

residue was distilled, bp 94–96 °C (0.3 mm), to give 1.1 g (32% yield) of **25**.

Anal. Calcd for C₇H₇F₆O₃S₂: C, 24.14; H, 2.01. Found: C, 24.15; H, 2.42.

The mass spectrum gave a molecular ion *m/e* 348 (calcd, 348).

The 100-MHz ¹H NMR spectrum of **25** in *o*-dichlorobenzene had a doublet centered at δ 3.51 (*J*_{POCH} = 17 Hz) which is assigned to the hydrogens of the methyl group. A complex multiplet was found between δ 3.73 and 4.37. The ¹H NMR spectrum did not change on heating to 130 °C.

The ³¹P NMR spectrum had an absorption at δ +16.5 and the ¹⁹F NMR spectrum had a doublet centered at δ +54.2 (*J*_{PSCCF} = 5.25 Hz).

Reaction of Trimethyl Phosphite with 2. A solution of 2.26 g (0.01 mol) of **2** in 2 mL of methylene chloride was added dropwise with stirring to a solution of 1.24 g (0.01 mol) of trimethyl phosphite in 2 mL of methylene chloride at –78 °C. The ³¹P NMR spectrum of the reaction mixture at ambient temperature had the following absorptions: δ +73 (10%), +19 (90%), and +1 (trace). The first absorption is assigned to trimethyl phosphorothionate, the second to the mixture of products, *cis*- and *trans*-**27**, and the third to the phosphorane **28**. The solvent was removed and the residue was distilled, bp 92–93 °C (0.4 mm), to give 1.2 g (34%) of **27** whose structures are tentatively assigned on the following evidence.

Anal. Calcd for C₇H₉F₆O₃PS₂: C, 23.99; H, 2.59. Found: C, 24.22; H, 2.71.

The mass spectrum revealed a molecular ion *m/e* 350 (calcd, 350).

The 60-MHz ¹H NMR spectrum had a doublet at δ 3.88 (*J*_{POCH} = 13 Hz) and another at δ 3.86 (*J*_{POCH} = 13 Hz); there was also found a broad singlet, δ 2.58, with a shoulder, δ 2.50. Integration gave a ratio of 3:1 for the areas of the doublets to those of the singlets. The ratio of areas of the doublets was 3.3:1.0.

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References and Notes

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Role of Through Space 2p–3d Overlap in the Alkylation of Phosphines

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Abstract: In order to gain additional insight into the scope of the through space 2p–3d overlap effect and into the structures of the transition states of the S_N2 reactions, we have prepared a wide variety of tertiary phosphines and have measured the rates of their reactions with benzyl chloride in benzene–methanol (3:2) solution. One of the most striking results is that diphenyl(2,6-dimethoxyphenyl)phosphine undergoes the quaternization reaction faster than any other phosphine we have used. In the attempted reaction of diphenyl(methoxymethyl)phosphine with benzyl chloride, the inductive, electron-withdrawing effect of the methoxy group bonded to a saturated carbon atom is so large that the rate of reaction with benzyl chloride in benzene–methanol at 31 °C is essentially zero. In spite of what must be large rate-depressing inductive effects in the reactions of diphenyl(2-methoxyethyl)phosphine and diphenyl(3-methoxypropyl)phosphine with benzyl chloride, these reactions are faster than those of diphenylethylphosphine and diphenyl-*n*-propylphosphine, respectively. Rationalizations for these and other results are presented.

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 presented in previous publications.^{1,2} Three particularly important effects were observed. (1) The presence of an *o*-methoxy substituent on an aryl group of the phosphine causes a significant increase in the rate of the reaction. (2) The ratio of the rates of reaction of a given triarylphosphine with benzyl chloride and with *n*-butyl chloride is about 20, probably the

smallest such ratio ever reported in S_N2 reactions of these alkyl chlorides. (3) Rate and activation parameter profiles for the reactions of the isomeric anisyldialkylphosphines and anisyldialkylamines, respectively, with alkyl halides are distinctly different. A rationalization of these effects has been presented, based partly on the concept of through-space overlap of a pair of 2p electrons of a 2-methoxyphenyl group with an empty 3d orbital (or hybrid orbital) of phosphorus in the transition state.³

It has also been suggested^{1,2} that, if such an effect exists in the transition state of an S_N2 reaction, it will also be apparent in the phosphonium cation which is the product of the reaction. Three lines of support for this concept have been offered. (1) An X-ray diffraction study⁴ of benzyl(2-methoxyphenyl)diphenylphosphonium bromide has revealed that the P-O distance is substantially shorter than the sum of the van der Waals radii of phosphorus and oxygen. Furthermore, calculations of bond angles indicate that the methoxyl oxygen is actually leaning toward the phosphorus, and energy minimization calculations, in which the total steric energy is made up primarily of bond stretching energies and van der Waals nonbonded interactions, also indicate a weak P-O bonding interaction. (2) For reasons cited in the earlier papers,^{1,2} the chemical shift of the protons of the methylene group directly bonded to phosphorus in the phosphonium salt represents the best probe of the overlap effect in the NMR spectrum of each compound. An upfield shift of the methylene hydrogens is expected when the electron density at phosphorus is increased owing to the overlap effect, and this is observed. (3) The rates of alkaline cleavage of a series of benzyltriarylphosphonium chlorides in 50% v/v aqueous dioxane at 10.1°C have been determined.⁵ The kinetics data for the cleavage of the meta- and para-substituted compounds can be correlated by the use of the Hammett equation ($\rho = +3.19$), but the salts containing *o*-methoxy groups undergo reaction much more slowly than those containing *p*-methoxy groups. For example, benzylbis(*o*-methoxyphenyl)phenylphosphonium chloride reacts but 2.6×10^{-3} times as fast as benzylbis(*p*-methoxyphenyl)phenylphosphonium chloride. This is the result anticipated based on the operation of the through space 2p-3d overlap effect in the ortho-substituted compound.

In order to gain additional insight into the scope of the 2p-3d overlap effect and into the structures of the transition states of the S_N2 reactions, we have now prepared a wide variety of tertiary phosphines and have measured the kinetics of their reactions with benzyl chloride in benzene-methanol (3:2) solution at 31°C. The data are summarized in Table I, which also includes some results previously published,^{1,2,6} selected for purposes of comparison.

One of the most striking results is that diphenyl(2,6-dimethoxyphenyl)phosphine undergoes the quaternization reaction faster than any of the other phosphines listed in Table I, or considered previously.^{1,2} Three possible reasons for this relatively high reactivity can be considered. (1) The previously cited through space 2p-3d overlap effect involving one *o*-methoxy group is augmented by the conventional electron-donating effect of the second methoxy group to the ring, this in turn promoting electron donation from the ring to the phosphorus atom. However, this cannot be the complete explanation of the high reactivity of diphenyl(2,6-dimethoxyphenyl)phosphine toward benzyl chloride, inasmuch as the reactivity of diphenyl(2,4-dimethoxyphenyl)phosphine toward benzyl chloride is but $\frac{1}{3}$ that of the 2,6-dimethoxy compound, and the conventional electron-donating effect of the *p*-methoxy group to the ring and from the ring to the phosphorus atom would be similar to that of a second *o*-methoxy group. (2) Each *o*-methoxy group of diphenyl(2,6-dimethoxyphenyl)phosphine overlaps an empty 3d orbital of phosphorus in the transition state of the S_N2 reaction. If this is the case, however, an explanation must be offered for the fact that the reactivity of bis(*o*-anisyl)phenylphosphine toward benzyl chloride is only about $\frac{1}{4}$ that of the 2,6-dimethoxy compound. A double through-space overlap effect should also be possible for the bis-*o*-anisyl compound. (3) Since triarylphosphines are known to be pyramidal about phosphorus in the crystalline state^{7,8} (and presumably also in solution), and since we have previously provided evidence that the transition states of the quaternization reactions under consideration are early ones,¹ it is rea-

