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Contrasting Chemical and Physical Properties of [*o*- and [*p*-(*N,N*-Dimethylamino) phenyl]phosphines and Phosphonium Salts

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ABSTRACT

The rate of alkylation of (2-N,N-*dimethylaminophenyl)diphenylphosphine with benzyl bromide in chloroform is faster than that of the corresponding reaction of* (4-N,N-*dimethylaminophenyl)diphenylphosphine. This result is discussed in terms of a through-space* N_{2p}–*P(IV) interaction for the former.*

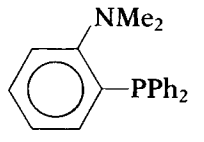
The rate of alkaline cleavage of benzyl(4-N,N-*dimethylaminophenyl)diphenylphosphonium bromide, which gives toluene, is slower than the rate of alkaline cleavage of benzyl*(2-N,N-*dimethylaminophenyl)diphenylphosphonium bromide, which gives dimethylaniline. This result is also discussed in terms of the through-space* N_{2p}–*P(IV) interaction.*

The ^{31}P *NMR spectra of a series of* ortho-*dimethylamino-substituted triarylphosphines and benzyltriarylphosphonium halides show that the phosphorus atom is more shielded than in the corresponding* para-*dimethylamino compounds, as anticipated on the basis of an* N_{2p}–*P(IV) interaction for the former.*

INTRODUCTION

Through-space interaction of a pair of 2*p* electrons of an alkoxy or dialkylamino group with a proximate P(IV) center produces important rate and stereochemical effects in substitution reactions at phosphorus. The designations "O_{2p}–P_{3d} overlap" and "N_{2p}–P_{3d} overlap" have previously been used to describe such effects, 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" and "N_{2p}–P(IV) interaction," because there are numerous theoretical treatments extant that 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].

The effects of through-space O_{2p}–P(IV) and N_{2p}–P(IV) interactions have been observed in quaternization reactions of tertiary phosphines, in alkaline decomposition reactions of quaternary phosphonium salts, in the Wittig reaction, in spectral studies of various types, and by x-ray diffraction studies. We have now made several comparisons of the reactivity and physical properties of [2-(*N,N*-dimethylamino)phenyl]diphenylphosphine **(1)**, [4-(*N,N*-dimethylamino)phenyl]diphenylphosphine **(2)**, and some of their derivatives. A small portion of the work has been reported in previous communications [3,4].



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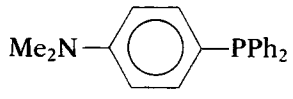

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QUATERNIZATION REACTIONS

Kinetics data for the S_N2 reactions of various triarylphosphines with benzyl chloride, benzyl bromide, and *n*-butyl chloride, and of aryldiethylphosphines with ethyl iodide have been reported [1,5,6].

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TABLE 1 Rate Data for the Alkylation of Triarylphosphines with Benzyl Bromide in Chloroform

Phosphine	10^4k (1 Mol^{-1} s^{-1})	*T* (°C) ± 0.05	k_{rel}
Triphenyl	6.72 ± 0.37	14.20	1.00
	24.92 ± 0.74	9.00	
1	65.12 ± 4.80	14.20	9.68
	100.3 ± 2.4	19.00	
	7.14 ± 0.36	9.00	
2	11.31 ± 0.84	14.20	1.68
	18.78 ± 0.56	19.00	
Bis[2-(*N*,*N*-dimethylamino)phenyl]phenyl, **3**	47.71 ± 3.70	14.20	7.10
	75.86 ± 6.80	19.00	
Bis[4-(*N*,*N*-dimethylamino)phenyl]phenyl, **4**	15.66 ± 1.30	14.20	2.33
Tris[2-(*N*,*N*-dimethylamino)phenyl], **5**	19.09 ± 1.70	14.20	2.84
	36.63 ± 3.30	19.00	
Triphenyl [8]		26.00	1.00[a]
(*o*-Methoxyphenyl)diphenyl [8]		26.00	4.88[a]
(*m*-Methoxyphenyl)diphenyl [8]		26.00	0.90
(*p*-Methoxyphenyl)diphenyl [8]		26.00	1.25
Bis(*o*-methoxyphenyl)phenyl [8]		26.0	6.28
Tris(*o*-methoxyphenyl) [8]		26.0	1.50

[a] New scale.

Six particularly important effects attributable to O_{2p}–P(IV) interactions have been observed.

1. The presence of an *o*-methoxy substituent on an aryl group of the phosphine causes a significant increase in the rate of reaction.
2. The ratio of the rates of reaction of a given triarylphosphine with benzyl chloride and with butyl chloride is about 20, probably the smallest ratio ever reported for S_N2 reactions of these alkyl chlorides, indicating an early transition state.
3. Rate and activation parameter profiles for the reactions of the isomeric anisyldialkylphosphines and anisyldialkylamines, respectively, are distinctly different.
4. Diphenyl(2,6-dimethoxyphenyl)phosphine undergoes the quaternization reaction with alkyl halides faster than any other phosphine we have used, including tris(*o*-methoxyphenyl)-phosphine and bis(*o*-methoxyphenyl)phenylphosphine.
5. The acceleration caused by the presence of one or more *o*-methoxyphenyl groups bonded to phosphorus is mainly attributable to a less negative value of $\Delta S^{\ddagger}$ relative to related reactions.
6. The preferred geometry of the O_{2p}–P(IV) interaction, as determined by rate studies of various methoxy-substituted 5-aryldibenzophospholes with benzyl chloride [7], is one in which a 5-(*o*-methoxyphenyl) group, which is orthogonal to the plane of the dibenzophosphole ring, is present.

