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Chemical and Physical Consequences of 2p–3d Overlap in *o*-Anisylphosphines and *o*-Anisylphosphonium Salts

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Abstract: Rate data for the quaternization reactions of various triarylphosphines with benzyl chloride, benzyl bromide, and *n*-butyl chloride are presented. There are two particularly striking effects. (1) The presence of an *o*-methoxy group in the phosphine causes a marked acceleration of the reaction. (2) The difference in the rates of reaction of a given triarylphosphine with benzyl chloride and *n*-butyl chloride is less than 20, probably the smallest difference ever found in SN2 reactions of these halides. An explanation of these effects is offered based partly on the concept of overlap of a pair of 2p electrons of an *o*-anisyl group with a 3d orbital (or hybrid orbital) of phosphorus in the transition state and partly on the concept that the transition state for each of the benzyl halide reactions lies much closer to the reagents than to the products along the reaction coordinate of the energy profile diagram. Additional evidence for the postulated 2p–3d overlap is found in the uv and NMR spectra of the phosphines and corresponding phosphonium salts. Finally, it has been found that *o*-anisyldiphenylphosphine exhibits mass spectral reactions not evidenced by the meta and para isomers. The eliminations of H_2O, $CH_3O\cdot$, and $C_7H_7\cdot$ from the molecular ion of the ortho isomer, involving skeletal and specific hydrogen rearrangements, have been studied by means of deuterium labeling.

Data which demonstrate that the presence of an *o*-anisyl group causes a marked acceleration of the SN2 reaction of a triarylarsine with benzyl bromide to give the quaternary arsonium bromide and of a triarylphosphine with benzyl chloride to give the quaternary phosphonium chloride have been presented in previous communications.[2] The major rationalization for these results consisted of the suggestion that overlap of a pair of 2p electrons of an *o*-methoxy group with a 4d orbital of arsenic or with a 3d orbital of phosphorus, respectively, lowers the energy of the transition state for each of these SN2 reactions. We now wish to present new data and to discuss the probable mechanism of reaction in greater detail.

Rate data for the quaternization reactions of various triarylphosphines with benzyl chloride, benzyl bromide, and *n*-butyl chloride are given in Table I. The activation parameters for some of these reactions are presented in Table II. Some of the highlights of the data are the following. (1) The relative rates of reaction of tris(*o*-anisyl)phosphine, bis(*o*-anisyl)phenylphosphine, *o*-anisyldiphenylphosphine, and triphenylphosphine with benzyl chloride in benzene–methanol (3:2 v/v) at 31.0° are 27.0, 20.2, 7.42, and 1.00, respectively. (2) The relative rates of reaction of *o*-anisyldiphenylphosphine and triphenylphosphine with benzyl chloride in chloroform at 31.0° are 5.07 and 1.00, and the reactions in this solvent are approximately 0.75–1.09 times as fast as those in benzene–methanol (3:2 v/v). (3) The relative rates of reaction of bis-*o*-anisylphenylphosphine, *o*-anisyldiphenylphosphine, tris-*o*-anisylphosphine, triphenylphosphine, and *m*-anisyldiphenylphosphine with benzyl bromide in chloroform at 31,0° are 6.45, 5.15, 1.59, 1.00, and 0.95, respectively; the benzyl bromide reactions are approximately 102–104 times more rapid than the corresponding benzyl chloride reactions. (4) The relative rates of reaction of bis(*o*-anisyl)phenylphosphine, *o*-anisyldiphenylphosphine, tris-*o*-anisylphosphine, and triphenylphosphine with *n*-butyl chloride in chloroform at 31.0° are 13.5, 4.68, 3.89, and 1.00, respectively; the benzyl chloride reactions are approximately 18.8–20.4 times faster than the corresponding *n*-butyl chloride reactions. (5) The k_o/k_p ratios for the trisanisyl, bisanisylphenyl, and anisyldiphenylphosphine reactions with benzyl chloride in benzene–methanol (3:2 v.v) at 31.0° are 4.1, 6.0, and 3.7, respectively; the k_o/k_p ratio for the anisyldiphenylphosphine reactions with benzyl bromide in chloroform at 31.0° is 4.0. (6) *m*-Anisyldiphenylphosphine reacts at a slower rate with benzyl bromide in chloroform than the *o*-anisyl or the *p*-anisyl isomers and even at a slower rate than triphenylphosphine. (7)

Table I. Rate Constants for Reactions of Triarylphosphines with Alkyl Halides

Triarylphosphine	Alkyl halide	Solvent	Temp, °C	l. mol^{-1} hr^{-1}
Triphenyl	Benzyl chloride	C_6H_6–MeOH (3:2)	31.0	7.22
o-Anisyldiphenyl				53.6
p-Anisyldiphenyl				14.6
Bis(*o*-anisyl)phenyl				146
Bis(*p*-anisyl)phenyl				24.3
Tris(*o*-anisyl)				195
Tris(*p*-anisyl)				47.8
Triphenyl		$CHCl_3$	26.0	5.38
			31.0	7.89
			36.0	11.0
o-Anisyldiphenyl			26.0	27.1
			31.0	40.0
			36.0	54.9
Triphenyl	Benzyl bromide		26.0	602
			31.0	803
			36.0	1140
o-Anisyldiphenyl			26.0	2937
			31.0	4143
			36.0	5913
m-Anisyldiphenyl			26.0	542
			31.0	760
			36.0	989
p-Anisyldiphenyl			26.0	751
			31.0	1040
			36.0	1441
Bis(*o*-anisyl)phenyl			26.0	3782
			31.0	5177
			36.0	7252
Tris(*o*-anisyl)			26.0	906
			31.0	1272
			36.0	1803
Triphenyl	*n*-Butyl chloride		31.0	0.419
o-Anisyldiphenyl			31.0	1.96
Bis(*o*-anisyl)phenyl			31.0	5.68
Tris(*o*-anisyl)			31.0	1.63

Table II. Activation Parameters for Reactions Carried Out in Chloroform Solution

Triarylphosphine	Benzyl halide	$\Delta E^{\ddagger}$	$\Delta S^{\ddagger}$ (26.0°)
Triphenyl	Benzyl chloride	13.2	−38.6
o-Anisyldiphenyl		12.9	−36.1
Triphenyl	Benzyl bromide	11.9	−33.5
o-Anisyldiphenyl		12.8	−27.3
m-Anisyldiphenyl		11.1	−36.3
p-Anisyldiphenyl		12.2	−32.0
Bis(*o*-anisyl)phenyl		11.9	−29.8
Tris(*o*-anisyl)		12.2	−31.6

All of the $\Delta E^{\ddagger}$ values listed in Table II are not greatly different. Differences in $\Delta S^{\ddagger}$ have a greater influence on the spread in rates than do the differences in $\Delta E^{\ddagger}$.

