrophilic and less accessible to react by this mechanism. Trippett<sup>12</sup> believed that this mechanism was not at all valid, for it would not take into account the fact that stable phosphoranes react only with carbonyls highly susceptible to nucleophilic addition.<sup>6</sup>

The Wittig reaction could also be used in another fashion to determine a relative scale of nucleophilicities for the ylids. The nucleo-

philicity of various ylids, an important factor in the Wittig reaction, could be attributed to many factors such as: basicity, polarizability, steric effects, associative effects, electrostatic interactions and changes in solvation.<sup>50</sup> For many species, ylids included, the basicity paralleled their nucleophilic strength in the attack of a carbonyl carbon.<sup>6</sup> Using the assumption that basicity would parallel nucleophilicity in carbonyl attack, Speziale<sup>6</sup> suggests that a competition reaction of two ylids for an aldehyde would reveal the reactivity of the ylids by measuring the ratio of products obtained from the reaction. The most nucleophilic ylid (i.e. the least amount of (p-d)pi overlap and the least delocalization by R' in I), would produce the most olefin. Consequently, another scale of relative reactivity could be obtained.

Bestmann<sup>51</sup> considered quaternary phosphonium salts and phosphine-alkylenes as corresponding acid-base pairs. He observed that triphenyl-alkylphosphonium salts and triphenylphosphinealkylenes could undergo intermolecular "transylidations" and that the composition of the equilibrium mixture was dependent upon the resonance and inductive effects of the substituents (equation 5). Working with various ylids and phosphonium salts of the type  $\text{Ph}_3\text{P}:\text{CHR}'$  and  $(\text{R}'\text{CH}_2\text{PPh}_3)^+\text{Br}^-$ , respectively, Bestmann derived a relative scale of ylid basicities. He found that ylids decreased in basicity in the order of R = alkyl, phenyl, carbomethoxy and



benzoyl, which was the same as the order of increasing carbanion stabilizing power. This, therefore, constituted another method for

determining the extent of the delocalization of electrons of the ylid carbanion by the carbon or phosphorus substituents.

The study of valence shell expansion of phosphorus is concerned primarily with the change in electron density about the phosphorus nucleus. As one can see from the discussion of the Wittig reaction, the use of chemical reactions elucidates this information in a somewhat indirect fashion. It should also be possible to utilize various physical measurements to supplement the chemical data.

An electron-diffraction investigation has revealed that phosphoryl halides of the type  $X_3PO$  (where X is a halogen, except iodine, or a mixture of these halogens) have little pi bonding character in the P-X portion of the molecule and substantial pi bonding character in the P-O bond.<sup>52,53</sup> The study included the following compounds containing a tetrahedrally surrounded phosphorus atom:  $POF_3$ ,  $POCl_3$ ,  $POBr_3$ ,  $POF_2Cl$  and  $POFCl_2$ . In all cases, the P-Cl bond distances corresponded to very little pi bonding, whereas the P-F and P-Br atom-center distances indicated that there was nearly one-third pi bond per sigma bond. In  $POCl_3$ , the P-O pi bond character was unduly large and indicated one pi bond per sigma bond. The same trend was found for  $POF_3$  from microwave spectra measurements.<sup>54</sup> This information could indicate that in the case of  $POCl_3$  and  $POF_3$ , the electron-withdrawing effect of the halogens caused the positive character to increase, which resulted in more (p-d)pi overlap with the oxygen atom.

In many phosphoryl molecules,  $X_3PO$ , the infrared P-O stretching frequencies and bond lengths, the XPX bonding angles and the relative XP bond distances have been found to vary as X is varied, which indicated significant changes in the P-O bond character. Bell et al.<sup>55</sup> have shown that there was a correspondence between phosphoryl frequency (P-O) and

the electronegativity of the substituent groups. They reported that the P-O bond frequency shifted to longer wavelength, which showed a decrease in the extent of pi bonding, in the order  $\text{Cl}_3\text{PO}$ ,  $\text{Cl}_2\text{PhPO}$  and  $\text{ClPh}_2\text{PO}$ . Thomas and Chittenden<sup>56</sup> believed that two effects influenced the absorption frequency in organophosphorus compounds. They were the inductive effects of substituents bonded to phosphorus and the effect, presumably resonance, of the number of phosphorus-carbon bonds in the molecule. In cases where the inductive effect was predominate, a linear relationship existed between absorption frequency and summed inductive effects of the groups attached. Daasch and Smith<sup>57</sup> have recorded the characteristic absorption bands for various phosphorus compounds ( $\text{X}_3\text{PO}$ ) and have shown that where X was halogen, alkyl, aryl, aryloxy and alkoxy the electronegativity had a similar effect on the infrared P-O stretching frequency. They concluded that the greater the positive character of the phosphorus atom in the phosphoryl molecule, the greater was the shift towards shorter wavelengths, which signified more double bond character associated with the P-O bond.

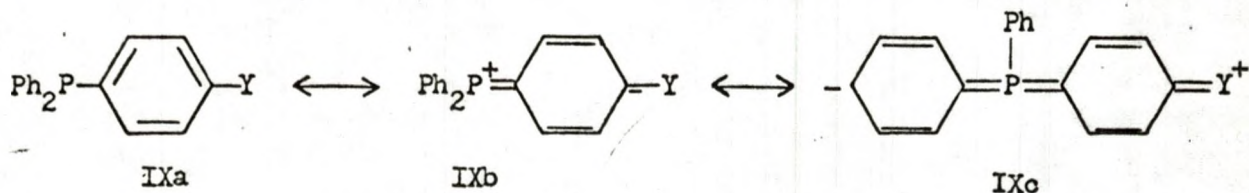
Wagner<sup>34</sup> has calculated the P-O pi bond orders of phosphoryl systems by the internally consistent molecular orbital method and has found a good correlation of these calculated values with the experimentally determined values. Working with  $\text{Ph}_3\text{PO}$ ,  $(\text{Cl}-\text{C}_6\text{H}_4-)_3\text{PO}$  and  $\text{Me}_3\text{PO}$ , and with calculated group electronegativities of 2.4, 2.2 and 2.0 respectively, the P-O stretching frequencies were found to shift to a lower value (less pi bonding) in the order listed for the phosphine oxides. This was expected if the positive character on phosphorus decreased in the order indicated. Therefore, the positive character of phosphorus appeared to affect the valence shell expansion in phosphoryl systems.

Studies conducted in the ultraviolet region have also presented considerable information as to the electron delocalization in phosphonium

systems, arylphosphines, substituted arylphosphines and phosphine oxides. Jaffe<sup>58</sup> has presented spectroscopic data that demonstrated that phenyl groups are only weakly conjugated with phosphorus when the unshared pair of electrons of phosphorus was unavailable, as in phosphine oxides. He concluded there was no resonance interaction between the several phenyl groups attached to the phosphorus, but that each phenyl group made an independent contribution to the extinction coefficient. These results were based on the ultraviolet absorption spectra of phenyl groups in  $\text{PhPO}_3\text{H}_2$ ,  $\text{Ph(H)PO}_2\text{H}$ ,  $\text{Ph(R)PO}_2\text{H}$ ,  $\text{Ph}_2\text{PO}_2\text{H}$ ,  $\text{Ph}_3\text{P}$  and  $\text{Ph}_3\text{PO}$ .<sup>58,59</sup> On the other hand, if the phosphorus had an unshared pair of electrons, as in phosphines, extensive conjugation with the phenyl groups was observed.<sup>59</sup> Additional studies in the ultraviolet region showed that the P-O bond in phosphine oxides exhibited little pi bonding.<sup>60</sup> Craig et al.<sup>18</sup> performed quantum mechanical calculations and concluded that the strength of bonds involving a d-orbital of one atom and a p-orbital of another atom was relatively independent of the electronegativity difference between the atoms. They found that in tri-substituted phosphorus, no (p-d)pi bonding was expected,<sup>18</sup> except for cases in which phosphorus carried highly electronegative ligands.<sup>61,62</sup> In general, quadruply connected phosphorus, which contained four sigma bonds, averaged one (p-d)pi bond per phosphorus atom. These generalities were also consistent with the quantum mechanical reasoning presented by Jaffe.<sup>61</sup> In studies conducted in the ultraviolet region on tri- and tetra-substituted group V elements, the same trends in bonding were observed.<sup>63</sup>

In view of the problem of charge distribution in organophosphorus compounds, Goetz et al.<sup>64</sup> investigated the influence of polar, para-substituents on the resonance exerted in triphenylphosphine and phosphine

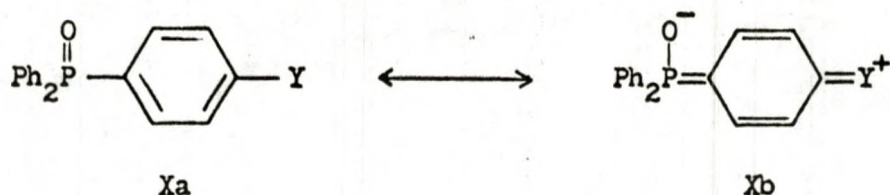
oxides by ultraviolet and infrared spectroscopy and dipole moment studies. For the investigation, phosphines, phosphine oxides and phosphine sulfides of the type  $\text{Ph}_2\text{P}-\text{C}_6\text{H}_4-\text{Y}-\text{p}(\text{IX})$ ,  $\text{Ph}_2\text{P}(\text{O})\text{C}_6\text{H}_4-\text{Y}-\text{p}(\text{X})$  and  $\text{Ph}_2\text{P}(\text{S})\text{C}_6\text{H}_4-\text{Y}-\text{p}(\text{XI})$ , respectively, where  $\text{Y} = \text{H}, \text{Cl}, \text{Br}, \text{MeO}$  and  $\text{NMe}_2$ , were employed. It was postulated from the ultraviolet experimental data that IXa existed in resonance forms IXb, involving the delocalization of the free electron



pair on phosphorus, and IXc, involving the delocalization of a free electron pair of Y. This resonance would occur in the ground state and should be influenced by Y, but the excited state was more polar than the ground state in all cases due to increased contribution of IXc. The contribution of IXb and IXc, for example, also would increase with an increase in the donor character of Y. A normal interaction of the substituent Y with its phenyl nucleus was observed, however. The authors have also stated that the halogen substituents showed predominately donor properties in the phosphines.

The oxides were believed to exist in the resonance forms Xa and Xb, with only slight dependence on the donor character of Y. The contribution of Xb was greater in the excited state and increased with increased donor properties of Y. Thus the halogens appeared to show a lesser degree of form Xb, due to weaker donating ability. It should be mentioned that Schiemenz<sup>65</sup> could not agree with Goetz. He felt that the ultraviolet spectra information was not sufficient to make all the statements concerning

electron distribution in the compounds IX, X and XI (having  $Y = NMe_2$ ).



Schiemenz said that theory would not allow for any  $n \rightarrow \pi^*$  transitions suggested by Goetz.

There existed other methods, besides chemical reactivity with carbonyls, that would determine the reactivity of an ylid. Among these was the method suggested by Johnson<sup>17</sup> who had shown that the greater the contribution to the ylene form (Ia) to the resonance hybrid of the ylid, the more acidic would be the conjugate acid. It was also stated that the more acidic was the conjugate acid, the less reactive would be the ylid. In addition, he demonstrated that in a series of ylids, which had a fluorene nucleus for the ylid carbon, dimethylsulfonium > triphenylphosphonium > triphenylarsonium > tributylphosphonium was the observed order of acidity of the conjugate acids of the ylids. The order of acidity of the conjugate acids was determined spectrophotometrically in the ultra-violet region. Therefore, one could conclude that as the reactivity of an ylid increased, the acidity of the conjugate acid should be decreased. Speziale and Ratts<sup>6</sup> observed the same trend in their work with stable ylids of the form  $\text{Ph}_3\text{P}:\text{C}(\text{X})\text{COR}$ , where  $\text{R} = \text{Ph}_2\text{N}$ ,  $\text{OEt}$ ,  $\text{CN}$  or  $\text{Ph}$  and  $\text{X} = \text{H}$ ,  $\text{Br}$ ,  $\text{Cl}$ ,  $\text{I}$  and  $\text{COEt}$ . Performing a potentiometric titration of the phosphonium salts in methanol with hydrochloric acid, they found that when  $\text{X} = \text{H}$ , the basicity, and thus reactivity, of the ylids roughly paralleled the ability of the attached groups to stabilize a negative charge on the alpha-methylene carbon. The order was:  $\text{CONPh}_2 < \text{COEt} <$



CN < CPh. Replacement of the alpha-hydrogen with a halogen decreased the basicity in each case, although the basicity of the ylids was opposite to that expected for the ability of a halogen to stabilize an adjacent carbanion (I > Br > Cl).

Royer<sup>11</sup> determined the pKa values for a series of ylids in which only R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> in III were varied (IIIg-n). The results revealed that groups pushing electron density towards the phosphorus atom (p-Me<sub>2</sub>N-Ph, p-MeO-Ph, Me, Et and Bu groups) caused the salts to have a higher pKa value (less acidic) than did groups that withdrew electron density away from phosphorus (ph). He also supplied data to prove that greater resonance stabilization of the ylid carbanion by the carbon substituents produced a more acidic conjugate acid.

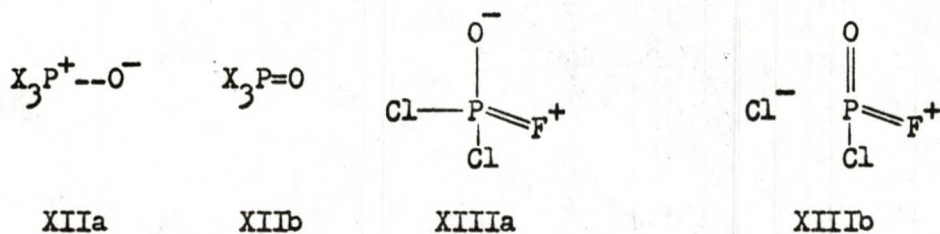
Therefore, by a pKa investigation one could determine the basicity of fluorenylides. The data, when correlated with the effect of substituents attached to phosphorus on the positive character of the central atom, could be considered essentially an indirect measurement of the degree of (p-d)pi overlap. The extent of this valence shell expansion was further verified by the reactivity of the ylids in the Wittig reaction, since basicity was correlated in this instance to nucleophilicity.<sup>6</sup>

More information about the electronic environment of phosphorus<sup>65</sup> could be obtained by nuclear magnetic resonance spectra (P<sup>31</sup>).<sup>66</sup> A change in the electron density about phosphorus with a change in substituents attached to phosphorus should alter the extent of shielding of the phosphorus nucleus and chemically shift its resonance position.<sup>67</sup>

There have been many studies in the literature primarily concerned with the shielding of phosphorus by various substituents. For instance, in the study of phosphorus halides, phosphorus shielding decreased in the

order  $\text{PF}_3$ ,  $\text{PI}_3$ ,  $\text{PCl}_3$  and  $\text{PBr}_3$  with the iodide out of sequence and the fluoride having the most shielding.<sup>68</sup> It was believed that both ionic and covalent bond character existed in these compounds. The electronegativity difference between phosphorus and halogen increased from  $\text{PI}_3$  to  $\text{PF}_3$  and so would the ionic bond character. In addition, fluorine, and to a lesser degree the other halogens, was capable of double bond formation. The observed shifts were reasonable and compatible with phosphorus shielding increasing with the increase of double bond character and shielding decreasing with increased ionic bonding. By analogy, one could expect greater shielding of phosphorus if the ylene form Ib predominated. The contribution of each to the resonance hybrid would, of course, determine the final chemical shift.

For quadruply substituted phosphorus,  $\text{POCl}_3$ ,  $\text{POCl}_2\text{F}$ ,  $\text{POClF}_2$  and  $\text{POF}_3$ , the shielding increased for both phosphorus and for fluorine as more fluorine atoms were added to the molecule. To explain this shielding effect, it was believed that these phosphorus oxyhalides had the structures XIIIa and XIIIb and that in order to give the experimentally observed trend



in the shifts, there had to exist some double bond structures XIIIa and XIIIb. They also observed that phosphorus had greater shielding in  $\text{POCl}_3$  than in  $\text{PSCl}_3$ . They used this information as direct verification that oxygen formed double bonds better than does sulfur. Therefore, XIIIb was thought to be more important than XIIIa in that investigation. It should be apparent that the increased positive character of phosphorus due to

increased substitution of fluorine for chlorine induced the valence shell expansion of phosphorus and, consequently, the formation of fluorine double bonds. The final result of this valence shell expansion was a greater shielding effect.

Muller et al.<sup>69</sup> reported that shielding increased from trivalent compounds ( $R_3P$ ) to thiophosphoryl compounds ( $R_3PS$ ) and then to phosphoryl compounds ( $R_3PO$ ). The chemical shift was found to depend upon the nature of the groups attached to phosphorus and the type of bonding involved. No simple quantitative correlations, such as an additive shift constant for a particular group or a relation between chemical shift and the groups attached to phosphorus were noted. Additional studies showed that trivalent phosphorus compounds had significantly larger chemical shifts than did tetravalent phosphorus compounds, as would be expected with resonance interaction occurring in the tri-substituted case. Morin<sup>70</sup> and Jones and Katritzky,<sup>71</sup> using a large number of phosphorus and organophosphorus compounds, reported more evidence pertaining to these shielding trends.