Table I. Rate Data for Reactions of Tertiary Phosphines with Benzyl Chloride in Benzene-Methanol (3:2) at 31.0 ± 0.1°C

phosphine	$k_2 \times 10^2$, L mol ⁻¹ h ⁻¹ ^a	rel rate
diphenyl(2,6-dimethoxyphenyl)	539 ± 32	74.7
tris(<i>o</i> -anisyl) ²	195 ± 4	27.0
diphenyl(2,4-dimethoxyphenyl)	173 ± 14	24.0
bis(<i>o</i> -anisyl)phenyl ²	146 ± 3	20.2
diphenyl(2-methoxy-4-methylphenyl)	113 ± 11	15.6
diphenyl(2-methoxy-4-phenylphenyl)	70.7 ± 0.8	9.80
bis(<i>p</i> -tolyl)- <i>o</i> -anisyl	61.7 ± 0.2	8.55
diphenyl- <i>o</i> -anisyl ²	53.6 ± 0.7	7.43
tris(<i>p</i> -anisyl) ²	47.8 ± 1.0	6.64
diphenyl(2-methoxy-6-methylphenyl)	47.3 ± 0.5	6.55
diphenylmethyl	35.5 ± 0.3	4.92
diphenyl(2-methoxy-6-phenylphenyl)	34.0 ± 0.5	4.70
diphenyl(2-methoxyethyl)	33.8 ± 0.3	4.68
tris(<i>p</i> -tolyl) ⁶	32.8 ± 0.9	4.55
diphenyl(3-methoxypropyl)	31.2 ± 0.2	4.31
diphenylethyl	27.1 ± 0.1	3.76
diphenyl- <i>n</i> -butyl	26.0 ± 0.1	3.60
diphenyl- <i>n</i> -propyl	25.9 ± 0.1	3.59
bis(<i>p</i> -anisyl)phenyl ²	24.3 ± 1.1	3.36
diphenyl(4-methoxybutyl)	21.1 ± 0.1	2.92
bis(<i>p</i> -tolyl)- <i>p</i> -anisyl	20.0 ± 0.2	2.78
diphenyl- <i>p</i> -anisyl ²	14.6 ± 0.3	2.02
diphenyl- <i>p</i> -tolyl ¹	9.44 ± 0.26	1.31
triphenyl ^{1,2}	7.22 ± 0.13	1.00
diphenyl- <i>p</i> -fluorophenyl	4.60 ± 0.24	0.64
diphenyl- <i>p</i> -chlorophenyl	3.78 ± 0.10	0.52
diphenyl- <i>o</i> -fluorophenyl	3.47 ± 0.02	0.48
diphenyl- <i>o</i> -tolyl ¹	2.16 ± 0.08	0.30
diphenyl- <i>p</i> -bromophenyl	2.10 ± 0.16	0.29
diphenyl- <i>o</i> -chlorophenyl	2.08 ± 0.17	0.29
diphenyl- <i>o</i> -bromophenyl	1.79 ± 0.03	0.25
bis(<i>o</i> -tolyl)- <i>o</i> -anisyl	1.09 ± 0.01	0.15
bis(<i>o</i> -tolyl)- <i>p</i> -anisyl	0.82 ± 0.14	0.11
tris(<i>o</i> -tolyl) ⁶	0.33 ± 0.01	0.046
diphenyl(methoxymethyl)	0.00 ^b	0.000

^a Average deviation based on four to ten experimental results. ^b Too slow to measure under conditions cited.

sonable to assume that the overlap effect caused by the presence of an *o*-methoxy group involves an empty 3d orbital of an essentially pyramidal phosphorus. The CPC bond angle reported⁷ for crystalline triphenylphosphine is 103°, but this could be modified somewhat as the transition state for the reaction with benzyl chloride is approached. It would be anticipated that, as the transition state for the reaction of diphenyl(2,6-dimethoxyphenyl)phosphine with benzyl chloride is being approached, the CPC bond angle would decrease somewhat in order to minimize steric interaction between, let us say, the 6-methoxy group and the benzyl chloride. This decrease in the CPC bond angle would then bring the 2-methoxy group closer to the phosphorus atom and therefore increase the magnitude of the 2p-3d overlap effect involving the 2-methoxy group. This greater overlap, combined with either the overall base-strengthening effect of the 6-methoxy group or a second, smaller overlap of the 2p electrons of the 6-methoxy group with a second, empty 3d orbital of phosphorus, could account for the relatively high reactivity of diphenyl(2,6-dimethoxyphenyl)phosphine in the quaternization reaction. In the case of bis(*o*-anisyl)phenylphosphine (or other di- or tri-ortho-substituted phenylphosphines) it might be expected that CPC bond angles would be increased slightly, thus diminishing the degree of 2p-3d overlap between an *o*-methoxy group and phosphorus in the transition state and thereby causing the rate of the quaternization reaction to be somewhat less than might otherwise have been expected.

The same line of reasoning can be used to rationalize the results obtained in the reactions of the other disubstituted or trisubstituted triphenylphosphines with benzyl chloride. As expected on the basis of steric considerations, diphenyl(2-methoxy-4-methylphenyl)phosphine and diphenyl(2-methoxy-4-phenylphenyl)phosphine undergo reaction with benzyl chloride faster than diphenyl(2-methoxy-6-methylphenyl)phosphine and diphenyl(2-methoxy-6-phenylphenyl)phosphine, respectively. The fact that, in spite of steric considerations, the latter two phosphines are almost as reactive toward benzyl chloride as diphenyl-*o*-anisylphosphine can be explained on the basis of a decrease in the CPC bond angles of the 2-methoxy 6-substituted phosphines, with a concomitant increase in the degree of 2p-3d overlap, as the transition states are being formed.

Such compression of CPC bond angles would not only be inhibited in tris-ortho-substituted triphenylphosphines, but, as mentioned above, it is likely that these bond angles would be increased relative to the triphenylphosphine case. Thus, bis(*o*-tolyl)-*o*-anisylphosphine, with the degree of 2p-3d overlap diminished in the transition state of its reaction with benzyl chloride, exhibits a relative rate of but 0.15. However, as expected, it undergoes reaction with benzyl chloride faster than bis(*o*-tolyl)-*p*-anisylphosphine. In like manner, bis(*p*-tolyl)-*o*-anisylphosphine is more reactive toward benzyl chloride than bis(*p*-tolyl)-*p*-anisylphosphine.

In the attempted reaction of diphenyl(methoxymethyl)phosphine with benzyl chloride, the inductive, electron-withdrawing effect of a methoxy group bonded to a saturated carbon atom is so large⁹ that the rate of reaction with benzyl chloride in benzene-methanol at 31 °C is essentially zero. In the reaction of diphenyl(4-methoxybutyl)phosphine with benzyl chloride, the inductive effect is still being felt, even though four methylene groups intervene between the phosphorus atom and the methoxy group. The evidence for this statement is the fact that the rate of reaction of diphenyl(4-methoxybutyl)phosphine with benzyl chloride is less than those of diphenyl-*n*-propylphosphine and diphenyl-*n*-butylphosphine, which have leveled off at about $k_2 = 0.26 \text{ L mol}^{-1} \text{ h}^{-1}$ at 31 °C. In spite of what must be large rate-depressing inductive effects of the methoxy group in the reactions of diphenyl(2-methoxyethyl)phosphine and diphenyl(3-methoxypropyl)phosphine with benzyl chloride, these reactions are faster than those of diphenylethylphosphine and diphenyl-*n*-propylphosphine, respectively. Thus, the 2p-3d overlap effect must be quite large in the cases of the 2-methoxyethyl and 3-methoxypropyl compounds, inasmuch as the overlap effects are being masked by the counterbalancing inductive effects. These results qualitatively parallel those of Winstein and his co-workers in their studies of classical anchimeric assistance effects in the solvolysis reactions of various methoxyalkyl brosylates.¹⁰ These results also have important implications with respect to hydrolysis and exchange reactions of biologically important phosphate esters, in which alkoxyl groups of carbohydrate moieties are almost always in close proximity to the phosphorus atom of the phosphate group.