Rate data for the reactions of **1**, **2**, and various other [(*N*,*N*-dimethylamino)phenyl]phosphines with benzyl bromide in chloroform solution have now been obtained, and the results are summarized in Table 1. Although all of the [(*N*,*N*-dimethylamino)phenyl]phosphines undergo the quaternization reactions at a greater rate than triphenylphosphine, there are anomalies in the data in comparison with the rate data for the previously reported analogous (*o*-methoxyphenyl)phosphine reactions, the relative rates of which are also included in Table 1 for comparison.

Calculations of the activation parameters for most of the compounds listed in Table 1 are presented in Table 2. Once again, there are anomalies in the data for the (methoxyphenyl)phosphine reactions as against those for the [(*N*,*N*-dimethylamino)phenyl]phosphine reactions.

Previously, for the reactions of (methoxyphenyl)phosphines with alkyl halides, we have presented arguments that the reactions have early transition states and that the observed anchimeric assistance in the cases of the (*o*-methoxyphenyl)phosphine reactions is attributable to a favorable through-space interaction between the 2*p* electrons of the methoxy group and the incipient P(IV) center in the transition state for the displacement reaction. The activation parameter data indicate that the anchimeric assistance arises mainly because the *o*-methoxy group provides intramolecular backside solvation of the phosphorus atom in the transition state, thus liberating solvent molecules from the necessity of providing such solvation. This leads to a less negative value for $\Delta S^{\ddagger}$.

TABLE 2 Activation Parameters for the Reactions of Triarylphosphines with Benzyl Bromide in Chloroform

Phosphine	$\Delta H^{\ddagger}$ (*kcal mol*$^{-1}$)	$\Delta S^{\ddagger}$ (*eu*)
Triphenyl [8]	11.9[a]	−33.5
1	22.5 ± 0.1	+9.4 ± 0.2
2	13.7 ± 1.3	−24.4 ± 4.8
3	27.0 ± 1.1	+24.5 ± 3.7
5	22.1 ± 0.1[b]	+6.0 ± 0.4[b]
(*o*-Methoxyphenyl)diphenyl [8]	12.8[a]	−27.3
(*m*-Methoxyphenyl)diphenyl [8]	11.1[a]	−36.3
(*p*-Methoxyphenyl)diphenyl [8]	17.2[a]	−32.0
Bis(*o*-methoxyphenyl)phenyl [8]	11.9[a]	−29.8
Tris(*o*-methoxyphenyl) [8]	12.2	−31.6

[a] $\Delta E^{\ddagger}$.
[b] Reasonably valid estimate based on reactions carried out at only two temperatures.

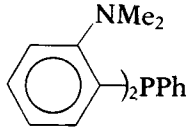
Thus, the presence of an *o*-methoxyphenyl group provides for a greater degree of acceleration than the presence of a *p*-methoxyphenyl group, even though both *o*-methoxy and *p*-methoxy substituents are considered to be electron-donating and therefore base-strengthening substituents. Both Davies and Lewis [9] and Henderson and Buckler [10] had previously demonstrated that arylphosphine reactivity in alkylation reactions was increased by the presence of electron-donating and decreased by the presence of electron-withdrawing substituents.

We have demonstrated previously that the presence of two *o*-methoxyphenyl groups bonded to the phosphorus brings about a greater degree of anchimeric assistance than the presence of only one such group, but unfavorable steric effects begin to compete with favorable intramolecular backside solvation effects when the attacking nucleophile is tris-(*o*-methoxyphenyl)phosphine. The latter compound reacts with some alkyl halides more slowly than (*o*-methoxyphenyl)diphenylphosphine and more rapidly with other alkyl halides [6,8].

The ortho/para rate ratios for the methoxyphenyl series indicate that the apparent magnitude of anchimeric assistance for the *o*-methoxyphenyl group is only 4–6. However, since ortho/para rate ratios for other substituents are all less than 1 [1,11], and since such rate reductions for the *o*-substituted compounds must be attributable at least in part to steric factors, the actual magnitude of anchimeric acceleration in the (*o*-methoxyphenyl)-phosphine reactions must be distinctly greater than 4–6. Nevertheless, the fact that the transition states for these quaternizations are early ones means that the degree of through-space electron-density transfer from the *o*-methoxy group to the developing P(IV) center will be relatively small.

Spectral data and evidence obtained by studies of the alkaline decompositions of quaternary phosphonium salts, to be presented later, indicate that, intrinsically, the *N,N*-dimethylamino group interacts more strongly with P(IV) than does the methoxy group. With this as the main consideration, let us examine more closely the rate data presented in Tables 1 and 2.

Whereas both *o*- and *p*-(*N,N*-dimethylamino)-substituted triarylphosphines exhibit an enhancement of the rate of alkylation with benzyl bromide relative to triphenylphosphine, the trend is not entirely the same as with the methoxy-substituted triarylphosphines. The presence of two [4-(*N,N*-dimethylamino)phenyl] groups, as in compound **4**, increases the rate of alkylation relative to the presence of only one such group, as in **2**, which, in turn, increases the rate relative to the triphenylphosphine reaction. These are the anticipated results, as is the observation that the presence of one [2-(*N,N*-dimethylamino)phenyl] group, as in **1**, increases the rate of alkylation more than the presence of two [4-(*N,N*-dimethylamino)phenyl] groups, as in **4**. However, the presence of two [2-(*N,N*-dimethylamino)phenyl] groups, as in **3**, decreases the rate of alkylation relative to the reaction of **1**, and tris[2-*N,N*-dimethylamino)phenyl]phosphine, **5**, is less reactive than **3**. Nevertheless, all three phosphines, **1**, **3**, and **5**, are more reactive than triphenylphosphine.



