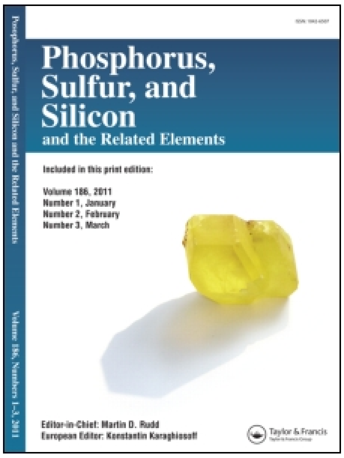

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THE ROLE OF O_{2p}-P(IV), N_{2p}-P(IV) AND SIMILAR INTERACTIONS IN HETEROATOM CHEMISTRY

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Phosphines having *o*-methoxyphenyl or *o*-(N,N-dimethylaminophenyl) groups bonded to the phosphorus atom exhibit moderate anchimeric assistance effects, attributable to through space O_{2p}-P(IV) or N_{2p}-P(IV) interactions, in reactions with alkyl halides. These S_N2 reactions have early transition states, and that is why the anchimeric assistance effects are only moderate. Quaternary phosphonium salts having *o*-methoxyphenyl groups bonded to phosphorus undergo slow alkaline decomposition reactions as expected because of O_{2p}-P(IV) interactions, but unusual effects are operative when *o*-(N,N-dimethylaminophenyl) groups are bonded to the phosphorus atom. Spectra of these types of compounds also show unusual characteristics. This review article provides rationalizations of these unusual data partly in terms of through space O_{2p}-P(IV) and N_{2p}-P(IV) interactions

Key words: Anchimeric assistance; alkylation; phosphines; phosphonium salts; phosphoranes; neighboring group interactions.

INTRODUCTION

It has been demonstrated that triarylphosphines in which at least one of the aryl groups is an *o*-methoxyphenyl group show a significant rate acceleration in their quaternization reactions with alkyl halides. This anchimeric assistance is thought to involve a through space interaction in which electron density from a 2*p* orbital of the methoxyl group is displaced in the direction of the developing P(IV) center, thereby lowering the energy of the transition state. The designation "O_{2p}-P_{3d} overlap" has previously been used to describe this effect, but with the proviso that this may be a convenient abbreviation rather than a statement of theory.[1] Now, however, it is time to change the abbreviation to "O_{2p}-P(IV) interaction" since there are numerous theoretical treatments in the literature which indicate that *d* orbital involvement may be only a minor component or even completely unnecessary in the description of either phosphorus "hypervalency" or a transition state interaction.[2]

Should such overlap occur in the transition state of the quaternization reaction, it should manifest itself to a greater extent in the resulting 'onium salt (partial positive charge versus a full positive charge on the phosphorus atom). There is much evidence supporting this idea. In benzyltriarylphosphonium salts in which at least one of the groups is an *ortho*-methoxyphenyl group, an upfield displacement in the chemical shift of the methylene hydrogens in the ^{1}H NMR spectrum is observed.[1] Support is also provided by the observation of a weak bonding interaction between the *ortho*-methoxyl oxygen and the positively charged phosphorus in the X-ray diffraction pattern of benzyl(2-methoxyphenyl)-diphenylphosphonium bromide.[3]

Perhaps the best evidence to date for this O_{2p}-P(IV) interaction is provided by the alkaline cleavage of benzyltriarylphosphonium halides containing *ortho*-methoxyphenyl groups. The rate of hydrolysis of these compounds is severely retarded compared with similar compounds which do not possess groups in the *ortho*-position capable of such interaction.[4] This is the expected result for an 'onium salt which has been rendered less electrophilic by such an interaction.

With such an O_{2p}-P(IV) interaction occurring with an *o*-methoxy group present, a substituent which is a better electron donor might be expected to show a greater amount of participation. This hypothesis was tested by studying the quaternization reactions of a series of triarylphosphines with *o*-(N,N-dimethylamino) groups present[5] as well as studying the alkaline cleavage reactions of a series of benzyltriarylphosphonium halides with *o*-(N,N-dimethylamino) groups present.[5,6] The effect of *o*-(N,N-dimethylamino) groups on the stereochemical outcome (*cis/trans* ratio of alkenes formed) of the Wittig reactions of benzyltriarylphosphonium ylides with aromatic aldehydes has also been studied.[7]

QUATERNIZATION REACTIONS

The base strengths of tertiary amines, phosphines and arsines have been shown to follow the order *t*-amine > *t*-phosphine > *t*-arsine.[8] However, the nucleophilic reactivity of these Lewis bases toward alkyl halides has been determined to follow the order *t*-phosphine > *t*-arsine > *t*-amine.[9]

The greater nucleophilicity of phosphines as compared to amines has been explained in a variety of ways. Davies[9] has suggested that this difference is due to the greater polarizability of the lone pair electrons on phosphorus. Henderson and Buckler[10] have compared the enthalpies and entropies of activation for the quaternization reactions of tertiary amines and phosphines, respectively, and have explained the reactivity difference as arising from a smaller degree of steric crowding around the larger phosphorus atom in the transition state. Another explanation may be offered based on Pearson's Hard and Soft Acid-Base Principle.[11] Alkyl halides, somewhat soft electrophiles, are more likely to react with a softer nucleophile, such as a tertiary phosphine, than a harder nucleophile, such as a tertiary amine.

While a great many and variety of quaternization reactions of tertiary phosphines have been reported, the background presented here will be limited mainly to quaternization reactions of triarylphosphines.

The quaternization reactions of tertiary phosphines with alkyl halides to form phosphonium salts are typical of S_N2 reactions of neutral reactants giving charged products. The rates of these reactions are ordinarily dependent on steric and electronic effects as well as on solvent polarity, inasmuch as charged species are formed.