The rate data for the reactions of the diphenyl-*p*-halophenylphosphines with benzyl chloride can be correlated by the Hammett equation ($\rho = -1.08$)⁵ and offer no surprises. Also, it would be anticipated that diphenyl-*o*-fluorophenylphosphine, because of the smaller size of the fluoro atom and its overall smaller electron-withdrawing effect (as reflected in the less negative σ_p value), would undergo reaction with benzyl chloride at a faster rate than diphenyl-*o*-chlorophenylphosphine or diphenyl-*o*-bromophenylphosphine, and the facts are in accord with this expectation. Also, even though the fluoride ion is a hard base according to HSAB theory¹¹ and comparable to the methoxy group in this regard, the same does not hold true for the *o*-fluorophenyl group. Thus, on the basis

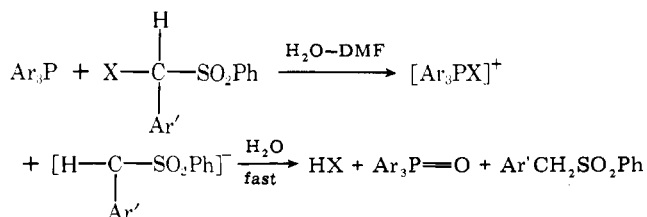
Table II. Activation Parameters for Reaction of Triarylphosphines with Benzyl Chloride in Benzene-Methanol (3:2)

phosphine	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu
triphenyl	13.2	-38.6 ¹ (26.0 °C)
<i>o</i> -anisyl diphenyl	12.9	-36.1 ¹ (26.0 °C)
diphenyl(2,6-dimethoxyphenyl)	12.9	-30.7 (24.0 °C)
diphenyl(2,4-dimethoxyphenyl)	13.2	-32.0 (24.0 °C)
diphenyl(2-methoxy-6-methylphenyl)	16.7	-23.0 (24.0 °C)
diphenyl(2-methoxy-4-methylphenyl)	16.0	-23.0 (24.0 °C)
diphenyl(2-methoxy-6-phenylphenyl)	15.4	-28.1 (24.0 °C)
diphenyl(2-methoxy-4-phenylphenyl)	16.5	-23.1 (24.0 °C)

of considerations presented previously,¹ an anchimeric assistance effect attributable to 2p-3d overlap would not be expected in the reaction of diphenyl-*o*-fluorophenylphosphine with benzyl chloride, and none is observed.

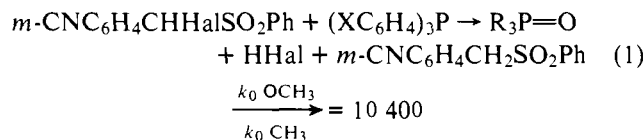
Activation parameters have been determined for a few of the reactions cited above and are presented in Table II. As in the related reactions with benzyl bromide,¹ the ΔS^\ddagger values are of greater importance in determining the relative rates of reaction than are the ΔH^\ddagger values. Again, we attribute this mainly to a decrease in backside solvation in the transition state as an *o*-methoxy group essentially takes the place of a solvent molecule, thus leading to an increase in mobility of some solvent molecules and an increase in ΔS^\ddagger (i.e., a less negative value of ΔS^\ddagger). A decrease in CPC bond angles in the transition states for the reactions of diphenyl-2-methoxy-6-methyl- (or phenyl-) phosphine with benzyl chloride, with a concomitant increase in the degree of 2p-3d overlap, should lead to an increase in the degree of "internal solvation" and to less negative values of ΔS^\ddagger , as observed. It is also not unreasonable that the increased F-strain^{12,13} in the transition states for these reactions should also lead to higher ΔH^\ddagger values.

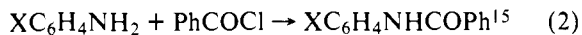
The possibility must be considered that the effects noted above are not a result of 2p-3d overlap, but are simply the result of a combination of inductive and steric factors. This view was stated recently by Jarvis and Marien.¹⁴ These workers examined the reactions of α -halobenzylphenyl sulfones with a number of sterically hindered triarylphosphines in aqueous DMF. This type of reaction is believed to involve nucleophilic



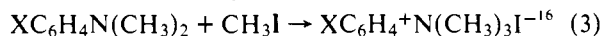
attack on halogen by phosphorus.

Jarvis and Marien¹⁴ compared the rate data for their reaction (1) to those of three other reactions.

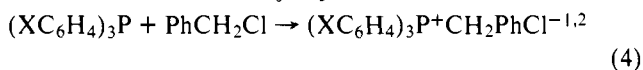




$$\frac{k_0 \text{OCH}_3}{k_0 \text{CH}_3} = 3.2$$



$$\frac{k_0 \text{OCH}_3}{k_0 \text{CH}_3} = 60$$



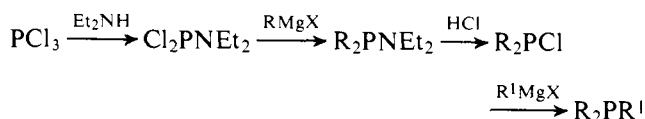
$$\frac{k_0 \text{OCH}_3}{k_0 \text{CH}_3} = 610$$

Jarvis and Marien¹⁴ conclude that "this interpretation (a through space 2p-3d overlap of *o*-anisyl groups with the incipient phosphonium cation in the transition state) loses force when one compares the (k_0/k_p)OCH₃ ratios for reactions (1-4); these ratios vary from 0.3 to 4. The (k_p/k_0)CH₃ ratios (2-4) are 11, 61, and 80, respectively. The small variation in (k_0/k_p) OCH₃ for reactions (1-4) seems inconsistent with a special electronic effect of an *o*-methoxy group; i.e., if 2p-3d overlap is important, then it seems most unlikely that this effect through bonds (viz., *p*-OCH₃) would parallel the effect through space (viz., *o*-OCH₃) for a series of such divergent reaction as (1-4)."

The data Jarvis and Marien presented are interesting, but their conclusions are questionable. Rather than refuting the concept of 2p-3d overlap, the data of Jarvis and Marien would appear to support it. We have suggested that 2p-3d overlap in the reaction of *o*-anisyl diphenylphosphine with benzyl chloride provides only a small degree of anchimeric assistance because the transition state of the reaction is an early one, and the developing positive charge on phosphorus is small.^{1,2} The rate is increased enough, however, to show the effects of anchimeric assistance when compared to the reactions of triphenylphosphine with other reagents, or to the reactions of the nitrogen compounds of the type shown in reaction 3. The data of Jarvis and Marien provide even more convincing proof of 2p-3d overlap because they state that, in the transition state of their reaction (1), a large degree of positive charge is present on the phosphorus atom, and the phosphorus-halogen bond formation process is very near completion.¹⁴ Consequently, if the theory postulated by us is correct, the $k_0 \text{OCH}_3/k_0 \text{CH}_3$ ratio for reaction 1, that of Jarvis and Marien, should be much greater than that of 4. This is clearly so, the $k_0 \text{OCH}_3/k_0 \text{CH}_3$ ratio for reaction 1 being 10 400 and that for 4 being 610.