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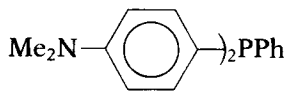

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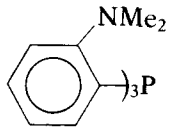

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Consideration of the activation parameters given in Table 2 helps to explain the divergencies between the methoxyphenylphosphine series and the dimethylaminophenylphosphine series in their relative rates of reaction with benzyl bromide. The $\Delta H^{\ddagger}$ values for the dimethylaminophenylphosphine alkylation reactions are greater than those for the analogous methoxyphenylphosphine reactions. This probably reflects greater steric hindrance in attainment of the transition states for the larger dimethylamino-substituted compounds than for the smaller methoxy-substituted compounds. However, in both the methoxy series and the dimethylamino series, the $\Delta S^{\ddagger}$ values are of much greater importance in determining relative rates. For example, the reaction of **1** with benzyl bromide in chloroform solution at 14.20°C is 9.68 times faster than that of triphenylphosphine, even though $\Delta H^{\ddagger}$ for the former is almost double that of the latter; it is the $\Delta S^{\ddagger}$ value of +9.5 eu for the reaction of **1**, as against a value of $\Delta S^{\ddagger}$ of −33.5 eu for the triphenylphosphine reaction, that causes **1** to react faster. Also, in all of the comparisons of the reactions of the dimethylaminophenylphosphines with the analogous methoxyphenylphosphine reactions, that $\Delta H^{\ddagger}$ values for the former are larger, but, at the same time, the $\Delta S^{\ddagger}$ values of the former are more positive (or less negative) than for the latter reactions. This is a reflection of the fact that the *N,N*-dimethylamino group (a stronger base) [12,13] interacts more strongly with P(IV), the acid center, than does the methoxy group (a weaker base). In turn, the greater degree of internal solvation in the transition states of the *o*-dimethylaminophenylphospine alkylation reactions liberates more solvent molecules from the necessity of playing this role than in the transition states of the *o*-methoxyphenylphosphine alkylation reactions. Thus, the mixture of more favorable internal solvation ($\Delta S^{\ddagger}$) effects and unfavorable steric (reflected in $\Delta H^{\ddagger}$) effects of the *o*-dimethylaminophenylphosphine alkylation reactions as against the analogous *o*-methoxyphenylphosphine reactions determines the relative rates and reactivity sequence series of these systems.

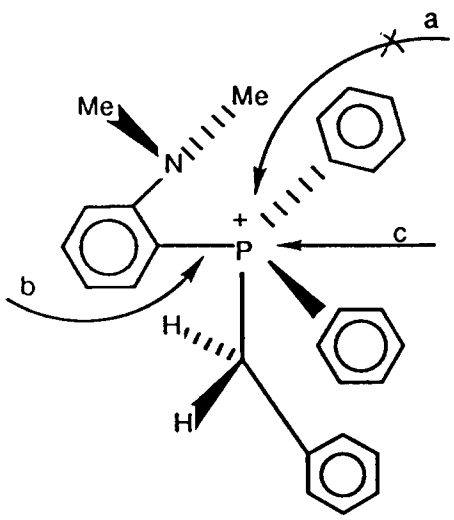
ALKALINE DECOMPOSITION REACTIONS

As we reported previously [4], benzyl[2-(*N,N*-dimethylamino)phenyl]diphenylphosphonium bromide **(6)** 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 [14] 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 ± 5.00 L^2 mol^{-2} s^{-1}), **6** 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 **(7)** 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.

Equally spectacular divergencies occur in the alkaline cleavage reactions of benzylbis[2-(*N,N*-dimethylamino)phenyl]phenylphosphonium bromide **(8)** and benzylbis[4-(*N,N*-dimethylaminophenyl)phenylphosphonium bromide **(9)**. Reaction of **8** under the standard conditions (relative rate = 0.11) gives *N,N*-dimethylaniline (94.2%) and benzene (1.05%), but no toluene is detected. Reaction of **9** under the same conditions (relative rate = 0.00070) affords toluene (100%) as the only hydrocarbon product; no $PhNMe_2$ or benzene is detectable.

We have previously reported [11] kinetics and product ratio data for the alkaline cleavage reactions of *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 benzylbis2-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 [11], 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 Pagilagan and McEwen [15] 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.

The mechanism of alkaline decomposition of ordinary acyclic quaternary phosphonium salts is well understood [16] 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) [17] 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 [18], it expels the apical group as a



Scheme 1

carbanion (k_3). This is protonated as it is being formed [19], with concomitant formation of a phosphine oxide. We have previously [11] 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 [8].

This same type of through-space interaction has been suggested to influence the alkaline cleavage reactions of (ω-*N*,*N*-dimethylaminoalkyl)benzyldiphenylphosphonium bromides [20]. 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 evidence 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) but a poorer electron-withdrawing group through the inductive effect than the methoxy group [22].

It is clear from all of the data presented above that the phosphonium salts **6** and **8** have a unique reactivity, particularly insofar as neither gives any toluene in its alkaline decomposition reaction, and **6** undergoes a faster reaction than benzyltriphenylphosphonium bromide.