Perhaps the most striking results of all those given in Table I are the relatively small differences in the rates of reaction of the triarylphosphines with benzyl chloride and *n*-butyl chloride. The average relative rates for benzyl vs. butyl substrates in a variety of S$_N$2 reactions are 120 vs. 0.4 (ethyl = 1.0).[3] The conventional explanation for this large rate difference is that π-bond overlap lowers the energy of the transition state for the benzyl system. This, in turn, requires the existence of a substantial degree of bond breaking between the methylene carbon and the departing group in the transition state for the benzyl system. Consequently, when the rate difference between a benzyl system and an *n*-butyl system is small, as in the examples provided in Table I, the explanation must be that the degree of bond breaking in the transition state of at least the benzyl system is small. In other words, the transition state for the reaction between each triarylphosphine and benzyl halide must lie close to the reactants in the energy profile diagram.

A similar rationalization has been offered by Hoffmann[4,5] for the variation in the k_{OTs}/k_{Br} ratio (0.36–5000) in nucleophilic displacement reactions of alkyl tosylates and bromides. Hoffmann has stated that "the ratio k_{OTs}/k_{Br} is small (large), if the nucleophile is powerful (weak) and the substrate has a poor (strong) ionization tendency". Furthermore, he has concluded that "even chloride, bromide, and iodide can become very selective, provided that charge separation in the transition state is advanced, and disturbances from hydrogen-bonding are eliminated." Accumulated experimental evidence[3] had indicated that an alkyl bromide reacts 30–100 times faster than the corresponding alkyl chloride in nucleophilic substitution reactions, irrespective of the alkyl group, whereas Hoffmann found reactions in which bromide is displaced 450–1000 times faster than chloride ion when dimethylformamide, which does not enter into hydrogen bonding[6] and thus permits leaving groups to be more selective, is used as the solvent.

The fact that the displacement reactions of triarylphosphines on benzyl chloride are about as fast in chloroform solution as they are in benzene–methanol (3:2 v/v) can also be explained in part in terms of a transition state which lies closer to the reactants than to the products along the reaction coordinate. Since, under these circumstances, there is relatively little development of additional charge in the transition state, the change from a less polar solvent (chloroform, dielectric constant = 4.64 at 25°) to a more polar solvent (40% methanol, dielectric constant = 32.6 at 25°; and 60% benzene, dielectric constant = 2.27 at 25°) will not necessarily lead to an increase in rate of reaction. Of course, specific interactions (e.g., hydrogen bonding with both reagents and products) complicate this particular comparison. (The change from benzene–methanol to chloroform was not undertaken primarily to study solvent effects in the quaternization reactions under consideration; rather,

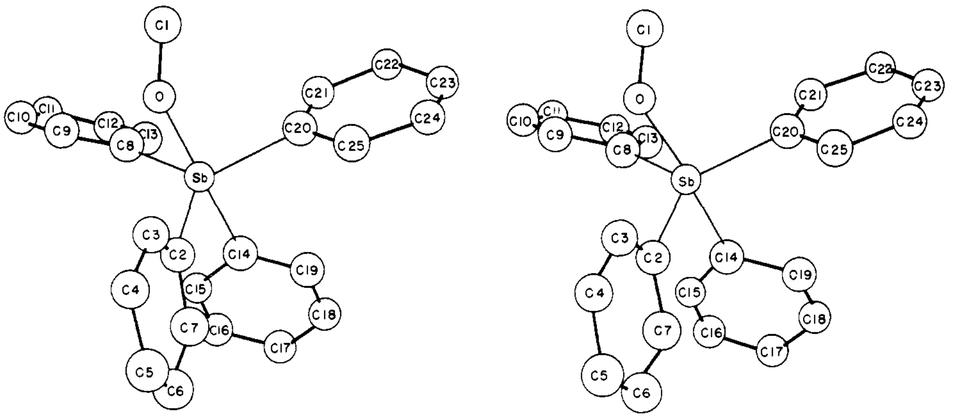


Figure 1. Stereoview of the structure of $(C_6H_5)_4SbOCH_3$.

it was done in order to avoid competing methanolysis of the benzyl bromide.)

The fact that rate acceleration caused by the presence of an *o*-anisyl group in the triarylphosphine in the reactions with alkyl halides is rather small can also, perhaps, be explained in terms of a transition state which lies closer to the reactants than to the products in the energy profile diagram. Under these circumstances, the degree of development of positive charge on the phosphorus atom is small, and consequently the degree of overlap of the 2p electrons of the methoxy group with a 3d orbital of phosphorus is small.

A convenient model for the geometry of the transition state for the SN2 reaction of *o*-anisyldiphenylphosphine with benzyl chloride may be derived by examination of the crystal and molecular structure of methoxytetraphenylantimony, as shown in Figure 1. It was stated in our previous article[7] that "an extremely short nonbonded distance of 2.20 Å exists between the phenyl proton associated with C_3 and the methoxy oxygen atom. With the aid of Figure 1 viewed stereoscopically, the "pseudo" planar five-membered ring formed by C_3, C_2, Sb, O, and H of C_3 (not shown) can easily be visualized."

All that is needed in order to transform Figure 1 into the probable transition state for the reaction of *o*-anisyldiphenylphosphine with benzyl chloride is to lift ring C_2–C_7 slightly, modify some of the bonds, and add the benzyl chloride.[8] As shown in Figure 2, the lifting of the ring A (which corresponds to C_2–C_7 in Figure 1) is beneficial, both in allowing the *o*-methoxy group to assume a quasi-apical position and in providing more room for the methylene carbon and attached hydrogens of the benzyl chloride.