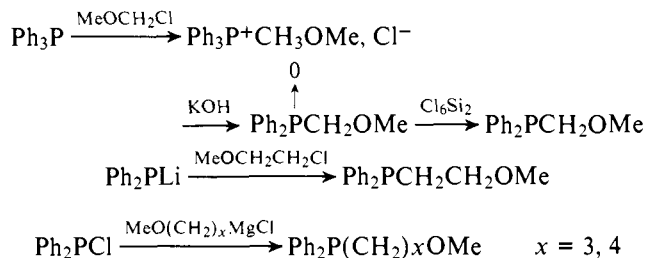
Jarvis and Marien also appear to have made a poor choice of nucleophiles for comparison with other systems. A tris-*o*-anisylphosphine is not a good choice when one wishes to distinguish between through space 2p-3d overlap, and through-bond (inductive) interactions. Our data^{1,2} clearly show that, in reactions of mono-, bis-, and tris-*o*-anisylphosphines with benzyl halides, the tris-*o*-anisylphosphine suffers from an unfavorable steric interaction which partially counteracts the effects of anchimeric assistance (i.e., through-space interactions). In addition, there is no logical basis for the comparison of reaction 2 with the other reactions considered by Jarvis and Marien.

Most of the syntheses of the previously unreported phosphines were unambiguous. The general procedure of Yudina, Medved', and Kabachnik¹⁷ was used to prepare bis(*p*-tolyl)-*p*-anisylphosphine, bis(*o*-tolyl)-*o*-anisylphosphine, and bis(*o*-tolyl)-*p*-anisylphosphine. The essential steps were the following:



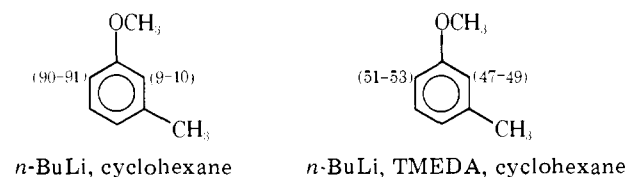
The diphenyl(halophenyl)phosphines were prepared by reaction of the appropriate halophenylmagnesium bromide or halophenyllithium with chlorodiphenylphosphine.

The various diphenyl(methoxyalkyl)phosphines were prepared by the reaction sequences:



Diphenyl(2,6-dimethoxyphenyl)phosphine was prepared by reaction of 2-lithioresorcinol dimethyl ether¹⁸ with chlorodiphenylphosphine. Diphenyl(2,4-dimethoxyphenyl)phosphine was obtained by reaction of 2,4-dimethoxyphenylmagnesium bromide with chlorodiphenylphosphine.

Only in the syntheses of diphenyl(2-methoxy-6-methylphenyl)phosphine, diphenyl(2-methoxy-4-methylphenyl)phosphine, diphenyl(2-methoxy-6-phenylphenyl)phosphine, and diphenyl(2-methoxy-4-phenylphenyl)phosphine were there possibilities of ambiguity, and therefore it was necessary to establish the identities of these compounds in a suitable manner. The method of preparation of the phosphines was adapted in part from the work of Shirley and his colleagues.¹⁹ They had found that, in the lithiation of *m*-methylanisole, the position of the entering lithium is determined by the relative acidities of the ring protons, the size of the reagent, RLi, and the nature of the solvent. The ratios of lithio derivatives formed under various conditions are shown below.



Compounds presumed to be diphenyl(2-methoxy-4-methylphenyl)phosphine and diphenyl(2-methoxy-4-phenylphenyl)phosphine were isolated by treatment of *m*-methylanisole and *m*-phenylanisole, respectively, first with *n*-BuLi in cyclohexane and then with chlorodiphenylphosphine. (The minor isomeric products remained in solution on crystallization of the crude reaction products from ethanol.) Then the same reactions were carried out with *N,N,N',N'*-tetramethylethylenediamine (TMEDA) present during the lithiation steps, and the crude reaction mixtures were separated by the triangular scheme²⁰ of fractional crystallization from absolute ethanol. In this way, the products mentioned above and also the isomeric compounds, diphenyl(2-methoxy-6-methylphenyl)phosphine and diphenyl(2-methoxy-6-phenylphenyl)phosphine, respectively, were isolated.

The identities of the isomeric products were confirmed by NMR spectroscopy. The rules for proton-phosphorus splitting are the same as those for proton-proton splitting, and the coupling between phosphorus and proton is observable through at least four bonds.²¹ In the NMR spectrum of the compound designated as diphenyl(2-methoxy-6-methylphenyl)phosphine by the approach described above, there is a singlet at δ 3.25 which is attributable to the three protons of the methoxy group. There is a doublet at δ 2.57, which is attributable to the protons of the methyl group in the 6 position of the ring. The phosphorus atom is four bonds removed and is the only nucleus which could cause the splitting. In the NMR spectrum of diphenyl(2-methoxy-4-methylphenyl)phosphine, on the other

hand, no such splitting is observed. There are two three-proton singlets at δ 2.6 and 3.3, respectively. These conclusions are further corroborated by examination of the NMR spectra of bis(*p*-tolyl)-*o*-anisylphosphine and bis(*o*-tolyl)-*o*-anisylphosphine, the methyl and methoxy protons of these compounds being easily distinguishable by integration. In the NMR spectrum of bis(*o*-tolyl)-*o*-anisylphosphine, the methyl protons at δ 2.4 are split, whereas in the NMR spectrum of bis(*p*-tolyl)-*o*-anisylphosphine, the methyl protons at δ 2.31 are not split.

The chemical shifts of the methoxy protons and the splitting patterns for the phenyl protons are helpful in confirming the identities of diphenyl(2-methoxy-4-phenylphenyl)phosphine and diphenyl(2-methoxy-6-phenylphenyl)phosphine, respectively. The chemical shifts of the methoxy protons in the isomeric compounds having a phenyl substituent match almost identically the corresponding chemical shifts of the methoxy protons in the compounds having a methyl substituent. Also, the splitting patterns of the phenyl protons in the trisubstituted phenyl groups match well the patterns described by Zanger²² for similar compounds.

Experimental Section

All reactions were conducted under an atmosphere of prepurified argon. Tetrahydrofuran (THF) was initially stored over potassium hydroxide just before use. Hexane was dried over size 3A molecular sieves. Melting points were determined in capillary tubes and are uncorrected. Analyses were obtained from Microanalytical Services, University of Massachusetts, Amherst, Mass.

***N,N*-Diethylaminodichlorophosphine.** *N,N*-Diethylaminodichlorophosphine was prepared in 72% yield by the method of Issleib and Seidel.²³

Chlorobis(*p*-tolyl)phosphine. To 28 g (1.15 g-atoms) of magnesium metal was added dropwise with stirring a solution of 171 g (1.0 mol) of *p*-bromotoluene in 1 L of dry THF. The mixture was heated at reflux for 2 h. The cooled mixture was filtered through a glass-wool plug into an addition funnel. The solution was added dropwise with stirring to an ice bath cooled solution of 87 g (0.5 mol) of *N,N*-diethylaminodichlorophosphine in 300 mL of dry THF. The mixture was heated at reflux for 6 h, the cooled reaction mixture filtered in vacuo, and the filtrate concentrated by evaporation under reduced pressure. The residual oil was slurried in dry hexane, and dry hydrogen chloride was bubbled into the stirred mixture. A white precipitate formed. When no more precipitate formed, the hydrogen chloride addition was stopped. The supernatant solution was decanted from the mixture of oil and precipitate. The solution was evaporated under reduced pressure, and the residue was distilled under reduced pressure to give 63.4 g (51.0%) of a viscous, pale yellow liquid, bp 125–127 °C (0.03 mm). The liquid was divided into two equal portions. Each portion was used to prepare a triarylphosphine.

