Additional Evidence of a New Type of Anchimeric Assistance in Quaternization Reactions of Phosphines and Arsines

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Rate data for the reactions of aryldiethylphosphines with ethyl iodide in acetone solution, of triarylphosphines with benzyl chloride in benzene–methanol (3:2) solution, and of triarylarsines with benzyl bromide in chloroform solution are presented. A comparison with literature data reveals that rate and activation parameter profiles are distinctly different for anisyldialkylphosphines and anisyldialkylamines in reactions with alkyl halides, and this supports the concept of an important contribution to the stabilization of the transition state caused by overlap of a pair of 2p electrons of the oxygen of an ortho methoxy group with an empty 3d (or hybrid) orbital of phosphorus. A similar effect shows up in the NMR spectra of the quaternary phosphonium salts. The effects of substituents other than methoxy in the reactions of triarylphosphines with benzyl chloride have been evaluated in terms of the geometry of the transition state, the HSAB principle, and ordinary substituent and steric effects. The fact that the presence of a ferrocenyl group has a larger effect in the retardation of the rate of alkaline cleavage of a ferrocenylphosphonium salt than it does in the acceleration of the rate of displacement of a ferrocenylphosphine on an alkyl halide provides additional evidence that the transition state for the latter type of reaction lies closer to the reagents than to the products along the reaction coordinate of the energy profile diagram. The greater degree of anchimeric assistance observed in the reactions of *o*-anisylarsines with alkyl halides than in the reactions of *o*-anisylphosphines with alkyl halides, even though the latter reactions are fundamentally much faster, is interpreted in terms of the principle that increasing electron demand results in increasing electron supply when an anchimeric assistance effect is operative. NMR spectral data and equilibrium considerations are also discussed with respect to the quaternary arsonium salts formed in the alkylation reactions.

Rate data for the quaternization reactions of various triarylphosphines with benzyl chloride, benzyl bromide, and *n*-butyl chloride have been presented in previous papers.[1,2] Two particularly striking effects were noted. (1) The presence of an *o*-methoxy group in the phosphine causes a marked acceleration of the reaction. (2) The ratio of the rates of reaction of a given triarylphosphine with benzyl chloride and *n*-butyl chloride is less than 20, probably the smallest such ratio ever found in SN2 reactions of these halides. An explanation of these effects was 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 reactions lies much closer to the reagents than to the products along the reaction coordinate of the energy profile diagram. We now wish to present new data with respect to substituent and structural effects and to evaluate these data in terms of the concepts cited above.

Since triarylamines (including tris-*o*-anisylamine) do not undergo quaternization reactions with *n*-butyl chloride, benzyl chloride, and benzyl bromide (at least under the reaction conditions employed in our previous[1,2] kinetics studies), we were unable in our previous papers to make a direct comparison between the phosphorus and nitrogen systems. (It would be anticipated that the postulated 2p–3d overlap would not occur in the amine reactions.) Therefore, we have now carried out kinetics studies of the reactions of selected aryldiethylphosphines with ethyl iodide in acetone solution. We selected this system for two reasons. (1) Henderson and Buckler[3] have developed a convenient procedure for studying the kinetics of the reaction of the parent phosphine, phenyldiethylphosphine, with ethyl iodide, and they consider this to be a "normal" system, based on several criteria (correlation of data by means of the Taft–Hammett equation, a reasonable reactivity–solvent polarity profile, etc.). (2) Evans, Watson, and Williams[4] have reported rate data for the reactions of dialkylanilines with alkyl halides which can be used for purposes of comparison. Our data for the reactions of aryldiethylphosphines with ethyl iodide in acetone solution are presented in Table I. It is clear that the new data on the phosphine reactions parallel the results presented previously.[1,2] The relative rates of reaction of *o*-anisyldiethylphosphine, *p*-anisyldiethylphosphine, phenyldiethylphosphine, and *m*-anisyldiethylphosphine with ethyl iodide in acetone solution at 35.0 °C are 6.96, 1.76, 1.00, and 0.91, respectively. By way of contrast, the relative rates of reaction of *o*-methoxydimethylaniline, *p*-methoxydimethylaniline, and dimethylaniline with methyl iodide in methanol solution at 35.0 °C are 1.88, 4.37, and 1.00, respectively.[4] These differences in reactivity profiles are readily explained in terms of overlap of the 2p electrons of the *o*-methoxy group with an empty 3d orbital (or hybrid orbital) of phosphorus in the transition state of the reaction of *o*-anisyldiethylphosphine with ethyl iodide, whereas there is no readily available d orbital in the nitrogen system to provide similar stabilization of the transition state.

Chock and Halpern[5] have suggested that a highly polar transition state, one closely resembling the product, is formed in the "oxidative addition" of iridium phosphine complexes of the type *trans*-[IrCl(CO)(PMe$_2$Ar)$_2$] with methyl iodide. Therefore, the degree of anchimeric assistance provided by an *o*-anisyl group in this system should be much larger than that in our system, the transition state of which is presumed to lie close to the reagents along the reaction coordinate of the energy profile diagram. The data of Miller and Shaw[6] illustrate this point nicely, the *o*-anisyl complex being 78 times more reactive than the *p*-anisyl complex. The presumed transition state for the reaction of the *o*-anisyl complex with methyl iodide is shown in Figure 1.

We speculated in our previous paper[1] that the transition state for the reaction of an *o*-anisylphosphine with an alkyl halide might be of the type depicted in Figure 2. As an additional test of this hypothesis, we have now investigated the effects of other substituents on the reactions of triarylphosphines with benzyl chloride in benzene–methanol (3:2) solution. The results are summarized in Table II.