The phenyl group (D) of the benzyl chloride would have to lie in a plane more or less parallel with those of rings B and C of the *o*-anisyldiphenylphosphine. This fact alone guarantees a situation in which the transition state lies relatively close to the reactants in the energy profile diagram. On the basis of data obtained from paracyclophanes,[9] the distance between these parallel rings should be at least 2.52 Å, and this serves as an approximation of the distance between phosphorus and the benzyl carbon atom in the transition state. Since the normal C–P bond length is about 1.87 Å,[10] this information provides additional support for the concept that the transition state lies closer to the reagents than to the products in the energy profile diagram.

Since the steric requirements of an *n*-butyl group are less than those of a benzyl group, it is probable that the transition state for the reaction of a triarylphosphine with *n*-butyl chloride is more nearly "normal" (see below) than that of the displacement reaction with benzyl chloride. Thus, the benzyl chloride reactions are only 18.8–20.4 times faster than the *n*-butyl chloride reactions instead of the normally much higher value owing to distortions caused by the presence of the benzyl chloride.

The probable structure of the transition state shown in Figure 2 provides for overlap of but one pair of 2p electrons of an *o*-methoxy group with a 3d orbital (or a hybrid orbital) of phosphorus. However, the k_o/k_h and k_o/k_p ratios indicate that the presence of a second *o*-anisyl group also promotes the displacement reaction. We attribute this to the superimposition of the favorable inductive effect of the second *o*-anisyl group on the favorable overlap effect of the first *o*-anisyl group. Since the presence of a *p*-anisyl group causes a small increase in rate over the unsubstituted case owing to a favorable inductive effect, the presence of a second *o*-anisyl group would do the same, even in the absence of a specific interaction. The emphasis is placed on an inductive effect rather than the occurrence of pπ–dπ overlap because of the existence of a considerable body of evidence[11–14] that phosphorus does not enter into any significant degree of direct interaction with the π-electron cloud of an attached aromatic ring. It also seems likely that unfavorable steric interactions would begin to arise in the case of the reaction of tris-*o*-anisylphosphine with a benzyl halide, and this could help to explain the fact that maximum efficiency of stabilization of the transition state (as measured by the k_o/k_p ratios) arises when two *o*-anisyl groups are present in the triarylphosphine.[15] This point will be developed further when the activation parameters are discussed. Also, the effect of a *m*-anisyl group will be considered at that time.

As mentioned previously, the $\Delta S^\ddagger$ values for the various reactions are of greater importance in determining the relative rates of reaction than are the $\Delta E^\ddagger$ values. For example, the reaction of *o*-anisyldiphenylphosphine with benzyl bromide in chloroform solution at 31° is 5.15 times faster than that of triphenylphosphine, even though $\Delta E^\ddagger$ of the former reaction is slightly greater than that of the latter. The less negative $\Delta S^\ddagger$ of the *o*-anisyl system controls the relative rate, and perhaps this less negative value can be attributed in part to the type of interaction depicted in Figure 2. As the *o*-methoxy group attains a quasi-apical position in the trigonal bipyramidal transition state, the *o*-anisyl group becomes more or less fixed in space, and there is more room for the other groups surrounding the phosphorus atom to rotate and vibrate. This could contribute to a less negative value of $\Delta S^\ddagger$ for this system as against the triphenylphosphine system. However, an even more important effect probably has to do with varying degrees of solvation of the transition states of the various systems. In the reaction of *o*-anisyldiphenylphosphine with benzyl bromide, for example, the *o*-methoxy group essentially takes the place of a

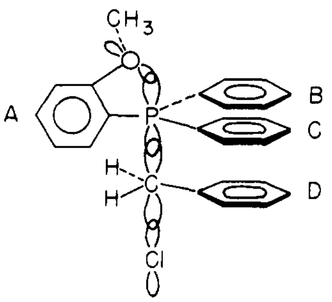


Figure 2. A possible transition state for the reaction of *o*-anisyldiphenylphosphine with benzyl chloride. Other geometries which would permit 2p–3d overlap are also possible.

solvent molecule in the transition state (as against the state of affairs for the triphenylphosphine system). The decrease in bonding to the solvent in the transition state leads to an increase in mobility of some solvent molecules, and this, in turn, causes an increase in the entropy of activation (i.e., this leads to a less negative value of $\Delta S^{\ddagger}$). At the same time, the interaction of the *o*-methoxy group with the phosphorus compensates for any possible loss of stabilization of the transition state by interaction with the solvent, and therefore there is little change in $\Delta E^{\ddagger}$ for the *o*-anisyl system as against the unsubstituted system.

Whereas the presence of an electron-donating *o*-methoxy or *p*-methoxy substituent would be expected to increase the nucleophilicity of a triarylphosphine relative to the unsubstituted case, and thereby cause a small increase in rate of reaction with an alkyl halide, the presence of a *m*-methoxy substituent, which is electron-withdrawing in nature (σ = +0.115), would cause a decrease in nucleophilicity of the phosphine and a consequent decrease in rate of reaction with an alkyl halide. Also, the presence of a meta substituent would hinder rotation of the aryl groups in the transition state of the SN2 reaction and thereby bring about a more negative value of $\Delta S^{\ddagger}$. Also, there might be a greater degree of solvation of the transition state for this reaction than in the others, leading to a smaller $\Delta E^{\ddagger}$ and a more negative $\Delta S^{\ddagger}$. These factors help to explain the fact that *m*-anisyldiphenylphosphine undergoes reaction with benzyl bromide at a slower rate than the *o*- or *p*-anisyl isomers, or even triphenylphosphine.