It is our belief that a reasonably strong N_{2p}–P(IV) through-space interaction exists in the cations of **6** and **8** (as shown previously for benzyl(2-methoxyphenyl)diphenylphosphonium bromide by x-ray diffraction [23]). As illustrated in Scheme 1, 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 [24–26], 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 **6** over the unsubstituted case.

Rationalization of the relative rates of alkaline decomposition of the remaining compounds, **7**, **8**, and **9**, depends on several factors. When benzyltriarylphosphonium salts are treated with sodium hydroxide solution and an incipient benzyl anion is the departing group, the presence of electron-donating substituents on the stationary aryl groups causes a decrease in rate; ρ values of +4.62 [27], +3.64 [28], and +3.19 [11] have been found for this and closely related systems. This is in qualitative accord with the fact that the relative rate for reaction of **9** (0.00070) is smaller than that for reaction of **7** (0.0043), and that the relative rate for reaction of **8** (0.11) is less than that for reaction of **6** (4.76). Furthermore, the departure of *N*,*N*-dimethylaniline in the reaction of **8** is aided by the Eaborn solvent effect but retarded by electron repulsion by unshared pairs on the hydroxyl group in the apical position of the trigonal-bipyramidal intermediate phosphorane and the unshared pair on the nitrogen atom of the stationary 2-(*N*,*N*-dimethylamino)-phenyl group in an equatorial position (reduction in the values of K_1 and K_2); thus, the balance of these effects provides an explanation for the greater reactivity of **6** over **8**.

In addition to the arguments favoring departure of *N*,*N*-dimethylaniline from **6** and **8** in their alkaline decomposition reactions, presented above, there are also reasons that departure of toluene (actually an incipient benzyl anion) would be inhibited. In order to have departure of an incipient benzyl anion from the conjugate bases of the phosphoranes initially formed, a Berry pseudorotation [18] 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 [29]. This would decrease the rate of this process relative to that which actu-

ally occurs. The alternative possibility, having the incipient benzyl anion depart from an equatorial position without a Berry pseudorotation, is contrary to theoretical treatments [29,30]; to the known stereochemistry of alkaline decomposition reactions of quaternary phosphonium salts having a chiral phosphorus atom, where inversion of configuration results [31–33]; and to the probable violation of the principle of microscopic reversibility, as pointed out by McDowell and Streitwieser [34].

SPECTRAL STUDIES

Although a much more extensive coverage of spectroscopic investigations of triarylphosphines and their corresponding quaternary phosphonium salts will be provided in a subsequent paper, a relatively brief coverage of this topic is required here. As we have pointed out in previous papers [1,6,8,20], the through-space O_{2p}–P(IV) and N_{2p}–P(IV) interactions, which involve transfer of electron density from the O and N atoms, respectively, to P(IV), should be of greater importance in quaternary phosphonium salts, where the P(IV) center is fully formed, than in the early transition states of S_N2 reactions, where the formation of the P(IV) center is at an incipient stage. This is reflected in the spread of rates for the quaternization reactions as against the spread of rates in the decomposition of the corresponding quaternary phosphonium hydroxides. For example, (2,6-dimethoxyphenyl)diphenylphosphine exhibits a 75-fold increase in rate of reaction with benzyl chloride in comparison with triphenylphosphine [1] whereas benzyl(2,6-dimethoxyphenyl)diphenylphosphonium hydroxide exhibits a 383-fold decrease in its rate of decomposition in comparison with benzyltriphenylphosphonium hydroxide [11].

A more convenient measure of the transfer of electron density from an *o*-methoxy group to P(IV) is achieved by examination of ^1H NMR spectra of the various benzyltriarylphosphonium salts. As described previously [8], the chemical shifts of the methoxyl hydrogens arise from ambiguous influences, but distinct upfield shifts of the benzyl methylene hydrogens are observed whenever an O_{2p}–P(IV) interaction is operative.

Chemical shift data for selected triarylphosphines and the corresponding benzyltriarylphosphonium bromides are given in Table 3. In agreement with previously given data for the corresponding methoxy compounds [8], increasing the number of *o*-dimethylamino groups causes an upfield shift of the methylene hydrogen resonances in the benzylphosphonium bromides, as does increasing the number of *p*-dimethylamino groups. However, there is a difference in the data presented here and those for the methoxy-substituted phosphonium salts. Unlike the methoxy-substituted cases, the occurrence of an N_{2p}–P(IV) interaction in **6** does not cause as great an upfield shift for the methylene hydrogens as does the presence of a *p*-dimethylamino group in **7**. The same holds true for the bis-substituted salts.

A possible explanation for the difference observed in these two systems could be the effect of an important through-ring resonance interaction in the *p*-dimethylamino-substituted salts. The x-ray diffraction data for the parent phosphine **2** indicate the existence of a partial double bond between the ring carbon atom and the nitrogen atom [35]. The increased electron density at the carbon bonded to phosphorus (para to the dimethylamino group) would, in turn, cause an inductive increase in electron density at the phosphine phosphorus atom. This effect is expected to be greater when the phosphorus has a positive charge, as in **7** and **9**. The fact that this effect is not seen in the case of the *o*-dimethylamino-substituted salts, **6** and **8**, appears to be attributable to a reduced interaction between the ring and the *o*-dimethylamino group; this would be expected owing to the operation of a through-space N_{2p}–P(IV) interaction, which reduces the electron density at nitrogen. In other words, the nitrogen atom will share the positive charge of the phosphonium salt. The nitrogen would have more of a positive charge than the oxygen in the analogous methoxy-substituted phos-