The effect of solvent polarity on the rate of alkylation of triphenylphosphine and tri-*n*-butylphosphine with ethyl iodide was studied by Henderson and

Buckler.[10] A quantitative correlation was not obtained between the reaction rates and solvent dielectric constants. It was observed, however, that the rates were faster in polar solvents. Davies and Lewis[9] found similar results for the reactions of aryldiethylphosphines with ethyl iodide. McEwen *et al.*, however, have found little effect on the rates of reaction of *o*-(methoxyphenyl)diphenylphosphine and triphenylphosphine with benzyl chloride upon changing the solvent from chloroform to benzene-methanol (3:2 v/v).[1]

A thorough study of the quaternization reactions of "normal" tertiary phosphines (i.e., tertiary phosphines with groups of moderate steric requirements) has been reported by Henderson and Buckler.[10] While the ethyl and iso-butyl groups have similar steric substituent constants (Es),[12] reactions of triethylphosphine with alkyl halides give a reasonable correlation by use of the Taft–Hammett equation, while tri-isobutylphosphine reacts much slower than expected. This apparent anomoly is explained by Henderson and Buckler, who point out that the ethyl groups in triethylphosphine can block the phosphorus lone pair occasionally, while the geometry of tri-iso-butylphosphine requires that one methyl group shields the lone pair at all times.

Pagilagan and McEwen[13] have observed rate retardation caused by steric interference by *ortho*-substituents in the reactions of tri-tolylphosphines with benzyl chloride (Table I). With only one *o*-methyl group present, similar effects have been observed by McEwen[14,15] and by Allen.[16]

Steric effects do not necessarily have to retard the reaction; they may, in fact, enhance the rate of reaction in some cases. G. B. Borowitz *et al.*[18] investigated a series of reactions of mono- and tri-substituted triarylphosphines with α-bromoacetophenone. A good correlation was found in the normal Hammett plot of these reactions, excluding the tris-*m*-substituted cases. The *tris*(*m*-tolyl)- and *tris*(*m*-methoxyphenyl)-phosphines were found to react faster than expected on the basis of the Hammett plot for the other phosphines. Borowitz suggested that, in the formation of the transition state, the bond angles about phosphorus are increased from 102° to almost 109.5° and that this relieves the steric strain originally present in the *tris*-*m*-substituted phosphines. This is, in fact, steric acceleration of the reaction.

The rates of reaction of a limited number of *p*-substituted phenyldiethylphosphines with alkyl halides were determined by Davies and Lewis.[9] The data indicate that the phosphine reactivity is increased by the presence of electron-donating substituents and decreased by the presence of electron-withdrawing substituents. Henderson and Buckler[10] utilized the data of Davies and Lewis and

TABLE I

Effect of *ortho*-methyl groups on the rate of alkylation of triarylphosphines with benzyl chloride in benzene-methanol (3:2 v/v) at 31.0 ± 0.1°C

Phosphine	10^2k(l mol^{-1} hr^{-1})	k rel
Triphenyl	7.22	1
Tris(*p*-tolyl)	25.82	3.6
Tris(*o*-tolyl)	0.32	0.44

prepared a Hammett plot for the reaction of the phosphines with ethyl iodide in acetone. The value of ρ obtained was -1.11. The sign of ρ is typical of reactions which are facilitated by the presence of electron-donating groups and retarded by electron-withdrawing substituents. The magnitude of ρ indicates that the reaction is only moderately susceptible to such substituent influences. Henderson and Buckler further report a ρ^* value of -0.767, obtained from a Hammett plot of their own data of the reactions of normal phosphines with ethyl iodide, which indicates the modest extent to which the presence of electron-donating substituents facilitate the reaction.

As mentioned above, Borowitz *et al.* have studied nucleophilic displacement reactions of α-bromoacetophenone with a series of mono- and tri-substituted triarylphosphines.[18] A ρ value of -1.22 was obtained for these reactions (excluding the *tris-m*-substituted cases). This again shows that, in the transition state, electron-donating groups delocalize the developing positive charge on the phosphorus, but that any resonance interaction between the phosphorus and the substituent is either quite weak or even non-existent.

Similar rate effects in the reactions of *m*- and *p*-substituted aryldiethylphosphines and triarylphosphines with benzyl chloride (or benzyl bromide or ethyl iodide) have been reported by McEwen and coworkers.[1,13,14,15,19] Some of these data are reported in Tables II–IV.

The rates of reaction of some heteroaryldiphenylphosphines with α-bromoacetophenone in nitromethane have been determined by Allen *et al.*[16] Some of these results may be found in Table V. These workers concluded from these data that "π-excessive" heteroaryl substituents are not significantly involved in $p\pi$-$d\pi$ conjugative stabilization of the developing phosphonium center in the transition state of the reaction. If such stabilization were important, one would expect the heteroarylphosphines to react faster than the phenylphosphines. The rate differences are due, therefore, to the overall inductive effects of the ring systems (especially notable in Ea) as well as related solvation effects (especially notable in ΔS^*).

Up to this point, discussion of cases where a substituent influences the phosphorus center in the course of a reaction has been limited to inductive

TABLE II

Rate data for reactions of triarylphosphines with benzyl chloride in benzene-methanol (3:2 v/v) at 31.0 ± 1°C.[19]

Phosphine	$10^2k(1\ mol^{-1}\ hr^{-1})$	k rel
p-Bromophenyldiphenyl	2.10	0.291
p-Chlorophenyldiphenyl	3.78	0.524
p-Fluorophenyldiphenyl	4.60	0.637
Triphenyl	7.22	1.000
p-Methylthiophenyldiphenyl	8.66	1.20
p-Tolyldiphenyl	9.44	1.31
p-Anisyldiphenyl[a]	14.6	2.02
Bis(*p*-anisyl)phenyl[a]	20.0	2.77
Tris(*p*-tolyl)	25.8	3.57
Tris(*p*-anisyl)[a]	47.8	6.62

[a] *p*-anisyl = (*p*-$MeOC_6H_4$).