Borowitz et al.[16] have reported that the points for tris-*m*-anisylphosphine and tris-*m*-tolylphosphine lie above the line defined by several para substituted triphenylphosphines in the Hammett plot for reaction with α-bromoacetophenone. These workers attributed these abnormalities mainly to steric acceleration caused by the decrease in steric crowding around phosphorus as the originally pyramidal triarylphosphine approaches sp^3 hybridization (with consequent opening of the phenyl–P–phenyl angle from 102 to 109.5°) in the transition state for the SN2 reaction with the α-bromoacetophenone. As evidence for this effect, they pointed out that the reactions of the two tris-meta-substituted triphenylphosphines have the least negative values of $\Delta S^{\ddagger}$ of the entire series. However, this effect was not apparent for the reaction of *m*-anisyldiphenylphosphine with the bromo ketone. In our studies, the value of $\Delta S^{\ddagger}$ for the reaction of *m*-anisyldiphenylphosphine with benzyl bromide was the most negative of the series. Thus, we can find no hint of this type of acceleration of reaction for our system. It should be noted, in passing, that the relative magnitudes of $\Delta E^{\ddagger}$ and $\Delta S^{\dagger}$ are about the same for our reactions and those reported by Borowitz et al.[16]

Probably the most thorough study of the SN2 reactions of phosphines with alkyl halides in the literature is that of Henderson and Buckler.[17] These workers found that the rates of such reactions are quite sensitive to changes in the phosphine, varying over a range of three powers of ten for the various phosphines. For the "normal" phosphines (tricyclohexyl-, tris-*n*-butyl-, triethyl-, tris-*n*-propyl-, tris-*n*-amyl-, diethylphenyl-, ethyldiphenyl-, tris-*p*-anisyl-, and triphenylphosphine) in reaction with ethyl iodide at 35° in acetone solution, the rates could be correlated by means of the Taft–Hammett equation

$$\log 10^5 k = 1.939 - 0.767\sigma^*$$

For the reactions of tris-*n*-butylphosphine with *n*-propyl halides, the rate ratios were found to be I:Br:Cl = 2660:248:1. Although the rates of reaction of tris-*n*-butylphosphine and of triphenylphosphine with ethyl iodide in solvents of differing polarity could not be correlated quantitatively with dielectric constant, *Y* values[18] or *Z* values,[19] it was found that the reactions take place faster in more polar solvents. These and other data provided by Henderson and Buckler[17] presumably define the attributes of a "normal" SN2 reaction, one in which the attacking and departing groups are roughly equidistant from the central carbon atom on which the displacement reaction is taking place. The deviations of our results with benzyl halides from these norms provide a further measure of the distortion of the transition states (displacement of the transition state along the reaction coordinate toward the reagents) of the triarylphosphine–benzyl halide systems. The results also indicate that we should extend our studies to include an evaluation of ortho effects with "normal" systems, and we are doing so. Since neither triphenylamine nor tris(*o*-anisyl)amine underwent any measurable reaction with benzyl chloride under the conditions of the quaternization reactions reported herein, a comparison of the behaviors of the nitrogen and phosphorus systems will have to await the completion of the new work.

The argument has been advanced in our previous communications[2] that, if the indicated 2p–3d overlap occurs in the transition state of the SN2 reaction of an *o*-anisylphosphine with a benzyl halide, it is also reasonable to expect it to occur in the ground state of the resulting phosphonium cation. Electron donation from the *o*-methoxy group to the phosphorus should cause a downfield shift for the methoxy protons and an upfield shift for the benzyl methylene protons in the nuclear magnetic resonance spectra of the salts. However, the chemical shifts of the methoxy hydrogens are also influenced by resonance interactions of the methoxy group with the aromatic ring to which it is bonded, and this effect will also cause a downfield shift of the methoxy protons of *o*-, *m*-, or *p*-methoxy groups. However, insofar as electron density is drained away from an *o*-methoxy group by 2p–3d overlap, interaction with the π-electron cloud of the ring to which it is bonded will be diminished. Thus, the chemical shifts of the methoxy hydrogens are subject to ambiguous influences, and this means that the chemical shifts of the benzyl methylene protons are of greater interest as a possible probe of the postulated 2p–3d overlap. These anticipated effects are highly visible in the spectra of the phosphonium chlorides and bromides, as shown by the data presented in Table III. Of course, the effects may also be attributable in part to magnetic anisotropy of the methoxy groups, and therefore they may not represent clear proof of the postulated 2p–3d overlap.

Another possible probe of 2p–3d overlap in the *o*-anisylphosphonium salts consists of a comparison of the ultraviolet spectra of selected compounds. Data for the B bands of the isomeric anisylbenzyldiphenylphosphonium chlorides are presented in Table IV. According to Silverstein and Bassler,[20] "substitution on the benzene ring of auxochromic

Table III. NMR Absorption Data Taken in $CDCl_3$ Solution for the Aliphatic Hydrogens of Triarylbenzylphosphonium Salts

Phosphonium cation	Anion	δ, ppm CH_2, d(J_{PH} = 14.4–15.6 Hz)	CH_3O, s
m-Anisylbenzyldiphenyl	Bromide	5.47	3.88
Benzyltriphenyl		5.32	
p-Anisylbenzyldiphenyl		5.24	3.89
o-Anisylbenzyldiphenyl		5.10	3.80
Bis(*o*-anisyl)benzylphenyl		4.82	3.80
Tris(*o*-anisyl)benzyl		4.67	3.70
Benzyltriphenyl	Chloride	5.42	
m-Anisylbenzyldiphenyl		5.50	3.84
p-Anisylbenzyldiphenyl		5.35	3.91
o-Anisylbenzyldiphenyl		5.15	3.84
Bis(*p*-anisyl)benzylphenyl		5.21	3.91
Bis(*o*-anisyl)benzylphenyl		4.76	3.80
Tris(*p*-anisyl)benzyl		5.10	3.91
Tris(*o*-anisyl)benzyl		4.61	3.68

Table IV. Ultraviolet Absorption Data for the B Bands of the Isomeric Anisylbenzyldiphenylphosphonium Chlorides in Chloroform Solution

Phosphonium salt	λ_{max}, nm	Log ε
o-Anisyl	243	3.78
	261	3.42
	268	3.55
	275	3.61
	290	3.65
m-Anisyl	244	3.86
	261	3.44
	268	3.52
	275	3.53
	292	3.53
p-Anisyl	252	4.33

groups (OH, NH_2, etc.) shifts the E and B bands to longer wavelengths, frequently with intensification of the B band and loss of its fine structure, because of n–π conjugation." The absorption data for *p*-anisylbenzyldiphenylphosphonium chloride indicate the occurrence of a much greater resonance interaction between the methoxy group and the ring to which it is bonded (n,π conjugation) than is the case with *o*-anisylbenzyldiphenylphosphonium chloride, the ultraviolet absorption spectrum of which is somewhat similar to that of *m*-anisylbenzyldiphenylphosphonium chloride, the methoxy group of which does not "feel" strongly the influence of the positively charged phosphorus atom as transmitted through the ring. Thus, this observation supports the concept of 2p–3d overlap, which diminishes the capacity of the *o*-methoxy group to conjugate with the π-electron cloud of the ring. Of course, the influence of the *o*-methoxy group on the ultraviolet spectrum may be partly, or even completely, the result of a field effect rather than an overlap effect.[21]