The effects of a methyl substituent are unexceptional. A methyl group in the para position is mildly electron donating by an inductive effect. This causes a small increase in the nucleophilicity of the phosphine and consequently a small increase in the rate of reaction. A methyl group in the ortho position obviously cannot enter into any kind of a direct bonding interaction with phosphorus in the transition state. The fact that the relative rate of the *o*-tolyl compound is but

Table I. Rate Data for Reactions of Aryldiethylphosphines with Ethyl Iodide in Acetone Solution

Registry no.	Phosphine	Temp, °C[a]	k_2, l. mol^{-1} h^{-1} [b]	E_a	$\Delta S^\ddagger$ (35.0 °C)
1605-53-4	Diethylphenyl	25.0	0.83 ±0.00		
		35.0	1.81 ±0.00	13.5	−31.8
		45.0	3.43 ±0.00		
58325-38-5	*o*-Anisyldiethyl	25.0	5.82 ±0.25		
		35.0	12.60 ±0.25	14.0	−26.2
		45.0	25.70 ±0.35		
58325-39-6	*m*-Anisyldiethyl	25.0	0.82 ±0.01		
		35.0	1.65 ±0.06	13.0	−33.6
		45.0	3.34 ±0.03		
17310-20-2	*p*-Anisyldiethyl	25.0	1.51 ±0.01		
		35.0	3.19 ±0.03	13.3	−31.2
		45.0	5.96 ±0.10		

[a] Maintained at ±0.1 °C. [b] Average deviation based on at least four experimental results.

Table II. Rate Constants for Reactions of Triarylphosphines with Benzyl Chloride in Benzene–Methanol (3:2) at 31.0 ± 0.1 °C

Registry no.	Phosphine	$k_2 \times 10^2$, l. mol^{-1} h^{-1} [a]	Rel rate
603-35-0	Triphenyl	7.22[8] ± 0.13	1.00
5931-53-3	*o*-Tolyldiphenyl	2.17 ± 0.08	0.30
1031-93-2	*p*-Tolyldiphenyl	9.44 ± 0.26	1.31
13175-76-3	*o*-(Methoxymethyl)phenyldiphenyl	2.50 ± 0.16	0.35
35542-35-9	*p*-(Methoxymethyl)phenyldiphenyl	6.50 ± 0.19	0.90
14791-94-7	*o*-Thiomethoxyphenyldiphenyl	8.32 ± 0.37	1.15
35542-36-0	*p*-Thiomethoxyphenyldiphenyl	8.66 ± 0.25	1.20
35612-21-6	*o*-(Thiomethoxymethyl)phenyldiphenyl	2.04 ± 0.13	0.28
12098-17-8	Ferrocenyldiphenyl	20.1 ± 1.4	2.78
12278-69-2	Diferrocenylphenyl	24.1 ± 0.7	3.34

[a] Average deviation based on four experimental results.

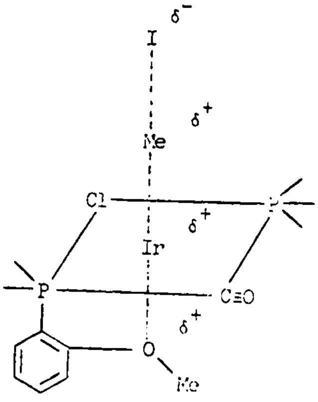

Figure 1. Proposed transition state for the reaction of *trans*-$[IrCl(CO)(o\text{-}anisylPMe_2)_2]$ with methyl iodide.

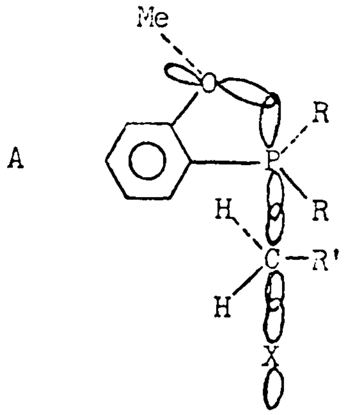

Figure 2. A possible transition state for the reaction of an *o*-anisylphosphine with an alkyl halide. Other geometries which would permit 2p–3d overlap are also conceivable.

0.30 indicates that an unfavorable steric compression in the transition state has a larger influence than the small, favorable inductive effect of the substituent.

The effect of a methoxy substituent has been discussed in detail previously.[1] The fact that the presence of an *o*-methoxymethyl substituent causes a decrease in the relative rate (0.35) can be understood in terms of the transition state depicted in Figure 2. The spatial requirements of the extra methylene group forces ring A down and to the right (in terms of Figure 2) so that it crowds the methylene group of $R'CH_2X$ and also causes more interference between R and R′ groups. Thus, this unfavorable steric effect in the transition state becomes more important than the otherwise favorable 2p–3d overlap effect, and the relative rate of reaction is lowered. The observation that the presence of a *p*-methoxymethyl group causes the relative rate to be slightly less than 1.00 reflects the fact that the methoxymethyl substituent is mildly electron withdrawing in nature, thus decreasing slightly the nucleophilicity of the phosphine.

The HSAB principle[7] can be invoked to explain why the presence of an *o*-MeS group has less ability to promote the rate of reaction than the presence of an *o*-MeO group. The phosphorus atom of the developing phosphonium cation is a hard acid center, and therefore overlap is more effective with the hard base center, OMe, than with the relatively soft base center, SMe. Thus, the relative rate for the *o*-methoxy system is 7.42,[1,2] while that for the *o*-thiomethoxy system is but 1.15. Also, the relatively large size of the *o*-SMe group probably causes the same unfavorable steric effect in the transition state as described previously for the *o*-methoxymethyl system, but to a smaller degree. The *p*-SMe group is mildly electron donating, and its presence therefore causes the relative rate of

Table III. NMR Absorption Data Taken in $CDCl_3$ Solution for the Hydrogen Atoms of the Methylene Group Directly Bonded to Phosphorus in the Phosphonium Salts