Speziale and Ratts<sup>6</sup> have shown that in stable ylids ( $Ph_3P:CXR$ , where  $X = H, Br, Cl, \text{ or } I$  and  $R = CN, COOMe \text{ or } CPh$ ) the  $P^{31}$  chemical shifts were very similar to the shifts exhibited by the corresponding phosphonium chloride or bromide. They attributed this information to very little  $P=C$  character, (p-d)pi overlap, in ylids. Thus NMR spectra of the ylids and the ylid salts resembled each other. This was surprising, since valence shell expansion was originally proposed to account for the stability of these ylids and, with valence shell expansion, one would expect increased phosphorus shielding. It appeared that something unknown, perhaps a different type of participation from the phenyl groups attached to phosphorus, was occurring that caused these similar shielding character-

istics. Mark<sup>7</sup> reported that ylids of the type  $(R_2N)_3P=CF_2$ , where R = Me and Et, possessed a highly shielded phosphorus atom, which was indicative of a pentacovalent phosphorus compound with a high degree of P-C double bond character (extensive (p-d)pi overlap). He also reported that these ylids would not react in a Wittig reaction with o-chlorobenzaldehyde or benzaldehyde. Nevertheless, it should be emphasized that if Speziale's proposal was applicable to fluorenylides, the trend would not be consistent with differences in reactivity observed in the Wittig reaction. Driscoll et al.<sup>16</sup> in their work with mesomeric phosphonium salts  $((Ph_3P)_2CH_2^{2+} 2Br^-)$  observed the same type of shifts in comparison to the NMR data of the mono-ylid  $(Ph_3P:CHPh_3^+ Br^-)$ . Additional studies are definitely needed in this area before any conclusions can be drawn.

Royer<sup>11</sup> recorded the  $P^{31}$  NMR spectra of triphenylphosphine, mono-, di and tri-p-methoxyphenylphosphines and their oxides, except the oxide of the dimethoxy derivative. In the phosphines, a definite increase in shielding from triphenylphosphine to tri-p-methoxyphenylphosphine was observed. Royer believed that the data implied the unshared pair of electrons of phosphorus was being delocalized into the phenyl rings<sup>59</sup> and that triphenylphosphine should have, correspondingly, the least amount of shielding. Each additional methoxy group, with an electron releasing effect, would then decrease the amount of delocalization into the rings from the phosphorus.

The oxides on the other hand showed relatively constant shifts. The chemical shift data indicated a large decrease in the amount of shielding from the phosphines, but the extent of shielding in the various oxides remained constant. Van Wazer's<sup>62</sup> studies with phosphonium systems indicated a similar trend in shielding.

NMR data on fluorenylides (IIIa-n) have been unattainable and could remain unavailable until some new techniques are developed for increasing the concentration of ylids in standard NMR solvents. Fortunately, however, NMR data on phosphine oxides, isoelectronic with ylids, was attainable and, consequently, electronic characteristics similar to those in ylids should be noted.

Upon closer inspection of the ylid molecule, it appeared that NMR spectra should not be able to supply as much significant shift data concerning changes in phosphorus shielding as expected. The degree of shielding about phosphorus should remain about the same in the series of substituted triphenylphosphoniumfluorenylides (IIIa-e, g-k) as was observed in the isoelectronic phosphine oxides used by Royer. In the case of ylids (IIIa-e, g-k), inductive effects of the phenyl groups would cause the positive character of phosphorus to increase by acting through the sigma bonds and in turn would create a demand for the available electrons of the ylid carbanion. In simple phosphoranes ( $\text{Ph}_3\text{P:CH}_2$ ), this demand could be met easily, due to the localization of the electrons on the ylid carbanion. In this situation, (p-d)pi overlap should truly affect the phosphorus shielding. In fluorenylides, the ylid carbanion electrons are so greatly delocalized through the fluorenyl system and relatively unavailable that the overall response would be a smaller increase in shielding than expected. Phosphorus should, however, try to keep a somewhat constant, stable, positive character.<sup>11</sup> This means that with increased positive character, phosphorus would seek electrons, presumably from the ylid carbanion, and alleviate the increased positive character. Electron-withdrawing substituents on the phenyl group should, of course, increase the demand for electrons from the ylid carbanion.

Where the phenyl groups were substituted with electron-donating groups, the inductive effects (-I) of the rings should be reduced and the demand for electrons from the ylid carbanion should be weaker. Therefore, using fluorenylides only and a representative series of substituted phenylphosphines in these ylids, small, but significant trends in the shielding with change in substituents should be present. This is inconsistent to what Speziale and Ratts<sup>6</sup> observed, but they were not working with a constant group for the CR<sub>2</sub>' in I.

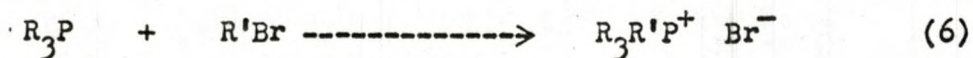
From this discussion, it is apparent there are many physical methods by which the extent of (p-d)pi overlap could be investigated. An X-ray crystallographic investigation of ylids would truly be beneficial, since it could furnish information concerning bond distances between the fluorenyl carbon and phosphorus. With increased (p-d)pi overlap, one would expect to see a corresponding decrease in bond length. Unfortunately, ylids are such complex molecules that an X-ray study would be too tedious to complete. Consequently, such studies have not been attempted. Infrared spectroscopic studies of ylids could possibly be used to investigate changes in bond order in the various P-C bonds of ylids through shifts in absorption wavelengths. Royer had attempted such a study basing his investigation on a 10 micron band being the corresponding phenyl-phosphorus absorption wavelength. However, it should be mentioned that this wavelength has not been fully verified and, until this is done, such work would not be valid. Of course, the study of pi bonding in P-O bonds by infrared spectroscopy would yield information about the effects of substituents attached to phosphorus, as indicated earlier.

Of the two remaining physical methods, NMR and UV spectroscopy, the latter appeared the most fruitful. PKa determinations performed spectrophotometrically in the UV region has correlated quite nicely with the electron distribution indicated by the Wittig reaction reactivity and

has become a very useful tool for estimating the extent of (p-d)pi overlap. NMR investigations, on the other extreme, left much to be desired. It appeared that only where the groups R in I were not carbon, was the shielding increased according to the proposals of "d-orbital resonance." This ambiguity must be eliminated before any further conclusions could be made. Thus, it seems reasonable that only Wittig reaction results and pKa measurements were employed to elucidate the extent of (p-d)pi overlap in the present investigation.

There existed a variety of methods available for the preparation of phosphorus ylids, but the most common procedure is to react a phosphonium salt with a suitable base. The strength of the base necessary to generate the ylid depended upon the acidity of the hydrogen on the carbon atom adjacent to the phosphorus atom and varied from a solution of sodium carbonate for  $((\text{Ph}_3\text{P})_2\text{CH}_2^{2+}) 2\text{Br}^-$  to alkyl-metals in nonpolar solvents for unsubstituted alkylphosphonium salts.<sup>16,72,73,74</sup>

Phosphines (aryl and alkyl) have been quaternized to phosphonium systems readily with primary alkyl halides,<sup>75</sup> as opposed to secondary and tertiary halides, which could form olefins by elimination according to the



following series:  $\text{I} > \text{Br} > \text{Cl}$  and  $\text{Me} > \text{Et} > \text{Pr}$ , etc. Other methods to prepare phosphonium systems have been outlined by Trippett.<sup>12</sup>

There are many methods known for preparing primary, secondary and tertiary phosphines. This includes phosphines which contain alkyl, aryl, substituted aryl groups and combinations thereof. Since this thesis is concerned primarily with the preparation of tertiary, substituted aryl-phosphines, only a discussion oriented in this direction will be given.

It is suggested that the reader refer to texts by Kosolapoff<sup>76</sup> and Van Wazer<sup>77</sup> for a comprehensive coverage of the chemistry of phosphines.

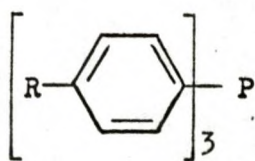
Phosphines possess a strong affinity for oxygen and must be handled with exclusion of air in most cases. Alkylphosphines are particularly susceptible to oxidation, especially the lower alkyl members, but aryl members are fairly stable in this respect and will not form oxides unless heated to high temperatures in the presence of air or treated with oxidizing reagents. For example, the lower-boiling, tertiary arylphosphines can be vacuum distilled with little or no oxidation occurring. The use of aryl iodides in the synthesis of arylphosphines is usually avoided for they are known to induce oxidation of the phosphine during isolation.<sup>78</sup> The use of methyl iodide or iodine to initiate the Grignard preparation is avoided, if possible, for the same reason. Reduction of phosphine oxides by reagents such as lithium aluminum hydride is possible, although one has to be concerned about other parts of the molecule being affected by the reduction.<sup>79</sup> Therefore, isolation and preparation procedures should exclude oxidizing conditions, since restoration of the original phosphine from the oxide may be very difficult.

Common synthetic techniques for tertiary, substituted arylphosphines have usually involved the displacement of the chlorine of phosphorus trichloride,<sup>80,81</sup> of an arylphosphorus dichloride ( $\text{RPhCl}_2$ , where R = Ph or a substituted phenyl group)<sup>78,82,83</sup> or of a diarylphosphinous chloride ( $\text{R}_2\text{P}(\text{OH})\text{Cl}$ , where R = Ph or a substituted phenyl group)<sup>78,84,85</sup> with a nucleophile. The nucleophile was usually a magnesium Grignard reagent, although other organometallic reagents ( $\text{Na}$ ,<sup>86,87,88, 89</sup>  $\text{K}$ ,<sup>90,91</sup>  $\text{Li}$ ,<sup>82,92,93</sup>  $\text{Hg}$ ,<sup>84</sup>  $\text{Zn}$ ,<sup>94</sup>  $\text{Al}$ ,<sup>95</sup> and etc.<sup>76</sup>) were known to react in the same manner.<sup>96,97</sup>

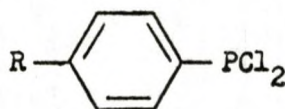


Another general method of phosphine preparation was to react an aryldihalide<sup>98</sup> or a substituted arylhalide with a nucleophile such as:  $M_3P$ ,  $M_2PR$  or  $MPR_2$  (where  $M = Na$ ,<sup>76,99,100</sup>  $Li$ ,<sup>101,102</sup> or  $K$ <sup>76,99</sup> and  $R = Ph$  or a substituted phenyl group).<sup>82,84</sup> It should be mentioned that very little work has been attempted, in comparison to  $MPR_2$  systems, on the reactions of either  $M_2PR$  or  $M_3P$  with arylhalide systems.

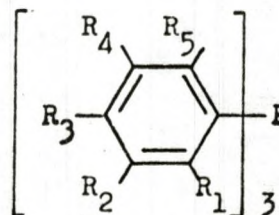
There are preparatory reactions where organometallic nucleophiles were not necessary. For instance, the reaction of phosphorus trichloride with a large excess of *N,N*-dimethylaniline, yielded tris(*p*-*N,N*-dimethylaminophenyl)phosphine ( $R = Me_2N$  in XIV) and the acid salt of *N,N*-



XIV



XV



XVI

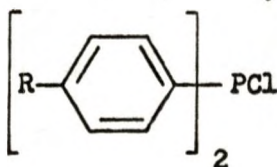
dimethylaniline.<sup>103</sup> The phosphines corresponding to IIIf<sup>104</sup> and VI<sup>44</sup> were prepared in an analogous manner from piperidine and morpholine respectively, with phosphorus trichloride.

Various approaches have been employed to prepare certain phosphines. For example, Davies and Morris<sup>105</sup> in their preparation of tris(*p*-phenoxyphenyl)phosphine ( $R = PhO$  in XIV), reacted diphenyl ether with aluminum chloride and phosphorus trichloride to prepare *p*-phenoxyphenylphosphonous chloride ( $R = PhO$  in XV). This was then converted to the desired product by reaction of the Grignard reagent of *p*-bromophenylphenyl ether with phosphorus trichloride. They also obtained the product, in an impure form only, by the reaction of the Grignard reagent of *p*-bromophenylphenyl ether with phosphorus trichloride. Michaelis<sup>106</sup> prepared the ortho, meta

and para isomerides of tris(methylphenyl)phosphine (XVI) ( $R_1 = \text{Me}$  and  $R_2-R_5 = \text{H}$  for ortho, and  $R_2 = \text{Me}$  and  $R_1, R_3-R_5 = \text{H}$  for meta and  $R_3 = \text{Me}$  and  $R_1, R_2, R_4$  and  $R_5 = \text{H}$  for para). Numerous other isomeric, methyl substituted arylphosphines, that contained up to three methyl groups per ring, were prepared also from the organosodium reagents of the corresponding bromo- and chloroaryl compound and phosphorus trichloride.<sup>106</sup> Later, Mann and Chaplin<sup>107</sup> prepared many of these same compounds by the magnesium Grignard with comparable yields.

From the literature, one could observe that it was common practice to first investigate the use of organomagnesium reagents for preparing phosphines, and if this failed to yield the product desired, lithium and sodium organometallic reagents were then employed. A typical situation was the observation that p-bromo-N,N-dimethylaminobenzene would not readily form a magnesium Grignard reagent, but the lithium derivative would form. This information concerning the reactivity of organometallics, combined with the fact that the order of ease of formation of an organometallic for arylhalides decreased in the order  $\text{I} > \text{Br} > \text{Cl}$ , enabled one to narrow the selection of possible starting materials for the investigation.

Unsymmetrical tertiary, substituted arylphosphines of the type  $R_2R'P$  (where  $R = \text{Ph}$  and  $R' =$  substituted phenyl group) have been prepared by the techniques mentioned earlier, with only small modifications necessary to produce other phosphines. Bartlett et al.<sup>78</sup> prepared (p-chlorophenyl)diphenylphosphine ( $R = \text{Ph}$  and  $R' = \text{p-Cl-Ph}$ ) by reaction of the Grignard of p-bromochlorobenzene and diphenylphosphinous chloride ( $R = \text{H}$  in XVII), whereas Gilman and Brown<sup>85</sup> prepared the corresponding bromo-derivative ( $R = \text{Ph}$  and  $R' = \text{p-Br-Ph}$ ) in an analogous manner using the mono-Grignard from p-dibromobenzene.<sup>108</sup> Other phosphines such as (p-

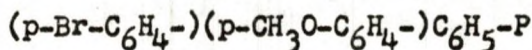
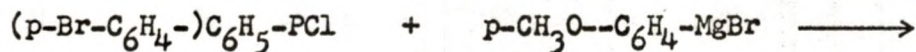
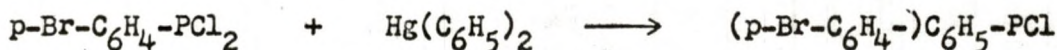
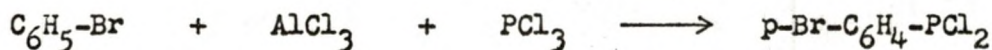


XVII

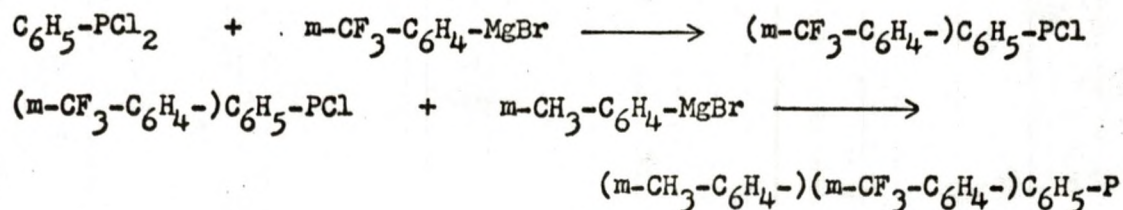
methoxyphenyl)diphenylphosphine (R = Ph and R' = p-MeO-Ph)<sup>81</sup> and (p-methylphenyl)diphenylphosphine (R = Ph and R' = p-Me-Ph)<sup>106,107</sup> have been prepared again using the Grignard of the corresponding bromoaryl compound and diphenylphosphinous chloride.