TABLE III

Rate data for reactions of triarylphosphines with benzyl bromide in chloroform at 26.0°C.[1]

Compound	$10^2k(1\ mol^{-1}\ hr^{-1})$	*k* rel	ΔE^*(kcal/mol)	ΔS^* (cal/moldeg)
$(C_6H_5)_3P$	602	1.00	11.9	−33.5
(*o*-$MeOC_6H_4)PPh_2$	2937	4.88	12.8	−27.3
(*m*-$MeOC_6H_4)PPh_2$	542	0.90	11.1	−36.3
(*p*-$MeOC_6H_4)PPh_2$	751	1.25	12.2	−32.0
(*o*-$MeOC_6H_4)_2PPh$	3782	6.28	11.9	−29.8
(*o*-$MeOC_6H_4)_3P$	906	1.50	12.2	−31.6

TABLE IV

Rate data for the reaction of ethyl iodide with aryldiethylphosphines in acetone at 35.0°C.[19]

$ArPEt_2$	$k(1\ mol^{-1}\ hr^{-1})$	k rel
Ar = phenyl	1.81	1.00
Ar = (*o*-$MeOC_6H_4$)	12.60	6.96
Ar = (*m*-$MeOC_6H_4$)	1.65	0.91
Ar = (*p*-$MeOC_6H_4$)	3.19	1.76

TABLE V

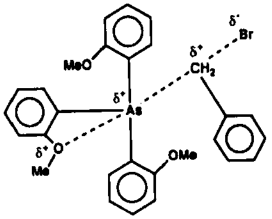
Rate data for the reaction of heteroaryldiphenylphosphines and aryldiphenylphosphines with α-bromoacetophenone in nitromethane at 30°C.[16]

$ArPPh_2$	k rel	Ea(KJ/mol)	Δ^*(J/mol deg)
Ar = 2-furyl	0.12	39.5	−162.9
Ar = 2-thienyl	0.33	42.1	−146.4
Ar = phenyl	1.00	45.2	−126.7
Ar = *p*-tolyl	1.67	41.5	−135.1
Ar = 2-pyrrolyl	2.12	37.4	−146.6
Ar = *p*-anisyl	2.33	41.4	−133.4
Ar = *o*-tolyl	0.15	47.3	−136.1
Ar = 1-methylpyrrol-2-yl	0.44	43.2	−140.1

(and/or field), resonance and steric effects. Another possibility is that of anchimeric assistance.[20]

While anchimeric assistance was originally proposed to explain the results obtained where carbon was the reacting center, other examples exist where the reacting center is an element other than carbon, such as iodine,[21] or sulfur.[22]

Fountaine and McEwen reported in 1971 that the k_o/k_p ratio for the reactions of tris(methoxyphenyl)arsines with benzyl bromide at 29.6° in chloroform is 14.3 ± 0.4, while the k_o/k_p ratio for the corresponding tris(tolyl)arsines under the same conditions is too small to be measured conveniently (presumably due to steric factors in the ortho case). The suggestion was made, based on these results, that the energy of the transition state for the reaction of tris(*o*-methoxyphenyl)arsine, compared with that of tris(*p*-methoxyphenyl)arsine, is lowered by a favorable interaction between 2*p* electrons on one or more of the methoxyl oxygens with the developing As(IV) center of the incipient quaternary arsonium salt. Here, the anchimeric assistance arises by an interaction of a neighboring group with the nucleophilic center of the attacking base and is therefore fundamentally different from the classical cases developed by Winstein and others.



With such an effect operating on arsenic compounds, one might suppose that a similar effect would be operating on analogous phosphorus compounds. This, in fact, has been shown to be the case.

In analogy with the triarylarsine system, McEwen and coworkers[1,14,15] have found a similar rate enhancement in the quaternization reactions of tertiary phosphines in which an *o*-methoxyphenyl group is present. Some examples have been presented earlier (cf. Tables III and IV). The k_o/k_p ratio for tertiary phosphines containing one methoxyphenyl group can be calculated from these data and found to be 3.9–4.0. Additional rate data may be found in Tables VI and VII.

The introduction of one *o*-methoxy group, in all cases for which data are available, causes a rate enhancement over that observed for the unsubstituted compound and over that observed for the corresponding *para*-substituted compound. These results have been interpreted, by analogy with the arsenic system, as arising through the interaction of 2*p* electrons on oxygen with a developing P(IV) center. This is now termed a through space O_{2P}-P(IV) interaction. For stronger interactions of a related nature, see recent publications by J. C. Martin *et al.* and by A. J. Arduengo, III, *et al.*[24]

The presence of a second *o*-methoxyphenyl group bonded to the phosphorus causes a still larger enhancement of the rate, but the presence of a third *o*-methoxyphenyl group causes somewhat anomalous results. The reaction of tris(*o*-methoxyphenyl)phosphine with either benzyl bromide or *n*-butyl chloride is slower than that of the mono-*o*-methoxy substituted phosphine. Steric crowding in the transition state has been suggested as a possible explanation.[1,15] However, the reaction of the same phosphine with benzyl chloride in 3:2 v/v benzene-methanol is faster than that of bis(*o*-methoxyphenyl)phenylphosphine. Solvation effects are presumed to play a strong role in this reaction.

Other examples of this O_{2p}-P(IV) interaction have been reported.[25,26] Alton and Kane-Maguire have reported a novel anchimeric assistance in the addition of triarylphosphines to $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}C_6H_7)]^+$. The results (Table VIII) show a rate retardation by the presence of an *o*-methyl substituent and a rate enhancement by an *o*-methoxy substituent relative to the unsubstituted case. These results indicate a strong steric effect operating in this reaction (cf. tris(*p*-tolyl)- and tris(*o*-tolyl)-phosphine in Table VIII), as well as a strong O_{2p}-P(IV) interaction.

TABLE VI

Rate data for reactions of tertiary phosphines with benzyl chloride in benzene-methanol (3:2 v/v) at 31.0 ± 0.1°C

Phosphine	10^2k(l mol^{-1} hr^{-1})	k rel
Diphenyl(2,6-dimethoxyphenyl)	539 ± 32	74.7
Tris(*o*-methoxyphenyl)	195 ± 4	27.0
Diphenyl(2,4-dimethoxyphenyl)	173 ± 14	24.0
Bis(*o*-methoxyphenyl)	146 ± 3	20.2
Diphenyl(*o*-methoxyphenyl)	53.6 ± 0.7	7.43
Tris(*p*-methoxyphenyl)	47.8 ± 1.0	6.64
Diphenylmethyl	35.5 ± 0.3	4.92
Diphenyl(2-methoxyethyl)	33.8 ± 0.3	4.68
Tris(*p*-tolyl)	32.8 ± 0.9	4.55
Diphenyl(3-methoxypropyl)	31.2 ± 0.2	4.31
Diphenylethyl	27.1 ± 0.1	3.76
Diphenyl(*n*-butyl)	26.0 ± 0.1	3.60
Diphenyl(*n*-propyl)	25.9 ± 0.1	3.59
Bis(*p*-methoxyphenyl)	24.3 ± 1.1	3.36
Diphenyl(4-methoxybutyl)	21.1 ± 0.1	2.92
Diphenyl(*p*-methoxyphenyl)	14.6 ± 0.3	2.02
Diphenyl(*p*-tolyl)	9.44 ± 0.26	1.31
Triphenyl	7.22 ± 0.13	1.00
Diphenyl(*p*-fluorophenyl)	4.60 ± 0.24	0.64
Diphenyl(*p*-chlorophenyl)	3.78 ± 0.10	0.52
Diphenyl(*o*-fluorophenyl)	3.47 ± 0.02	0.48
Diphenyl(*o*-tolyl)	2.16 ± 0.08	0.30
Diphenyl(*p*-bromophenyl)	2.10 ± 0.16	0.29
Diphenyl(*o*-chlorophenyl)	2.08 ± 0.17	0.29
Diphenyl(*o*-bromophenyl)	1.79 ± 0.03	0.25
Tris(*o*-tolyl)	0.33 ± 0.01	0.046
Diphenyl(methoxymethyl)	0.00	