Registry no.	Phosphonium cation	Anion	δ, ppm, CH_2	J_{PH}, Hz
1100-88-5	Triphenylbenzyl	Cl^-	5.42, d	15
14479-51-7	*o*-Tolyldiphenylbenzyl	Cl^-	5.32, d	15
13432-86-5	*p*-Tolyldiphenylbenzyl	Cl^-	5.64, d	15
58325-40-9	*o*-Thiomethoxyphenyldiphenylbenzyl	Cl^-	5.68, d	15
58325-41-0	*p*-Thiomethoxyphenyldiphenylbenzyl	Cl^-	5.51, d	15
58325-42-1	*o*-(Methoxymethyl)phenyldiphenylbenzyl	Cl^-	5.58, d	15
58325-43-2	*p*-(Methoxymethyl)phenyldiphenylbenzyl	Cl^-	5.67, d	14.5
58325-44-3	*o*-(Thiomethoxymethyl)phenyldiphenylbenzyl	Cl^-	5.76, d	14.5
58384-30-8	Ferrocenyldiphenylbenzyl	Cl^-	5.02, d	14
3040-69-5	Phenyltriethyl	I^-	2.93, d of q	13
58325-45-4	*o*-Anisyltriethyl	I^-	2.82, d of q	13
58325-46-5	*m*-Anisyltriethyl	I^-	2.95, d of q	13
58325-47-6	*p*-Anisyltriethyl	I^-	2.87, d of q	13

its reaction system to be 1.20. The presence of an *o*-CH_2SMe group, which combines an unfavorable steric effect with a relatively unfavorable HSAB effect, causes the relative rate to drop to 0.28.

Another (although not mutually exclusive with the HSAB concept) explanation for the lower reactivity of the *o*-thiomethoxyphenylphosphine as against the *o*-methoxyphenylphosphine lies in the strength of the partial bond formed in the neighboring group interaction of the ortho substituent with the central phosphorus atom. The energy of the phosphorus–oxygen bond is substantially greater than that of the phosphorus–sulfur bond.[9]

As in the reactions described previously,[1,2] the $\Delta S^{\ddagger}$ values for the reactions of aryldiethylphosphines with ethyl iodide (see Table I) are of greater importance in determining the relative rates of reaction than are the E_a values. An explanation for this effect was offered in a previous paper[1] and need not be repeated here. Although Evans, Watson, and Williams[4] did not calculate values of $\Delta S^{\ddagger}$ for the reactions of the various dimethylanilines with methyl iodide in methanol solution, their data permit such calculations to be made. For the reaction of *o*-methoxydimethylaniline, $E_a = 15.9$ and $\Delta S^{\ddagger} = -25.5$; for the *p*-methoxydimethylaniline reaction, $E_a = 14.3$ and $\Delta S^{\ddagger} = -29.0$. In this series, it is significant that the greater rate of the *p*-methoxy compound is attributable to a lower value of E_a.

The rate acceleration caused by the presence of a ferrocenyl group is relatively small. As shown in Table II, the relative rate of reaction of ferrocenyldiphenylphosphine with benzyl chloride is 2.78, while that of diferrocenylphenylphosphine is 3.34. On the other hand, the relative rates of reaction of benzyltriphenylphosphonium iodide, benzylferrocenyldiphenylphosphonium iodide, and benzyldiferrocenylphenylphosphonium iodide with sodium hydroxide in dimethoxyethane–water (1:1) at 62.2 °C are 163, 2.75, and 1.00, respectively.[10] These results support the concept that the transition state for the SN2 reaction of a tertiary phosphine with an alkyl halide lies closer to the reagents than to the products in the energy profile diagram. Thus, overlap of the ha_g molecular orbital[11] of a ferrocenyl group with a 3d (or hybrid) orbital of phosphorus in the transition state is relatively slight. However, in the phosphonium salts, a significant degree of overlap between the filled molecular orbital of the ferrocenyl group with an empty 3d orbital of phosphorus exists, and this results in a significant degree of stabilization of a ferrocenylphosphonium ion, as is also true with α-ferrocenylcarbonium ions.[12–17] Therefore, the phosphorus atom of the ferrocenylphosphonium ion is relatively resistant to attack by the hydroxide ion (cf. our earlier papers[18,19] for the detailed mechanism of phosphonium hydroxide decomposition), and this accounts for the marked decrease in rate when a ferrocenyl group is one of the substituents bonded to the phosphorus atom. The fact that the presence of a second ferrocenyl group does not further affect to any marked extent the rate of either the SN2 reaction of a phosphine or the rate of attack of a hydroxide ion on a phosphonium cation is consistent with the type of interaction depicted in Figure 2, in which only one such group can engage in a direct overlap interaction.

Additional support for the concept of 2p–3d overlap can be gained by examination of the ^1H NMR spectra of the phosphonium salts formed in the SN2 reactions of the various phosphines with alkyl halides. For reasons cited in the previous paper,[1] the chemical shift of the methylene group directly bonded to phosphorus in the phosphonium salt represents a better probe of the overlap than the chemical shift of a substituent on an aryl group bonded to the phosphorus. An upfield shift of the methylene hydrogen atoms is expected when the electron density at phosphorus is increased owing to an overlap effect. This anticipated effect is visible only in the spectra of the phosphonium salts formed by reactions in which anchimeric assistance is in evidence, as shown by the data presented in Table III. Of course, the effects may also be attributable in part to magnetic anisotropy of the substituent groups, and therefore they may not represent clear proof of the postulated overlap.

Additional insight into the potential reactivity of triarylphosphines with alkyl halides can sometimes be obtained by examination of the ultraviolet spectra of the phosphines. Previously,[1] we reported that the uv spectrum of *o*-anisyldiphenylphosphine possesses an "extra" band at 284 nm, presumably attributable to intramolecular charge transfer absorption. This observation presaged the 2p–3d overlap in the transition states of its reactions with alkyl halides. No such extra value of λ_{max} has been found in the uv spectra of the *o*-tolyl-, *o*-methoxymethyl-, and *o*-thiomethoxymethyldiphenylphosphines, and this coincides with the absence of anchimeric assistance in their reactions with alkyl halides. On the other hand, the *o*-thiomethoxy compound does possess an extra uv absorption peak at 304.5 nm, which suggests that this group has the requisite geometry for p–d overlap. However, the rate data for the reaction of this compound with benzyl chloride (Table II) show but a small enhancement of SN2 reactivity. Apparently, the proper spatial arrangement is offset by the unfavorable HSAB effect (vide supra).