Unsymmetrical, tertiary, substituted arylphosphines of the type R<sub>2</sub>R'P (where R = a substituted phenyl group and R' = Ph) have been prepared by the general techniques previously discussed. Examples of these phosphines were di(p-N,N-dimethylaminophenyl)phenylphosphine (R = p-Me<sub>2</sub>N-Ph and R' = Ph)<sup>82</sup> prepared by the reaction of phenylphosphonous chloride (R = H in XV) with the organolithium reagent of p-bromo-N,N-dimethylaniline and di(p-methoxyphenyl)phenylphosphine (R = p-MeO-Ph and R' = Ph) prepared from phenylphosphonous dichloride and the Grignard of p-bromoanisole.<sup>81</sup>

Many unsymmetrical, tertiary, substituted arylphosphines of the type RR'R''P have been prepared where R ≠ R' ≠ R''. Davies and Mann<sup>84</sup> have prepared (p-bromophenyl)(p-methoxyphenyl)phenylphosphine according to the following sequence of reactions:



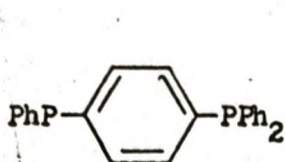
Campbell and Hatton<sup>109</sup> have prepared (m-trifluoromethylphenyl)(m-methylphenyl)phenylphosphine by the fast reaction of the Grignard of m-bromotrifluoromethylbenzene with phenylphosphonous chloride followed by another reaction with the Grignard of m-bromotoluene. Other mixed, tertiary arylphosphines have been listed by Kosalopoff.<sup>76</sup>



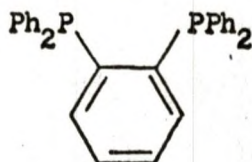
Symmetrical, tertiary, substituted and unsubstituted arylphosphines of the type RR'R''P (where R = R' = R'') have been conveniently prepared by a reaction that eliminates hydrochloric acid as described earlier. The simplest arylphosphine (triphenylphosphine) has been known for a long time and many preparations have since been recorded.<sup>80,90,95,110</sup> However, the most common laboratory method was the reaction of the Grignard of bromobenzene with phosphorus trichloride.<sup>80</sup> As already mentioned, other symmetrical substituted arylphosphines have been prepared by the same method using either magnesium, sodium or lithium organometallics as the nucleophile. Tris(pentafluorophenyl)phosphine,<sup>111</sup> tris(p-methoxyphenyl)phosphine<sup>112</sup> and tris(p-fluorophenyl)phosphine<sup>40</sup> have been prepared from the Grignard reagent of the corresponding arylbromide with phosphorus trichloride and could serve as additional evidence for the number and variety of substituents that could be attached to the phenylgroup of the arylphosphine.

In addition, other methods have been employed to prepare symmetrical phosphines. Aguiar,<sup>98</sup> for example, has reported the preparation of p-bis(diphenylphosphino)benzene (XVIII) from the reaction of p-dibromobenzene with lithium diphenylphosphide (prepared from lithium, triphenyl-

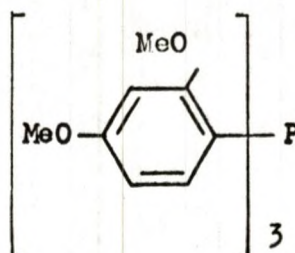
phosphine and t-butylchloride). The ortho isomeride (XIX) has been pre-



XVII



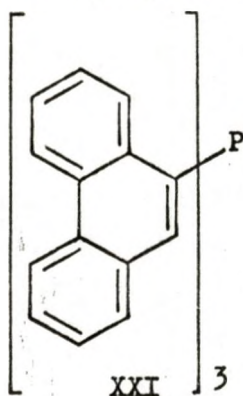
XIX



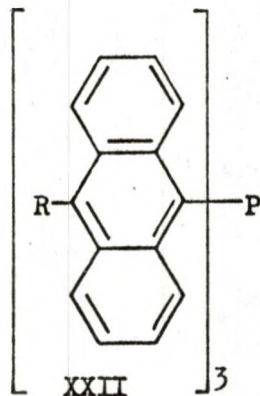
XX

pared from the reaction of (o-chlorophenyl)diphenylphosphine and lithium metal with diphenylphosphinous chloride.<sup>93</sup> Tris(2,4-dimethoxyphenyl)-phosphine (XX)<sup>113</sup> has been prepared in a slightly different manner by boiling three moles of 1,3-dimethoxybenzene with one mole of phosphorus trichloride and an equimolar amount of zinc chloride. It was also reported that phenol esters or substituted phenol esters react to yield triarylphosphines under the same conditions.

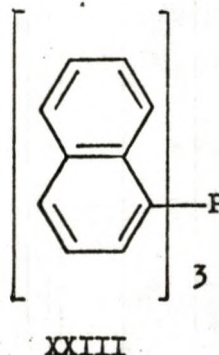
Aromatic analogs of triphenylphosphine such as tris(9-phenanthryl)-phosphine (XXI),<sup>110</sup> tris(9-anthryl)phosphine (XXII, R = H), tris(9-bromo-10-anthryl)phosphine (XXII, R = Br) and tris(1-naphthyl)phosphine (XXIII)<sup>114</sup> have been prepared from the action of organolithium reagents of 9-bromo-



XXI



XXII



XXIII

phenanthrene, 9-bromoanthracene, 9,10-dibromoanthracene and bromonaphthalene, respectively, with phosphorus trichloride.

Isolation procedures for the phosphines discussed varied considerably. However, arylphosphine reactions, in general, are usually quenched with either dilute sodium hydroxide, dilute hydrochloric acid, water or an ammonium chloride solution. The product is often isolated by either distillation, extraction with acid, fractional recrystallization of the reaction mixture and column or gas<sup>115</sup> chromatography.<sup>76</sup>

Royer<sup>11</sup> prepared tertiary, substituted arylphosphines (XIV) having groups (R) which were known to be electron-donating ( $\text{Me}_2\text{N}$  and  $\text{MeO}$ ). He synthesized the mono, di- and tri-p-methoxy derivatives of triphenylphosphine and tris(p-N,N-dimethylaminophenyl)phosphine as described earlier. The phosphines were isolated by extraction of the phosphine in a benzene solution with concentrated hydrochloric acid followed by neutralization of the acid layer with ammonium hydroxide. Although he quenched his reaction with ice-water exposed to air, Royer reported no oxide formation.

Substituted phosphines could be prepared from some of the unsubstituted phosphines already discussed, limited to the extent that the reactivity of the reagents employed would alter the valence state of phosphorus. Those phosphines containing bromine on a phenyl group could undergo a displacement by a nucleophile<sup>116,117,118</sup> or metallation<sup>93</sup> with magnesium or lithium. Gilman<sup>85</sup> found that treating (p-bromophenyl)diphenylphosphine with butyl lithium and carbon dioxide gave (p-carboxyphenyl)diphenylphosphine. The same product was obtained with triphenylphosphine under the same conditions.

Neunhoeffer and Lamza<sup>112</sup> subjected (p-methoxyphenyl)diphenylphosphine to ether cleavage conditions with hydroiodic acid and hypophosphorous acid and obtained (p-hydroxyphenyl)diphenylphosphine. They

also prepared the di-p-hydroxy and tri-p-hydroxy derivatives of tri-phenylphosphine employing similar techniques.

Thus from this discussion, it should be evident that many different tertiary, substituted arylphosphines could be prepared and that more than one pathway for preparing the phosphine was usually available (see Table 1).

Basically, the main objective of this research investigation was to synthesize new derivatives of triphenylphosphine containing meta and para electron-withdrawing substituents on the phenyl groups and to convert those phosphines to the corresponding phosphoniumfluorenylides. The information, obtained from Wittig reactions and pKa determinations on the ylid conjugate acids, was desired to further reveal the effect of substituents attached to phosphorus on (p-d)pi overlap ("d-orbital resonance").

Table 1. Tertiary Aryl Derivatives of Phosphorus Trichloride

No.	Aryl Substituents Attached to Phosphorus			Lit. Ref.
	1	2	3	
1.	$C_6H_5-$	$C_6H_5-$	$C_6H_5-$	80
2.	$o-Cl-C_6H_4-$	$C_6H_5-$	$C_6H_5-$	93
3.	$p-Cl-C_6H_4-$	$C_6H_5-$	$C_6H_5-$	78
4.	$p-Br-C_6H_4-$	$C_6H_5-$	$C_6H_5-$	85
5.	$p-Me-C_6H_4-$	$C_6H_5-$	$C_6H_5-$	106
6.	$p-HO-C_6H_4-$	$C_6H_5-$	$C_6H_5-$	112
7.	$p-MeO-C_6H_4-$	$C_6H_5-$	$C_6H_5-$	81
8.	$p-HOOC-C_6H_4-$	$C_6H_5-$	$C_6H_5-$	85
9.	$p-Br-C_6H_4-$	$p-MeO-C_6H_4-$	$C_6H_5-$	84
10.	$m-Me-C_6H_4-$	$m-CF_3-C_6H_4-$	$C_6H_5-$	109
11.	$p-HO-C_6H_4-$	$p-HO-C_6H_4-$	$C_6H_5-$	112
12.	$p-MeO-C_6H_4-$	$p-MeO-C_6H_4-$	$C_6H_5-$	81
13.	$p-Me_2N-C_6H_4-$	$p-Me_2N-C_6H_4-$	$C_6H_5-$	82
14.	$p-F-C_6H_4-$	$p-F-C_6H_4-$	$p-F-C_6H_4-$	40
15.	$o-Me-C_6H_4-$	$o-Me-C_6H_4-$	$o-Me-C_6H_4-$	106
16.	$m-Me-C_6H_4-$	$m-Me-C_6H_4-$	$m-Me-C_6H_4-$	106
17.	$p-Me-C_6H_4-$	$p-Me-C_6H_4-$	$p-Me-C_6H_4-$	106
18.	$p-HO-C_6H_4-$	$p-HO-C_6H_4-$	$p-HO-C_6H_4-$	112
19.	$p-MeO-C_6H_4-$	$p-MeO-C_6H_4-$	$p-MeO-C_6H_4-$	112
20.	$p-PhO-C_6H_4-$	$p-PhO-C_6H_4-$	$p-PhO-C_6H_4-$	105
21.	$p-Me_2N-C_6H_4-$	$p-Me_2N-C_6H_4-$	$p-Me_2N-C_6H_4-$	103
22.	$C_6F_5-$	$C_6F_5-$	$C_6F_5-$	111



Table 1, continued

No.	Aryl Substituents Attached to Phosphorus (all three groups are the same)	Lit. Ref.
23.	2,4-dimethoxyphenyl	113
24.	1-naphthyl	114
25.	9-phenanthryl	110
26.	9-anthryl	110
27.	9-bromo-10-anthryl	110

## RESULTS

The mono-para-bromo-, tri-para-bromo-, tri-para-chloro-, mono-meta-trifluoromethyl-, tri-meta-trifluoromethyl-, mono-para-cyano- and tri-para-cyano- derivatives of triphenylphosphine were prepared by Grignard reactions, using the para bromo-derivatives of the substituted phenyl ligands, with either phosphorus tri-chloride or diphenylphosphinous chloride or by the displacement of the bromine atom of the two bromo-substituted phenylphosphines with cuprous cyanide. Samples were purified by chromatographic and recrystallization techniques. All of the above mentioned phosphines were alkylated with 9-bromofluorene in acetone according to the procedure of Pinck and Hilbert.<sup>119</sup>

It was found that neither the tri-meta-trifluoromethyl- nor tri-para-cyano- derivatives of triphenylphosphine afforded a phosphonium salt. Repeated attempted alkylations in toluene, xylene and diethylene glycol dimethyl ether afforded no phosphonium salts, even with prolonged reaction times. Alkylation with benzyl chloride, using benzyl chloride as a solvent, again afforded no recognizable phosphonium salt. Infra-red analysis indicated the absence of a P-O bond in both cases and elemental analysis of tris(m-trifluoromethylphenyl)phosphine also indicated that absence of a P-O bond.

The phosphine oxides of the various listed phosphines were prepared for future NMR investigations. It was noted that neither the tri-

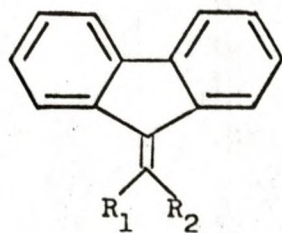
para-cyano- nor the tri-meta-trifluoromethyl- derivatives of triphenylphosphine could be converted to the corresponding phosphine oxides with 10% hydrogen peroxide.<sup>81</sup> Subjection of the tris(m-trifluoromethylphenyl)phosphine to stronger oxidative conditions (sodium dichromate in sulfuric and acetic acid)<sup>111</sup> yielded only the unchanged phosphine. However, being incapable of undergoing any further oxidation or alkylation, lacking the characteristic phosphine odor and removal from an alumina chromatographic column occurring quite late in the elution scheme could be interpreted as indicating the existence of tris(m-trifluoromethylphenyl)phosphine oxide. A trial reduction of this compound with lithium aluminum hydride produced the characteristic phosphine odor. The phosphine was not isolated.

After recrystallization of the phosphonium salts from appropriate solvents, the dried salts were dissolved in absolute ethanol and treated with concentrated ammonium hydroxide. The reaction gave brightly colored ylids (IIIa, IIIb, IIIc and IIIe) in good yields, but which were difficult to recrystallize from appropriate solvent pairs and melted with decomposition. Ylid IIIf could not be generated with ammonium hydroxide and was not used further in this investigation. Ylids IIIa-c were reacted with various substituted benzaldehydes (p-NO<sub>2</sub>, p-Cl, p-OMe, p-NMe<sub>2</sub> and p-H) under Wittig reaction conditions according to the procedure suggested by Johnson.<sup>120</sup> The reactions were conducted under standardized conditions to obtain a relative series of reactivity for the various ylids. This data was then compared with the data of previous work.<sup>11,17,120</sup> It was hoped that with the Wittig reaction results, the effect of electron-withdrawing para-substituents on the phenyl rings bonded to the phosphorus on the degree of "d-orbital resonance" would be clarified.

The yield of olefin, obtained by fractional recrystallization techniques, was compared to the theoretical yield, based both on the total ylid added (table 2) and the total ylid reacted (table 3), to determine the relative reactivity. The amount of reacted ylid was also recorded in the form of "per-cent ylid reacted," to verify the reactivity sequence obtained from the recovered olefin. These values were recorded in table 4. Melting point ranges of the isolated olefins are presented in table 5 as an indication of the purity of the products and a justification for some inconsistent percentages for the ylid reacted and the corresponding olefin reactivity. The benzalfluorenes obtained in the reaction of ylids IIIa-c with the substituted benzaldehydes are listed in chart 2.

The effect of substituents attached to phosphorus on the positive character of phosphorus was investigated by a ultraviolet spectrophotometric determination of the pKa of the ylid conjugate acids. Unlike Johnson<sup>17</sup> and Royer,<sup>11</sup> a new system involving 95% ethanol as a solvent and tris(hydroxymethyl)aminomethane in 95% ethanol as a buffer solution, was employed. The acidic and basic solution contained hydrochloric acid and sodium hydroxide, respectively, in 95% ethanol. The pKa values for the conjugate acids of ylids IIIa-c, IIIe, IIIg and IIIj were determined and recorded in table 6. The pKa values of the ylid salts investigated by Royer<sup>11</sup> and Johnson<sup>17</sup> are listed in tables 7 and 8 respectively.

Chart 2



R <sub>1</sub>	R <sub>2</sub>
XXIVa H	-C <sub>6</sub> H <sub>4</sub> -NO <sub>2</sub> -p
XXIVb H	-C <sub>6</sub> H <sub>4</sub> -Cl-p
XXIVc H	-C <sub>6</sub> H <sub>5</sub>
XXIVd H	-C <sub>6</sub> H <sub>4</sub> -OMe-p
XXIVe H	-C <sub>6</sub> H <sub>4</sub> -NMe <sub>2</sub> -p

Table 2. Reaction of Ylids With Carbonyls

Carbonyl	Percent Olefin (XXIV) from Ylids*		
	IIIa	IIIb	IIIc
p-Nitrobenzaldehyde	91	95	96
p-Chlorobenzaldehyde	93	88	78
Benzaldehyde	77	21	57
p-Anisaldehyde	17	21	17
p-Dimethylaminobenzaldehyde	9	3	10

\*Yields based on total ylid added.

Table 3. Reaction of Ylids With Carbonyls

Carbonyl	Percent Olefin (XXIV) from Ylids*		
	IIIa	IIIb	IIIc
p-Nitrobenzaldehyde	91	95	96
p-Chlorobenzaldehyde	93	97	92
Benzaldehyde	79	41	73
p-Anisaldehyde	35	91	63
p-Dimethylaminobenzaldehyde	32	26	71

\*Yields based on amount of ylid reacted.