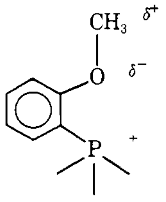


Table V. Ultraviolet Absorption Data for Selected Triarylphosphines, Triarylstibines, and Triarylamines in Cyclohexane Solution

Substrate	λ_{max}, nm
Triphenylamine	228, 297[20]
Triphenylphosphine	261[20]
Triphenylstibine	256[20]
o-Anisyldiphenylphosphine	260.5, 266, 284
p-Anisyldiphenylphosphine	260.5, 264
Bis(*o*-anisyl)phenylphosphine	266, 287.5
Bis(*p*-anisyl)phenylphosphine	263.5
Tris(*o*-anisyl)phosphine[a]	
Tris(*p*-anisyl)phosphine	264
Tris(*o*-anisyl)amine	216, 302
Tris(*o*-anisyl)stibine	257, 271, 279, 286

[a] Insoluble in cyclohexane.

Table VI. ^{31}P Nuclear Magnetic Resonance Spectral Data for the Isomeric Anisyldiphenylphosphines in Chloroform Solution

Phosphine	$\delta_{^{31}P}$, ppm relative to 85% H_3PO_4
o-Anisyldiphenyl	13.5 ± 0.5
m-Anisyldiphenyl	4.0 ± 0.5
p-Anisyldiphenyl	6.0 ± 0.5

It was also of interest to us to examine various spectra of the triarylphosphines used in the kinetics studies. An important feature of the ultraviolet absorption spectra, shown in Table V, of the triarylphosphines is the appearance of extra absorption bands at 284 and 287.5 nm in the ultraviolet absorption spectra of *o*-anisyldiphenylphosphine and bis(*o*-anisyl)phenylphosphine, respectively. Since these new bands are not found in triphenylphosphine, *p*-anisyldiphenylphosphine, or bis(*p*-anisyl)phenylphosphine, and since they are not solvent dependent, they are probably not K, E, or B bands. Our belief that these extra absorption bands involve intramolecular charge transfer from the p electrons of a methoxy oxygen to a vacant d orbital of phosphorus receives additional support from the observation that there is also an extra band in the spectrum of tris(*o*-anisyl)stibine but not in those of triphenylstibine,[22] triphenylamine,[22] or tris(*o*-anisyl)amine.

The ^1H NMR spectra of the various triarylphosphines are given in the Experimental Section. There were no unusual features in these spectra, and no comment about them is needed. The ^{31}P NMR spectra of the isomeric anisyldiphenylphosphines were taken in chloroform solution, and the data are given in Table VI. The fact that the chemical shift of the *o*-anisyl compound is at lower field than those of the meta and para isomers is probably attributable to an anisotropic effect.[23]

Mass spectral fragmentation studies can also be used to good advantage in mechanistic studies of the ortho effect, and they are also of use in analysis. The specificity observed for some reactions of ortho-substituted aromatic compounds under electron impact, as compared with the corresponding meta and para isomers, is attributed to neighboring group participation.[24] Specific loss of an ortho hydrogen,[25] or an ortho substituent[26] from triphenylphosphine and other aromatic phosphorus compounds, is interpreted in terms of anchimeric assistance of another phenyl group in these compounds.[26] Support for this mechanism has been provided by kinetic[27] and energetic[24,28] considerations. Thus, several ortho-effect reactions have been found to be low-energy processes accompanied by low frequency factors typical of rearrangements.[29] Many other similar reactions are obvious rearrangements, and the proximity of another group is a prerequisite for their occurrence. Recently we have reported[28] that bis(*o*-anisyl)phenylphosphine exhibits a prominent elimination of $CH_3O\cdot$ from its molecular ion and a rearrangement in which an oxygen has migrated to the phosphorus atom.

The present mass spectral work was designed to study a possible ortho effect in *o*-anisyldiphenylphosphine under

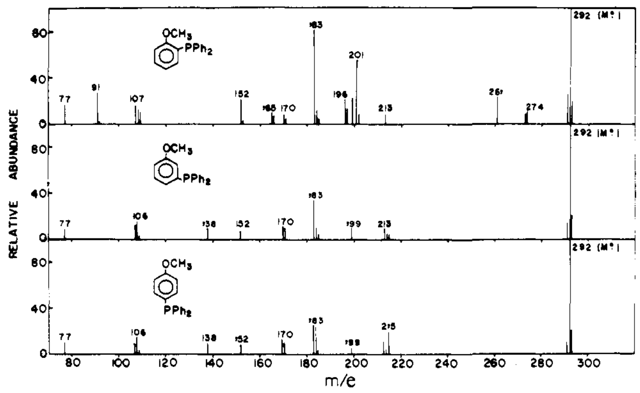
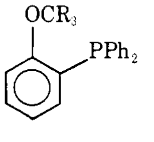
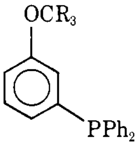


Figure 3. Mass spectra of *o*-anisyldiphenylphosphine, *m*-anisyldiphenylphosphine, and *p*-anisyldiphenylphosphine.