Our first observations of a new and unusual anchimeric assistance effect were made when we first studied the rates of the quaternization reactions of triarylarsines with benzyl bromide in chloroform solution.[20] The pertinent data are summarized in Table IV. For purposes of comparison, the specific rate constant for the reaction of triphenylphosphine with benzyl bromide at 31.0 °C is 803×10^{-2} l. mol^{-1} h^{-1}, as reported in the previous publication.[1] Thus, triphenylphos-

Table IV. Rate and Equilibrium Constants for Reactions of Triarylarsines with Benzyl Bromide in Chloroform Solution at 29.6 ± 0.1 °C

Registry no.	Arsine	$k_2 \times 10^2$, l. mol^{-1} h^{-1}	K_{eq}
603-32-7	Triphenyl	3.58 ± 0.02	70.5 ± 2.1
2896-10-8	Tris(*p*-tolyl)	15.5 ± 0.1	$1.5 \pm 0.1 \times 10^4$
2417-85-8	Tris(*o*-tolyl)	0.00[a]	
35569-46-1	Tris(*p*-anisyl)	22.2 ± 0.3	$9.0 \pm 0.6 \times 10^5$
21920-60-5	Tris(*o*-anisyl)[b]	319.5 ± 7.0	

[a] The reaction was too slow to permit measurement of the rate. A sensitive qualitative test[23] for the formation of benzyltris(*o*-tolyl)arsonium bromide was found to be faintly positive after 1 week of reaction. [b] The concentration of tris(*o*-anisyl)arsine at equilibrium is too small to be measured accurately; thus, no meaningful value of K_{eq} could be obtained. It is obviously distinctly larger than 9×10^5, the value reported for the tris(*p*-anisyl) reaction.

phine is approximately 220 times more reactive than triphenylarsine in the quaternization reaction, and this reflects the well-documented greater nucleophilicity of a phosphine as against a corresponding arsine.[21] Another important point of comparison is that tris(*o*-anisyl)phosphine is 1.59 times more reactive than triphenylphosphine toward benzyl bromide in chloroform solution at 31.0 °C.[1] From the data presented in Table IV, it is apparent that tris(*o*-anisyl)arsine is 89.3 times more reactive than triphenylarsine toward benzyl bromide in chloroform solution at 29.6 °C. Undoubtedly, one of the major influences here is based on a steric effect; there is more room for the nonparticipating methoxy groups about the larger arsenic atom. Another important effect is based on the principle that increasing electron demand results in increasing electron supply when an anchimeric assistance effect is operative.[22,23] We consider the results cited above to represent yet another substantial line of evidence in support of the postulated 2p–3d overlap in the transition states of the *o*-anisylphosphine–alkyl halide reactions and of 2p–4d overlap in the *o*-anisylarsine–alkyl halide reactions.

As anticipated on the basis of known electronic effects of the substituents, and also on the basis of analogy with the SN2 reactions of triarylphosphines with alkyl halides,[1,2] the presence of *p*-methyl and *p*-methoxy substituents on the arsine brought about a relatively small increase in the rate of reaction as against the triphenylarsine result. Also, on the basis of the obvious steric effect, the presence of *o*-methyl substituents caused the reaction to be too slow to permit measurement of the rate. Rate data for the reactions of tri-*p*-chlorophenylarsine and tri-*p*-bromophenylarsine with benzyl bromide could not be obtained. Nevertheless, some useful information about these reactions was obtained. When these arsines were mixed with benzyl bromide in chloroform, they gave a positive qualitative test[24] for the arsonium ion after the solutions had been allowed to stand for 1 week at room temperature. However, when these solutions were warmed to 50–55 °C for a few minutes and tested again for the presence of the arsonium cation, a negative result was obtained. A positive test again resulted when the solution had been allowed to stand at room temperature for 1 week. Evidence for reversal of quaternary salt formation has also been reported by a number of other workers.[25,26] Consequently, we have determined the equilibrium constants for several of the reactions of triarylarsines with benzyl bromide, and these are given in Table IV. The order of the K_{eq} values parallels that of the specific rate constants.

The rates of the reactions of tris(*o*-anisyl)arsine and tris(*p*-anisyl)arsine with benzyl bromide in chloroform solution were also measured at 25.0 and 35.0 °C. The values for the ortho isomer were 233.9×10^{-2} l. mol^{-1} h^{-1} (25.0 °C) and 446.3×10^{-2} l. mol^{-1} h^{-1} (35.0 °C). The values for the para isomer were 15.5×10^{-2} l. mol^{-1} h^{-1} (25.0 °C) and 29.59×10^{-2} l. mol^{-1} h^{-1} (35.0 °C). From these data we could calculate $\Delta H^{\ddagger}$ values of 11.8 and 11.7 kcal mol^{-1} for the reactions of the ortho and para compounds, respectively, and $\Delta S^{\ddagger}$ values of −35 and −41 eu, respectively. As in the tertiary phosphine–alkyl halide reactions, the value of $\Delta S^{\ddagger}$ controls the rate more than the value of $\Delta H^{\ddagger}$ (or E_a). The proposed 2p–4d interaction in the *o*-anisyl reaction decreases the need for external solvation, and this leads to a markedly less negative value of $\Delta S^{\ddagger}$ and a faster rate of reaction. A more complete explanation of this effect has been given in our previous publication.[1]

The chemical shift effect cited previously is also apparent in the NMR spectra of the arsonium salts. The δ values found for the methylene protons in deuteriochloroform solution are 5.38 for benzyltriphenylarsonium bromide, 5.22 for benzyltris(*p*-tolyl)arsonium bromide, 5.15 for benzyltris(*p*-anisyl)arsonium bromide, and 4.70 for benzyltris(*o*-anisyl)arsonium bromide. Again, the apparent increased electron density at arsenic in the *o*-anisyl salt, presumably caused by 2p–4d overlap, brings about a pronounced upfield shift in the absorption of the methylene protons.

Experimental Section

The general statements with regard to physical constants, spectral data, analyses, the preparation of triarylphosphines, and the procedures used in the kinetics studies are the same as those given in the previous paper.[1] The physical constants and spectral data for the tertiary phosphines are presented in Table V, and the properties of the quaternary phosphonium halides are given in Table VI.