Table 4. Percent Ylid Reacted in the Wittig Reaction

Carbonyl	Percent Ylid Reacted		
	IIIa	IIIb	IIIc
p-Nitrobenzaldehyde	100	100	100
p-Chlorobenzaldehyde	100	90	84
Benzaldehyde	97	51	77
p-Anisaldehyde	48	23	27
p-Dimethylaminobenzaldehyde	29	11	14

Table 5. Melting Points of Olefins Obtained from the Wittig Reaction

Olefins	Lit. M.P. <sup>120</sup>	Observed Uncorrected M.P. of Olefins from Ylids		
		IIIa	IIIb	IIIc
XXIVa	167°	165-167°	167.5-.69.0°	168-169°
XXIVb	149°	146.5-148.0°	147-148°	147.0-148.5°
XXIVc	76°	74-75°	74.0-75.5°	73.5-75.0°
XXIVd	128-129°	129-130°	130.0-131.5°	130-132°
XXIVe	135-136°	135-137°	134.0-135.5°	135-137°

Table 6. pKa of Ylid Conjugate Acids (Buffers at pH of 9.20 and 8.20)

Ylids	pKa at	pKa at
	buffer pH=9.20	buffer pH=8.20
1. Tris(p-methoxyphenyl)phosphoniumfluorenylide (IIIj)	10.71	10.35
2. Triphenylphosphoniumfluorenylide (IIIg)	9.69	9.47
3. (p-bromophenyl)diphenylphosphoniumfluorenylide (IIIa)	9.30	9.23
4. (p-cyanophenyl)diphenylphosphoniumfluorenylide (IIIe)	8.88	8.71
5. Tris(p-bromophenyl)phosphoniumfluorenylide (IIIb)	8.62	8.57
6. Tris(p-chlorophenyl)phosphoniumfluorenylide (IIIc)	8.49	8.55

Table 7. pKa of Ylid Conjugate Acids by Royer<sup>11</sup>

Ylids and Phenol	pKa
1. Dimethylsulfoniumfluorenylide*	9.72
2. Phenol (actual pKa in water is 9.99) <sup>121</sup>	9.65
3. Tri-p-N,N-dimethylaminophenylphosphoniumfluorenylide	9.22
4. Tri-n-butylphosphoniumfluorenylide*	9.12
5. Tri-p-methoxyphenylphosphoniumfluorenylide	9.00
6. Trimethylphosphoniumfluorenylide*	8.85
7. Triphenylarsoniumfluorenylide*	8.79
8. Di-(p-methoxyphenyl)phenylphosphoniumfluorenylide	8.77
9. Triphenylphosphonium-1-aminofluorenylide*	8.75
10. Triphenylphosphoniumdiphenylmethylide*	8.73
11. Ethylmethylphenylphosphoniumfluorenylide*	8.60
12. Triphenylphosphoniumfluorenylide	8.51
13. p-Methoxydiphenylphosphoniumfluorenylide	8.42
14. Triphenylphosphonium-4,5-benzofluorenylide*	8.11

\*Compounds furnished by A. Wm. Johnson

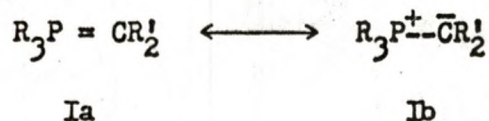


Table 8. pKa of Ylid Conjugate Acids by Johnson<sup>17</sup>

<u>Ylids</u>	<u>pKa</u>
1. Triphenylphosphoniumfluorenylide	7.5
2. Triphenylarsoniumfluorenylide	7.8
3. Tri-n-butylphosphoniumfluorenylide	8.0
4. Dimethylsulfoniumfluorenylide	7.3

## DISCUSSION

The discussion that follows is basically concerned with the statement by Johnson,<sup>17</sup> that the extent of (p-d)pi bonding in phosphorus ylids should be dependent upon the positive character of the phosphorus atom in the ylid. This statement was assumed to hold in the case of phosphorus ylids, but it was based on the evidence presented earlier for other systems exhibiting the property of valence shell expansion of phosphorus. An important consideration in this discussion, is the fact that the carbanion portion of the ylids being studied ( $\text{CR}_2^{\ominus}$  in I) was always the fluorenylidene



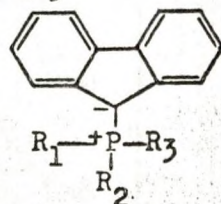
group. Consequently, changes which occurred in the physical and chemical properties of the various ylids employed could be attributed directly to the changes in substituents attached to phosphorus within the given series of ylids (IIIa-c). The second assumption, made earlier, was that with an increase in the positive character of phosphorus, the contribution of form Ia to the resonance hybrid increased by way of "d-orbital resonance." The opposite effect would occur, more contribution of form Ib, if the positive character of phosphorus decreased. Therefore, with our fluorenylides the results of Wittig reaction measurements and pKa determinations measured the effect of various substituents attached to phosphorus on the positive character of phosphorus. Even though Jaffe,<sup>20</sup> Rao<sup>60</sup> and Mann<sup>107</sup>

have qualified the statement that resonance interactions are relatively non-existent between tetravalent phosphorus and benzenoid rings, interactions affecting the positive character of phosphorus are assumed to be the result of inductive effects. Royer<sup>11</sup> provided evidence that the preceding statements held for the fluorenylides IIIg-k, all of which had electron-donating substituents on the phenyl groups. The next portion of the discussion is devoted to verifying the above statements using fluorenylides (IIIa-c) which had electron-withdrawing substituents on the phenyl groups.

Chart I

III	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
a	p-Br-C <sub>6</sub> H <sub>4</sub> -	C <sub>6</sub> H <sub>5</sub> -	C <sub>6</sub> H <sub>5</sub> -
b	p-Br-C <sub>6</sub> H <sub>4</sub> -	p-Br-C <sub>6</sub> H <sub>4</sub> -	p-Br-C <sub>6</sub> H <sub>4</sub> -
c	p-Cl-C <sub>6</sub> H <sub>4</sub> -	p-Cl-C <sub>6</sub> H <sub>4</sub> -	p-Cl-C <sub>6</sub> H <sub>4</sub> -
d	m-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -	C <sub>6</sub> H <sub>5</sub> -	C <sub>6</sub> H <sub>5</sub> -
e	p-CN-C <sub>6</sub> H <sub>4</sub> -	C <sub>6</sub> H <sub>5</sub> -	C <sub>6</sub> H <sub>5</sub> -
f	C <sub>5</sub> H <sub>10</sub> N-	C <sub>5</sub> H <sub>10</sub> N-	C <sub>5</sub> H <sub>10</sub> N-
g	C <sub>6</sub> H <sub>5</sub> -	C <sub>6</sub> H <sub>5</sub> -	C <sub>6</sub> H <sub>5</sub> -
h	p-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -	C <sub>6</sub> H <sub>5</sub> -	C <sub>6</sub> H <sub>5</sub> -
i	p-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -	p-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -	C <sub>6</sub> H <sub>5</sub> -
j	p-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -	p-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -	p-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -
k	p-Me <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> -	p-Me <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> -	p-Me <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> -
l	n-C <sub>4</sub> H <sub>9</sub> -	n-C <sub>4</sub> H <sub>9</sub> -	n-C <sub>4</sub> H <sub>9</sub> -
m	CH <sub>3</sub> -	CH <sub>3</sub> -	CH <sub>3</sub> -
n	C <sub>6</sub> H <sub>5</sub> -	C <sub>2</sub> H <sub>5</sub> -	CH <sub>3</sub> -

III



Inspection of the results shows that each ylid decreased in its reactivity from p-nitrobenzaldehyde to p-dimethylaminobenzaldehyde. This trend was reasonable if one considered the nitro group to facilitate the reaction mechanism by increasing the positive character of the carbonyl atom, thus increasing the susceptibility towards nucleophilic attack.<sup>9,120,122</sup> The opposite effect, a decrease in the positive character of the carbonyl carbon atom, would be expected to decrease the reactivity.

Examination of tables 2, 3 and 4 revealed that the reactivity of the ylids, determined by the Wittig reaction with various carbonyls, was in the order IIIa > IIIb = IIIc. The difference between the reactivity of IIIb and IIIc was, in most cases, very small for the same carbonyl. It appeared that the effect of the chlorines and bromines was approximately the same.

It was observed that even by allowing the experimental error to be an extreme limit of 10%, ylids IIIa-c were slightly less reactive than the ylids containing electron-donating substituents used by Royer (IIIg-k).<sup>11</sup> This expectation was verified by the fact that all the ylids used by Royer reacted quantitatively with p-chlorobenzaldehyde, whereas only ylid IIIa reacted in that manner (see table 2). It is, however, difficult to explain on the same basis why the ylids used by Royer would not react with p-dimethylaminobenzaldehyde and ylids IIIa-c would react to a significant degree.

Upon closer examination of the results recorded by Royer, it became obvious that the isolation procedures for the Wittig reactions must have been very difficult and inadequate. Royer reported, for instance, that in the case of ylid IIIj reacting with p-dimethylaminobenzaldehyde, only 0.14 g. of the original 1.017 g. of ylid was recovered from the reaction and that no olefin (XXIVe) was isolated at all. Fractional

crystallizations of XXIVc, XXIVd and XXIVe were very difficult to carry out, particularly where the reaction proceeded in low yields. Similarly, low yields of isolated olefins were reported for the present work. However, in each instance 90% or more of the ylid added was accounted for in the present work. These results imply a need for more refined isolation procedures, perhaps those which involved column or gas chromatographic analysis of the reaction mixture, less the unreacted ylid. Otherwise, the only difference in the techniques used by Royer and the present author was the use of 0.5 g. samples of ylids, whereas Royer used approximately 1.0 g.

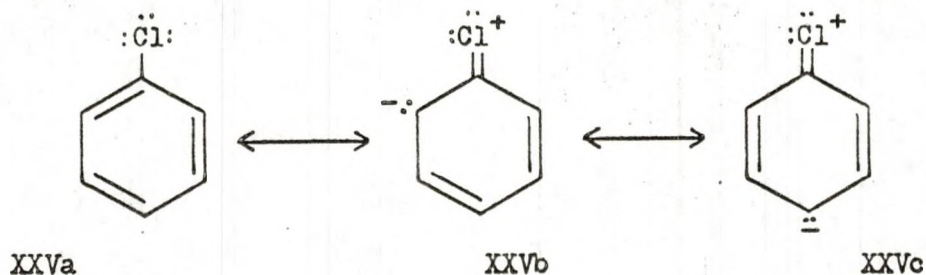
In a trial run to correlate the work of the present investigation with work by Royer, 0.5g. of triphenylphosphoniumfluorenylide was reacted with an equimolar quantity of p-anisaldehyde according to the standard procedure. The results are given in table 9. Apparently then, there are small, but significant differences in the results due to variations in the techniques employed for the Wittig reactions. However, the fact that the

Table 9. Wittig Reaction of p-Anisaldehyde With Triphenylphosphoniumfluorenylide

	Work By Royer	Present Work
Percent olefin (XXIVd) formed, based on the total ylid added	20%	12%
Percent olefin (XXIVd) formed, based on the amount of ylid reacted	82%	68%
Percent ylid (IIIj) reacted	25%	17%
Weight of ylid (IIIj) reacted	0.840	0.500
M.P. of olefin (XXIVd)	129.5-131.0°	131.0-131.5°

values are correspondingly smaller for the present work could be attributed to the degree of purity of olefin (XXIVd) recovered (smaller melting point range).

The fact that ylids IIIa-c are slightly less reactive than ylids IIIg-k can be accounted for by investigation of the electronic effects of the halogens on the phenyl groups attached to phosphorus. According to Gould,<sup>123</sup> both chlorine and bromine can exhibit two electronic effects, an inductive and a resonance effect. The lighter halogen atoms are, because of their greater measure of unscreened nuclear charge, better electron attractors than either carbon or hydrogen. This is a permanent property of the atoms. Therefore, substitution of a halogen for a carbon atom or a hydrogen atom will cause the electron density to be pulled towards the halogen by an inductive effect (-I). However, the halogens in aryl halides have lobes of two of the unshared electrons lying perpendicular to the benzene ring and these lobes can become a part of the pi electron system lying above and below the plane of the molecule. Consequently, the C-Cl bond in chlorobenzene can assume some double bond character. This is shown by XXV. Bond length data substantiates the partial double bond character represented in XXV. Thus it appears that chlorine and to a



lesser extent bromine, although permanently capable of withdrawing electron density from saturated carbon atoms by induction, can supply electron density to conjugated systems. However, aryl halides are known to be more

resistant to electrophilic substitution than benzene.<sup>124</sup> This is attributed to the inductive effect (-I) of the halogen decreasing the electron density of the ring, lowering the susceptibility towards electrophilic substitution. In aryl systems, therefore, the halogens appear to exhibit a resonance effect (+R) and an inductive effect (-I). These two effects are both always present, but the resonance effect can be called into stronger participation upon demand to facilitate an aromatic substitution reaction if necessary in the transition state of the reaction.

Royer<sup>11</sup> stated from his experimental findings that in para-substituted triphenylphosphoniumfluorenylides, there appeared to be resonance interaction between the substituent and the phenyl group, but little or no resonance interaction between the phosphorus and the substituted phenyl group, as indicated by Johnson.<sup>17</sup> Provided one accepted the fact that the phenyl groups in tri-phenylphosphoniumfluorenylide exerted a -I effect, as seemed likely, the fact that IIIa was less reactive than IIIg appeared reasonable. The bromine atom, which apparently acted through its inductive properties, could increase the positive character of phosphorus slightly over that of the IIIg case to create more (p-d)pi overlap and thus the overall reactivity of the ylid would become slightly less than that of IIIg through "d-orbital resonance." The idea of halogens inductively withdrawing electron density from the ring, thus facilitating the -I effect of the ring on phosphorus could be applied further to ylids IIIb and IIIc. With a halogen on each ring, the overall degree of (p-d)pi overlap should be increased over that of IIIa and the reactivity of the ylid should, correspondingly, decrease. Indeed, this was what table 2 revealed.

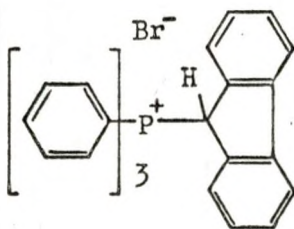
Cook and Allen<sup>37</sup> found that the electron accepting properties of phosphorus in platinum complexes, containing para-substituted triphenyl-

phosphines as ligands, decreased in the order  $((p\text{-F-C}_6\text{H}_4\text{-})_3\text{P}$  and  $(p\text{-Cl-C}_6\text{H}_4\text{-})_3\text{P}$ ),  $(\text{C}_6\text{H}_5\text{-})_3\text{P}$  and  $((p\text{-Me-C}_6\text{H}_4\text{-})_3\text{P}$  and  $(p\text{-MeO-C}_6\text{H}_4\text{-})_3\text{P}$ ). In the phosphine ligands, the functional group attached to the phenyl group appeared to either hinder (Me and MeO) or aid (F and Cl) the inductive effect of the phenyl group, causing a corresponding change in the electron attracting power of phosphorus. This implied, in the case of the halogen substituted phenyl groups that resonance interactions from the rings to phosphorus were at a minimum and that the inductive effect of the halogen overcame the resonance effect in the phosphines. If, on the other hand, the resonance effect of the halogens in ylids IIIa-c had priority over the inductive effect, according to the structures of XXV, the positive character of phosphorus should have decreased sufficiently to nearly eliminate (p-d)pi overlap in the ylid.

Perhaps an answer to the recurring question of whether or not resonance interaction actually exists between the para-substituted phenyl groups and the phosphorus atom in the fluorenylides, would be another investigation similar to work by Royer and the present work employing the same substituted phenyl groups, but with the substitution in the meta positions. This would remove the functional group from direct resonance with the carbon atom of the ring that is attached to phosphorus. The overall change in the positive character of phosphorus and thus the physical and chemical properties of the ylids would be, supposedly, a result of the inductive effects of the substituted phenyl groups alone. Thus, regardless of whether resonance interaction existed between the benzene rings and the substituents, the difference in the properties of the meta substituted ylids should reflect only increased inductive effects.



As mentioned earlier, the effect of substituents attached to phosphorus on the positive character of phosphorus could be investigated by a pKa determination of the conjugate acids of the fluorenylides. With increased positive character of phosphorus, an increase in attracting power would be expected. In ylid salts, the attracting power of phosphorus for the available electron pair bonding the hydrogen atom to the ylid carbon (XXVI) should increase with increased positive character of phos-



XXVI

phorus. The results of this increased electron attracting power would be a more acidic salt and an easily generated and less basic ylid.

Johnson,<sup>17</sup> and Royer<sup>11</sup> and Speziale and Ratts<sup>6</sup> have shown that the greater the contribution of the ylene form (Ia) to the resonance hybrid of the ylid, the more acidic would be the conjugate acid and the less reactive would be the ylid. Royer<sup>11</sup> and Speziale and Ratts<sup>6</sup> have also shown that the greater the extent of delocalization of the ylid carbanion throughout the carbon portion of the ylid the more acidic was the conjugate acid (see numbers 10, 12 and 14 of table 7). Utilizing only fluorenylides, however, would completely eliminate this variable.

Coordination of the results of Speziale and Ratts with the Work of Johnson and Royer is not possible, since Speziale and Ratts did not study any fluorenylides. Examination of the pKa values determined by Royer (see table 7) and the results of the investigation conducted by Johnson (see table 8), revealed that an accurate correlation of the two sources of fluorenylide data could not be made. An explanation for this was the fact that Royer did not use the same organic acid-inorganic salt

buffer system employed by Johnson and was confronted with serious solubility problems of the buffer in his solvent pair. For lack of a better solvent, he altered the ratio of dioxane to water from the ratio used by Johnson to insure solution of the buffer analysis. Thus Royer and Johnson both conducted their measurements in dioxane-water solutions, but had substantially different ratios of the two solvents. Unfortunately, Royer encountered solubility problems with the phosphonium salts and the ylids and had difficulty maintaining a constant solvent ratio throughout the solutions for the analysis. It was these factors that led to results inconsistent with those of Johnson. However, the results of Royer were, nevertheless, internally consistent.