TABLE VII

Rate data for reactions of triarylphosphines with alkyl chlorides in chloroform at 31.0°[1]

Phosphine	Alkyl halide	10^2k(l mol^{-1} hr^{-1})	k rel
Triphenyl	*n*-BuCl	0.419	1.00
Diphenyl(*o*-methoxyphenyl)	*n*-BuCl	1.96	4.68
Bis(*o*-methoxyphenyl)	*n*-BuCl	5.68	13.5
Tris(*o*-methoxyphenyl)	*n*-BuCl	1.63	3.89
Triphenyl	$PhCH_2Cl$	7.89	1.00[a]
Diphenyl(*o*-methoxyphenyl)	$PhCH_2Cl$	40.0	5.07[a]

[a] A new series of relative rates.

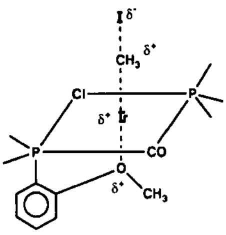
TABLE VIII

Rate data for addition of triarylphosphines to $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}C_6H_7)]^+$ in acetone at 20°.

Phosphine	10^2k(mol^{-1} dm^3 s^{-1})	k rel
Triphenyl	74.6	1.00
Tris(*p*-tolyl)	283	3.8
Tris(*o*-tolyl)	0.077	0.001
Tris(*p*-methoxyphenyl)	642	8.6
Tris(*o*-methoxyphenyl)	68000	91

These authors suggest a transition state in which phosphorus-carbon bond formation is considerable, but not complete, based on $k(o\text{-CH}_3\text{O})/(k(\text{H})$ ratios of analogous systems.[25]

In another organometallic system, Miller and Shaw[26] have studied the kinetics of the oxidative addition of methyl iodide to iridium phosphine complexes of the type *trans*$[\text{IrCl(CO)(PMe}_2\text{Ar)}_2]$ where Ar = Ph, $o\text{-CH}_3\text{OC}_6\text{H}_4$ or $p\text{-CH}_3\text{OC}_6\text{H}_4$. The results showed (1) that the complex containing *o*-methoxyphenyldimethylphosphine reacts 78 times faster than the complex containing the *p*-methoxyphenyl group (in toluene at 25.3°C), (2) that all three reactions involve similar large negative $\Delta S^{\neq}$ values and (3) that the *o*-methoxyphenyl reaction has a much lower $\Delta H^{\neq}$ value than do the reactions of the other two complexes. It was suggested earlier by Chock and Halpern[27] that the reaction where Ar = phenyl involves a highly polar transition state which closely resembles the products. This suggestion may be modified to allow interaction between the 2*p* electrons of the methoxyl oxygen with the iridium atom with a consequent lowering of $\Delta H^{\neq}$.



While *o*-methoxy groups show a through space interaction with P(IV), they are not the only groups to do so. McEwen and coworkers studied the alkylation of (ω-N,N-dimethylaminoalkyl)diphenylphosphines with benzyl chloride in benzene-methanol (3:2 v/v) at 31.0 ± 0.1°C. The results, summarized in Table IX, indicate the operation of a modest degree of N_{2p}-P(IV) interaction in the transition state of the reaction. The apparent effects of the dimethylamino group on the rates of alkylation are not great. However, an argument for at least a weak through space interaction $[\text{N}_{2p}\text{-P(IV)}]$ can be raised. The inductive electron-withdrawing effect of a dimethylamino groups bonded to a saturated carbon atom is appreciable.[29] Despite this fact, each (ω-N,N-dimethylaminoalkyl)phosphine undergoes reaction with benzyl chloride at approximately the same rate as the

TABLE IX

Rate data for reactions of (ω-N.N-dimethylaminoalkyl)diphenylphosphines with benzyl chloride in benzene-methanol (3:2) at 21.0 ± 0.1°C

Phosphine	$10^2k(\text{l mol}^{-1}\text{ hr}^{-1})$
(N,N-Dimethylaminomethyl)diphenyl	26.6 ± 0.2
(β-N,N-Dimethylaminoethyl)diphenyl	18.9 ± 0.2
(γ-N,N-Dimethylaminopropyl)diphenyl	13.7 ± 0.2
(δ-N,N-Dimethylaminobutyl)diphenyl	26.5 ± 0.2
Diphenylmethyl	35.5 ± 0.3
Diphenylethyl	27.1 ± 0.1
Diphenyl(*n*-propyl)	25.9 ± 0.1
Diphenyl(*n*-butyl)	26.0 ± 0.1

corresponding unsubstituted alkylphosphine. The ratio of the rates of reaction of N,N-dimethylaminomethyl/methyl = 0.75, β-N,N-dimethylaminoethyl/ethyl = 0.70, γ-N,N-dimethylaminopropyl/*n*-propyl = 0.53 and δ-N,N-dimethylaminobutyl/*n*-butyl = 1.02. Therefore, the through space N_{2p}-P(IV) interaction compensates for the rate retarding inductive effects of the dimethylamino group, causing the ratios cited above to be close to unity.

Cairns and McEwen[30] have determined that the rate of alkylation of (2-N,N-dimethylaminophenyl)diphenylphosphine with benzyl bromide in chloroform solution (rel. rate = 9.68) is greater than that of (4-N,N-dimethylaminophenyl)diphenylphosphine (rel. rate = 1.68) and both are greater than that of triphenylphosphine (rel. rate = 1.00).