Preparation of Triarylphosphines by the Grignard Reaction. The procedure in each case was essentially the same as that reported for the preparation of *o*-anisyldiphenylphosphine in the previous paper.[1]

Preparation of *o*-(Methoxymethyl)phenyldiphenylphosphine. To a stirred mixture of 182 ml of a 2.25 M (0.41 mol) solution of *n*-butyllithium in hexane (Alfa Inorganics) and 30 ml of anhydrous diethyl ether contained in a three-necked flask under argon at 0 °C was added a solution of 82.4 g (0.41 mol) of *o*-bromobenzyl methyl ether[35] in 175 ml of anhydrous diethyl ether over a 30-min period. After the mixture had been stirred for an additional 1 h, a solution of 90.6 g (0.41 mol) of chlorodiphenylphosphine in 90 ml of anhydrous diethyl ether was added over 30 min at 0 °C. The mixture was allowed to warm to room temperature, and then it was refluxed for 1 h. Hydrolysis at 0 °C with 5% hydrochloric acid followed, and the mixture was extracted with diethyl ether. The ether layer was washed with water until neutral to litmus paper and subsequently concentrated with the aid of a rotary evaporator. The residue was dissolved in acetone at room temperature and then refrigerated at −15 °C; *o*-(methoxymethyl)phenyldiphenylphosphine, mp 94.0–95.5 °C, crystallized from the acetone solution and weighed 50.9 g (41%).

Preparation of Other Triarylphosphines by Use of a Lithium Reagent. *p*-Bromobenzyl methyl ether was prepared by the method of Supniewski and Adams[36] and converted to *p*-(methoxymethyl)phenyldiphenylphosphine by essentially the same method as that described for the ortho isomer, with the exception that the product was purified by vacuum distillation. *o*-Bromobenzyl methyl sulfide was prepared by the method of Breslow, Garratt, Kaplan, and La-Follette[37] and converted to *o*-(thiomethoxymethyl)phenyldiphenylphosphine by the method described above.

Preparation of *m*-Anisyldichlorophosphine. To the Grignard reagent prepared in a 500-ml three-necked flask under nitrogen from 4.8 g (0.2 g-atom) of magnesium turnings, 30 ml of dry tetrahydrofuran, and a solution of 37.4 g (0.2 mol) of *m*-bromoanisole in 150 ml of dry tetrahydrofuran was added slowly a solution of 27.2 g (0.2 mol) of zinc chloride[38] in 180 ml of dry tetrahydrofuran at 0 to −5 °C, with stirring. The organozinc halide reagent was transferred under nitrogen to a 500-ml dropping funnel.

A solution of 50 ml (0.57 mol) of phosphorus trichloride in 100 ml of dry tetrahydrofuran was prepared in a 1000-ml three-necked flask, and the contents were kept in the vicinity of −20 °C.[39] The organozinc halide reagent was added slowly to the chilled solution under nitrogen with stirring. The reaction mixture was then refluxed for 4 h, cooled

Table V. Physical Constants and Spectral Data for Tertiary Phosphines

Phosphine	Reagents (solvent)	Mp or bp, °C	Reported mp or bp, °C	Cryst solvent (% yield)	NMR, δ ($CDCl_3$)
o-Tolyldiphenyl	*o*-TolylMgCl + Ph_2PCl (THF)	69–71	73[27]	MeOH (72)	3.74 s, 6.97–7.64 m
p-Tolyldiphenyl	*p*-TolylMgBr + Ph_2PCl (THF)	65.2–66.8	66.5[28]	EtOH (55)	2.28 s, 7.01–7.30 m
o-(Methoxymethyl)phenyldiphenyl	*o*-$MeOCH_2C_6H_4Li$ + Ph_2PCl (hexane–ether)	94.0–95.5[a]		Acetone (41)	3.22 s, 4.61 s, 6.78–7.30 m
p-(Methoxymethyl)phenyldiphenyl	*p*-$MeOCH_2C_6H_4Li$ + Ph_2PCl (hexane–ether)	157–160 (0.05 mm)		(40)	3.26 s, 4.30 s, 7.04–7.48 m
o-Thiomethoxyphenyldiphenyl	*o*-$MeSC_6H_4MgBr$ + Ph_2PCl (THF)	104.5–105.2	101–102[29]	EtOH (36)	2.46 s, 6.97–7.67 m
p-Thiomethoxyphenyldiphenyl	*p*-$MeSC_6H_4MgBr$ + Ph_2PCl (THF)	109.0–110.5[b]		MeOH (40)	2.44 s, 7.41–7.67 m
o-(Thiomethoxymethyl)phenyldiphenyl	*o*-$MeSCH_2C_6H_4Li$ + Ph_2PCl (hexane–ether)	155–163 (0.05 mm)[c]		(33)	1.86 s, 3.91 s, 6.87–7.41 m
Ferrocenyldiphenyl	Ferrocene + Ph_2PCl (heptane, $AlCl_3$)	122–124	122–124[30,31]	EtOH (45)	4.04–4.50 m, 7.15–7.60 m
Diferrocenylphenyl	Ferrocene + $PhPCl_2$ (heptane, $AlCl_3$)	193–195	191–193[30,31]	Benzene–heptane	3.8–4.3 m, 7.1–7.6 m
Diethylphenyl	EtMgBr + $PhPCl_2$ (ether)	69–70 (0.18 mm)	65–67 (1 mm)[32]	(54)	0.98 d of t (J_{P-CH} = 15 Hz), 1.64 q, 7.1–7.75 m
o-Anisyldiethyl	EtMgBr + *o*-$MeOC_6H_4PCl_2$ (ether)	107–108 (0.9 mm)		(85)	1.0 d of t (J_{P-CH} = 14.4 Hz), 1.66 q, 3.75 s, 6.65–7.50 m
m-Anisyldiethyl	EtMgBr + *m*-$MeOC_6H_4PCl_2$ (ether)	101–102 (1.3 mm)		(78)	1.0 d of t (J_{P-CH} = 15 Hz), 1.66 q, 3.72 s, 6.70–7.46 m
p-Anisyldiethyl	EtMgBr + *p*-$MeOC_6H_4PCl_2$ (ether)	92–93 (0.5 mm)	108 (1.5)[33]	(57)	0.97 d of t (J_{P-CH} = 15 Hz), 1.64 q, 3.72 s, 6.75–7.05 m, 7.25–7.65 m