Therefore, it was necessary to develop a new solvent system to facilitate the determination of pKa's of all the known unreactive, easily generated fluorenylides. The criteria for a solvent system included the ability to dissolve phosphonium salts, dissolve ylids, dissolve either an inorganic or an organic acid, dissolve either an organic or an inorganic buffer system, dissolve a rather strong organic or an inorganic base, be miscible with water, buffer effectively in nonaqueous media and finally be non-absorbing in the ultraviolet region of the spectrum.<sup>125,126</sup> Among the solvents under consideration were methyl cellosolve,<sup>127</sup> ethanol, methanol, ethylene glycol, dioxane and tetrahydrofuran. The problem of selecting a solvent could be greatly simplified if an organic buffer system were used, since it is the solubility of inorganic material that demands a higher ratio of water to organic solvent and lowers the solubility of the ylids and the ylid salts in the solutions necessary for the analysis. Since we were primarily concerned with the 320-400 millimicron region of the spectra, organic compounds, even those with chromophores, could be used

as long as they didn't absorb in the region under observation. Thus amines and amino acids could be considered, for example. The system finally selected for the analysis used 95% ethanol as a solvent. The buffer consisted of tris(hydroxymethyl)aminomethane combined with hydrochloric acid.<sup>128</sup> The basic and acidic solution contained sodium hydroxide and hydrochloric acid, respectively, in 95% ethanol. Buffers at two different pH ranges (8.20 and 9.20) were prepared in 95% ethanol and pH readings were recorded with a Beckman Expanded Scale pH meter. Analyses were conducted using both of these buffer systems and comparable results were obtained in each case. The results of the analyses conducted with the buffers having a pH of 8.20 and 9.20 are recorded in table 6. These buffer regions were selected because they facilitated the interpretation of the spectra.

It should be emphasized that the results presented are not absolute values, for the calculations for the analysis demands an accurate reading of the buffer solution. Since the pH readings recorded were taken in non-aqueous media, the values are not totally reliable. However, the buffers, when prepared in 95% ethanol in the same proportions for aqueous solutions having pH values of 8 and 9, gave readings of 8.20 and 9.20 respectively on the pH meter. It should be mentioned that Speziale and Ratts<sup>6</sup> performed their potentiometric titrations reading directly on a standard pH meter using 100% methanol as the solvent for the ylids. A description of the problems of the determination of the pH in nonaqueous media is available in references 129-132.

Besides obtaining only relative values and having to work with very small quantities of phosphonium salts to maintain solution of the ylids in alcohol, the only other problem with this system is the fact

that the sodium hydroxide-ethanol solution, as expected, turns turbid upon standing exposed to air. This is not too critical, since the results should not change significantly provided sufficient base is present to generate the ylid and a large excess of the base was employed. Perhaps a solution to this problem would be the use of ammonium hydroxide in place of sodium hydroxide.

Even though the results presented are relative values, inspection of the results in table 6 are still quite informative. Since the order of reactivity determined from Wittig reaction measurements was IIIa > IIIb = IIIc, one would expect that the pKa value of IIIa would be higher than either IIIb or IIIc. This was observed. In addition, the pKa results revealed that IIIc was more acidic than IIIb, a result not discernible from Wittig reaction data. This seemed reasonable if inductive effects and not resonance effects predominated in the ylids. Since chlorine has a greater electronegativity value than bromine (3.15 and 2.95 respectively), a decrease in reactivity and an increase in acidity (lower pKa value) would be expected due to more (p-d)pi overlap. However, the substituent constants for the Hammett equation ( $\sigma$ ) for both bromine and chlorine is +0.23 and does not distinguish their ability to distort the electron density about the benzene ring.

The pKa values for ylids IIIa and IIIc are very significant. According to Fieser and Fieser,<sup>133</sup> the dipole moments of benzonitrile and bromobenzene (3.90 and 1.53 respectively) are indicative of the direction and magnitude of the inductive effects of the groups on the ring. This seems reasonable, since the cyano group can display both inductive and resonance effects more easily than can a halogen. Consequently, the cyano group appears to have a greater effect on distorting

the electron density of the ring. This effect is further indicated by the cyano group deactivating a benzene ring for electrophilic substitution more so than a halogen.<sup>133</sup> It is interesting to note that the substituent constants for the Hammett equation for bromine and a cyano group are +0.23 and +0.63 respectively. This too indicates greater distortion of the electron density about the benzene ring by a cyano group than by a halogen. In the case of ylids, increased distortion of the electron density of a phenyl group away from the phosphorus atom, creating greater positive character on phosphorus, would be expected to create more (p-d)pi overlap in IIIe than IIIa and a lower pKa value. The value given in table 6 complies with this view very well. On the other hand, electron-donating substituents, as pointed out by Royer,<sup>11</sup> have just the opposite effect on the extent of (p-d)pi overlap, resulting in a weaker conjugate acid, but a more reactive ylid. This is shown in table 6 through the value of ylid IIIj.

The Wittig reaction results revealed that the halogen-substituted phenyl groups have a greater inductive effect than the unsubstituted phenyl group, resulting in increased (p-d)pi overlap and a less reactive ylid. Although the Wittig reaction results were crude, the data indicated that ylids IIIa-c < IIIh-k and that IIIb and IIIc < IIIa in reactivity with the same carbonyls. As would be expected, the pKa results were more conclusive. The pKa study verified the electronic effects indicated by the Wittig reaction rate data for Ylids IIIa-c, IIIe, IIIg and IIIj and also distinguished the reactivity of IIIe from IIIa and IIIb from IIIc.

Naturally, with any newly developed technique, there always remain openings for improvement. With reference to pKa studies, new techniques involving new solvents, new buffer systems for a spectrophotometric

analysis and reproducibility studies should be investigated to further improve the present system. In addition, potentiometric titrations, similar to that used by Speziale and Ratts<sup>6</sup> should be investigated. With the development of an answer to the solubility problems of fluorenylides in standard solvents, NMR studies will be planned that will hopefully clear up the present ambiguity in the literature concerning the contribution of form Ia to the resonance hybrid of the ylid. The NMR results will be combined with the information obtained from the intended dipole moment measurements of the fluorenylides, similar to the one determined by Johnson<sup>120</sup> for triphenylphosphoniumfluorenylide. The results of these studies should be sufficient to verify pKa and Wittig reaction rate data. More refined studies, kinetic and material balance, should be conducted on the Wittig reaction to more fully establish the results of the work by Royer and the present investigation. It should be mentioned that more functional groups are still needed in this study ( $\text{NO}_2$ , CN and  $\text{CF}_3$ ) to produce bigger differences in the results than obtained for the halogens. This would provide sufficient groups for a complete Hammett rho-sigma study that could be conducted both spectrophotometrically and kinetically.

The actual key to the success of this investigation remained in the preparation of the arylphosphines containing electron-withdrawing para substituents. The synthesis of many of these phosphines had been previously attempted, but never succeeded. An example, was the preparation of tris-(p-bromophenyl)phosphine. Many attempts to prepare this compound, both in this laboratory and in others, failed to yield a solid or any identifiable species. Application of a vast array of known and original techniques was probably the only reason that this compound was ever isolated.

It could be shown that many of the phosphines corresponding to the fluorenylides in chart I have somewhat unique procedures for their preparation. In particular, the phosphines involved in this investigation had a greater tendency towards oxidation than the phosphines employed by Royer. Where reaction energetics required, as a final resort, the use of aryl iodides to prepare the phosphines, oxidation occurred to a significant degree even under a nitrogen atmosphere. In the preparation of the phosphines corresponding to ylids IIIa-c, the problem of oxidation was not experienced as long as aryl iodides, iodine or methyl iodide were not used in the reaction.

In the preparation of the arylphosphines containing trifluoromethyl groups from *m*-bromobenzotrifluoride, just the opposite occurred. The preparation of the tris(*m*-trifluoromethylphenyl)phosphine was attempted first and from infrared data and qualitative and quantitative elemental analysis data, it appeared that indeed the phosphine had been prepared. However, extensive chemical oxidation and alkylolation reactions on this compound were found to be useless, as mentioned earlier. This indicated that either the  $\text{CF}_3$  groups were so strongly electron-withdrawing (3.3 on the Pauling electronegativity scale) that the phosphine no longer possessed its nucleophilic character or that the compound was actually a phosphine oxide and not a phosphine. Two other pieces of information were available to further establish that a phosphine was not present. The compound had lost its characteristic odor and, unlike other phosphines, was not removed from an aluminum oxide chromatography column until quite late in the elution scheme (chloroform-ether eluent). A trial reduction of the compound produced the characteristic phosphine odor; however, the phosphine was not isolated.

Recently when the known (*m*-trifluoromethylphenyl)diphenylphosphine was desired to determine if it could be alkylated, it was discovered that vacuum distillation under nitrogen followed by chromatography on aluminum oxide gave a product other than the phosphine. It was suspected to be the oxide. This helped to confirm the suspicion that the supposed tris(*m*-trifluoromethylphenyl)phosphine was actually an oxide. Because vacuum distillation procedures under nitrogen did not destroy the characteristic phosphine odor of the trifluoromethyl-substituted arylphosphines, the oxidation was attributed partially to both quenching procedures employed in the synthesis and to inducement by the aluminum oxide employed for purification. Nevertheless, it appears that more refinements are needed before isolation of the phosphine could be made. It is suggested that fractional recrystallization of the reaction mixture, as suggested in procedure I for the preparation of (*m*-trifluoromethylphenyl)diphenylphosphine be tried again in order to isolate the tris(*m*-trifluoromethylphenyl)-phosphine and thus eliminate the vacuum distillation and chromatography procedures which produced an oxide. Further, it may be even advantageous not to isolate the phosphine, but react the phosphine during the preparation, before quenching with 20% ammonium chloride, with 9-bromofluorene. This could be done for both of the trifluoromethyl-substituted arylphosphines and would eliminate extensive work-up procedures.

The preparation of nitro-substituted arylphosphines, which also has been unsuccessfully attempted many times, have now been attempted with both the lithium and magnesium reagents of an aryl iodide. A product was obtained for both the (*p*-nitrophenyl)diphenylphosphine and tris(*p*-nitrophenyl)phosphine, but in very low yields. Again the products obtained would not alkylate or oxidize and showed no definite P-O peak (there could, however, be an interaction with another absorption frequency associated



with the molecule to hide the P-O absorption) in the infrared region. It was believed that phosphine oxides were again present.

More work is, however, needed to increase the yields of phosphine or oxides in the reactions. This could possibly be accomplished by using dioxane or diphenyl ether as a solvent in place of tetrahydrofuran to help the energetics of the reaction and by employing the lithium reagent of p-iodonitrobenzene (see Experimental). However, if phosphine oxide is going to be the only isolable product, other methods should be considered. For example, for both the (p-nitrophenyl)diphenylphosphine and tris(p-nitrophenyl)phosphine, the phosphine should be alkylated in solution in the same manner as suggested for the trifluoromethyl-substituted arylphosphines to circumvent the isolation of the phosphines.

Royer<sup>11</sup> reported that neither p-chloronitrobenzene nor m-bromonitrobenzene would form a lithium reagent, thus making the use of aryl iodides compulsory for the preparation of the nitro-substituted arylphosphines, whereas Bartlett has shown that these aryl iodides could induce phosphine oxidation. Oxidation would lead to compounds that could not be restored readily to their phosphine state. This was the reason for making the preceding suggestion for future work. In conclusion, the experimental procedures presented were the procedures that produced the most product, with that product in the best form for isolation purposes.

The same situation is now thought to have occurred in the preparation of tris(p-cyanophenyl)phosphine. Royer observed that the lithium reagent of p-bromobenzonitrile would not form and he could not, consequently, prepare the cyanosubstituted arylphosphine. This compound was formed in the present investigation from a nucleophilic aromatic substitution reaction of cuprous cyanide with tris(p-bromophenyl)phosphine. The reaction was conducted with the exclusion of oxygen and, after chromato-

graphy on aluminum oxide, yielded a product that would not alkylate under the most rigorous conditions. It displayed a very small, almost insignificant, peak in the P-O absorption frequency range of the infrared region (8.4 microns). The absence of the characteristic phosphine odor and the fact that chromatographic elution was quite late was indicative of an oxide. The results of the elemental analysis will reveal the final situation. If it is oxide, the only solution is to react the phosphine, without purification by chromatography, with 9-bromofluorene.

It is unfortunate that break throughs in the preparation of these phosphines have come so slow and too late for continued investigation by this researcher. It is the hope of the author, however, that this thesis will enable the reader to develop the slowly learned techniques at a faster rate than previous workers. In this way the problems stated within this thesis will be solved.

## EXPERIMENTAL

All chemicals used, whether commercially obtained or not, were purified where necessary and made anhydrous unless otherwise specified. All the ether and tetrahydrofuran used was dried by distillation over lithium aluminum hydride under a nitrogen atmosphere. Because of the toxicity associated with most phosphorus compounds, all reactions were performed in a hood. The preparation of organometallic reagents and their corresponding reactions, and other reactions susceptible to air oxidation or reaction with water, were all conducted in an atmosphere of dry, oxygen-free nitrogen and in oven-dried, ground-glass jointed apparatus. To start the Grignard Reagents, it was found that heating the magnesium before adding the aryl halide facilitated the reaction. Addition of either methyl iodide or a crystal of iodine was avoided because side reactions were observed. Air-sensitive, liquid reagents were transferred by means of a calibrated, oven-dried syringe. Where stirring was required, as in all Grignard reactions, a mechanical glass stirring rod and blade, operated at maximum speed, was used. Where chromatography was employed, the columns were packed dry with Merck 71707 alumina, flushed with skelly solve B and finally irrigated with anhydrous organic solvents according to the elution scheme suggested by Fieser.<sup>134</sup> Qualitative elemental analyses were performed according to procedures by Vogel.<sup>135</sup> Melting points were taken in capillary tubes or on a Bausch and Lomb hot stage and were uncorrected. Refractive indices were obtained using a Bausch

and Lomb Refractometer, Model ABBE-3L. Elemental analyses by A. Bernhardt Microanalytical Laboratories, Max Planck Institute, Mulheim (Ruhr), Germany. Ultraviolet spectra were recorded on a Bausch and Lomb Spectronic 505 spectrophotometer. A Perkins-Elmer Infrared, Model 137, spectrophotometer was used to obtain all infrared spectra data. Finally, pH measurements were taken on a Beckman Expanded Scale pH meter.

2-Bromofluorene.- -9-Bromofluorene was prepared according to the procedure of Ross, Finkelstein and Peterson.<sup>136</sup> Recrystallization from hexane, after washing the product with a small volume of skelly solvent B, yielded colorless needles, m.p. 104-5° (Lit.<sup>136</sup> m.p. 102-4°). The needles turned from colorless to amber upon standing for long periods of time. For another procedure, see Wittig and Felletschin.<sup>137</sup>

p-Iodonitrobenzene.- -p-Nitroaniline (100 g., 0.72 moles) was dissolved in 300 ml. of concentrated hydrochloric acid and 300 ml. of water, cooled to 0°C. then 56 g. (0.81 moles) of sodium nitrite in 120 ml. of water was added slowly with vigorous stirring. After diazotization was complete, as indicated by starch iodide paper (positive test is a development of a blue color upon immediate contact) the solution was added to a solution of potassium iodide (200 g. in 400 ml. of water), stirred for 15 minutes, filtered with suction and washed with ice water. The residue was taken up in ether and washed with dilute sodium hydroxide, dilute hydrochloric acid, twice with water, then treated with norite, filtered and the solvent removed by distillation. The residue crystallized from ethanol to yield 101 g. (60%) of pale yellow needles, m.p. 172-3° (Lit.<sup>138</sup> m.p. 170-1°).

p-Bromiodobenzene.- -p-Bromoaniline (100 g., 0.58 moles) was dissolved in 300 ml. of concentrated hydrochloric acid and 300 ml. of

water, cooled to 0°C. and 56 g. (0.81 moles) of sodium nitrite in 120 mg. of water was added slowly with vigorous stirring. After diazotization was complete, as indicated by starch iodide paper (positive test is a development of a blue color upon immediate contact), the solution was added to a solution of potassium iodide (200 g. in 400 ml. of water), stirred for 15 minutes, filtered with suction and washed with ice water. The residue was steamed distilled until no more product was carried over. Care was taken that the distillate did not solidify in the condenser to create a closed system. The distillate was filtered and the residue dissolved in ether. The ether solution was washed with dilute sodium hydroxide, dilute hydrochloric acid, and twice with water, then treated with norite, filtered and the ether removed by distillation. The residue crystallized from ethanol to yield 124 g. (76%) of colorless needles, m.p. 90-92° (Lit. <sup>139</sup> m.p. 92°).

p-Bromochlorobenzene. - -To 122 g. (1.07 moles of chlorobenzene and 150 mg. iron turnings heated to 45°C. under agitation was introduced 176 g. (1.1 moles) of bromine during 1.5 hours at such a rate as to maintain the temperature between 45-55°C. The temperature was raised to 80°C. until the hydrobromic acid evolution ceased then the reaction was quenched with water. After cooling, the product was filtered with suction, rinsed with a dilute solution of sodium bisulfite, washed with water and dried. The 171.5 g. of colorless plates (82.6%), free of liquid isomers, was dissolved in absolute ethanol, treated with norite and allowed to crystallize, m.p. 67-8° (Lit. <sup>140,141</sup> m.p. 67.4°).

(p-Bromophenyl)diphenylphosphine. - -A solution of 55.1 g. (0.25 moles of diphenylphosphinous chloride (1.23 g./cc.) in 150 ml. of ether was added dropwise with cooling to a Grignard Reagent prepared from 64.9 g.