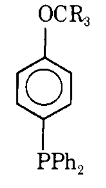
electron impact by means of deuterium labeling. Compounds **1a–3a** and **1b–3b** have been investigated. The mass spectra of the unlabeled, isomeric phosphines at 70 eV are summarized in Figure 3. The isotopic purity of the labeled compounds **1b–3b** is 98% d_3 and 2% d_2. This has been calculated from low-voltage spectra in which no M − 1 peaks are shown by **1a–3a**.[30]



1a, R = H
b, R = D



2a, R = H
b, R = D

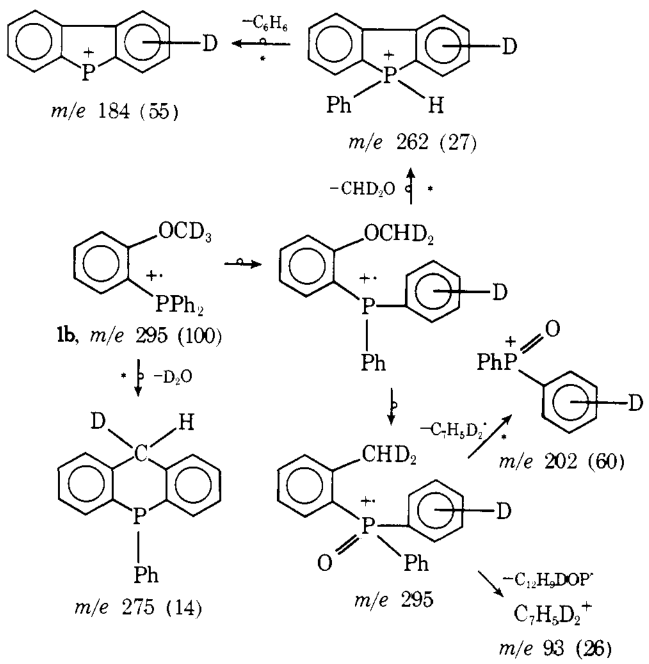


3a, R = H
b, R = D

The mass spectra of **2a** and **3a** are qualitatively the same, while there are several important differences between them and the spectrum of **1a**. The latter shows inter alia peaks at *m/e* 274 $(M - H_2O)\cdot^+$, 273 $(M - H - H_2O)^+$, 261 $(M - CH_3O)^+$, 201 $(M - C_7H_7)^+$, 197 $(C_{13}H_{10}P)\cdot^+$, 196 $(C_{13}H_9P)^+$, 166 $(C_{13}H_{10})\cdot^+$, 165 $(C_{13}H_9)^+$, and 91 $(C_7H_7)^+$, which are absent in the spectra of **2a** and **3a**, and does not contain peaks at *m/e* 215 $(M - C_6H_5)^+$ and 138 $(C_7H_7OP)\cdot^+$, which appear in the spectra of the meta and para isomers. The reactions indicated above in parentheses are accompanied by the corresponding metastable transitions, except for $(M - C_6H_5)^+$. The assignments of ion compositions are confirmed by appropriate shifts in the spectra of the deuteriated derivatives **1b–3b** and by exact mass measurements.

The M − 1 ions are not shifted in the spectra of the deuterated analogs, showing that aromatic hydrogens are eliminated to produce these ions in all the three isomers. The H_2O expulsion from both $M\cdot^+$ and $(M - 1)^+$ of **1a** is also specific in the sense that no aromatic hydrogens are incorporated into the water molecule, as only D_2O is lost from $M\cdot^+$ or $(M - 1)^+$ of **1b**. The specific elimination of $CH_3O\cdot$ from the molecular ion of the ortho isomer (**1a**) was expected.[28] We find now that it is preceded by a specific rearrangement of one hydrogen between the methoxy and one of the two unsubstituted phenyl groups. This is concluded from the expulsions of $CHD_2O\cdot$ and $C_7H_5D_2\cdot$ from the molecular ion of **1b**. The latter reaction involves the transfer of the methoxy oxygen to the phosphorus with a simultaneous C–C bond formation to produce the C_7H_7 unit. (See Scheme I.) This is the lowest energy process which gives the most intense metastable transition.[29] This evidence suggests a relatively slow reaction with a low frequency factor, properties associated with a rearrangement reaction.[31] Indeed, an intense peak at *m/e* 91 $(C_7H_7)^+$ is also observed in the spectrum of **1a** and is shifted mainly to *m/e* 93 $(C_7H_5D_2)^+$ in that of **1b** (Scheme I). Exact mass measurements showed a doublet at *m/e* 199 in the mass spectrum of **1a**, consisting of 80% $(M - C_6H_5O)^+$ and 20% of $(M - C_7H_9\cdot)^+$, but only the latter appears in the spectra of **2a** and **3a**. Indeed, the spectra of **2b** and **3b** show no shift in the *m/e* 199, but the corresponding ions produced from **1a** are mostly shifted to *m/e* 202 in the spectrum of **1b**.

Scheme I. Partial Mass Spectral Fragmentation of **1b** (Relative Intensities in Parentheses)



The mass spectral decompositions of **2a** and **3a** are typical of aromatic phosphines[25] and are confirmed by those of the deuterated analogs **2b** and **3b**, which show no aliphatic–aromatic hydrogen randomization. The latter observation further demonstrates the specificity of the hydrogen rearrangement in the ortho isomer, thus showing it also to be due to the ortho effect.

Experimental Section

Melting points were obtained by use of either a Mel-Temp or a Fisher-Johns melting point apparatus and are uncorrected. Proton nuclear magnetic resonance spectra were taken on a Varian Model A-60 spectrometer with tetramethylsilane as the internal reference standard. Chemical shifts are reported in parts per million (δ) with reference to tetramethylsilane, and coupling constants are reported in hertz (Hz). ^{31}P NMR spectra were taken on a JEOL C-60 HL spectrometer, 85% H_3PO_4 being used as an external standard. Ultraviolet spectra were taken either on a Perkin-Elmer 202 or else on a Cary 14 spectrophotometer. Infrared spectra were taken on a Beckman Model IR-10 spectrophotometer. Mass spectra were taken on a Hitachi Perkin-Elmer RMU 6 single focusing mass spectrometer by the direct inlet procedure at 70 and 20 eV and at source temperatures of 170–200°. Exact mass measurements were obtained with an AEI MS 902 instrument. Analyses were carried out either by the Microanalysis Laboratory, University of Massachusetts, Amherst, Mass., or else by Galbraith Laboratories, Knoxville, Tenn.