[a] Anal. Calcd for $C_{20}H_{19}OP$: C, 78.41; H, 6.25; P, 10.11; O, 5.22. Found: C, 78.36; H, 6.16; P, 10.00; O, 5.20. [b] Anal. Calcd for $C_{19}H_{17}PS$: C, 74.00; H, 5.56; P, 10.05. Found: C, 73.89; H, 5.51; P, 10.15. [c] Anal. Calcd for $C_{20}H_{19}PS$: C, 74.51; H, 5.94; P, 9.61. Found: C, 74.86; H, 5.96; P, 9.49.

to room temperature, and filtered. The light yellow filtrate was distilled to remove the solvent. The remaining liquid was fractionated under reduced pressure. The product was obtained as a colorless liquid, 18.2 g (44%), bp 76–78 °C (0.5 mm).

The ^1H NMR spectrum of this compound in deuteriochloroform showed a singlet at δ 3.70 ppm (3 H) and a multiplet at δ 6.65–7.62 ppm (4 H).

Synthesis of *m*-Anisyldiethylphosphine. To the Grignard reagent prepared in a three-necked flask under nitrogen from 9.6 g (0.4 g-atom) of magnesium turnings, 110 ml of anhydrous diethyl ether, and a solution of 44 g (0.4 mol) of ethyl bromide in 150 ml of anhydrous diethyl ether was added dropwise a solution of 17.8 g (0.085 mol) of *m*-anisyldichlorophosphine in 40 ml of anhydrous diethyl ether at −10 to −15 °C with stirring over a period of 0.5 h. The reaction mixture was refluxed for 1 h. It was then hydrolyzed at 0 °C with 110 ml of saturated ammonium chloride solution, and additional water was added to dissolve a white solid which had formed. The ether layer was separated from the aqueous solution and dried over anhydrous magnesium sulfate. Removal of the solvent by simple distillation left a faint-colored liquid, which was fractionated under reduced pressure, bp 101–102 °C (1.3 mm). The yield of the colorless liquid was 13 g (78%).

The ^1H NMR spectrum of this compound in deuteriochloroform showed a doublet of triplets centered at δ 1.0 ppm (6 H, J_{P-CH} = 15 Hz), a quartet coupled with the phosphorus centered at δ 1.66 ppm (4 H), a singlet at δ 3.72 ppm (3 H), and a multiplet at δ 6.70–7.46 ppm (4 H).

Other Aryldiethylphosphines. These were prepared in essentially the same manner as that described for *m*-anisyldiethylphosphine. *o*-Anisyldichlorophosphine was obtained in 60% yield as a colorless liquid: bp 124.6–125.0 °C (1.2 mm) [lit.[40] 88.5–89.0 °C (0.52 mm)]; NMR ($CDCl_3$) δ 3.78 (s, 3 H) and 6.70–8.05 (m, 4 H). *o*-Anisyldiethylphosphine was obtained in 85% yield: bp 107–108 °C (0.9 mm); NMR ($CDCl_3$) δ 1.0 (d of t, 6 H, J_{P-CH} = 14.4 Hz), 1.66 (q, 4 H, J_{P-CH} = 14.4 Hz), 3.75 (s, 3 H), and 6.67–7.50 (m, 4 H). *p*-Anisyldichlorophosphine was obtained in 52% yield, bp 103–104 °C (0.23 mm) [reported 150 °C (13 mm),[41] 140 °C (10 mm)[33]]; NMR ($CDCl_3$) δ 3.72 (s, 3 H), 6.8–7.1 (m, 2 H), 7.6–8.0 (m, 2 H). *p*-Anisyldiethylphosphine was obtained in 57% yield: bp 92–93 °C (0.5 mm) [reported 166–171 °C (40 mm),[41] 108 °C (1.5 mm)[33]]; NMR ($CDCl_3$) δ 0.97 (d of t, 6 H, J_{P-CH} = 15 Hz), 1.64 (q, 4 H, J_{P-CH} = 15 Hz), 3.72 (s, 3 H), 6.75–7.05 (m, 2 H), 7.25–7.65 (m, 2 H).

Preparation of Benzyltriarylphosphonium Chlorides. The same procedure as described in the previous paper[1] was used to prepare these salts.

Preparation of Aryltriethylphosphonium Iodides. These salts were isolated directly from the reaction solutions of the kinetics experiments by evaporation of the solvent under nitrogen.

Kinetics Procedure for Quaternization Reactions of Triarylphosphines with Benzyl Chloride. The procedure was identical with that described previously.[1] In the reactions with the ferrocenylphosphines and *o*-(thiomethoxymethyl)phenyldiphenylphosphine, the colored aliquots were titrated by use of an Aminco-Cotlove Automatic Chloride Titrator.

Kinetics Procedure for the Reactions of Aryldiethylphosphines with Ethyl Iodide in Acetone. The procedure of Henderson and Buckler[3] was followed. The titrations were carried out by the Volhard method.

Preparation of Triarylarsines. Triphenylarsine, mp 59–60 °C (reported[42] mp 61 °C), tri-*p*-anisylarsine, mp 156–158 °C (reported[43] mp 158 °C), and tri-*o*-anisylarsine, mp 201.5–203.0 °C (reported[44] mp 200 °C), were prepared by the Wurtz-type reaction described in "Organic Syntheses".[42] Tri-*p*-tolylarsine, mp 148–150 °C (reported[45] mp 146 °C), tri-*o*-tolylarsine, mp 110–112 °C (reported[46] 108–109 °C), tri-*p*-chlorophenylarsine, mp 113–114 °C, and tri-*p*-bromophenylarsine, mp 140–141 °C, were prepared by the diazonium salt procedure of Hanby and Waters.[47]

Anal. Calcd for $C_{18}H_{12}AsCl_3$: C, 52.78; H, 3.95; As, 18.29. Found: C, 53.14; H, 3.30; As, 18.32.