(0.275 moles) of p-dibromobenzene and 6.7 g. (0.275 g-atm.) of magnesium in a total volume of 325 ml. of ether. The dibromide was added at a fast rate once the Grignard Reagent started to form (noted by a color change from colorless to brown). After completion of the addition the mixture was refluxed for 0.5 hours then cooled and 100 ml. of 20% ammonium chloride was added slowly to the stirred reaction mixture still under a nitrogen atmosphere. The reaction mixture was transferred to a separatory funnel and dilute sodium hydroxide was added to make the aqueous layer definitely basic. The layers were separated and the aqueous layer very gently extracted with 2-100 ml. portions of chloroform. The chloroform extracts were added to the ether extracts and the combined organic layer was washed with 2-200 ml. portions of water and distilled. The product fraction was collected at 187-224°C./0.2 mm. and solidified immediately upon cooling in the refrigerator. Recrystallization from acetone-water gave 51 g. (60%) of leaflets, m.p. 78-79° (Lit.<sup>63</sup> m.p. 78-79°). Gilman and Brown<sup>85</sup> reported the compound to be an oil with a b.p. of 205-10°C/4mm.

Tris(p-bromophenyl)phosphine.- -A Grignard Reagent was prepared from 34 g. (0.165 moles) of p-dibromobenzene and 4.4 g (0.183 g-atm.) of magnesium in a total of 250 ml. of ether. The dibromide was added at a fast rate once the Grignard Reagent started to form (noted by a color change from colorless to brown). The excess of magnesium was removed by filtration through a coarse porosity sintered glass funnel under nitrogen then a solution of 6.9 g. (0.05 moles) of phosphorus trichloride (1.574 g./cc.) in 75 ml. of ether was added dropwise to the Grignard Reagent at 0-10°C. After completion of the addition the mixture was refluxed for 0.5 hours, cooled to 0-10°C. then 100 ml. of 20% ammonium chloride slowly was added to the stirred reaction mixture, still under a nitrogen atmosphere. The

reaction mixture was transferred to a separatory funnel and dilute sodium hydroxide was added to make the aqueous layer definitely basic. The layers were separated and the aqueous layer was very gently extracted with 2-100 ml. portions of chloroform. The chloroform extracts were added to the ether extract and the combined organic layer was washed with 2-200 ml. portions of water and distilled. The product fraction was collected at 240-60°C./0.2 mm. and solidified upon cooling in the refrigerator. Recrystallization from acetone-water gave 11.25 g. (45%) of needles, m.p. 118-19°. p-Bromiodobenzene also produced the phosphine, but oxide formation occurred to decrease yields of phosphine.

Anal. Calcd. for  $C_{18}H_{12}PBr_3$ : C, 43.32; H, 2.42; P, 6.22;  
Br, 48.04.

Found: C,       ; H,       ; P,       ; Br,       .

Tris(p-chlorophenyl)phosphine.- -To a Grignard Reagent prepared from 40.12 g. (0.21 moles) of p-bromochlorobenzene and 10.2 g. (0.42 g-atm.) of magnesium in 150 ml. of ether and cooled to 0-10°C. slowly was added 6.4 g. (0.047 moles) of phosphorus trichloride (1.574 g./cc.) in 50 ml. of ether. After completion of the addition the mixture was refluxed for 0.5 hours, cooled to 0-10°C. and 150 ml. of 20% ammonium chloride was slowly added to the stirred reaction mixture, still under a nitrogen atmosphere. The reaction mixture was transferred to a separatory funnel containing sufficient dilute sodium hydroxide to make the aqueous layer definitely basic. The layers were separated and the aqueous layer was very gently extracted with 2-100 ml. portions of chloroform. The chloroform extracts were added to the ether extract and the combined organic layer was washed with 2-200 ml. portions of water and distilled. The product fraction was collected at 200-210°C./0.2 mm. and solidified upon cooling in the refrigerator. Recrystallization from acetone-water gave 8.6 g. (50%) of colorless needles, m.p. 102-3° (Lit. <sup>78,107</sup> m.p. 102-3°).

(m-Trifluoromethylphenyl)diphenylphosphine. - A solution of 33.1 g. (0.15 moles) of diphenylphosphinous chloride in 75 ml. of ether was added dropwise to a Grignard Reagent prepared from 37.1 g. (0.165 moles) of m-bromobenzotrifluoride and 4.4 g. (0.18 g-atm.) of magnesium in a total of 50 ml. of ether. The reaction mixture was maintained at 10-15°C. during this addition. After completion of the addition the mixture was refluxed for 0.5 hours, cooled, and 200 ml. of 20% of ammonium chloride was slowly added to the stirred reaction mixture, still under a nitrogen atmosphere. The reaction mixture was transferred to a separatory funnel and treated by either of the two following procedures:

I. The organic layer was separated and washed with water. After drying, the solvent was evaporated and the residual oil crystallized from ethanol to give material of m.p. 47-49°C. Recrystallization from ethanol gave 28.5 g. (58.7%) of colorless needles, m.p. 49-50° (Lit.<sup>118</sup> m.p. 49-50°).

II. The organic layer was separated and washed with dilute sodium hydroxide to make the organic layer definitely basic. The layers were separated and the combined aqueous layers were very gently extracted with 2-200 ml. portions of chloroform. The chloroform extracts were added to the ether extract and the combined organic layer was washed with 2-200 ml. portions of water then distilled under nitrogen. The product fraction was collected at 140-150° C./0.2 mm. and solidified slowly upon cooling in the refrigerator. Recrystallization from ethanol, after purifying by column chromatography using aluminum oxide, gave colorless needles in about the same yield as procedure I above, m.p. 116-17°. This was believed to be the phosphine oxide.



Anal. Calcd. for  $C_{19}H_{14}PF_3O$ : C, 65.89; H, 4.08; P, 8.95; F, 16.46;  
O, 4.62.

Found: C.       ; H.       ; P.       ; F.       ; O.       .

Tris(m-trifluoromethylphenyl)phosphine.- -To a Grignard Reagent

prepared from 4.9 g. (0.025 moles) of m-bromobenzotrifluoride (1.637 g./cc.) and 0.67 g. (0.0275 g-atm.) of magnesium in 50 ml. of ether, cooled to 0-10°C., was slowly added 1.15 g. (0.0083 moles) of phosphorus trichloride (1.574 g./cc.) in 50 ml. of ether. After completion of the addition the mixture was refluxed for 0.5 hours, cooled to 0-10°C. and 100 ml. of 20% ammonium chloride was slowly added to the stirred reaction mixture, still under a nitrogen atmosphere. The reaction mixture was transferred to a separatory funnel and treated by either of the two following procedures:

I. The organic layer was separated and washed with water. After drying, the solvents were evaporated and the residual oil crystallized from ethanol to give material that was very difficult to recrystallize, but had the characteristic phosphine odor.

II. The organic layer was separated and washed with dilute sodium hydroxide to make the organic layer definitely basic. The layers were separated and the aqueous layer was very gently extracted with 2-100 ml. portions of chloroform. The chloroform extracts were added to the ether extract and the combined organic layer was washed with 2-100 ml. portions of water and distilled under nitrogen. The product fraction was collected at 155-65°C./0.2 mm. and was reluctant to solidify upon cooling in the refrigerator. Crystallizations from acetone-water failed, probably due to the presence of small amounts of m-bromobenzotrifluoride. Chromatography of the oily material yielded 1.55 g. (40%) of a relatively odorless solid (chloroform-ether eluent) that was recrystallized from acetone-

water as long, colorless needles, m.p. 99-100°. This was suspected of being the phosphine oxide.

Anal. Calcd. for  $C_{21}H_{12}PF_9$ : C, 54.09; H, 2.60; P, 6.64; F, 36.67.

Calcd. for  $C_{21}H_{12}PF_9O$ : C, 52.27; H, 2.51; P, 6.42; F, 35.45;

O, 3.32.

Found: C, 53.84; H, 2.87; P, 6.23; F, 37.01.

Tris(p-cyanophenyl)phosphine. - A mixture of 10.6 g. (0.021 moles) of tris(p-bromophenyl)phosphine, 19.5 g. (0.218 moles) of cuprous cyanide and 30 ml. of dimethylformamide was refluxed under nitrogen for 15 hours, cooled and poured into a mixture of 150 ml. of a 25% solution of ethylenediamine in water and 150 ml. of chloroform, based on the procedures of Friedman and Shechter<sup>116</sup> and Newman and Boden.<sup>117</sup> The organic layer was separated and the aqueous phase thoroughly extracted with 3-100 ml. portions of chloroform. The organic phase and the extracts were combined, washed with 100 ml. of 10% sodium cyanide, 50 ml. of 10% sodium cyanide, 3-100 ml. portions of water and dried over magnesium sulfate. Evaporation of the solvent in vacuo left 6 g. of a light-brown syrup of which 4 g. was taken up in the minimum amount of benzene and chromatographed on a 2.5 X 60 cm. column packed dry with 100 g. of aluminum oxide and irrigated with the standard eluents, starting with skelly solve B. Approximately 0.75 g. of odorless product (chloroform-ether eluent) was obtained and recrystallization from acetone-water afforded colorless needles, m.p. 184-5°. Crystallization of the remaining 2 g. of oily residue from ethanol-water was unsuccessful.

Anal. Calcd. for  $C_{21}H_{12}PN_3$ : C, 74.77; H, 3.59; P, 9.18; N, 12.46.

Calcd. for  $C_{21}H_{12}PN_3O$ : C, 71.39; H, 3.42; P, 8.77; N, 11.89;

O, 4.53.

Found: C, ; H, ; P, ; N, ; O, .

(p-Cyanophenyl)diphenylphosphine.- -A mixture of 45.6 g. (0.134 moles) of p-bromophenyl)diphenylphosphine, 40.2 g. (0.46 moles) of cuprous cyanide and 75 ml. of dimethylformamide was refluxed for four hours. The cooled reaction mixture was then poured into a mixture of 300 ml. of a 25% solution of ethylenediamine in water and 300 ml. of chloroform. The organic phase was separated and the aqueous phase extracted with 3-200 ml. portions of chloroform. The chloroform extracts were added to the organic phase which was then washed with 100 ml. of 10% sodium cyanide, 50 ml. of 10% sodium cyanide and 3-150 ml. portions of water. The organic phase was then dried over sodium sulfate and the solvent evaporated. The residual oil solidified when triturated with ethanol. This solid was recrystallized from ethanol to give 24 g. (62.5%) of distorted hexagonal prisms, m.p. 86.5-87.5° (Lit.<sup>118</sup> m.p. 86.5-87.5°).

Tripiperidylphosphine.- -This compound was prepared according to the procedure suggested by Michaelis and Luxembourg<sup>142</sup> using 20 g (0.245 moles) of piperidine and 5.4 g. (0.039 moles) of phosphorus trichloride in ether, with the exception that an atmosphere of nitrogen was used throughout the reaction and filtration of the amine acid salt was performed through a coarse porosity, sintered, glass funnel. The reaction gave 5.75 g. (52%) of oily material that crystallized from dry benzene, but decomposed when exposed to air and water, m.p. 34-7° (Lit.<sup>142</sup> m.p. 37-8°).

Tris(p-nitrophenyl)phosphine.- -To a refluxing solution of a Grignard Reagent prepared from 6.23 g. (0.025 moles) of p-iodonitrobenzene and 0.67 g. (0.0275 g-atm.) of magnesium in 50 ml. of tetrahydrofuran, was slowly added 1.15 g. (0.0083 moles) of phosphorus trichloride (1.574 g./cc.) in 25 ml. of tetrahydrofuran. After completion of the addition the mixture was refluxed for 0.5 hours, cooled then 20 ml. of 20% ammonium chloride was

slowly added to the stirred reaction mixture, still under a nitrogen atmosphere. The solvent was removed in vacuo until only water remained then the residue was dissolved in chloroform. The solution was transferred to a separatory funnel and dilute sodium hydroxide was added to make the aqueous layer definitely basic. The layers were separated and the aqueous layer was very gently extracted with 2-50 ml. portions of chloroform. The combined chloroform extracts were washed with 2-50 ml. portions of water and dried over anhydrous magnesium sulfate. Evaporation of the solvent in vacuo left approximately 6 g. of yellow-brown solid material. The residue was dissolved in the minimum quantity of benzene and placed on a 25 X 60 cm. column containing 150 g. of aluminum oxide, packed dry, and irrigated with the standard eluents. Approximately 0.4 g. (10%) of solid material (benzene-chloroform eluent) was obtained and recrystallization from acetone-water afforded gold plates, m.p. 201-2°. The later fractions (ether-acetone eluents), upon standing for very long periods of time, solidified and were suspected to be oxides of the phosphine, most likely the result of using aryl iodides. In addition, it was suspected that the aluminum oxide of the column may have induced a portion of this conversion. These phosphine oxides could not be readily reduced without affecting the nitro group. Preparation of the organolithium reagent of p-iodonitrobenzene was attempted, but was obtained in very low yields (based on the amount of lithium reacted). The product, also in very low yields, corresponded to the product obtained from the Grignard Reagent reaction with phosphorus trichloride. It is suggested that at the reaction temperatures lithium could react with nitrogen and the nitride formed could hinder the preparation of the lithium reagent.

Anal. Calcd. for  $C_{18}H_{12}N_3O_6P$ : C, 54.42; H, 3.04; N, 10.58; O, 24.16;  
P, 7.80.

Calcd. for  $C_{18}H_{12}N_3O_7P$ : C, 52.31; H, 2.93; N, 10.17; O, 27.10;  
P, 7.49.

Found: C,       ; H,       ; N,       ; O,       ; P,       .

(p-Nitrophenyl)diphenylphosphine. - (A.) To a Grignard Reagent

prepared from 6.23 g. (0.025 moles) of p-iodonitrobenzene and 0.67 g. (0.0275 g-atm.) of magnesium in 50 ml. of tetrahydrofuran, was slowly added, while refluxing, 5.51 g. (0.025 moles) of diphenylphosphinous chloride in 25 ml. of tetrahydrofuran. After completion of the addition the mixture was refluxed for 0.5 hours, cooled and 40 ml. of 20% ammonium chloride was added slowly to the stirred reaction mixture, still under a nitrogen atmosphere. The work up was continued as described above for the tris(p-nitrophenyl)phosphine. Approximately 0.1 g. (1.3%) of solid material (benzene-chloroform eluent) was obtained and recrystallization from acetone-water afforded red-orange plates, m.p. 214-16°.

(B.) To 2.0 g. (0.288 g-atm.) of lithium, rolled and cut into small pieces, in 250 ml. of refluxing tetrahydrofuran was slowly added 25 g. (0.088 moles) of diphenylphosphinous chloride in 50 ml. of tetrahydrofuran. The reaction was allowed to reflux until the mixture turned a deep red color and the lithium pieces disappeared. The reaction mixture was then decanted (leaving behind any excess pieces of lithium) under nitrogen into a side arm separatory funnel and slowly added to a well-stirred refluxing solution of 21.91 g. (0.088 moles) of p-iodonitrobenzene in 150 ml. of tetrahydrofuran under nitrogen. After completion of the addition the reaction was allowed to reflux for an additional 0.5 hours. The reaction was cooled and 40 ml. of water was slowly added to the stirred

reaction mixture, still under a nitrogen atmosphere. The work up was continued as described above for the tris(p-nitrophenyl)phosphine. Approximately 0.1 g. (1.3%) of solid material (benzene-chloroform eluent) was obtained and was recrystallized from acetone-water affording red-orange flakes, m.p. 214-16°.

Anal. Calcd. for  $C_{18}H_{14}PNO_2$ : C, 70.36; H, 4.59; P, 10.08; N, 4.56;  
O, 10.41.

Calcd. for  $C_{18}H_{14}PNO_3$ : C, 66.87; H, 4.37; P, 9.58; N, 4.33;  
O, 14.85.

Found: C,       ; H,       ; P,       ; N,       ; O,       .

Preparation of Ylid Salts.- -A general procedure was employed to prepare all of the ylid salts needed for the analyses involving Wittig reactions and pKa determinations.<sup>119</sup>

Equimolar amounts of the substituted phenylphosphine and 9-bromofluorene were added to an appropriate sized flask, dissolved in a minimum volume of acetone, refluxed for 4 hours, cooled in the refrigerator and the crystals formed were filtered. A large portion of the acetone of the filtrate was removed by evaporation on a Rinco evaporator and the clear solution was again cooled in the refrigerator. The precipitate was filtered and the remaining acetone of the filtrate was removed in vacuo. The residue was treated with a small volume of skelly solve B (or benzene) and the undissolved crystals were filtered and recrystallized from an appropriate solvent pair, dried and weighed.

(p-Bromophenyl)diphenylfluorenylphosphonium bromide.- -This compound was prepared from 18.79 g. (0.0551 moles) of (p-bromophenyl)diphenylphosphine and 13.48 g. of 9-bromofluorene in 50 ml. of acetone. The reaction afforded 28.8 g. (89%) of salt which crystallized as colorless microcrystals from chloroform-skelly solve B, m.p. 201-3° (dec.).

Tris(p-bromophenyl)fluorenylphosphonium bromide. - This compound was prepared from 5.27 g. (0.0106 moles) of tris(p-bromophenyl)phosphine and 2.59 g. of 9-bromofluorene in 25 ml. of acetone. The reaction afforded 6.2 g. (89%) of salt which crystallized as colorless, rectangular plates from ethanol-water, m.p. 261-3° (dec.).