Surely, one of the most interesting results of those reported in Table VI is that, in chloroform at 31.0°C, the reactions of (*o*-methoxyphenyl)diphenylphosphine and triphenylphosphine with benzyl chloride are, respectively, only 20.4 and 18.8 times faster than their reactions with *n*-butyl chloride. These are probably the smallest such ratios ever reported for the S_N2 reactions of these alkyl chlorides. As a comparison, the reaction of iodide ion with benzyl chloride in acetone at 60°C is 179 times faster than its reaction with *n*-butyl chloride, and its reaction with benzyl chloride in ethanol at 50°C is 205 times faster than its reaction with *n*-butyl chloride.[31]

The general explanation for the large rate differences in the latter two cases is that π-bond overlap lowers the transition state energy for the benzyl system. Overlap of this type will be most effective when a substantial degree of bond breaking between the methylene carbon and the leaving group exists. As a result of this, McEwen *et al.*[1] suggest that, when the rate difference between a benzyl system and an *n*-butyl system is not large, as in the phosphine cases above, the degree of bond breaking, at least in the benzyl system, must be small. This would necessitate an early transition state, one which would lie close to the reactants in the energy profile diagram.

In an early transition state there would be relatively little development of charge. McEwen *et al.*[1] have found that a change from the less polar chloroform (dielectric constant = 4.64 at 25°C) to the more polar 60% benzene (dielectric constant = 2.27 at 25°C)—40% methanol (dielectric constant = 32.6% at 25°C) does not lead to a rate increase for the reaction; the rates of the reaction of the phosphines mentioned above with benzyl chloride are comparable in the two different solvent systems.

Also, the small amount of rate acceleration caused by the presence of an *o*-methoxy group in the reactions of triarylphosphines with alkyl halides is consistent with the idea of an early transition state. Since the charge developed in an early transition state is small, the degree of interaction of the 2*p* valence electrons with the incipient P(IV) center of phosphorus would also be small.

McEwen and coworkers[1,15] note that the $\Delta S^{\neq}$ values have a greater influence on the difference in reaction rates than do the $\Delta H^{\neq}$ values. The reaction of (*o*-methoxyphenyl)diphenylphosphine with benzyl bromide in chloroform at 31° is 5.15 times faster than the corresponding reaction with triphenylphosphine, even though $\Delta H^{\neq}$ of the former is slightly greater than that of the latter; therefore, the less negative $\Delta S^{\neq}$ of the former controls the relative rates (Table III). This less negative $\Delta S^{\neq}$ value may be due in part to an O_{2p}-P(IV) interaction in the transition state. It is suggested[1] that the *o*-methoxy group may take the place of a solvent molecule in the transition state (as compared to the triphenyl system). This decrease in backside solvation in the transition state results in an increased freedom of movement for some of the solvent molecules, which, in turn, leads to a more positive, or less negative, entropy of activation (as compared to the triphenyl system). This internal interaction of the *o*-methoxy group with the phosphorus also compensates for any loss of stabilization of the transition state by backside interaction with the solvent. As a result, there is little change in the $\Delta H^{\neq}$ value for the *o*-methoxy system compared to the triphenyl system.

It may be recalled that Chock and Halpern[27] suggested the formation of a highly polar transition state, one resembling products, in the reaction of *trans*[$IrCl(CO)(PMe_2Ar)_2$] with methyl iodide. McEwen and coworkers[15] suggest that the degree of anchimeric acceleration provided by an *o*-methoxyphenyl group in the reaction of the iridium-phosphine complex should be distinctly greater than in the phosphine alkylation reactions (where the transition state is an early one). In fact, the data of Miller and Shaw[26] confirm this suggestion. The *o*-methoxyphenyl complex is 78 times more reactive than the *p*-methoxyphenyl complex, as compared to k_o/k_p ratios of only 3.7–6.0 for the more simple alkylation reactions.

The preferred geometry of the O_{2p}-(P(IV) interaction, has been determined by rate studies of the reactions of various methoxy-substituted 5-aryldibenzophospholes with benzyl chloride.[32] The greatest degree of anchimeric assistance (i.e., the fastest rate) occurs when a 5-(*o*-methoxyphenyl) group, which is orthogonal to the dibenzophosphole ring, is present.

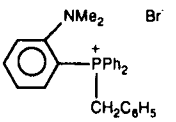
ALKALINE DECOMPOSITION REACTIONS

The mechanism of alkaline decomposition of ordinary acyclic quaternary phosphonium salts is well understood[32] and need not be given in detail here. It is sufficient to state that, with an uncomplicated, noncyclic quaternary phosphonium cation, hydroxide ion first adds reversibly (K_1) to the tetrahedral phosphorus to form a trigonal bipyramidal intermediate in which the hydroxyl and the most apicophilic group originally bonded to phosphorus (benzyl > aryl > alkyl)[33] occupy apical positions. The conjugate base is formed by the reaction of the phosphorane with hydroxide ion (K_2), and, without the necessity for a Berry pseudorotation,[34] it expels the apical group as a carbanion (k_3) which is protonated as it is being formed,[35] with concomitant formation of a phosphine oxide.

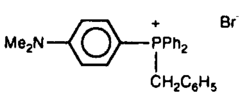
Keldsen and McEwen[4] reported kinetics and product ratio data for the alkaline cleavage reactions of quaternary *o*- and *p*-methoxyphenylphosphonium salts in 50 v/v % dioxane-water at 10.1°C in the presence of 0.4000 *M* KCl. The relative rates are 1.00 for benzyltriphenylphosphonium bromide, 0.0269 for benzyl(2-methoxyphenyl)diphenylphosphonium bromide, 0.139 for benzyl(4-methoxyphenyl)diphenylphosphonium bromide, 0.00036 for benzylbis(2-methoxyphenyl)-phenylphosphonium bromide, and <0.0003 for benzyltris(2-methoxyphenyl)phosphonium bromide. In all of these reactions, toluene was the major hydrocarbon produced, with benzene being a very minor product in some instances. No anisole was detected as a product of any of these reactions. As previously discussed by Keldsen and McEwen,[4] these rate differences cannot be rationalized on the basis of resonance interactions between the respective methoxy groups and the phenyl groups to which they are bonded. It is also unlikely that the rate retarding effect of an *o*-methoxy group arises from steric hindrance, as it has been shown by Pagilagen and McEwen[13] that, in the alkaline cleavage of phosphonium salts in which one, two or three *o*-tolyl groups are present, the relative rate retardations are not large. Keldsen and McEwen[4] have previously invoked the concept of through space "O_{2p}-P_{3d}" overlap between the methoxyl oxygen and the phosphonium phosphorus to explain the rate reductions in the alkaline cleavage reactions of phosphonium salts containing *o*-methoxyphenyl groups. This will reduce the magnitude of K_1, at least, and lead to an overall rate reduction. The same would hold true for an essentially electrostatic attraction of the O_{2p}-P(IV) type.[1]