Anal. Calcd for $C_{18}H_{12}AsBr_3$: C, 40.20; H, 2.23; As, 13.97; Br, 44.60. Found: C, 39.78; H, 2.33; As, 14.00; Br, 44.69.

Analysis of Triarylarsines. An accurately weighed sample of the arsine (ca. 0.4 mmol) was dissolved in 10.00 ml of chloroform and titrated with a standardized 0.050 M solution of bromine in glacial acetic acid. The end point was determined by use of a pH meter equipped with glass and platinum electrodes. It was necessary to

Table VI. Properties of Quaternary Phosphonium Halides

Phosphonium cation	Anion	Cryst solvent	Mp, °C	Reported mp, °C	Anal.[a]	NMR, δ ($CDCl_3$)[b] (J, Hz)
o-Tolyldiphenylbenzyl	Cl^-	EtOH–AcOEt	280–283 dec	280–283 dec[34]	C, H, P, Cl[34]	2.17 s, 5.32 d ($J = 15$)
p-Tolyldiphenylbenzyl	Cl^-	EtOH–AcOEt	246–248 dec	246–248 dec[34]	C, H, P, Cl[34]	2.52 s, 5.64 d ($J = 15$)
o-(Methoxymethyl)phenyldiphenylbenzyl	Cl^-	$CHCl_3$–ether	252–254		P	2.98 s, 4.40 s, 5.58 d ($J = 15$)
p-(Methoxymethyl)phenyldiphenylbenzyl	Cl^-	$CHCl_3$–ether	214–217		P	3.60 s, 4.79 s, 5.67 d ($J = 14.5$)
o-Thiomethoxyphenyldiphenylbenzyl	Cl^-	$CHCl_3$–ether	240–243		P	2.37 s, 5.68 d ($J = 15$)
p-Thiomethoxyphenyldiphenylbenzyl	Cl^-	EtOH–AcOEt	220–222		P	2.64 s, 5.51 d ($J = 15$)
o-(Thiomethoxymethyl)phenyldiphenylbenzyl	Cl^-	$CHCl_3$–ether	234–236		P	1.80 s, 3.51 s, 5.76 d ($J = 14.5$)
Ferrocenyldiphenylbenzyl	Cl^-	EtOH–ether	178–179		C, H, Cl, P	5.02 d ($J = 14$)
Diferrocenylphenylbenzyl	Cl^-	EtOH–ether	205–206		C, H, Cl, Fe	
Phenyltriethyl	I^-	EtOH–AcOEt	141–142	140–141[3]		1.28 d of t ($J_{PH} = 18, J_{HH} = 7.5$), 2.93 d of q ($J_{PH} = 13, J_{HH} = 7.5$)
o-Anisyltriethyl	I^-	EtOH–AcOEt	193–194		C, H, I, P	4.1 s, 1.26 d of t ($J_{PH} = 18, J_{HH} = 7.5$), 2.82 d of q ($J_{PH} = 13, J_{HH} = 7.5$)
m-Anisyltriethyl	I^-	EtOH–AcOEt	154–155		C, H, I, P	4.0 s, 1.29 d of t ($J_{PH} = 18, J_{HH} = 7.5$), 2.95 d of q ($J_{PH} = 13, J_{HH} = 7.5$)
p-Anisyltriethyl	I^-	EtOH–AcOEt	140–141		C, H, I, P	3.92 s, 1.29 d of t ($J_{PH} = 18, J_{HH} = 7.5$), 2.87 d of q ($J_{PH} = 13, J_{HH} = 7.5$)

[a] Found values were within ±0.3% of calculated values. [b] δ (7.0–8.0, m) for aromatic protons not listed.

obtain a titration curve, millivolts being plotted against milliliters. This method was also used to check the purity of the arsines, the respective molecular weights being found to agree within ±2 units with the calculated values.

Kinetics Procedure for Reactions of Triarylarsines with Benzyl Bromide. Contained in an accurately tared 50-ml volumetric flask, an accurately weighed sample of benzyl bromide (approximately 0.09 mol) was diluted with spectral grade chloroform to within 1 cm of the mark. The flask was allowed to equilibrate in a constant-temperature bath for several hours and then filled to the mark with thermally equilibrated chloroform, mixed thoroughly, and replaced in the bath.

An accurately weighed sample of a triarylarsine (exactly one-tenth the mole quantity of the benzyl bromide) was weighed in a tared 50-ml Erlenmeyer flask. The arsine was dissolved in spectral grade chloroform, transferred to a 100-ml volumetric flask, diluted to a point 1 cm below the flask's neck, and allowed to equilibrate overnight in the constant-temperature bath.

A 5.00-ml sample of the benzyl bromide–chloroform solution was transferred to the flask containing the equilibrated arsine solution, diluted to the mark with thermally equilibrated chloroform, and mixed thoroughly. With the mark on the neck of the volumetric flask showing just above the water level, the volume within the flask was adjusted if necessary. Concentrations of both reactants were approximately 0.09 M.

A 5.00-ml pipet was used to transfer each 5.0-ml aliquot into a 50-ml beaker containing 5 ml of chloroform. The unreacted arsine was titrated with a standard solution of bromine (0.05 M) in glacial acetic acid as described previously.

All concentrations of tri-*o*-anisylarsine were approximately 0.045 M because of its low solubility.

The titer of the bromine–acetic acid solution changes slowly, necessitating daily standardizations against three samples of triphenylarsine.

Determination of Equilibrium Constants. A solution of 1.9287 g (1.1278 mmol) of benzyl bromide in chloroform was added to a 25-ml volumetric flask containing 1.13 mmol of the triarylphosphine (0.565 mmol in the case of tri-*o*-anisylarsine). After dilution to the mark with chloroform, the solution was allowed to stand at room temperature for 10 months. Then it was placed in a constant-temperature bath maintained at 29.63 °C for 2 weeks. Duplicate 5.00-ml aliquots of the solution were titrated for unreacted triarylarsine as described previously.