Chlorobis(*o*-tolyl)phosphine. To an ice bath cooled solution of 87 g (0.5 mol) of *N,N*-diethylaminodichlorophosphine in 300 mL of anhydrous THF was added dropwise with stirring a solution of 1 mol of *o*-tolylmagnesium chloride in THF. The mixture was allowed to warm to room temperature and then heated at reflux overnight. Approximately 350 mL of THF was removed by distillation. To the residue was added 700 mL of dry hexane. The solution was distilled with periodic addition of fresh hexane until no more THF could be detected by gas chromatography. To the cooled, stirred solution was added dry hydrogen chloride through a gas dispersion tube. When no more precipitate formed, the hydrogen chloride addition was stopped. The mixture was allowed to stand overnight. The precipitate was removed by filtration in vacuo. The solvent was removed by evaporation under reduced pressure, and the residue was distilled under reduced pressure to give 100.6 g (81%) of a colorless liquid, bp 120–122 °C (0.03 mm), which solidified when cooled. The solid was dissolved in dry THF. The solution was divided into two equal portions. Each portion was used to prepare a triarylphosphine.

Anisylbis(*p*-tolyl)phosphines. To 4.25 g (0.175 g-atom) of magnesium was added with stirring 28.1 g (0.15 mol) of *o*- or *p*-bromoanisole, respectively, in 200 mL of dry THF. Each Grignard reagent was heated at reflux for 1 h. To the ice bath cooled mixture was added dropwise with stirring 31.7 g (0.127 mol) of chlorobis(*p*-tolyl)phosphine in 200 mL of dry THF. The mixture was heated at reflux for

6 h. The cooled mixture was hydrolyzed with 200 mL of water and 200 mL of saturated ammonium chloride solution. The mixture was separated, and the aqueous portion was extracted with three 100-mL portions of ether. The combined organic portion was dried over anhydrous magnesium sulfate. The drying agent was removed by filtration, and the solvent was removed by evaporation under reduced pressure to give a solid residue. Each of the phosphines was recrystallized from 95% ethanol.

There was obtained 34.1 g (84%) of bis(*p*-tolyl)-*p*-anisylphosphine, mp 122–123 °C.

Anal. Calcd for C₂₁H₂₁OP: C, 78.73; H, 6.61; O, 4.99; P, 9.67. Found: C, 78.85; H, 6.52; O, 4.98; P, 9.60.

There was obtained 27.1 g (66%) of bis(*p*-tolyl)-*o*-anisylphosphine, mp 104–105 °C.

Anal. Calcd for C₂₁H₂₁OP: C, 78.73; H, 6.61; O, 4.99; P, 9.67. Found: C, 78.90; H, 6.53; O, 5.00; P, 9.60.

Anisylbis(*o*-tolyl)phosphines. To 5.5 g (0.226 g-atom) of magnesium was added with stirring 36.7 g (0.21 mol) of *o*- or *p*-bromoanisole, respectively, in 200 mL of dry THF. Each Grignard reagent was heated at reflux for 1 h. To the ice bath cooled mixture was added dropwise with stirring 50.3 g (0.203 mol) of chlorobis(*o*-tolyl)phosphine in 200 mL of dry THF. The mixture was heated at reflux for 6 h. The cooled mixture was hydrolyzed with 200 mL of water and 200 mL of saturated ammonium chloride solution. The mixture was separated and the aqueous layer was extracted with three 100-mL portions of ether. The combined organic portion was dried over magnesium sulfate. The drying agent was removed by filtration, and the solvent was removed by evaporation under reduced pressure to give a solid residue. Each of the phosphines was recrystallized from 95% ethanol.

There was obtained 53.7 g (83%) of bis(*o*-tolyl)-*p*-anisylphosphine, mp 119.5–121 °C.

Anal. Calcd for C₂₁H₂₁OP: C, 78.73; H, 6.61; O, 4.99; P, 9.67. Found: C, 78.81; H, 6.51; O, 5.02; P, 9.68.

There was obtained 50.7 g (78%) of bis(*o*-tolyl)-*o*-anisylphosphine, mp 130–132 °C.

Anal. Calcd for C₂₁H₂₁OP: C, 78.73; H, 6.61; O, 4.99; P, 9.67. Found: C, 78.67; H, 6.51; O, 5.11; P, 9.62.

***o*-Fluorophenyldiphenylphosphine.** To a dry ice-acetone-cooled solution of 22.2 mL of 2.25 M (0.05 mol) *n*-butyllithium in ether and 35 mL of additional anhydrous ether was added dropwise with stirring a solution of 8.74 g (0.05 mol) of *o*-fluorobromobenzene in 60 mL of ether. The rate of addition was such that the temperature of the reaction mixture was not allowed to rise above –65 °C. Ten minutes after the addition had been completed, a solution of 11.0 g (0.05 mol) of chlorodiphenylphosphine in 20 mL of ether was added dropwise with stirring, again such that the temperature did not rise above –65 °C. The reaction mixture was stirred for 7 days at –70 °C and then gradually allowed to come to ambient temperature. The mixture was hydrolyzed with 100 mL of 10% hydrochloric acid. The ether layer was separated and dried over anhydrous magnesium sulfate. Filtration of the drying agent followed by evaporation of the solvent left a solid which, after two recrystallizations from 95% ethanol, produced 4.06 g (29%) of *o*-fluorophenyldiphenylphosphine, mp 88–89 °C.

Anal. Calcd for C₁₈H₁₄FP: C, 77.14; H, 5.04; F, 6.78; P, 11.05. Found: C, 77.38; H, 5.02; F, 6.81; P, 10.98.

Diphenylalkylphosphines. Diphenylmethylphosphine was prepared by the reaction of diphenylchlorophosphine with methylmagnesium chloride in THF. The boiling point of the product was 130–131 °C (1 mm) (reported²⁴ bp 125–128 °C (0.1 mm)). Diphenylethylphosphine and diphenyl-*n*-butylphosphine were purchased from Orgmet, Inc.,²⁵ and redistilled in vacuo before use in kinetics experiments. Diphenyl-*n*-propylphosphine, bp 108–110 °C (0.5 mm) (reported²⁶ bp 138 °C (1 mm)), was prepared by the reaction of diphenylchlorophosphine with *n*-propylmagnesium bromide in THF.

Diphenyl(methoxymethyl)phosphine. A solution consisting of 104.9 g (0.40 mol) of triphenylphosphine and 32.2 g (0.40 mol) of methyl chloromethyl ether²⁷ in 200 mL of absolute benzene was heated at reflux with stirring for 8 h. After having been stirred for an additional 48 h at ambient temperature, a total of 105 g (0.3 mol) of triphenyl(methoxymethyl)phosphonium chloride which had precipitated was collected by filtration.