All aryl Grignard reagents were prepared by the method of Normant[32] from the corresponding halides. Phosphines were prepared by normal addition of phosphorus halides to Grignard reagents. Phosphines used in kinetics experiments were crystallized to constant melting point. We noticed that benzene–methanol solutions of several phosphines became yellow when allowed to stand, and the rate constants found when the aged solutions were employed were somewhat lower than those found when fresh solutions were used. A similar aging effect (presumably attributable to oxidation)

Table VII. Physical Constants and Spectral Data for Triarylphosphines

Phosphine	Reagents	Cryst solvent (% yield)	Mp, °C	Reported mp, °C	δ (nmr, $CDCl_3$)
o-Anisyldiphenyl	*o*-Bromoanisole + Ph_2PCl	MeOH (72)	122.5–123.5		3.74 s, 6.97–7.64 m
m-Anisyldiphenyl	*m*-Bromoanisole + Ph_2PCl	EtOH–H_2O (46)	54–55^a	60–61[34]	3.73 s, 6.80–7.40 m
p-Anisyldiphenyl	*p*-Bromoanisole + Ph_2PCl	EtOH (75)	64.5–65.5^b	78[35] 62–64[36] 78–79[37,38] 68–69[37,38]	3.75 s, 6.70–7.42 m
Bis-*o*-anisylphenyl	*o*-Bromoanisole + $PhPCl_2$	C_6H_6–EtOH (77)	164–165^c		3.70 s, 6.62–7.32 m
Bis-*p*-anisylphenyl	*p*-Bromoanisole + $PhPCl_2$	EtOH (75)	80–82^d	89–90[37,38] 90[39]	3.79 s, 6.76–7.44 m
Tris-*o*-anisyl	*o*-Bromoanisole + PCl_3	C_6H_6–EtOH (72)	204	204[40,41] 203–205[42]	3.69 s, 6.50–7.41 m
Tris-*p*-anisyl	*p*-Bromoanisole + PCl_3	EtOH (71)	134.5–135.5	131[41,43,44] 135[45]	3.80 s, 6.72–7.43 m

^{a}Anal. Calcd for $C_{19}H_{17}OP$: C, 78.07; H, 5.86; P, 10.60. Found: C, 77.80; H, 5.91; P, 10.42. ^{b}Anal. Calcd for $C_{19}H_{17}OP$: C, 78.07; H, 5.86; P, 10.60. Found: C, 77.86, 78.07; H, 6.00, 5.85; P, 10.53. ^{c}Anal. Calcd for $C_{20}H_{19}O_2P$: C, 74.54; H, 5.90; P, 9.61. Found: C, 74.61; H, 5.85; P, 9.60. ^{d}Anal. Calcd for $C_{20}H_{19}O_2P$: C, 74.59; H, 5.90. Found: C, 74.38; H, 5.81.

Table VIII. Properties of Quaternary Phosphonium Halides

Phosphonium cation	Anion	Cryst solvent	Mp, °C	Reported mp, °C	Analyses^a
Benzyltriphenyl	Cl^-	EtOH–AcOEt	333–337	338[48]	C, H, Cl
o-Anisylbenzyldiphenyl			196–198 dec^b 208–209 dec 254–256 dec		C, H, P, Cl
m-Anisylbenzyldiphenyl		$CHCl_3$–AcOEt	262–263		C, H, P, Cl
p-Anisylbenzyldiphenyl		EtOH–AcOEt	202–203		C, H, P, Cl
Bis-*o*-anisylbenzylphenyl			196–198		C, H
Bis-*p*-anisylbenzylphenyl			207–208		Cl
Tris-*o*-anisylbenzyl^c			201–202 dec		C, H, P, Cl
Tris-*p*-anisylbenzyl			206–208		Cl
Benzyltriphenyl	Br^-	EtOH–ether	297–299	295[49]	
o-Anisylbenzyldiphenyl		EtOH–AcOEt	229–231		C, H, Br, P
m-Anisylbenzyldiphenyl		EtOH–ether	264–266		C, H, Br, P
p-Anisylbenzyldiphenyl		EtOH–AcOEt	225–228		C, H, Br, P
Bis-*o*-anisylbenzylphenyl			214–217		C, H, Br, P
Tris-*o*-anisylbenzyl			241–244		C, H, Br, P
n-Butyltriphenyl	Cl^-		228–229.5	220[50]	
n-Butyl-*o*-anisyldiphenyl^c			147–149 dec		C, H, Cl, P
n-Butylbis-*o*-anisylphenyl^c			171–172 dec		C, H, Cl, P
n-Butyltris-*o*-anisyl^c			204–208 dec		C, H, Cl, P

^{a}Found values were within ±0.3 of calculated values. ^{b}Melting point varied with rate of heating of bath. ^{c}Contains one molecule of water of crystallization.

had been observed by Bartlett and his coworkers[33] for the reaction of triphenylphosphine with elemental sulfur in benzene solution. Therefore, to ensure reproducibility of kinetics results, we found it advisable to use freshly prepared phosphine solutions and to carry out the quaternization reactions in an inert atmosphere. All chemicals and solvents used in this study were of at least reagent grade quality. Solvents used in kinetics determinations were subjected to additional treatment. For example, methanol was refluxed over magnesium, distilled from the same metal, and stored over 3 Å molecular sieves. Benzene was redistilled from sodium and stored over 4 Å molecular sieves. Chloroform was of "spectranalyzed" grade and was degassed by passing argon through the refluxing liquid. All other solvents were also deoxygenated in the same manner. Reagent grade benzyl chloride, *n*-butyl chloride, and benzyl bromide were redistilled before use.

All quaternization reactions followed the second-order rate law. Most of the rate constants were obtained by use of a computer program which provided the slope of the line (rate constant), the standard deviation of the slope, and the extrapolated intercept for the best straight line (method of least squares). These calculations were carried out on a CDC 3600 computer.

Preparation of *o*-Anisyldiphenylphosphine. To the Grignard reagent prepared from 56.0 g (0.30 mol) of *o*-bromoanisole in 120 ml of dry tetrahydrofuran (distilled from $LiAlH_4$) at 0° was added a solution of 45.0 g (0.20 mol) of chlorodiphenylphosphine in 25 ml of dry tetrahydrofuran. After all of the halophosphine had been added, the mixture was refluxed for 2 hr. The reaction mixture was cooled to 0° and hydrolyzed with a saturated solution of ammonium chloride. The product was extracted into benzene, washed with water, and dried over magnesium sulfate. Evaporation of the solvent left 42.0 g (72%) of *o*-anisyldiphenylphosphine; this material was recrystallized fom methanol, mp 122.5–123.5°.