TABLE 3 Chemical Shift Data for Selected Triarylphosphines and the Corresponding Benzyltriarylphosphonium Bromides in $CDCl_3$ Solution

Substrate	δ^1H CH_2	$\delta^{31}P$	$\delta^{13}C$ $N(CH_3)_2$	$\delta^{13}C$ CH_2
Triphenylphosphine	—	−4.69	—	—
1	—	−13.55	45.58	—
2	—	−6.54	40.36	—
3	—	−21.88	45.49	—
4	—	−13.17	40.27	—
Benzyltriphenylphosphonium bromide	5.34	23.60	—	117.13
6 Bromobenzylate of **1**	5.12	19.74	45.91	106.34
7 Bromobenzylate of **2**	4.91	22.32	40.05	112.38
8 Bromobenzylate of **3**	4.68	17.87	46.04	108.07
9 Bromobenzylate of **4**	4.54	20.52	40.03	112.49

phonium salts, as the dimethylamino group is a better electron donor than the methoxy group, as shown previously. This charge distribution in the *o*-dimethylamino-substituted salts would counteract, to some extent, the upfield shift of the methylene hydrogens caused by the N_{2p}–P(IV) interaction, as observed.

The ^{31}P NMR spectra for selected compounds have been examined, and the hydrogen-decoupled phosphorus resonances are presented in Table 3. 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 triarylphosphines. In agreement with the reports of Grim [36–39] and Quin [40], 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 because 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. As mentioned previously, 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, whereas 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.

The ^{13}C NMR chemical shifts of the $-N(CH_3)_2$ carbons of the phosphines and of both the $-N(CH_3)_2$ and benzyl carbons of the phosphonium salts are presented in Table 3. It is of interest that when *o*-(*N*,*N*-dimethylamino)phenyl groups are bonded to the phosphorus atom, the benzyl carbon shows a downfield shift, indicative of apparent decreased electron density at phosphorus. It is possible that this apparent decrease in electron density at phosphorus actually arises by the imposition of a field effect. Since the *o*-dimethylamino group is a good through-space donor, it is reasonable to assume that the nitrogen has developed an appreciable degree of positive charge. This (these) positive nitrogen(s) would probably set up a field effect that would decrease the electron density about the benzyl carbon.

For any of the related pairs of phosphine–phosphonium salt compounds, (**1** and **6**; **2** and **7**; **3** and **8**; **4** and **9**) there is not much change in the ^{13}C chemical shifts for the methyl groups. This provides additional evidence that benzylation has occurred at phosphorus rather than nitrogen. Of course, the chemical reactivity evidence (the phosphonium hydroxide decomposition reactions and the Wittig reactions of ylides derived from **6, 7, 8,** and **9** [3]) is also unambiguous in this regard.

As mentioned previously, a much more complete coverage of spectral effects in *o*- and *p*-methoxyphenylphosphines and phosphonium salts and of *o*- and *p*-(*N*,*N*-dimethylamino)phenylphosphines and phosphonium salts will be forthcoming in a future paper.

EXPERIMENTAL

General Procedures

All newly obtained melting points were taken in open capillary tubes using a Mel-Temp melting point apparatus and are uncorrected. Ultraviolet spectra were recorded on a Perkin-Elmer 202 ultraviolet–visible spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 1310 infrared spectrophotometer. Gas chromatographic analyses were performed on a Varian 1200 Series Aerograph. Proton NMR spectra were recorded on a Varian A-60 NMR, a Perkin-Elmer R12 NMR, or a Varian XL-200 NMR instrument. Phosphorus-31 NMR spectra were recorded on a Varian XL-300 NMR instrument and ^{13}C NMR spectra were recorded on a Varian XL-200 NMR or on a Varian XL-300 NMR instrument. Elemental analyses were performed by the Microanalysis Laboratory of the University of Massachusetts, Amherst.

Silica gel used for column chromatography was 100–200 mesh, Fisher reagent grade; 10% deactivated, where specified, was achieved by thoroughly mixing fresh silica gel with an amount of water equal to one-tenth the mass of the silica gel. Thin-layer chromatography was conducted on precoated silica-gel plates (with fluorescent indicator), Eastman Chromatogram Sheet No. 13181.

Standard procedures were employed in drying solvents. Thus, hexane was distilled from calcium hydride. Tetrahydrofuran and 1,4-dioxane were distilled from sodium benzophenone ketyl. Chloroform was washed with concentrated sulfuric acid and water, predried over potassium carbonate, and distilled under argon.

An inert atmosphere in experiments employing air-sensitive reagents was provided by charging the system with an inert gas, which means that after the apparatus had been assembled, it was evacuated by use of a vacuum pump and then backflushed with argon.

Synthetic Procedures

*Preparation of (2-*N,N*-Dimethylaminophenyl)diphenylphosphine* (**1**). The method of Horner and Simons [41] was used to prepare **1**, colorless needles, mp 116.5–118.5°C; results by UV (cyclohexane), λ_{max} = 223 (ε = 13,900), λ = 264 (ε = 6,700); by IR ($CHCl_3$), 940 cm^{-1} (P Ar_3), 1430 cm^{-1}; by ^1H NMR ($CDCl_3$), δ = 7.29–6.80 (m, 14H), 2.60 (s, 6H); by ^{31}P NMR ($CDCl_3$), δ = −13.55 (s); by ^{13}C NMR ($CDCl_3$): δ = 45.58 (N-CH_3) (decoupled).