The 105 g of triphenyl(methoxymethyl)phosphonium chloride was heated for 1 h at reflux in 800 mL of 1.0 N potassium hydroxide solution. When cooled to ambient temperature, the reaction mixture was extracted with two 200-mL portions of benzene. The combined benzene extract was dried over anhydrous sodium sulfate. The drying

Table III. Physical Constants and Spectral Data for Tertiary Phosphines

phosphine	reagents (solvent)	mp or bp, °C	crystn solvent (% yield)	NMR, δ (CDCl ₃)
diphenyl(2,6-dimethoxyphenyl)	<i>f</i>	114.5–115	EtOH (31)	3.45 s, 6.38–6.75 m, 7.08–7.65 m
diphenyl(2,4-dimethoxyphenyl)	<i>f</i>	134–135	EtOH (24)	3.68 s, 3.75 s, 6.25–6.90 m, 7.10–7.55 m
diphenyl(2-methoxy-4-methylphenyl)	<i>f</i>	107.5–108.5	EtOH (16)	2.33 s, 3.70 s, 6.65 m, 7.30 d
diphenyl(2-methoxy-4-phenylphenyl)	<i>f</i>	136.5–137.5	EtOH (15)	3.78 s, 7.35 m
bis(<i>p</i> -tolyl)- <i>o</i> -anisyl	<i>f</i>	104–105	95% EtOH (66)	2.31 s, 3.70 s, 6.55–7.80 m
diphenyl(2-methoxy-6-methylphenyl)	<i>f</i>	111–112	EtOH (15)	2.57 d, 3.25 s, 6.25 m, 7.25 m
diphenyl(2-methoxy-6-phenylphenyl)	<i>f</i>	156.5–158	EtOH (15)	3.22 s, 7.25 m
diphenyl(2-methoxyethyl)	<i>f</i>	153–156 (0.6 mm)	(31)	2.33 t (<i>J</i> = 8 Hz), 3.22 s, 3.45 m (<i>J</i> = 8 Hz), 2.5–2.9 m
diphenyl(3-methoxypropyl)	<i>f</i>	152–155 (0.5 mm)	(77)	1.3–2.3 m, 3.23 s, 3.37 t (<i>J</i> = 11 Hz), 7.1–7.6 m
diphenyl(4-methoxybutyl)	<i>f</i>	161–163 (0.25 mm)	(75)	1.2–2.3 m, 3.25 s, 3.33 t (<i>J</i> = 10 Hz), 7.1–7.6 m
bis(<i>p</i> -tolyl)- <i>p</i> -anisyl	<i>f</i>	122–123	95% EtOH (84)	2.28 s, 3.72 s, 6.6–7.7 m
diphenyl- <i>p</i> -fluorophenyl ^a	<i>p</i> -BrC ₆ H ₄ F, <i>n</i> -BuLi, then Ph ₂ PCl (ether, –70 °C)	149–152 (0.03 mm)	(19)	
diphenyl- <i>p</i> -chlorophenyl ^b	<i>p</i> -BrC ₆ H ₄ Cl, <i>n</i> -BuLi, then Ph ₂ PCl (ether, –70 °C)	155–157 (0.02 mm)	(18)	
diphenyl- <i>o</i> -fluorophenyl	<i>f</i>	88–89	95% EtOH (29)	
diphenyl- <i>p</i> -bromophenyl ^c	<i>p</i> -BrC ₆ H ₄ Br, <i>n</i> -BuLi, then Ph ₂ PCl (ether, –70 °C)	188–195 (0.05 mm)	(44)	
diphenyl- <i>o</i> -chlorophenyl ^d	<i>o</i> -CLC ₅ H ₄ MgBr, Ph ₂ PCl (ether, 25–35 °C)	106–108	EtOH–CH ₂ Cl ₂ (34)	
diphenyl- <i>o</i> -bromophenyl ^e	<i>o</i> -BrC ₆ H ₄ MgBr, Ph ₂ PCl (ether, 25 °C)	113–114.2	95% EtOH (9)	
bis(<i>o</i> -tolyl)- <i>o</i> -anisyl	<i>f</i>	130–132	95% EtOH (78)	2.48 d, 3.70 s, 6.60–7.35 m
bis(<i>o</i> -tolyl)- <i>p</i> -anisyl	<i>f</i>	119.5–121	95% EtOH (83)	2.41 d, 3.79 s, 6.78–7.48 m
diphenyl(methoxymethyl)	<i>f</i>	134–136 (0.25 mm)	(50)	3.38 s, 4.14 d (<i>J</i> = 8 Hz), 7.20–7.70 m

^a Anal. Calcd for C₁₈H₁₄FP: C, 77.14; H, 5.04; F, 6.78; P, 11.05. Found: C, 77.25; H, 5.15; F, 6.80; P, 11.00. ^b Anal. Calcd for C₁₈H₁₄ClP: C, 72.86; H, 4.76; Cl, 11.95; P, 10.44. Found: C, 72.63; H, 4.89; Cl, 11.70; P, 10.75. ^c Anal. Calcd for C₁₈H₁₄BrP: C, 63.37; H, 4.14; Br, 23.42; P, 9.08. Found: C, 63.66; H, 4.33; Br, 23.10; P, 9.00. ^d Anal. Found: C, 72.87; H, 5.03; Cl, 11.90; P, 10.40. ^e Anal. Found: C, 63.16; H, 4.32; Br, 23.45; P, 8.96. ^f See Experimental Section.

agent was removed by filtration, and the filtrate was concentrated to 150 mL by distillation. Crystallization of the phosphine oxide commenced as the solution was allowed to cool to ambient temperature; 68 g (0.27 mol, 90%) of diphenyl(methoxymethyl)phosphine oxide, mp 112–14 °C (reported²⁸ mp 116–117 °C), was obtained by filtration.

To a rapidly stirred solution of 61.5 g (0.25 mol) of diphenyl(methoxymethyl)phosphine oxide in 400 mL of absolute benzene was added over a period of 15 min a solution of 80.7 g (0.30 mol) of hexachlorodisilane in 100 mL of absolute benzene. When the addition was complete, the mixture was heated at reflux for 1.5 h. The mixture was cooled in an ice bath and 100 mL of 30% sodium hydroxide solution was added dropwise with stirring over a period of 1.5 h (vigorous frothing occurred during the addition of the first few milliliters of sodium hydroxide solution). When the addition was complete, the organic layer was removed by decantation. The benzene solution was washed twice with 50-mL portions of water and dried over anhydrous sodium sulfate. The mixture was filtered and the benzene was removed by atmospheric pressure distillation. Reduced pressure distillation of the oily residue produced 29 g (0.13 mol, 50%) of diphenyl(methoxymethyl)phosphine, bp 134–135 °C (0.25 mm) (reported²⁸ bp 138–139 °C (0.1 mm)).

Diphenyl(2-methoxyethyl)phosphine. A solution of 18.8 g (0.20 mol) of 2-methoxychloroethane²⁹ in 100 mL of anhydrous THF was added dropwise with stirring over a period of 1 h to a solution heated at reflux of lithium diphenylphosphide in 200 mL of THF that had been made from 0.20 mol of triphenylphosphine.³⁰ When the addition was complete, the reflux was maintained for an additional 15 min, after which time the mixture was allowed to cool to ambient temperature.

Deaerated, saturated ammonium chloride solution (300 mL) was added, and the organic layer was separated from the aqueous phase and dried over anhydrous sodium sulfate. The THF was removed by distillation at atmospheric pressure, and the oily residue was fractionally distilled under reduced pressure with the fraction boiling at 146–175 °C (0.5 mm) being retained. Redistillation produced 15 g of a liquid, bp 153–156 °C (0.6 mm). The NMR spectrum of this liquid was consistent with that predicted for diphenyl(2-methoxyethyl)phosphine with the exception of a doublet at δ 1.25 and 1.05.³¹ Purification was accomplished by successively (five times) dissolving a sample of the mixture in four to five volumes of spectral grade pentane and freezing out the phosphine by immersing the solution in a dry ice–ethanol bath. The cold supernatant liquid was removed from the solid by decantation. Changing vessels twice during this procedure eliminated a pentane-insoluble scum that was deposited on the sides of the vessel. The NMR spectrum of phenyl(2-methoxyethyl)phosphine purified in this manner indicated only a trace of the original impurity.

Anal. Calcd for C₁₅H₁₇OP: C, 73.75; H, 7.02; P, 12.68. Found: C, 73.90; H, 7.07; P, 12.98.