This same type of through space interaction has been suggested to influence the alkaline cleavage reactions of (ω-N,N-dimethylaminoalkyl)benzyldiphenylphosphonium bromides.[28] The simple alkylbenzyldiphenylphosphonium hydroxides undergo alkaline cleavage in DMSO at 22.0°C at too rapid a rate to be measured conveniently, whereas the corresponding phosphonium hydroxides containing the ω-N,N-dimethylaminoalkyl groups react at rates several orders of magnitude slower. It is of interest that no compelling evicence for a strong O_{2p}-P(IV) interaction has been observed in the alkaline decomposition reactions of the corresponding ω-methoxyalkylbenzyldiphenylphosphonium iodides. Here, the strong inductive electron-withdrawing effect of a methoxymethylene group overwhelms an electron donating through space O_{2p}-P(IV) interaction. Evidently the dimethylamino group is a better through space donor to P(IV) because of its greater basicity, but it is a poorer electron-withdrawing group through the inductive effect than the methoxy group. The latter is consistent with the greater electronegativity of oxygen over nitrogen.[36]

As we have reported previously,[6] benzyl[2-(N,N-dimethylamino)phenyl]diphenylphosphonium bromide (**1**) undergoes alkaline cleavage [KOH] at 37.70 ± 0.05°C in 1:1 1,4-dioxane-water containing 0.400 *M* potassium bromide in a third-order reaction[37] having a relative rate of 4.76 in comparison with a value of 1.00 for the alkaline cleavage of benzyltriphenylphosphonium bromide under the same conditions. Whereas the latter reaction gives toluene and triphenylphosphine oxide ($10^3k = 730.3 \pm 5.00\ L^2\ mol^{-2}\ s^{-1}$), **1** affords N,N-dimethylaniline (96.5%), benzene (3.5%), and benzyldiphenylphosphine oxide (96%). On the other hand, benzyl[4-(N,N-dimethylamino)phenyl]diphenylphosphonium bromide (**2**) undergoes alkaline cleavage under the same conditions to give toluene (100%) as the sole hydrocarbon product and at a relative rate of 0.0043. No benzene or N,N-dimethylaniline can be detected.

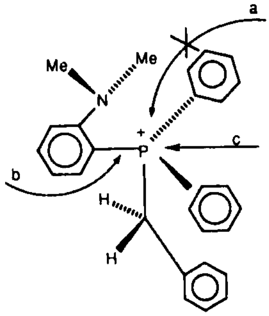


1



2

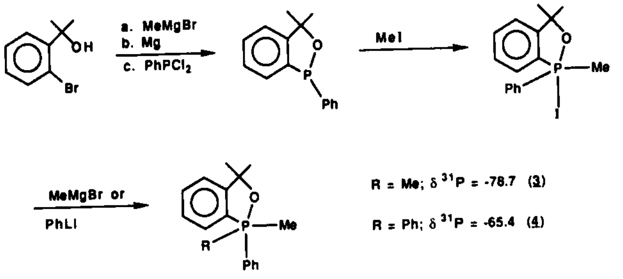
It is clear from the data presented above that the phosphonium salt **1** has a unique reactivity, particularly insofar as it gives no toluene in its alkaline decomposition reaction and yet it undergoes a faster reaction than benzyltriphenylphosphonium bromide. We believe that a reasonably strong N_{2p}-P(IV) through space interaction exists in the cation of **1**. Therefore, as depicted in the accompanying scheme, attack by hydroxide ion does not occur by path *a* because the dimethylamino group is strongly attracted to the positive phosphorus atom and shields the face of the phosphorus tetrahedron opposite to the benzyl group. Since Eaborn's concept of electrophilic participation by a protic solvent molecule (hydrogen bonding in the transition state) can apply well to the departure of N,N-dimethylaniline,[38–40] path *c* for attack of hydroxide ion is favored over path *b*. This, and the fact that electron repulsion by unshared pairs on N and O are at a minimum when the hydroxyl group and the 2-(N,N-dimethylamino)phenyl group occupy apical positions in the intermediate phosphorane (also its conjugate base), provide a rationalization for the greater rate of alkaline decomposition of **1** over the unsubstituted case.



In addition to the above arguments favoring departure of N,N-dimethylaniline from **1** in its alkaline decomposition reaction, there are also reasons why departure of toluene (actually an incipient benzyl anion) would be inhibited. In order to have departure of an incipient benzyl anion from the conjugate base of the phosphorane initially formed, a Berry pseudorotation[34] would be necessary to bring the benzyl group into an apical position, from which departure of a group ordinarily occurs in a trigonal bipyramidal unstable intermediate.[41] This would decrease the rate of this process relative to that which actually occurs. The alternative possibility of having the incipient benzyl anion depart from an equatorial position, without a Berry pseudorotation, is contrary to theoretical treatments,[41,42] the known stereochemistry of alkaline decomposition reactions of quaternary phosphonium salts having a chiral phosphorus atom, where inversion of configuration results,[43–45] and to the probable violation of the Principle of Microscopic Reversibility, as pointed out by McDowell and Streitwieser.[46]

SIGMA DELOCALIZED BONDING IN HYPERVALENT HETEROATOMIC SPECIES[24]

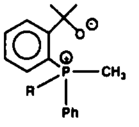
Hypervalent heteroatomic compounds represent the extremes of a spectrum of compounds involving O_{2p}-P(IV), N_{2p}-P(IV), O_{2p}-S(III), N_{2p}-Si(IV) and similar interactions. Only a few representative examples of such compounds will be presented here.