The physical properties are in good agreement with those reported by Horner and Simons [41] and by Fritz et al. [42].

*Preparation of bis-(2-*N,N*-Dimethylaminophenyl)phenylphosphine* **(3).** The method of Horner and Simons [41] was used to prepare **3**, colorless crystals, mp 82–85°C; results by UV (cyclohexane), λ_{max} = 218 (ε = 15,350), λ = 285 (ε = 8,700); by IR ($CHCl_3$), 940 cm^{-1} (P-Ar_3), 1430 cm^{-1} (P-Ph); by ^1H NMR ($CDCl_3$), δ = 7.30–6.75 (m, 13H), 2.60 (s, 12H); by ^{31}P NMR ($CDCl_3$), δ = −21.88 (s) (decoupled); by ^{13}C NMR ($CDCl_3$), δ = 45.49 (N-CH_3) (decoupled).

The physical properties are in excellent agreement with those reported by Horner and Simons [41] and by Fritz et al. [42].

*Preparation of tris-(2-*N,N*-Dimethylaminophenyl)phosphine* **(5).** The method of Bone et al. [43] was used to prepare **5**, colorless needles, mp 109–110°C; results by UV (cyclohexane), λ_{max} = 229 (ε = 23,000), λ = 297 (ε = 9800); by IR ($CHCl_3$), 940 cm^{-1} (P-Ar_3), 1425 cm^{-1} (P-Ph); by ^1H NMR ($CDCl_3$), δ = 7.70–6.85 (m, 12H), 2.40 (s, 18H); by ^{31}P NMR ($CDCl_3$), δ = −27.78 (s), −33.01 (s) (decoupled); by ^{13}C NMR ($CDCl_3$), δ = 45.34 (N-CH_3) (decoupled).

The physical properties are in excellent agreement with those reported by Horner and Simons [41] and by Fritz et al. [42].

*Preparation of (4-*N,N*-Dimethylaminophenyl)diphenylphosphine* **(2).** The method of Schiemenz [44] was used to prepare **2**, mp 149–151°C; results by UV (cyclohexane), λ = 218 (ε = 16,100), λ_{max} = 283 (ε = 25,900); by IR ($CHCl_3$), 940 cm^{-1} (P-Ar_3), 1100 cm^{-1} (P-Ar_3), 1355 cm^{-1}; by ^1H NMR ($CDCl_3$), δ = 7.36–6.76 (m, 14H), 2.95 (s, 6H); by ^{31}P NMR ($CDCl_3$), δ = −6.54 (s), (decoupled); by ^{13}C NMR ($CDCl_3$), δ = 40.36 (N-CH_3).

The physical properties are in excellent agreement with those reported by Horner and Simons [41] and by Schiemenz [44].

*Preparation of bis-(4-*N,N*-Dimethylaminophenyl)phenylphosphine* **(4).** The method of Schiemenz [44] was used to prepare **4**, colorless crystals, mp 149.5–151.0°C; results by UV (cyclohexane), λ = 223 (ε = 12,500), λ_{max} = 287 (ε = 23,950); by IR ($CHCl_3$), 940 cm^{-1} (P-Ar_3), 1100 cm^{-1} (P-Ar_3), 1355 cm^{-1}; by ^1H NMR ($CDCl_3$), δ = 7.35–6.60 (m, 13H), 2.95 (s, 12H); by ^{31}P NMR ($CDCl_3$), δ = −13.17 (s), (decoupled); by ^{13}C NMR ($CDCl_3$), δ = 40.27 (N-CH_3) (decoupled).

The physical properties are in good agreement with those reported by Horner and Simons [41] and by Schiemenz [44].

General Procedure for the Benzylation of Triarylphosphines. A weighed quantity of the triarylphosphine was added to a round-bottom flask equipped with a magnetic stirring bar and a reflex condenser. Benzene (70 ml for 5 g of the triarylphosphine) was then added and stirring was begun. Once all the phosphine had dissolved, the solution was set up for reflux. One equivalent of benzyl bromide was added dropwise at reflux. The reaction mixture was allowed to reflux for 24 h. The white precipitate that formed was collected by filtration and recrystallized from ethyl acetate–ethanol (95%) (5 : 1).

Benzyl(2 - N,N *- dimethylaminophenyl)diphenylphosphonium Bromide* **(6).** From 5.0 g (1.6×10^{-2} mol) of (2-*N,N*-dimethylaminophenyl)diphenylphosphine **(1)**, 70 mL of benzene, and 2.0 mL of benzyl bromide was obtained 7.75 g (99.2%) of the salt, mp 278–279°C (decomp.); results by UV ($CHCl_3$), λ_{max} = 244 (ε = 6,400), λ = 263 (ε = 4100), λ = 269 (ε = 4000), λ = 277 (ε = 3300); by IR ($CHCl_3$), 660 cm^{-1} (R-P^+Ar_3), 1435 cm^{-1} (P-Ph); by ^1H NMR ($CDCl_3$), δ = 8.20–6.70 (m, 19H), 5.10 (d, 2H), 2.07 (s, 6H); by ^{31}P NMR ($CDCl_3$), δ = 19.74 (s, IP) (decoupled); by ^{13}C NMR ($CDCl_3$), δ = 106.34 (d, P-CH_2—), 45.91 (N-CH_3).