Diphenyl(3-methoxypropyl)phosphine. To an ice bath cooled, rapidly stirred solution of 47 g (0.50 mol) of 3-chloropropanol and 142 g (1 mol) of iodomethane in 300 mL of dry THF was added in small portions 24 g (1 mol) of sodium hydride.³² Upon completion of the addition, the mixture was allowed to warm to ambient temperature and to stir overnight. The mixture was cooled in an ice bath and 150 mL of water was added dropwise with stirring. The organic layer was separated from the aqueous layer and dried over anhydrous sodium sulfate. After filtration of the drying agent, the THF was removed by

Table IV. Properties of Quaternary Phosphonium Chlorides

phosphonium cation	crystn solvent	mp, °C dec	NMR (CDCl ₃), J _{PH} = 14.5–16.3 Hz
benzylidiphenyl(2,6-dimethoxyphenyl) ^a	ether-CH ₂ Cl ₂	175–182	3.70 s, 4.92 d, 6.75–8.05 m
benzylidiphenyl(2,4-dimethoxyphenyl) ^b	EtOH-AcOEt	218–222	3.83 s, 3.98 s, 4.88 d, 6.75–8.05 m
benzylbis(<i>p</i> -tolyl)- <i>o</i> -anisyl	EtOH-ether	242–245	2.47 s, 4.85 d, 5.15 s, 6.42–7.28 m
benzylbis(<i>p</i> -tolyl)- <i>p</i> -anisyl	EtOH-ether	222–225	2.44 s, 3.88 s, 5.08 d, 6.62–7.65 m
benzylidiphenyl- <i>p</i> -fluorophenyl ^c	CHCl ₃	280–283	5.80 d, 7.25–8.27 m
benzylidiphenyl- <i>p</i> -chlorophenyl ^d	CHCl ₃ -CCl ₄	250–255	5.91 d, 7.30–8.15 m
benzylidiphenyl- <i>o</i> -fluorophenyl ^e	CHCl ₃	307–308	5.71 d, 7.30–8.09 m
benzylidiphenyl- <i>p</i> -bromophenyl ^f	CHCl ₃ -CCl ₄	261–262	5.87 d, 7.30–8.12 m
benzylidiphenyl- <i>o</i> -chlorophenyl ^g	CHCl ₃ -CCl ₄	288–290	5.75 d, 7.16–8.20 m
benzylidiphenyl- <i>o</i> -bromophenyl ^h	CHCl ₃ -CCl ₄	268–269	5.73 d, 7.10–8.15 m
benzylbis(<i>o</i> -tolyl)- <i>o</i> -anisyl	EtOH-ether	202–205	1.93 s, 4.73 d, 5.11 s, 6.34–7.62 m
benzylbis(<i>o</i> -tolyl)- <i>p</i> -anisyl	EtOH-ether	219–222	2.09 s, 3.88 s, 5.08 d, 6.33–7.62 m

^a Anal. Calcd for C₂₇H₂₆O₂CIP: C, 72.24; H, 5.84; Cl, 7.90; P, 6.90. Found: C, 72.21; H, 6.03; Cl, 7.88; P, 6.99. ^b These data are for the phosphonium bromide. Anal. Calcd for C₂₇H₂₆O₂BrP: C, 65.73; H, 5.31; Br, 16.19; P, 6.27. Found: C, 65.62; H, 5.16; Br, 16.38; P, 6.15. ^c Anal. Calcd for C₂₅H₂₁FCIP: C, 73.80; H, 5.20; P, 7.61. Found: C, 73.89; H, 5.09; P, 7.60. ^d Anal. Calcd for C₂₅H₂₁Cl₂P: C, 70.93; H, 5.00; Cl, 16.75; P, 7.32. Found: C, 70.40; H, 5.11; Cl, 16.65; P, 7.21. ^e Anal. Found: C, 73.67; H, 5.17; P, 7.60. ^f Anal. Calcd for C₂₄H₂₁BrCIP: C, 64.19; H, 4.53; P, 6.62. Found: C, 63.86; H, 4.51; P, 6.58. ^g Anal. Found: C, 70.44; H, 4.92; Cl, 16.66; P, 7.23. ^h Anal. Found: C, 63.90; H, 4.63; P, 6.60.

distillation at atmospheric pressure. The residue was fractionally distilled at atmospheric pressure to produce 27 g (0.25 mol, 50%) of a liquid, bp 111–114 °C.³³

To the ice bath cooled, rapidly stirred Grignard reagent, which had been prepared from 6 g (0.25 g-atom) of magnesium metal turnings, 27 g (0.25 mol) of 3-methoxychloropropane, and 150 mL of dry THF, was added dropwise over a period of 1 h 44 g (0.20 mol) of diphenylchlorophosphine in 100 mL of dry THF. When the addition was complete, the mixture was heated at reflux for 20 min, after which time the mixture was cooled in an ice bath. Saturated, deaerated ammonium chloride solution (75 mL) was added dropwise with stirring. The organic layer was separated from the aqueous layer and dried over anhydrous sodium sulfate. Filtration of the drying agent was followed by removal of most of the THF by distillation at atmospheric pressure. The oily residue was fractionally distilled under reduced pressure to produce 39.5 g (77%) of diphenyl(3-methoxypropyl)phosphine, bp 152–155 °C (0.5 mm).

Anal. Calcd for C₁₆H₁₉OP: C, 74.40; H, 7.41; P, 11.99. Found: C, 74.42; H, 7.30; P, 11.97.

Diphenyl(4-methoxybutyl)phosphine. In an ice bath cooled, rapidly stirred suspension of 24 g (1 mol) of sodium hydride,³² 142 g (1 mol) of iodomethane, and 350 mL of dry THF was added dropwise over a period of 1.5 h a solution of 54 g (0.5 mol) of 4-chlorobutanol³⁴ in 50 mL of dry THF. When the addition was complete, the mixture was allowed to warm to ambient temperature and to stir overnight. To the mixture was added dropwise with stirring 100 mL of saturated, deaerated ammonium chloride solution, and the organic layer was separated from the aqueous layer and dried over anhydrous sodium sulfate. Distillation at atmospheric pressure produced 12 g (20%) of 4-methoxychlorobutane, bp 144–148 °C.³⁴

To the ice bath cooled, rapidly stirred Grignard reagent, prepared from 3.8 g (0.16 g-atom) of magnesium metal turnings, 19 g (0.15 mol) of 4-methoxychlorobutane, and 120 mL of dry THF, was added dropwise, over a period of 1 h, 29 g (0.13 mol) of diphenylchlorophosphine in 50 mL of dry THF. Upon completion of the addition, 50 mL of saturated, deaerated ammonium chloride solution was added dropwise with stirring. The organic layer was removed from the inorganic salts by decantation and dried over anhydrous sodium sulfate. After removal of the drying agent by filtration, the THF was removed by distillation at atmospheric pressure, and the oily residue was fractionally distilled under reduced pressure to produce 26.6 g (0.098 mol, 75%) of diphenyl(4-methoxybutyl)phosphine, bp 161–163 °C (0.25 mm).

Anal. Calcd for C₁₇H₂₁OP: C, 74.98; H, 7.77; P, 11.37. Found: C, 74.88; H, 7.70; P, 11.45.