R = Me; $\delta\,^{31}P$ = -78.7 (3)

R = Ph; $\delta\,^{31}P$ = -65.4 (4)

Granoth and Martin[47] have reported the synthesis of the phosphoranes **3** and **4**. Based on the ^{31}P NMR chemical shifts of these compounds, these workers suggested the phosphorane structures shown, **3** and **4**, rather than the other possible structure, a phosphonium alkoxide, **5**. Reaction of either **3** or **4** with excess Grignard or organolithium reagent does not give rise to a compound of the type shown in **6**. These workers report that this may be due to the well established five-membered ring effect, a known source of stabilization of hypervalent derivatives of phosphorus and sulfur in which the heteroatom is included in a five-membered ring.[47,48]



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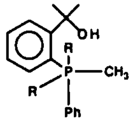
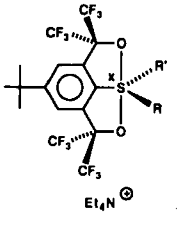


6

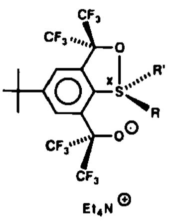
Hypervalency is by no means limited to phosphorus alone. Another report by Martin and coworkers[49] provides an example of hypervalency at sulfur. These workers reported extensive studies, including X-ray crystallographic data, pK_a measurements, as well as low temperatures NMR spectra, which showed that the closed structures **7**, **8**, and **9** (hypervalency at sulfur) are at least 2.6, 5.9, and 7.5 kcal/mol, respectively, more stable than their corresponding open-chain analogs, **10**, **11**, and **12**.



(7) X = +1, R = R' = O^-

(8) X = 0, R = electron pair, R' = O^-

(9) X = -1, R = R' = electron pair



(10) X = +2, R = R' = O^-

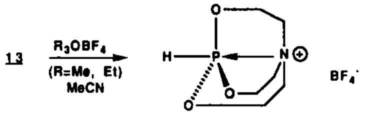
(11) X = +1, R = electron pair, R' = O^-

(12) X = 0, R = R' = electron pair

Examples of hypervalency where the electron-rich moiety is a dimethylamino group and the central atom is Si(IV) have been reported. West, Corriu and their colleagues[50] have examined the equilibrium between the open and closed structures shown below. Some of these data are presented in Table X. The presence of N→Si coordination was determined from their low temperature ^1H NMR spectra in which the Me_2 groups become diastereotopic. When the fluorine substituent in the compounds listed in Table X was replaced with an alkoxy substituent, no closed structures were observed, presumably due to competitive back-bonding by the lone pairs on oxygen.

The presence of an N→P coordinate bond has also been reported.[51-53] The synthesis and crystal structure of **14** were reported by Verkade and coworkers.[52] The second step of the reaction shown below normally gives the expected alkylphosphonium cation $(RP(OR)_3^+)$ with acylic phosphite esters or bicyclic phosphites.

$$P(NMe_2)_3 + (HOCH_2CH_2)_3N \longrightarrow \underset{\mathbf{13}}{P(OCH_2CH_2)_3N}$$



14 $\delta\ ^{31}P = -20.2$

In the system reported, the phosphorus, as evidenced by its apparent proton abstracting ability, shows a considerable basicity enhancement owing to an interaction with the nitrogen lone pair ($\delta\ ^{31}P = -20.2$). This idea is supported by the X-ray crystallographic data which gives the structure indicated, (**14**). The P←N dative bond length was determined to be 1.986 Å with the phosphorus atom being trigonal bipyramidal; O—P—O angles of 120°, O—P—N angles of 87° and an H—P—N angle of 172°. The P—H bond distance is 1.35 Å, only somewhat shorter than the sum of the covalent radii (1.38 Å).[51]

TABLE X

Equilibrium constants for the open/closed structure ratio of o-$(Me_2NCH_2)C_6H_4$ substituted silanes

Silane	K
$ArMeSiF_2$	1.6
ArMeSiHF	2.5
Ar_2SIF_2	1.0
$ArSiF_3$	8.1

Ar = o-$(Me_2NCH_2)C_6H_4$; K = (open)/(closed)

SPECTRAL DATA

Schiemenz has devoted much attention to the electronic nature of quaternary phosphonium salts.[54–56] In an investigation of the electron acceptor ability of phosphonium centers, he examined the UV spectra of a series of quaternary triarylphosphonium salts (Table XI). The main absorption in all the compounds listed in Table XI is due to a $\pi \rightarrow \pi^*$ transition. Compared with the dimethylamino group, the phosphonium phosphorus shows a clear −M effect.[55] This −M effect of the 'onium phosphorus decreases with increasing electron density at the phosphorus. This is explained by Schiemenz as an interaction of the phosphorus 3*d* orbitals with the aromatic rings, which have an increased electron density due to interactions with the dimethylamino group.[54]

McEwen *et al.* have also investigated the UV spectra of a series of benzyltriarylphosphonium chlorides.[1] These data are presented in Table XII. According to McEwen and coworkers, the absorption data for (*p*-methoxyphenyl)diphenylbenzylphosphonium chloride indicate the presence of a much

TABLE XI

UV absorption data for quaternary phosphonium salts of the structure $(p\text{-}Me_2NC_6H_4)_nP^+R_{3-n}R'$ Hal^- in methanol[55]

n	R	R'	Hal	$\lambda_{max}(cm^{-1})$	ε
1	CH_3	CH_3	I	35,400	28,400
1	C_6H_5	CH_3	I	33,400	26,300
1	C_6H_5	$PhCH_2$	Cl	33,000	27,400
2	C_6H_5	CH_3	I	32,900	45,000
3		C_2H_5	Br	33,200	80,800
3		$p\text{-}Me_2NC_6H_4$	I	33,200	110,400

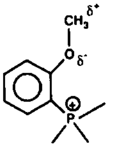


TABLE XII

UV absorption data for the B bands of the isomeric (methoxyphenyl)-benzyldiphenylphosphonium chlorides in chloroform.[1]