Analysis, calculated for $C_{27}H_{27}NPBr$, C, 68.06; H, 5.72; N, 2.94; P, 6.50; Br, 16.77; found, C, 67.96; H, 5.76; N, 2.82; P, 6.54; Br, 16.66.

Benzylbis(2 - N,N *- dimethylaminophenyl)phenylphosphonium Bromide* **(8).** From 6.60 g (1.9×10^{-2} mol) of bis(2-*N,N*-dimethylaminophenyl)-phenylphosphine **(3)**, 100 mL of benzene and 2.3 mL of benzyl bromide was obtained 9.0 g (92%) of the salt, mp 254–257°C (decomp.); results by UV ($CHCl_3$), λ_{max} = 245 (ε = 7150), λ = 263 (ε = 4450), λ = 271 (ε = 3900), λ = 276 (ε = 3400); by IR ($CHCl_3$), 690 cm^{-1} (R-P^+Ar_3), 1435 cm^{-1} (P-Ph), 1475 cm^{-1}; by ^1H NMR ($CDCl_3$), δ = 8.18–6.42 (m, 18H), 4.68 (d, 2H), 2.02 (s, 12H); by ^{31}P NMR ($CDCl_3$), δ = 17.87 (s, IP) (decoupled); by ^{13}C NMR ($CDCl_3$), δ = 108.07 (d, P-CH_2—), 46.04 (N-CH_3).

Analysis, calculated for $C_{29}H_{32}N_2PBr$, C, 67.05; H, 6.21; N, 5.39; P, 5.96; Br, 15.38; found, C, 67.41; H, 6.02; N, 4.95; P, 5.76; Br, 15.20.

Benzyl(4 - N,N *- dimethylaminophenyl)diphenylphosphonium Bromide* **(7).** From 6.2 g (2.0×10^{-2} mol) of (4-*N,N*-dimethylaminophenyl)diphenylphosphine **(2)**, 100 mL of benzene and 2.4 mL of benzyl bromide was obtained 9.6 g (99.5%) of the salt, mp 222–226°C; results by UV ($CHCl_3$), λ = 243 (ε = 4300), λ_{max} = 310 (ε = 22,000); by IR ($CHCl_3$), 680 cm^{-1} (R-P^+Ar_3), 1105 cm^{-1} (P-Ar_3), 1435 cm^{-1} (P-Ar_3), 1705 cm^{-1} (P=C?); by ^1H NMR ($CDCl_3$), δ = 7.76–6.64 (m, 19H), 4.90 (d, 2H), 3.02 (s, 6H); by ^{31}P NMR ($CDCl_3$), δ = 22.32 (s) (decoupled); by ^{13}C NMR ($CDCl_3$), δ = 112.38 (d, P-CH_2—), 40.05 (N-CH_3).

Analysis, calculated for $C_{27}H_{27}NPBr$, C, 68.06; H, 5.72; N, 2.94; P, 6.50; Br, 16.77; found, C, 68.17; H, 5.75; N, 2.83; P, 6.39; Br, 16.97.

Benzylbis(4 - N,N - dimethylaminophenyl)phenylphosphonium Bromide **(9).** From 7.8 g (2.3×10^{-2} mol) of bis-(4-*N,N*-dimethylaminophenyl)-phenylphosphine **(4)**, 100 mL of benzene and 2.7 mL of benzyl bromide was obtained 11.0 g (91.3%) of the salt, mp 270°C (decomp.); results by UV ($CHCl_3$), $\lambda = 244$ ($\varepsilon = 4600$), $\lambda_{max} = 313$ ($\varepsilon = 39{,}300$); by IR ($CHCl_3$), 690 cm^{-1} (R-P^+Ar_3), 1105 cm^{-1} (P-Ar_3), 1375 cm^{-1}, 1435 cm^{-1} (P-Ar_3); by ^1H NMR ($CDCl_3$), δ = 7.65–6.62 (m, 18H), 4.47 (d, 2H), 2.98 (s, 12H); by ^{31}P NMR ($CDCl_3$), δ = 20.52 (s, 1P) (decoupled); by ^{13}C NMR ($CDCl_3$), δ = 112.49 (d, P-CH_2—), 40.03 (s, N-CH_3).

Analysis, calculated for $C_{29}H_{32}N_2PBr$, C, 67.05; H, 6.21; N, 5.39; P, 5.96; Br, 15.38; found, C, 66.54; H, 6.77; N, 5.31; P, 5.74; Br, 15.10.

Kinetics Procedures

The kinetics runs were carried out in a Precision Scientific bath (No. 66580) with water as the bath medium. The water surface was covered with polystyrene foam packing material to help prevent evaporation and provide insulation. Time was recorded by use of a Precision Scientific timer (No. 69235). Cooling was provided by use of a Lauda cooling unit (No. IC-6). A Corning pH meter (No. 125) was used to obtain pH measurements.

General Procedure for the Decomposition of Benzyltriarylphosphonium Bromides. The solvent, 50 v/v% of distilled water–1,4-dioxane, was prepared as follows: A 50-mL pipet was used to deliver three 50-mL portions of 0.8000 ± 0.0002 *M* aqueous potassium bromide into a 1000-mL volumetric flask. The same pipet, after being rinsed and dried, was used to transfer three 50-mL portions of 1,4-dioxane, freshly distilled, to the same volumetric flask. The heat of mixing being positive, the solution was cooled to room temperature in a water bath. This solution was then transferred into a plastic squeeze bottle. This was used to transfer a weighed quantity of phosphonium salt (1–2 mmol) quantitatively to a 100-mL volumetric flask, which was then diluted to the mark. The solution was transferred to a 250-mL Erlenmeyer flask equipped with a 24/40 ⧩ joint. The flask was stoppered with a 24/40 ⧩ stopper fitted with a teflon sleeve. This flask was then placed in the constant temperature bath at least 2 h prior to use.