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Registry No.—Ethyl iodide, 75-03-6; benzyl chloride, 100-44-7; benzyl iodide, 100-39-0; *o*-bromobenzyl methyl ether, 52711-30-5; chlorodiphenylphosphine, 1079-66-9; *m*-anisyldichlorophosphine, 58325-48-7; *m*-bromoanisole, 2398-37-0; phosphorus trichloride, 7719-12-2; diethyl ether, 60-29-7; *o*-anisyldichlorophosphine, 58325-49-8; *p*-anisyldichlorophosphine, 19909-85-4; tri-*p*-chlorophenylarsine, 17314-57-7; tri-*p*-bromophenylarsine, 6306-93-0.

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Carbon-13 Nuclear Magnetic Resonance Spectroscopy in the Study of Conformational Effects among Cyclohexyl Phosphorus Compounds

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^{13}C NMR spectra were obtained for the cis and trans isomers resulting from situating each of the following functions at the 4 position of *tert*-butylcyclohexane: PH_2, PMe_2, PCl_2, $P(OMe)_2$, $PSMe_2$, $^+PMe_3I^-$. For the trans isomers, the ^{13}C spectra were consistent with diequatorial substitution. In the cis isomers, the trivalent functions occupied the normal axial position but the larger $PSMe_2$ and $^+PMe_3$ groups, as seen from chemical shift effects, caused considerable distortion of the ring, either through flattening about the 1,4-ring carbons or by adoption of a twist conformation. C–P coupling constants favor the former explanation. When $PSMe_2$ and $^+PMe_3$ are placed in the cis 4 position of methylcyclohexane, the ^{13}C NMR evidence suggests that they adopt the equatorial position and force methyl into the axial position. A minimum *A* value for these phosphorus functions derived from this information is 3.0 kcal/mol. The PMe_2 group has an *A* value similar to that for methyl, and the ^{13}C NMR spectrum for the 1,4 cis isomer is consistent with an approximately 1:1 mixture of equilibrating conformers. Among the trivalent functions, the three-bond ^{13}C–^{31}P coupling constant was found to be under strong steric control for the primary phosphines alone; the other functions showed only a small difference in $^3J_{PC}$ between the cis and trans isomers. The spectra of 24 cyclohexane derivatives were recorded during this study and interpreted by existing generalities.

^{13}C NMR spectroscopy is firmly established as a technique providing valuable information about conformational aspects of six-membered rings.[2,3a] We have now applied it in a systematic way to cyclohexanes containing various phosphorus functions and report our results in this paper.[4] We have done this first to test the validity of our *A* values for some trivalent functions, which we have recently determined by ^{31}P NMR spectroscopy,[5] and then to obtain qualitative information on some tetravalent phosphorus functions, which could not be determined by the ^{31}P approach used. Since the trivalent groups studied [PH_2, PCl_2, PMe_2, and $P(OMe)_2$] all had sizable *A* values (±0.2 kcal/mol of that for methyl,[7] 1.7), it might be expected that tetravalent functions would show even larger values, indeed possibly approaching that of *tert*-butyl. A precise value for this group is still lacking but the range 4–5 kcal/mol has been proposed.[7,8]

^{13}C Spectral Data and Assignments. All data for the 24 compounds studied are recorded in Table I. For measurements on cis, trans isomers (whose structures have been determined in previous work[5]), data were obtained on samples enriched in the pertinent form, in some cases as high as 95%. Assignments are easily made on the following lines: (1) C-1 and C-4 are of half the intensity of C-2,6 and C-3,5. C-1 is always a doublet through coupling to ^{31}P; C-4 shows no coupling. (2) Methyls on phosphorus are always the most upfield doublets. (3) Methyls on C-4 are the most shielded of the uncoupled carbons, and are of unit intensity. (4) *tert*-Butyl carbons are recognized from their intensities (weak quaternary signal, strong methyl signal) and near identity of position in both cis and trans forms. (5) Differentiation between C-2,6 and C-3,5 was based on a combination of shift and P–C coupling effects. For PH_2, the differentiation is easy; C-2,6 are well downfield (δ 36.0) of C-3,5 (27.4) since the former carbons feel a strong β effect due to phosphorus, while the latter carbons are not greatly shifted from the cyclohexane value (27.7). The same effect is seen for NH_2[9] (δ $C_{2,6}$ 37.7; δ $C_{3,5}$ 25.8). For all other phosphorus functions, the atoms replacing hydrogen can be expected to exert an additional upfield γ effect at C-2,6, compensating in part for the β effect acting in the opposite direction. As a result signals for C-2,6 move closer to those for C-3,5, as is true in many cyclohexyl derivatives.[9] We have reported on the same effect in noncyclic phosphorus derivatives.[10] To distinguish between these carbons, P–C coupling constants were used. Among the noncyclic trivalent derivatives, ^2J is larger than ^3J, and the values found for the cyclohexyl derivatives were very similar to those seen for *n*-butyl derivatives.[10] For the tetravalent functions, ^3J is considerably larger than ^2J in the *n*-butyl series,[10] and comparable values were obtained for the cyclohexyl derivatives.

For derivatives bearing trans 4-alkyl substituents, assignments were straightforward; shift effects occurred that resembled closely those seen on placing the same alkyl group on cyclohexane. For the cis derivatives, additional effects are present owing to the placement of one group in the axial position; these effects are more appropriately discussed in later sections of this paper.

Effects of Phosphorus Functions on the Carbon Signals of Cyclohexane. It is known from our previous studies based on ^{31}P NMR spectroscopy[5] that the six phosphorus functions are of considerable size (*A* > 1.5 kcal/mol) and will occupy the equatorial position on cyclohexane to a very large extent. Therefore, spectra for monosubstituted cyclohexanes can be taken as arising from the equatorial conformers. The shifts caused by these equatorial phosphorus substituents on the cyclohexane carbons are summarized in Table II in terms of α, β, γ, and δ effects at C-1, C-2,6, C-3,5, and C-4, respectively.