$ArP(C_6H_5)_2CH_2C_6H_5$	$\lambda_{max}(nm)$	log ε
Ar = *o*-methoxyphenyl	243	3.78
	261	3.42
	268	3.55
	275	3.61
	290	3.65
Ar = *m*-methoxyphenyl	244	3.86
	261	3.44
	268	3.52
	275	3.53
	292	3.53
Ar = *p*-methoxyphenyl	252	4.33

greater resonance interaction between the methoxy group and the aromatic ring to which it is bonded (n, π conjunction) than is observed with the *o*-methoxyphenyl case. The UV spectrum of the *o*-methoxyphenyl compound is similar to that of the *m*-methoxyphenyl isomer. This is indicative of the fact that the *o*-methoxy group does not "feel" the presence of the 'onium center through the ring to any great extent. This lends support to the concept of an O_{2p}-P(IV) interaction, which lessens the ability of the *o*-methoxy group to participate in a resonance interaction with the aromatic ring. The effect of the *o*-methoxy group could be due to a field effect.[1,57]

As mentioned previously, the chemical shift in the ^1H NMR spectra of the methylene hydrogens of the benzyl group is used as a tool in assessing the existence of a 2*p*-P(IV) interaction. Some ^1H NMR absorption data have been reported by McEwen and coworkers[1] and are presented in Table XIII. Through space electron-donation from the *o*-methoxy group to the positive phosphorus should cause a downfield shift for the methoxy protons and an upfield shift for the benzyl methylene protons in the ^1H NMR spectra of these salts. The chemical shifts of the methoxy protons are also influenced by resonance interactions with the aromatic ring to which it is bonded, this effect also causing a downfield shift of the methoxy progons of *o*-, *m*-, and *p*-methoxy groups. Since electron density is removed from the *o*-methoxy group by an O_{2p}-P(IV) interaction, an additional interaction with the π-electron cloud of the aromatic ring to which it is bonded will be diminished. Therefore, the chemical shifts of the methoxy hydrogens are subject to ambiguous influences, making the shifts of the benzyl methylene protons of greater interest as a probe of the postulated O_{2p}-P(IV) interaction. These effects can indeed be seen in the data reported in Table XIII.

The ^{31}P NMR spectra for selected organophosphorus compounds have been examined, and the hydrogen decoupled phosphorus resonances are presented in Table XIV. From the data presented, it can be seen that increasing the electron density on the aryl rings causes a shielding effect of the phosphorus in the triaryl

TABLE XIII

^1H NMR absorption data for the aliphatic hydrogens in benzyltriarylphosphonium salts in $CDCl_3$ solution

Phosphonium Ion	Halide	δ(ppm)CH_2	δ(ppm)MeO
(*m*-Methoxyphenyl)benzyldiphenyl	Br^-	5.47	3.88
Benzyltriphenyl		5.32	
(*p*-Methoxyphenyl)benzyldiphenyl		5.24	3.89
(*o*-Methoxyphenyl)benzyldiphenyl		5.10	3.80
Bis(*o*-methoxyphenyl)benzylphenyl		4.82	3.80
Tris-(*o*-methoxyphenyl)benzyl		4.67	3.70
(*m*-Methoxyphenyl)benzyldiphenyl	Cl^-	5.50	3.84
Benzyltriphenyl		5.42	
(*p*-Methoxyphenyl)diphenyl		5.35	3.91
(*o*-Methoxyphenyl)benzyldiphenyl		5.15	3.84
Bis-(*p*-Methoxyphenyl)benzylphenyl		5.21	3.91
Bis-(*o*-Methoxyphenyl)benzylphenyl		4.76	3.80
Tris-(*p*-Methoxyphenyl)benzyl		5.10	3.91
Tris-(*o*-Methoxyphenyl)phenyl		4.61	3.68

TABLE XIV

Hydrogen decoupled ^{31}P NMR chemical shift data for selected triarylphosphines and the corresponding benzyltriaryl-phosphonium bromides in $CDCl_3$ solution[63]

Phosphines or Phosphonium Cation	δ ^{31}P
Triphenylphosphine	−4.69
Benzyltriphenylphosphonium	23.60
(*o*-Methoxyphenyl)diphenylphosphine	−13.81
Benzyl(*o*-methoxyphenyl)diphenylphosphonium	22.25
(*m*-Methoxyphenyl)diphenylphosphine	−1.76
Benzyl(*m*-methoxyphenyl)diphenylphosphonium	24.50
(*p*-Methoxyphenyl)diphenylphosphine	−4.10
Benzyl(*p*-methoxyphenyl)diphenylphosphonium	23.52
(*o*-N,N-Dimethylaminophenyl)diphenylphosphine	−13.55
Benzyl(*o*-N,N-dimethylaminophenyl)diphenylphosphonium	19.74
(*p*-N,N-Dimethylaminophenyl)diphenylphosphine	−6.54
Benzyl(*p*-dimethylaminophenyl)diphenylphosphonium	22.32

phosphines. In agreement with the reports of Grim[58–61] and Quin,[62] the *o*-substituted phosphines show a large upfield shift, presumably due to the γ-effect. The ^{31}P chemical shift data for the phosphonium bromides show a similar increasing upfield shift of the phosphorus resonances with increasing electron density at phosphorus. This cannot be explained by invoking the γ-effect, as the phosphorus is quaternized. However, this upfield shift can be explained by the operation of an inductive or field effect, respectively, for the *p*-substituted and *o*-substituted salts. Of course, the inductive effect for the *p*-substituted compounds is superimposed on a resonance interaction between the substituent and the ring to which it is attached, while, in the case of the *o*-substituted compounds, the electron density increase at phosphorus is attributable, at least in part, to the through space (N_{2p}-P(IV) interaction.

CONCLUDING STATEMENTS

It is our opinion that we have presented only the tip of the iceberg in this review of through space O_{2p}-P(IV), N_{2p}-P(IV) and similar interactions in heteroatom chemistry. As mentioned previously, "hypervalency" represents one end of the spectrum of such interactions, and the literature of this topic is huge. Also, the literature of biochemistry, particularly of compounds containing oxygen and/or amino functions proximate to P(V) functions (i.e., phosphate groups), must surely contain many examples of (apparently as yet unrecognized) O_{2p}-P(V) and N_{2p}-P(V) interactions.

Although they fall outside the scope of this review, the recent papers of Musker and Doi[64] deserve attention with respect to anchimeric assistance effects which involve electron donation by neighboring groups to nucleophilic centers of compounds of third group elements. Last, but by no means least, we continue to fumble our way to a better understanding of the role of O_{2p}-P(IV) and N_{2p}-P(IV) interactions in the Wittig reaction and of the mechanism of the Wittig reaction itself.[7,65,66–68]

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