2,4-Dimethoxyphenyldiphenylphosphine. To the Grignard reagent prepared under nitrogen from 32 g (0.15 mol) of 1-bromo-2,4-dimethoxybenzene in 60 mL of dry tetrahydrofuran and 3.6 g (0.15 g-atom) of magnesium turnings in 60 mL of dry tetrahydrofuran was added dropwise at 0 °C a solution of 31 g (0.14 mol) of chlorodiphenylphosphine in 30 mL of dry THF. After all of the halophosphine had been added, the reaction mixture was refluxed for 3 h. The reac-

tion mixture was cooled to 0 °C and hydrolyzed with 70 mL of saturated ammonium chloride solution. An additional 100 mL of water was added. The THF layer was separated from the aqueous layer, which was extracted with 30 mL of THF. The extract was combined with the THF layer and dried over anhydrous magnesium sulfate. After removal of the drying agent by filtration, evaporation of the solvent under nitrogen left a viscous, brown liquid. This product was induced to crystallize from absolute ethanol, a light brown solid weighing 10.9 g (24%) being obtained. One more recrystallization from absolute ethanol coupled with charcoal decolorization gave white crystals, mp 134–135 °C.

Anal. Calcd for C₂₀H₁₉O₂P: C, 74.52; H, 5.94; P, 9.61. Found: C, 74.19; H, 6.08; P, 9.76.

2,6-Dimethoxyphenyldiphenylphosphine. To a stirred mixture of 50 mL of a 2.2 M solution (0.11 mol) of *n*-butyllithium in hexane and 100 mL of anhydrous diethyl ether, maintained under nitrogen at –78 °C, was added dropwise a solution of 15.2 g (0.11 mol) of resorcinol dimethyl ether in 120 mL of anhydrous diethyl ether over a 1.5-h period. After the addition had been completed, the reaction mixture was allowed to warm to room temperature with stirring, and was then refluxed for an additional 4 h. The reaction mixture was allowed to stand for 1.5 days, and a single, large, white crystal of 2-lithioresorcinol dimethyl ether was observed to have been formed.

To 0.165 mol of 2-lithioresorcinol dimethyl ether suspended in a mixture of anhydrous hexane and anhydrous ethyl ether was added dropwise with stirring a solution of 35.4 g (0.16 mol) of diphenylchlorophosphine in 75 mL of anhydrous ether at –5 °C. The reaction mixture was refluxed for 3 h. It was then hydrolyzed at 0 °C with 120 mL of water. Filtration of the mixture and evaporation of the solvent from the organic layer gave a light yellow solid. Recrystallization from absolute ethanol gave a yellow solid, mp 114.5–115.5 °C.

Anal. Calcd for C₂₀H₁₉O₂P: C, 74.52; H, 5.94; P, 9.61. Found: C, 74.12; H, 5.84; P, 9.54.

Diphenyl(2-methoxy-6-methylphenyl)- and Diphenyl(2-methoxy-4-methylphenyl)phosphine. By the method of Shirley,¹⁹ 34.86 g (0.300 mol) of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) in 100 mL of dry cyclohexane was cooled in an ice bath. To the stirred TMEDA solution was added 131 mL (0.300 mol) of 2.9 M *n*-butyllithium in hexane. The resulting solution was stirred for 0.5 h at ice bath temperature, after which time a solution of 36.65 g (0.300 mol) of *m*-methylanisole in 100 mL of dry cyclohexane was added dropwise over a period of 45 min. The mixture was allowed to warm to ambient temperature and to stir overnight, approximately 15 h. The reaction mixture was cooled in an ice bath, and a solution of 58 mL (0.300 mol + 10%) of diphenylchlorophosphine in 100 mL of dry cyclohexane was added dropwise with stirring. After the addition was complete, the reaction mixture was allowed to warm to ambient temperature and stirred for approximately 8 h, after which time 175 mL of saturated ammonium chloride solution was added, followed by an additional 100 mL of water. The resulting layers were separated, and the cyclohexane layer was washed with three 75-mL portions of water. The combined aqueous solution was extracted with four 75-mL por-

tions of methylene chloride. The combined methylene chloride solution was added to the cyclohexane solution and dried over anhydrous magnesium sulfate. After removal of the drying agent by filtration, the solution was concentrated by evaporation under reduced pressure, which produced a viscous, brown oil. The oil was stirred with Skellysolve F under a stream of air, which eventually caused the oil to solidify, producing a beige-colored solid. The solid was triturated with 10 mL of absolute ethanol and the mixture was filtered. The dark orange filtrate was allowed to stand overnight and produced a white solid, which was collected by filtration. The solid materials were combined and recrystallized from absolute ethanol to give a white, crystalline material. NMR spectral analysis demonstrated that the crystalline material was predominantly a mixture of the two desired isomers. Triangular fractional crystallization²⁰ from ethanol eventually resulted in the separation of the two isomers. There was obtained 23.60 g of diphenyl(2-methoxy-4-methylphenyl)phosphine, mp 107.5–108.5 °C, and 13.72 g of diphenyl(2-methoxy-6-methylphenyl)phosphine, mp 111–112 °C.

Anal. Calcd for C₂₀H₁₉OP: C, 78.41; H, 6.25; P, 10.11. Found for diphenyl(2-methoxy-4-methylphenyl)phosphine: C, 78.46; H, 6.18; P, 9.91. Found for diphenyl(2-methoxy-6-methylphenyl)phosphine: C, 78.32; H, 6.24; P, 10.05.

Diphenyl(2-methoxy-4-phenylphenyl)- and Diphenyl(2-methoxy-6-phenylphenyl)phosphine. In the manner described above, a solution of 20 g (0.172 mol) of *N,N,N',N'*-tetramethylethylenediamine in 120 mL of dry cyclohexane and 71.7 mL (0.172 mol) of 2.4 M *n*-butyllithium in hexane were caused to react. To the resulting solution was added dropwise with stirring 31.60 g (0.172 mol) of *m*-phenylanisole³⁵ in 100 mL of dry cyclohexane. The mixture was stirred at ambient temperature for approximately 16 h, after which time the mixture was cooled in an ice-salt bath. A solution consisting of 34 mL (0.172 mol + 10%) of diphenylchlorophosphine in 75 mL of cyclohexane was added dropwise with stirring. The mixture was allowed to warm to ambient temperature and was stirred for an additional 7 h. Saturated, deaerated ammonium chloride (100 mL) was then added, followed by 150 mL of distilled water. The two-phase mixture was separated, and the aqueous layer was washed twice with 75-mL portions of methylene chloride. The combined organic layer and methylene chloride extract was washed twice with 75-mL portions of water and dried over anhydrous magnesium sulfate. After filtration to remove the drying agent, the solvents were removed by evaporation under reduced pressure. The viscous, orange residue was triturated in Skellysolve F, which produced a beige-colored solid. Trituration of the solid with approximately 25 mL of absolute ethanol removed most of the colored impurities. Prolonged fractional crystallization²⁰ separated the isomers. There were obtained 12.55 g of diphenyl(2-methoxy-4-phenylphenyl)phosphine, mp 136.5–137.5 °C, and 9.60 g of diphenyl(2-methoxy-6-phenylphenyl)phosphine, mp 156.5–158.0 °C.

Anal. Calcd for C₂₅H₂₁OP: C, 81.50; H, 5.75; P, 8.41. Found for diphenyl(2-methoxy-4-phenylphenyl)phosphine: C, 81.64; H, 5.98; P, 8.60. Found for diphenyl(2-methoxy-6-phenylphenyl)phosphine: C, 81.54; H, 6.00; P, 8.44.

Triarylbenzylphosphonium Chlorides. To ca. 5 g (0.0156 mol) of the phosphine in 35 mL of benzene was added 10 ml (0.0866 mol) of benzyl chloride. The solution was heated at reflux for 1–3 days. The cooled mixture was filtered in vacuo, and the solid residue was washed with ether. The residue was recrystallized from a suitable solvent (see Table IV). The resulting crystals were dried at 78 °C under reduced pressure. When heated in melting point capillary tubes, many of the salts seemed to effervesce somewhere in the range 50–150 °C, after which the melt resolidified and eventually melted at the temperatures listed in Table IV.

Kinetics Experiments. These were carried out as described previously.

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References and Notes

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