Tris(p-chlorophenyl)fluorenylphosphonium bromide. - This compound was prepared from 3.37 g. (0.0092 moles) of tris(p-chlorophenyl)phosphine and 2.26 g. of 9-bromofluorene in 40 ml. of acetone. The reaction afforded 4.13 g. (73%) of salt which crystallized as colorless needles from ethanol-skelly solve B, m.p. 273-4° (dec.).

(p-Cyanophenyl)diphenylfluorenylphosphonium bromide. - This compound was prepared from 1.10 g. (0.0038 moles) of (p-cyanophenyl)diphenylphosphine and 0.93 g. of 9-bromofluorene in 25 ml. of acetone. The reaction afforded 1.5 g. (75%) of salt which crystallized as colorless microcrystals from chloroform-skelly solve B, m.p. 273-4° (dec.).

Tripiperidylfluorenylphosphonium bromide. - This compound was prepared from 11.5 g. (0.0407 moles) of tripiperidylphosphine and 9.98 g. of 9-bromofluorene in 100 ml. of dry acetone under a nitrogen atmosphere. The reaction afforded colorless needles which crystallized readily from chloroform as colorless needles, m.p. 244-5°.

Anal. Calcd. for  $C_{28}H_{39}PNBr$ : C, 63.63; H, 7.44; P, 5.86; N, 7.95;  
Br, 15.12.

Found: C,       ; H,       ; P,       ; N,       ; Br,       .

Preparation of Ylids. - All the ylids were prepared by the following procedure.<sup>120</sup>

A weighed quantity of purified ylid salt was dissolved in boiling absolute ethanol, filtered with suction, and cooled to room temperature.

A slight excess of one equivalent of concentrated ammonium hydroxide was added with thorough mixing and the solution cooled in the refrigerator. The product was isolated, immediately after cooling, by filtration then it was dried in a vacuum oven and weighed. The ylids were recrystallized from chloroform-ethanol and the melting points determined.

(p-Bromophenyl)diphenylphosphoniumfluorenylide.- -This compound was prepared from 11.71 g. (0.0199 moles) of (p-bromophenyl)diphenylfluorenylphosphonium bromide in 800 ml. of absolute ethanol and 10 ml. of concentrated ammonium hydroxide. The reaction afforded 8.1 g. (81%) of yellow-orange plates that were recrystallized from chloroform-ethanol, m.p. 110-12°.

Anal. Calcd. for  $C_{31}H_{22}PBr$ : C, 73.67; H, 4.39; P, 6.13; Br, 15.81.

Found: C,       ; H,       ; P,       ; Br,       .

Tris(p-chlorophenyl)phosphoniumfluorenylide.- -This compound was prepared from 7.8 g. (0.0128 moles) of tris(p-chlorophenyl)fluorenylphosphonium bromide in 800 ml. of absolute ethanol and 5 ml. of concentrated ammonium hydroxide. The reaction afforded 5.16 g. (76.5%) of golden-yellow needles that crystallized from chloroform-ethanol as needles, m.p. 226-7°.

Anal. Calcd. for  $C_{31}H_{20}PCl_3$ : C, 70.27; H, 3.80; P, 5.85; Cl, 20.08.

Found: C,       ; H,       ; P,       ; Cl,       .

Tris(p-bromophenyl)phosphoniumfluorenylide.- -This compound was prepared from 7.55 g. (0.0101 moles) of tris(p-bromophenyl)fluorenylphosphonium bromide in 700 ml. of absolute ethanol and 5 ml. of concentrated ammonium hydroxide. The reaction afforded 5.9 g. (88%) of golden-yellow needles that crystallized from chloroform-ethanol as needles, m.p. 266-8°.



Anal. Calcd. for  $C_{31}H_{20}PBr_3$ : C, 56.14; H, 3.04; P, 4.67; Br, 36.15.

Found: C,       ; H,       ; P,       ; Br,       .

(p-Cyanophenyl)diphenylphosphoniumfluorenylide.- -This compound was prepared from 1.10 g. (0.0021 moles) of (p-cyanophenyl)diphenylfluorenylphosphonium bromide in 25 ml. of absolute ethanol and 0.5 ml. of concentrated ammonium hydroxide (dissolved in 5 ml. of water). The reaction afforded 0.8 g. (95%) of red-brown plates that crystallized from chloroform-ethanol as needles, m.p. 133-35° (dec.).

Anal. Calcd. for  $C_{32}H_{22}PN$ : C, 85.13; H, 4.91; P, 6.86; N, 3.10.

Found: C,       ; H,       ; P,       ; N,       .

Preparation of Phosphine Oxides.- -The phosphine, dissolved in acetone, was treated with an equimolar amount of 10% hydrogen peroxide and refluxed for an hour. The acetone was removed, the residue re-dissolved in benzene and treated, until peroxide free, with freshly prepared ferrous ammonium sulfate. The benzene solution was washed with water, dried over magnesium sulfate, filtered and the benzene removed. The residue was then recrystallized from an appropriate solvent. The yields were effectively quantitative.

Tris(p-bromophenyl)phosphine Oxide.- -This compound was crystallized from acetone-water as colorless clusters, m.p. 174-175.5° (Lit.<sup>118</sup> m.p. 173-5°).

Tris(p-chlorophenyl)phosphine Oxide.- -This compound was crystallized from acetone-water as colorless needles, m.p. 173-4° (Lit.<sup>107</sup> m.p. 171.5-172.0°).

(p-bromophenyl)diphenylphosphine Oxide.- -This compound was crystallized from acetone-water as colorless needles, m.p. 153-54° (Lit.<sup>63</sup> m.p. 133-34°.)

Reaction of ylids IIIa, IIIb and IIIc with carbonyls. - A standard procedure was used in all the Wittig reactions. Exactly 0.500 g. of the various ylids were weighed into a 100 ml. round bottom flask and dissolved in 35 ml. of chloroform. An equimolar amount of the carbonyls (see table 2) was added to the reaction flask and the mixture was allowed to reflux for exactly three hours, after which the reaction mixtures were worked up in the following manner.

The chloroform was evaporated on a Rinco Evaporator under vacuum. After all of the solvent was removed, 20 ml. of absolute ethanol was added to dissolve all components except the unreacted ylid. The latter was filtered into a pre-weighed funnel and filter paper. The reaction flask was rinsed with 10 ml. of absolute ethanol (making sure to remove all ylid remaining on the walls of the flask) and filtered through the same funnel as before. The combined filtrates were transferred to a 50 ml. beaker. Distilled water was added until the olefin just began to precipitate and the beaker was then set on the steam bath and the crystals were redissolved. The solution was then allowed to cool, whereupon crystals began to form. When precipitation was assumed to be complete, additional amounts of water were added to assure complete precipitation. The olefin was then filtered into a preweighed funnel (including filter paper). The funnels now containing the unreacted ylid and the olefin were placed in a vacuum drying oven for drying. They were allowed to dry for 2-3 hours and then reweighed. The amount of olefin and unreacted ylid were then obtained, from which the relative reactivity was calculated, based upon both the total ylid added and the total ylid reacted. The observed melting points for the isolated olefins have been listed in table 5.

The other reaction product, the respective phosphine oxides, were also isolated by flooding the remaining filtrate from the olefin isolation with water. Colorless crystals of the oxides were formed, filtered from the aqueous mixture, and identified according to their melting points.<sup>11</sup>

pKa determination. - The pKa's of the conjugate acids of various ylids were measured spectrophotometrically and the following general procedure was used. Four solutions were necessary to carry out the measurements and they were prepared in the following manner:

a) Solution I - An approximately 95% aqueous ethanol solution was prepared by pipetting 10 ml. of distilled water into a dry 200 ml. volumetric flask and diluting to the mark, with shaking, with reagent grade absolute ethanol.

b) Base Solution - To a dry 200 ml. volumetric flask was added 0.80 g. of reagent grade sodium hydroxide, 10 ml. of distilled water from a pipette and the contents shaken until the base was dissolved. The solution was diluted to the mark, with mixing, with reagent grade absolute ethanol.

c) Buffer Solution - To a dry 200 ml. volumetric flask was added 1.214 g. of tris(hydroxymethyl)aminomethane (Fisher Certified Reagent), 150 ml. of reagent grade absolute ethanol and the solid was brought into solution by heating on a hot plate. An approximately 1 N hydrochloric acid solution was prepared by diluting 1 ml. of concentrated hydrochloric acid with 12 ml. of distilled water. Into the volumetric flask was pipetted 5.36 ml. of the hydrochloric acid solution and 4.64 ml. of distilled water. The cooled solution, while being mixed, was diluted to the mark with more absolute ethanol. pH = 9.20 was recorded on a Beckman Expanded scale pH meter standardized at pH = 7.02 at 20°.

d) Acid Solution - To a dry 200 ml. volumetric flask was pipetted 1.66 ml. of concentrated hydrochloric acid and 8.34 ml. of distilled water. The cooled solution was diluted to the mark, with shaking, with reagent grade absolute ethanol.

Approximately 0.006 g. of ylid salt was accurately weighed into a 10 ml. volumetric flask (A), dissolved in about 7 ml. of solution I with heating on a hot plate, cooled to room temperature and diluted to the mark with more solution I. To each of three 10 ml. volumetric flasks (B), (C) and (D), was carefully pipetted 1.0 ml. of (A) and the solutions were then diluted to their respective volumes with the acid, buffer and base solutions (making sure that each flask was thoroughly mixed before reaching the mark). The reference cell of the spectrophotometer was filled with solution I and capped. The sample cell was first filled with solution I and the base line for the solvent adjusted to zero absorbance in the region of 300-400 millimicrons. The sample cell was emptied, air dried, rinsed with acid solution (B) and filled with acid solution (B). The spectrum of the acid solution was recorded from 200 to 450 millimicrons. Upon completion of the spectrum, the sample cell was emptied, washed with absolute ethanol, air dried, rinsed with buffer solution (C) and filled with buffer solution (C). The spectrum of the buffer solution was recorded from 200 to 450 millimicrons on the same graph paper. The same process was performed for the spectrum of the base solution (D) on the same graph paper.

Calculations of the pKa values were made by obtaining absorbance values from the spectra and using them in the following equation:<sup>125,126</sup>

$$\text{pKa} = \text{pH}_{\text{Buffer}} - \log \frac{A_1 - A_2}{A_3 - A_1} \quad (7)$$

where  $A_1$  = absorbance of buffer

$A_2$  = absorbance of acid

$A_3$  = absorbance of base

$\text{pH}_{\text{Buffer}} = 9.20$

Absorbance values  $A_1$ ,  $A_2$  and  $A_3$  were taken at 10 millimicron intervals from 320 to 390 millimicrons and the average of the eight values resulting from equation (7) was taken to be the actual pKa.

Table 10. pKa Spectra Data for IIIa (Buffer pH = 9.20)

Wave- Length millimicrons	$A_1 \times 10^3$	$A_2 \times 10^3$	$A_3 \times 10^3$	pKa
320	262	12	581	9.31
330	208	6	474	9.32
340	206	7	458	9.30
350	217	8	480	9.30
360	242	9	527	9.29
370	260	10	585	9.31
380	273	6	597	9.28
390	242	5	539	9.30

Buffer pH = 8.20

320	63	18	542	9.23
330	48	11	463	9.25
340	46	10	450	9.25
350	48	10	465	9.24
360	52	12	500	9.25
370	54	11	535	9.25
380	56	7	544	9.20
390	49	4	492	9.19

Table 11. pKa Spectra Data for IIIb (Buffer pH = 9.20)

Wave- Length millimicrons	$A_1 \times 10^3$	$A_2 \times 10^3$	$A_3 \times 10^3$	pKa
320	326	27	408	8.64
330	279	8	355	8.70
340	281	7	354	8.63
350	304	8	382	8.68
360	342	8	428	8.61
370	383	10	478	8.62
380	419	9	515	8.57
390	397	4	482	8.53

Buffer pH = 8.20

320	162	30	445	8.70
330	140	17	405	8.70
340	139	12	410	8.70
350	148	13	438	8.53
360	164	15	485	8.53
370	185	13	525	8.50
380	197	12	543	8.47
390	185	9	490	8.44

Table 12. pKa Spectra Data for IIIc (Buffer pH = 9.20)

Wave- Length millimicrons	$A_1 \times 10^3$	$A_2 \times 10^3$	$A_3 \times 10^3$	pKa
320	400	24	475	8.50
330	348	8	415	8.49
340	349	8	420	8.52
350	379	8	453	8.50
360	435	12	518	8.49
370	488	11	576	8.47
380	522	6	620	8.48
390	490	6	577	8.45

Buffer pH = 8.20

320	177	18	549	8.57
330	149	6	509	8.60
340	154	2	505	8.56
350	168	7	549	8.57
360	192	8	599	8.55
370	213	9	652	8.53
380	225	5	676	8.51
390	205	1	616	8.50

Table 13. pKa Spectra Data for IIIe (Buffer pH = 9.20)

Wave- Length millimicrons	$A_1 \times 10^3$	$A_2 \times 10^3$	$A_3 \times 10^3$	pKa
320	415	40	605	8.90
330	327	20	495	8.94
340	312	10	472	8.92
350	333	11	495	8.90
360	377	12	550	8.88
370	419	9	598	8.84
380	444	8	624	8.82
390	395	4	565	8.84

Buffer pH = 8.20

320	185	50	672	8.76
330	144	22	580	8.75
340	137	11	560	8.73
350	144	10	586	8.72
360	158	11	640	8.72
370	172	9	687	8.61
380	176	8	713	8.71
390	157	1	638	8.69



Table 14. pKa Spectra Data for IIIg (Buffer pH = 9.20)

Wave- Length millimicrons	$A_1 \times 10^3$	$A_2 \times 10^3$	$A_3 \times 10^3$	pKa
320	176	17	675	9.70
330	138	11	542	9.70
340	138	12	525	9.69
350	146	14	542	9.68
360	154	18	578	9.69
370	161	16	613	9.69
380	173	13	627	9.65
390	147	10	595	9.71

Buffer pH = 8.20

320	50	11	655	9.39
330	38	8	563	9.44
340	37	6	550	9.42
350	37	10	575	9.50
360	40	12	609	9.51
370	40	11	634	9.51
380	39	10	650	9.52
390	36	8	592	9.50

Table 15. pKa Spectra Data for IIIj (Buffer pH = 9.20)

Wave- Length millimicrons	$A_1 \times 10^3$	$A_2 \times 10^3$	$A_3 \times 10^3$	pKa
320	37	8	772	10.60
330	26	9	633	10.75
340	28	6	602	10.62
350	27	7	592	10.65
360	29	12	578	10.72
370	26	11	590	10.78
380	27	12	582	10.77
390	23	8	574	10.77

Buffer pH = 8.20

320	12	4	900	10.25
330	11	4	765	10.23
340	10	3	727	10.21
350	11	6	703	10.34
360	--	--	---	-----
370	11	9	690	10.73
380	--	--	---	-----
390	7	2	671	10.32

### Attempted Syntheses

a) An attempt to prepare tris(p-N-acetylamino-phenyl)phosphine from the reaction of the Grignard reagent of p-bromoacetanilide and phosphorus trichloride resulted only in a red-brown polymeric-like material, insoluble in the common organic solvents.

b) An attempted alkylation of tris(m-trifluoromethylphenyl)-phosphine with 9-bromofluorene in acetone, toluene, xylene and diethylene glycol dimethyl ether gave only the starting materials in each case after a reflux time of three hours.

c) Alkylation of tris(p-cyanophenyl)phosphine with 9-bromofluorene in acetone, toluene, xylene and diethylene glycol dimethyl ether gave only starting materials after a reflux time of three hours.

d) Both tris(m-trifluoromethylphenyl)phosphine and tris(p-cyanophenyl)phosphine when refluxed for three hours in a large excess of benzyl chloride, in an attempt to prepare the benzylphosphonium salts, gave only the starting materials after removal of the excess benzyl chloride in vacuo.

e) An attempt to prepare (p-bromophenyl)diphenylphosphine from the reaction of lithium diphenylphosphide (made from diphenylphosphinous chloride and a slight excess of lithium metal in tetrahydrofuran under nitrogen) and p-dibromobenzene in a molar ratio of 1:1, failed to give the desired product in an appreciable yield. The main product obtained, but not purified, melted very close to the product synthesized by an alternate method, p-bis(diphenylphosphino)benzene (m.p. 166-7°).

Another attempt using the above conditions and p-bromiodobenzene gave a product that melted at 123-5° and was not identified. Oxide formation was suspected in both of the reactions.

### SUGGESTED SYNTHESIS

1. The preparation of (p-cyanophenyl)diphenylphosphine should be attempted using the reaction between p-cyanophenylphosphonous chloride, prepared according to the procedure suggested by Quin and Humphrey,<sup>83</sup> and phenylmagnesium bromide.

## SUMMARY

The influence of electron-withdrawing substituents attached to phosphorus on the valence shell expansion of a phosphorus atom was studied employing ylids IIIa-c, IIIe, IIIg and IIIj. The ylids, resonance hybrids of an ylene form (Ia) and an ylid form (Ib), were used to investigate the effect electron-withdrawing groups have on the relative contribution of the two forms to the hybrid and thus the extent of valence shell expansion through the contribution of Ia. With increased positive charge on phosphorus, created by the electron-withdrawing effects of attached substituents, the valence shell expansion of phosphorus (by (p-d)pi overlap) should increase the importance of the contributing form Ia and vice versa.