A quantity of standardized aqueous sodium hydroxide exactly equivalent to the quantity of the phosphonium salt was dispensed from a 5-mL class A microburet into a 6-dram vial. The vial was immediately closed with a tightly fitting screw cap. This was placed in the bath at least 2 h prior to use.

The mixing of the base and phosphonium salt solutions was accomplished by use of a 9-in. disposable pipet and a rubber pipet bulb. The base solution was withdrawn from the vial via the pipet and directly added to the phosphonium salt solution. This point is taken as time = zero. The stoppered Erlenmeyer flask was vigorously shaken 20 times. Some of the solution was then withdrawn via the pipet and transferred to the base vial in order to rinse it. This rinse was then returned to the flask and it was shaken another 20 times. The rinsing procedure was repeated two more times.

Class A volumetric pipets (10 mL) were used to transfer aliquots of the reaction mixture to 100-mL beakers containing 50–60 mL of distilled water as a quench. The time at which a particular aliquot was quenched was taken to be the average of the time at which the aliquot started to flow into the quenching solution and the time at which it stopped flowing. The quench solution was then titrated with 0.1000 *M* hydrochloric acid dispensed from a 5-mL class A microburet. The titration was followed by means of a pH meter. End points were determined by calculating ($\Delta^2pH/\Delta mL^2$) [46].

General Procedure for the Benzylation of Triarylphosphines. A weighed quantity of phosphine (1–2 mmol) was added to a 100-mL class A volumetric flask and diluted to the mark with chloroform (distilled under argon and degassed by bubbling argon through it for 1 h. A 50-mL class A pipet was used to transfer 50 mL of this solution to a 250-mL Erlenmeyer flask, equipped with a stopper having a teflon sleeve. The flask had previously been flushed with argon. The remaining 50 mL of solution was transferred in a similar manner to another 250-mL ⧩ Erlenmeyer flask (flushed with argon) and stoppered. These flasks were allowed to equilibrate in the constant temperature bath for 2 h prior to use.

Two 6-dram vials of 1 equiv each of a 1.000 *M* benzyl bromide–chloroform solution (under an argon blanket) were also placed in the bath to equilibrate for 2 h prior to use.

The mixing of the two solutions was performed as in the decomposition procedure.

Aliquots of 2 mL were added to a 100-mL beaker containing 20 mL of degassed, distilled water as a quench solution. The quench solution was then cooled and the resulting two-phase system was titrated with a 0.0100 *M* aqueous silver nitrate solution dispensed from a class A microburet using 3 drops of 5% aqueous potassium chromate as indicator (Mohr titration for bromide ion).

Study of the Decomposition of Benzyl(2-N,N-dimethylaminophenyl)diphenylphosphonium Bromide (6) in Alkaline Solution. A weighed quantity of phosphonium salt (1.5–2.0 mmol) was transferred to a 100-mL class A volumetric flask and diluted to the mark with 50 v/v% aqueous 1,4-dioxane (0.4000 *M* KBr). This was transferred to a 250-mL ⧩ 19/22 round-bottom flask equipped with a magnetic stirring bar. To this was added 1 equiv of 1.0000 *M* sodium hydroxide. The apparatus was set up to reflux for 3.5 h. After reflux, the solution was allowed to cool and a 10.0-mL aliquot (dispensed from a 10-

mL class A volumetric pipet) was taken and quenched in a beaker containing 50 mL of distilled water. The quench was then titrated with 0.0200 *M* aqueous hydrochloric acid.

The remainder of the reaction mixture was added to a 125-mL separatory funnel together with 50 mL of hexane. A white precipitate formed and remained with the aqueous layer. The extraction was repeated with another 50 mL of hexane. The clear hexane layers were combined and examined by gas chromatography. The precipitate was filtered from the aqueous layer and dried; mp 194–195°C, yield = 96%. The mp (also in admixture) was identical with that of an authentic sample [45] of benzyldiphenylphosphine oxide. Proton NMR and IR spectra of the two samples were identical.

Study of the Decomposition of Benzylbis(2-N,N-dimethylaminophenyl)phenylphosphonium Bromide **(8)** *in Alkaline Solution.* A weighed quantity of phosphonium salt (1.5–2.0 mmol) was transferred to a 100-mL class A volumetric flask and diluted to the mark with 50 v/v% aqueous 1,4-dioxane (0.4000 *M* KBr). This was transferred to a 250-mL ℑ 19/22 round-bottom flask equipped with a magnetic stirring bar. To this was added 1 equiv of 1.0000 *M* aqueous sodium hydroxide. The apparatus was set up to reflux for 16.5 h. After refluxing, the solution was allowed to cool and a 10.0-mL aliquot was taken and titrated with 0.0200 *M* aqueous hydrochloric acid.

The remainder of the reaction mixture was treated as described in the decomposition study of benzyl(2-*N*,*N*-dimethylaminophenyl)diphenylphosphonium bromide **(6)**.

The kinetics data for the alkylation reactions and for the alkaline decomposition reactions were treated as described previously [1,5,7,8,11, 14,20,28,31,32]. The calculated values of the various rate constants are given in Table 1 and in the text. The detailed data are available [47].

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