The ^1H NMR spectrum of this compound in deuteriochloroform showed a singlet at δ 3.74 ppm and a multiplet at δ 6.97–7.64 ppm (relative to TMS).

Anal. Calcd for $C_{19}H_{17}OP$: C, 78.07; H, 5.86; P, 10.60. Found: C, 78.19, 78.07; H, 5.92, 5.75; P, 10.60, 10.41.

Preparation of Diphenyl-*o*-trideuteriomethoxyphenylphosphine. An *n*-hexane solution of *n*-butyllithium (4.7 ml of 2.13 *N*, 10 mmol) was added under a nitrogen atmosphere to a solution of phenyl trideuteriomethyl ether (1.1 g, 10 mmol) in 5 ml of tetrahydrofuran and 7 ml of diethyl ether. The mixture was refluxed for 2 hr, treated dropwise with diphenylphosphinous chloride (2.2 g, 10 mmol), and then again refluxed for 2 hr. After treatment with 30 ml of water, the organic layer was evaporated to give the solid product, which was recrystallized from ethanol, yield, 1.4 g (47%), mp 122–124°.

Preparation of Other Triarylphosphines. The method was essentially the same as that for *o*-anisyldiphenylphosphine, and details are provided in Table VII. Similarly, diphenyl-*m*-trideuteriomethoxyphenylphosphine was prepared from *m*-bromophenyl trideuteriomethyl ether and diphenyl-*p*-trideuteriomethoxyphenylphosphine was prepared from *p*-bromophenyl trideuteriomethyl ether.

Preparation of Benzyltriarylphosphonium Chlorides. The phosphines (0.04 mol quantities) were dissolved in 100-ml portions of dry benzene. To these solutions were added 0.12 mol quantities of benzyl chloride. The mixtures were refluxed from 12 to 96 hr, depending upon the reactivity of the phosphines. In all cases, the corresponding triarylbenzylphosphonium chlorides precipitated directly from the reaction mixtures. The ^1H NMR spectra of these compounds were characteristic of triarylalkylphosphonium halides (J_{pch} = 14–15 Hz).[46] Also, all quaternization products gave positive "onium tests".[47] These salts were recrystallizable from chloroform–ether, ethanol–ether, or ethyl acetate–ether solvent pairs. The properties of these phosphonium salts are listed in Table VIII.

Preparation of Benzyltriarylphosphonium Bromides. The phosphines (0.01–0.025 mol) were dissolved in anhydrous benzene (25–30 ml), and slight excesses of benzyl bromide (0.015–0.030 mol) were added. The clear solutions were flushed with nitrogen, and then refluxed with stirring for 10–20 hr, depending on the reactivity of the phosphines. In all cases, the triarylbenzylphosphonium bromides precipitated directly from the reaction mixtures and were recrystallized from ethanol–ether or from ethanol–ethyl acetate. The properties of these phosphonium salts are listed in Table VIII.

Preparation of *n*-Butyltriarylphosphonium Chlorides. The phosphines (0.02 mol) were dissolved in spectranalyzed chloroform (20 ml), and an excess (0.08 mol) of *n*-butyl chloride was added to each solution. The clear solutions were flushed with nitrogen and then heated under reflux for 156 hr. The solutions were concentrated to dryness and the residues washed thoroughly with anhydrous ether. The solid which remained in each case was digested in ethanol–ethyl acetate. The properties of the salts are listed in Table VIII.

Kinetics Procedure for Quaternization Reactions with Benzyl Chloride in Benzene–Methanol. A 60% benzene–methanol solution was prepared by pipetting the appropriate amounts of both degassed (air removed by bubbling argon through the solvent for several hours) anhydrous benzene and degassed absolute methanol into an erlenmeyer flask and covering the mixture with a blanket of argon before agitation. After thorough mixing, the homogeneous solution was stored under a positive argon pressure until it was used.

An accurately weighed sample of the phosphine was added to a 250-ml volumetric flask and filled to the mark with the 60% benzene–methanol solvent ($\simeq$0.02 *N*). The solution was briefly covered with a blanket of argon and subsequently mixed thoroughly. A 100-ml portion of freshly prepared 0.02 *N* phosphine solution was pipetted into a 200-ml erlenmeyer flask, fitted with a ₸ joint, and equilibrated at 31.0 ± 0.1° under a positive argon pressure for 2 hr. After this period, the required volume (2–3 ml) of a 0.9918 *N* solution of benzyl chloride in benzene–methanol was added.

At various time intervals, a 10-ml aliquot of the reaction mixture was pipetted into 5.0 ml of water (distilled from alkaline potassium permanganate solution) to quench the quaternization reaction. The resulting two-phase system was titrated with a standard solution of silver nitrate (0.01 *N*), 5% potassium chromate solution being used as the indicator (Mohr method for chloride analysis).

Kinetics Procedure for Quaternization Reactions with Benzyl Bromide, Benzyl Chloride, and *n*-Butyl Chloride in Chloroform. An accurately weighed sample of the triarylphosphine was dissolved in about 98 ml of chloroform contained in a 100-ml volumetric flask, and this solution was flushed with argon and allowed to attain thermal equilibrium in the oil bath for 2 hr. Then the flask was filled to the mark with fresh, degassed, thermally equilibrated chloroform (concentration = 0.015–0.025 *N*). Concurrently, a solution of the alkyl halide in chloroform (concentration = 0.5–1.0 *N*) was prepared in the same manner. A 50-ml portion of the freshly prepared phosphine solution was transferred under a positive argon pressure to a fresh, thermally equilibrated 100-ml volumetric flask, and the required volume of alkyl halide solution was added.

At various time intervals, a 2-ml aliquot of the reaction mixture was pipetted into 15.0 ml of chilled, deionized water to quench the reaction. The two-phase system which resulted was cooled in an ice bath and titrated with a standard solution of silver nitrate (0.01 *N*), 5% potassium chromate being used as the indicator (Mohr method).

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