Ylids IIIa-c were reacted in the Wittig reaction with various substituted benzaldehydes (p-NO<sub>2</sub>, p-Cl, p-H, p-MeO and p-Me<sub>2</sub>N) and their relative reactivity determined by isolation of both the olefin product and the unreacted ylid. The results revealed that the order of reactivity was IIIa > IIIb = IIIc. The results also revealed that the ylids IIIa-c were less reactive than IIIg-k used by Royer.<sup>11</sup>

An ultraviolet spectrophotometric determination of the pKa of the ylid conjugate acids confirmed the proposal that the most reactive ylid was also the most basic. The basicity increased in the order IIIc < IIIb < IIIe < IIIa < IIIg < IIIj.

The combined results indicated that the electron-withdrawing substituents on the phenyl groups attached to phosphorus increased the inductive effect of the phenyl group, increasing the positive character of phosphorus, and induced the valence shell expansion of phosphorus through increased (p-d)pi overlap with the adjacent ylid carbanion. The valence shell expansion of phosphorus in the ylids was exhibited through decreased reactivity in the Wittig reaction and increased acidity of the ylid conjugate in comparison to IIIg.

LITERATURE CITED

1. D. P. Craig, J. Chem. Soc., 997 (1959).
2. D. P. Craig and N. L. Paddock, J. Chem. Soc., 4118 (1962).
3. W. Von E. Doering and A. K. Hoffman, J. Am. Chem. Soc., 77, 521 (1955).
4. H. B. Henbest, Ann. Repts. Chem. Soc., 53, 137 (1956).
5. F. Ramirez and S. Dershowitz, J. Org. Chem., 22, 41 (1957).
6. A. J. Speziale and K. W. Ratts, J. Am. Chem. Soc., 85, 2790 (1963).
7. V. Mark, Tetrahedron Letters, 3139 (1964).
8. G. Aksnes, Acta. Chem. Scand., 15, 692 (1961).
9. A. J. Speziale and K. W. Ratts, J. Org. Chem., 28, 465 (1963).
10. A. J. Speziale and D. E. Bissing, J. Am. Chem. Soc., 85, 3873 (1963).
11. L. Royer, "Electronic Effects of Substituents on Phosphonium Compounds," Dissertation in partial fulfillment of the requirements for a M.S. Degree in chemistry at the University of North Dakota, 1962.
12. S. Trippett, Quart. Rev., 4, 406 (1963).
13. F. Ramirez and S. Levy, J. Org. Chem., 21, 488 (1956).
14. F. Ramirez and S. Levy, J. Am. Chem. Soc., 79, 67 (1957).
15. H. J. Bestmann, D. Kratzer and H. Simon, Chem. Ber., 95, 2750 (1962).
16. J. S. Driscoll and D. W. Grisley, J. Org. Chem., 29, 2427 (1964).
17. A. Wm. Johnson and R. B. LaCount, Tetrahedron, 9, 130 (1960).
18. D. P. Craig, H. Maccoll, R. S. Nyholm, L. E. Sutton and L. E. Orgel, J. Chem. Soc., 332 (1954).
19. D. P. Craig and E. A. Magnusson, J. Chem. Soc., 4895 (1956).
20. H. H. Jaffe, J. Phys. Chem., 58, 185 (1954).
21. J. Chatt and A. A. Williams, J. Chem. Soc., 3061 (1951).



22. E. W. Abel, M. A. Bennett and G. Wilkinson, J. Chem. Soc., 2323 (1959).
23. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., U. S. A., 1962, p. 611.
24. M. Schlosser and K. F. Christmann, Angew. Chem., 76, 683 (1964).
25. J. Levisalles, Bull. soc. Chim. France, 1021 (1958).
26. U. Schollkopf, Angew. Chem., 71, 260 (1959).
27. G. Wittig, Experientia, 12, 41 (1956).
28. S. Trippett, "Advances in Organic Chemistry: Methods and Results," v. 1, Interscience Publishers, Inc., New York, 1960, p. 83.
29. L. Horner and H. Oediger, Chem. Ber., 91, 437 (1958).
30. A. Wm. Johnson, J. Org. Chem., 24, 282 (1959).
31. B. M. Wepster, Rec. Trav. Chem., 71, 1171 (1952).
32. R. S. Mulliken, J. Am. Chem. Soc., 72, 4500 (1950).
33. G. W. Fenton and C. K. Ingold, J. Chem. Soc., 2342 (1929).
34. E. L. Wagner, J. Am. Chem. Soc., 85, 161 (1963).
35. J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1962, p. 90.
36. E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, Inc., New York, 1963, p. 207.
37. C. D. Cook and A. D. Allen, Can. J. Chem., 41, 1235 (1963).
38. M. Grayson, Chem. and Eng. News, 40, No. 49, Dec. 3, 1962, p. 90.
39. A. F. Bedford and C. T. Mortimer, J. Chem. Soc., 1622 (1960).
40. H. J. Bestmann and O. Kratzer, Chem. Ber., 95, 1894 (1962).
41. G. Wittig, H. Weigmann and M. Schlosser, Chem. Ber., 94, 676 (1961).
42. S. Trippett and D. M. Walker, Chem. and Ind., 933 (1960).
43. A. Wm. Johnson and R. B. LaCount, Chem. and Ind., 52 (1959).
44. A. J. Speziale and D. E. Bissing, J. Am. Chem. Soc., 85, 1888 (1963).
45. L. D. Bergelson and M. M. Shemyakin, Tetrahedron, 19, 149 (1963).

46. L. D. Bergelson and M. M. Shemyakin, Chem. & Eng. News, 40, No. 29, July 23, 1962, p. 36.
47. L. D. Bergelson, V. A. Vaver, L. I. Barsukov and M. M. Shemyakin, Tetrahedron Letters, 2669 (1964).
48. G. Witschard and C. W. Griffin, J. Org. Chem., 29, 2335 (1964).
49. L. D. Bergelson and M. M. Shemyakin, Angew. Chem. (Int. Edn.), 3, 113 (1964).
50. J. O. Edwards and R. G. Pearson, J. Am. Chem. Soc., 84, 16 (1962).
51. H. J. Bestmann, Chem. Ber., 95, 58 (1962).
52. J. R. Van Wazer, "Phosphorus and Its Compounds," Interscience Publishers, Inc., New York, 1958, p. 246.
53. P. W. Allen and L. E. Sutton, Acta. Cryst., 3, 66 (1950).
54. Q. Williams, J. Sheriden, and W. Gordy, J. Chem. Phys., 20, 164 (1952).
55. J. V. Bell, J. Husler, H. Tennenbaum and J. Goldenson, J. Am. Chem. Soc., 76, 5185 (1954).
56. L. C. Thomas and R. A. Chittenden, Chem. and Ind., 1913 (1961).
57. L. W. Daasch and D. C. Smith, Anal. Chem., 23, 853 (1951).
58. H. H. Jaffe, J. Chem. Phys., 22, 1430 (1954).
59. H. H. Jaffe and L. B. Friedman, J. Am. Chem. Soc., 74, 1069, 2930 (1952).
60. C. N. R. Rao, Nature, 183, 1475 (1959).
61. H. H. Jaffe, J. Inorg. Nucl. Chem., 4, 372 (1957).
62. K. Bowden and E. A. Braude, J. Chem. Soc., 1068 (1952).
63. H. Goetz, F. Nerdel, K. H. Wiechel, Ann., 665, 1 (1963).
64. G. P. Schiemenz, Tetrahedron Letters, 2729 (1964).
65. W. D. Knight, Phys. Rev., 76, 1259 (1949).
66. J. Packer, J. Chem. Soc., 960 (1963).
67. H. S. Gutowsky and D. W. McCall, J. Chem. Phys., 22, 162 (1954).
68. N. Muller, P. C. Lauterbur and J. Goldense, J. Am. Chem. Soc., 78, 3557 (1956).
69. C. Morin, Bull. soc. chim. France, 1446 (1961).

70. R. Jones and A. R. Katritzky, Angew. Chem., 74, 60 (1962).
71. J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, J. Am. Chem. Soc., 78, 5715 (1956).
72. F. Ramirez, N. B. Desai, B. Hansen and N. McKelvie, J. Am. Chem. Soc., 83, 3539 (1961).
73. G. Wittig and M. Rieber, Ann., 562, 177 (1949).
74. D. Seyferth, J. K. Heeren and W. B. Hughes, J. Am. Chem. Soc., 84, 1764 (1962).
75. W. A. Henderson and S. A. Buckler, J. Am. Chem. Soc., 82, 5794 (1960).
76. G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley & Sons, Inc., New York, 1950.
77. Reference 52, p. 193.
78. P. D. Bartlett and G. Meguerian, J. Am. Chem. Soc., 78, 3710 (1956).
79. K. Issleib and G. Grams, Z. anorg. u. allgem. chem., 58, 299 (1959).
80. J. Dodonow and H. Medox, Chem. Ber., 61, 907 (1928).
81. A. E. Sinear, W. Valient and J. Wirth, J. Org. Chem., 25, 2001 (1960).
82. H. Gilman and C. G. Stuckwisch, J. Am. Chem. Soc., 63, 2844 (1941).
83. L. D. Quin and J. S. Humphrey, J. Am. Chem. Soc., 82, 3795 (1960).
84. W. C. Davies and F. G. Mann, J. Chem. Soc., 276 (1944).
85. H. G. Gilman and G. E. Brown, J. Am. Chem. Soc., 67, 824 (1945).
86. D. E. Worrall, J. Am. Chem. Soc., 62, 2514 (1940).
87. G. Wittig, German patents 955, 596 and 1,003,731, Chem. Abs. 53, P13108g, P16064a (1959).
88. A. A. Morton and H. E. Romsden, J. Am. Chem. Soc., 70, 3132 (1948).
89. Symposium Report, Angew. Chem., 76, 754 (1964).
90. H. Gilman, A. L. Jacoby and H. Ludeman, J. Am. Chem. Soc., 60, 2336 (1938).
91. G. Wittig, German patent 1,054,992, Chem. Abs. 56, P503f (1962).
92. C. Screttas and A. F. Isbell, J. Org. Chem., 27, 2573 (1962).
93. F. A. Hart, J. Chem. Soc., 3324 (1960).

94. Th. Weil, Helv. Chim. Acta., 37, 654 (1954).
95. H. Lautenschlager and D. Wittenberg, German patent 1,131,669, Chem. Abs. 58, P1490f (1963).
96. G. Wittig, "New Methods of Preparative Organic Chemistry," Interscience Publishers, New York, 1948.
97. E. G. Rochow, D. T. Hurd and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley & Sons, Inc., New York, 1957, p. 69.
98. A. M. Aguiar, H. J. Greenberg and K. E. Rubenstein, J. Org. Chem., 27, 619 (1954).
99. H. Albers and W. Schuler, Chem. Ber., 76, 23 (1943).
100. W. Hewertson and H. R. Watson, J. Chem. Soc., 1490 (1962).
101. K. Issleib and A. Tzschach, Chem. Ber., 92, 1118 (1959).
102. C. Tamborski, J. Org. Chem., 27, 619 (1962).
103. H. Raudnitz, Chem. Ber., 60, 743 (1927).
104. S. Goldschmidt and F. Obermeier, Ann., 588, 24 (1954).
105. W. C. Davies and C. J. O. L. Morris, J. Chem. Soc., 2880 (1932).
106. A. Michaelis, Ann., 315, 43 (1901).
107. F. G. Mann and E. J. Chaplin, J. Chem. Soc., 527 (1937).
108. L. W. Breed, W. J. Haggerty and F. Baiocchi, J. Org. Chem., 25, 1633 (1960).
109. R. Campbell and R. E. Hatton, Chem. Abs., 56, P12948b (1962).
110. B. M. Mikhailov and N. F. Kucherove, Zhur. Obshehei. Khim. 22, 792 (1952).
111. L. A. Wall, R. E. Donadio and W. J. Pummer, J. Am. Chem. Soc., 82, 4846 (1960).
112. O. Heuhoefler and L. Lamza, Chem. Ber., 94, 2514 (1961).
113. I. S. Protopopov and M. Ya Kraft, Chem. Abs., 54, 10913h (1960).
114. L. Anschutz, H. Kraft and K. Schmidt, Ann., 542, 14 (1939).
115. B. J. Gudzinowicz and R. H. Campbell, Anal. Chem., 33, 1510 (1961).
116. L. Friedman and H. Shechter, J. Org. Chem., 26, 2522 (1961).

117. M. S. Newman and H. Boden, J. Org. Chem., 26, 2525 (1961).
118. Private communication from Hooker Chemical Corp.
119. L. A. Pinck and G. E. Hilbert, J. Am. Chem. Soc., 69, 723 (1947).
120. A. Wm. Johnson, J. Org. Chem., 25, 183 (1960).
121. Reference 35, p. 64.
122. R. Oda, J. Kawabata and S. Tanimoto, Tetrahedron Letters, 1653 (1964).
123. Reference 36, p. 217.
124. R. T. Morrison and R. N. Boyd, "Organic Chemistry," Allyn and Bacon, Inc., Boston, 1961, p. 388.
125. L. A. Flexser, L. P. Hammett and A. Dingwall, J. Am. Chem. Soc., 57, 2103 (1935).
126. W. Stenstrom and N. Goldsmith, J. Phys. Chem., 30, 1683 (1926).
127. F. Westheimer, J. Am. Chem. Soc., 56, 1962 (1934).
128. S. P. Colowick and N. O. Kaplan, "Methods in Enzymology," Academic Press Inc., Publishers, New York, Vol. I, 1955, p. 138.
129. C. L. de Ligny, P. F. M. Luykx, M. Rehbach and A. A. Wieneke, Rec. Trav. Chim., 79, 699 (1960).
130. C. L. de Ligny and M. Rehbach, Rec. Trav. Chim., 79, 727 (1960).
131. R. G. Bates, "Electrometric pH Determinations," John Wiley and Sons, Inc., New York, 1954, p. 122.
132. R. G. Bates, "Determination of pH: Theory and Practice," John Wiley and Sons, Inc., New York, 1964.
133. L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corporation, New York, 1962, p. 627.
134. L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, Boston, 1957, p. 90.
135. A. I. Vogel, "Elementary Practical Organic Chemistry," Longmans, Green and Co. Inc., New York, 1958, p. 477.
136. S. D. Ross, M. Finkelstein and R. C. Peterson, J. Am. Chem. Soc., 80, 4329 (1958).
137. G. Wittig and G. Felletschin, Ann., 555, 133 (1944).

117. M. S. Newman and H. Boden, J. Org. Chem., 26, 2525 (1961).
118. Private communication from Hooker Chemical Corp.
119. L. A. Pinck and G. E. Hilbert, J. Am. Chem. Soc., 69, 723 (1947).
120. A. Wm. Johnson, J. Org. Chem., 25, 183 (1960).
121. Reference 35, p. 64.
122. R. Oda, J. Kawabata and S. Tanimoto, Tetrahedron Letters, 1653 (1964).
123. Reference 36, p. 217.
124. R. T. Morrison and R. N. Boyd, "Organic Chemistry," Allyn and Bacon, Inc., Boston, 1961, p. 388.
125. L. A. Flexser, L. P. Hammett and A. Dingwall, J. Am. Chem. Soc., 57, 2103 (1935).
126. W. Stenstrom and N. Goldsmith, J. Phys. Chem., 30, 1683 (1926).
127. F. Westheimer, J. Am. Chem. Soc., 56, 1962 (1934).
128. S. P. Colowick and N. O. Kaplan, "Methods in Enzymology," Academic Press Inc., Publishers, New York, Vol. I, 1955, p. 138.
129. C. L. de Ligny, P. F. M. Luykx, M. Rehbach and A. A. Wieneke, Rec. Trav. Chim., 79, 699 (1960).
130. C. L. de Ligny and M. Rehbach, Rec. Trav. Chim., 79, 727 (1960).
131. R. G. Bates, "Electrometric pH Determinations," John Wiley and Sons, Inc., New York, 1954, p. 122.
132. R. G. Bates, "Determination of pH: Theory and Practice," John Wiley and Sons, Inc., New York, 1964.
133. L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corporation, New York, 1962, p. 627.
134. L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, Boston, 1957, p. 90.
135. A. I. Vogel, "Elementary Practical Organic Chemistry," Longmans, Green and Co. Inc., New York, 1958, p. 477.
136. S. D. Ross, M. Finkelstein and R. C. Peterson, J. Am. Chem. Soc., 80, 4329 (1958).
137. G. Wittig and G. Felletschin, Ann., 555, 133 (1944).

138. R. L. Datta and P. S. Varma, J. Am. Chem. Soc., 41, 2047 (1919).
139. H. Hirtz, Chem. Ber., 29, 1405 (1896).
140. G. Losco, G. Speroni and C. A. Peri, Chimica e Industria (Milan), 37, 691 (1955, Chem. Abs., 50, 13797a (1956)).
141. J. Narbutt, Chem. Ber., 52, 1031 (1919).
142. A. Michaelis and K. Luxembourg, Chem. Ber., 28, 2208 (1895).