

Kinetics of the Photopolymerization. Pyrex tubes, each containing an equal amount of a 0.10 M solution of **1a** or **1b** in dichloromethane, were degassed in four successive freeze-thaw cycles and irradiated in a "merry-go-round" apparatus with lamps with λ_{\max} 350 nm for **1a** or λ_{\max} 310 nm for **1b**. All the incident light was absorbed by the system up to about 70–90% conversion. The solutions remained colorless during irradiation, and no precipitate was formed. The absorbance of the solution and the molecular weights of the formed polymers were measured as a function of the irradiation time. The intrinsic viscosities of the polymers were measured as a function of the degree of conversion.

Quenching of the Photopolymerizations. Different samples (5 ml) with a given concentration of *N,N'*-undecamethylenebis(dimethylmaleimide) or *N,N'*-nonamethylenebis(dimethylmaleimide), but with various concentrations of quencher (ferrocene or 3,3,4,4-tetramethyl-1,2-diazetidine 1,2-dioxide) in dichloromethane or acetonitrile, were degassed in four freeze-thaw cycles and irradiated in parallel in a "merry-go-round" apparatus, equipped with lamps that have a maximum intensity at 352 nm (band width 40 nm). The conversion in each sample was determined by means of the optical density. The change in optical density in each sample was compared with that in the reference samples containing no quencher and was, when ferrocene was used as the quencher, eventually corrected for partial light absorption by the quencher. Such a quenching was carried out for different dimethylmaleimide chromophore

concentrations. The maximum conversion in the reference sample never exceeded 10%.

Quantum Yields. A solution (3 ml) with a given dimethylmaleimide chromophore concentration in dichloromethane or acetonitrile was degassed in four freeze-thaw cycles. The solution was then poured into a quartz cell which was connected to the degassing flask. The cell was placed in a thermostated block at 20° in front of the monochromator, in a fixed position, and irradiated. All the incident light was absorbed. During irradiation the solution was stirred with a magnetic stirrer. The degree of conversion was determined directly by measuring the optical density of the undiluted solution. The maximum conversion was about 8%. The amount of light absorbed was calculated from the optical density differences. The incident light intensity was measured by actinometry with *N,N'*-hexamethylenebismaleimide in dichloromethane.³

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Chemical Transformations with Regenerable, Polymer-Supported Trisubstituted Phosphine Dichlorides. The Efficacious Incorporation of Phosphorus Reagents on Polymer Supports

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Abstract: Trisubstituted phosphine dichloride reagents have been prepared chemically bound to cross-linked polystyrene beads. The reaction of phosgene with the corresponding phosphine oxide reagents was the final step in the three synthetic approaches used. The reagents were employed successfully for the preparation of acid chlorides from acids, an imidoyl chloride from an anilide, a nitrile from a primary amide, an alkyl chloride from an alcohol, and a chloroolefin from a ketone. Each reaction simultaneously regenerated the resin-bound phosphine oxide reagent, which was readily recovered and rephosgenated for subsequent use.

A limited number of publications dealing with polymer-supported organophosphorus reagents have appeared in the past few years. Three groups¹ have prepared polymeric Wittig reagents by treating cross-linked polymeric triarylphosphines (**5**) with alkyl halides and then strong base. The reactions of ketones or aldehydes with these reagents then led to various olefins which were separated from the resulting cross-linked polymeric triarylphosphine oxide (**7**) by filtration. Several other reports² have indicated that metal com-

plexes of **4**, **5**, or similar polymeric trisubstituted phosphines could be prepared and used for a variety of transition-metal-catalyzed reactions, such as olefin hydrogenation, hydroformylation, and arylacetylene cyclotrimerization.

In this paper we report the synthesis and synthetic utility of cross-linked, polymeric trisubstituted phosphine dichlorides. Not only can these materials be used for carrying out a wide variety of organic chemical transformations³ and separating the reaction products conveniently by simple filtration,^{1,2} but the nature of

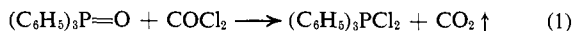
(1) (a) W. Heitz and R. Michels, *Angew. Chem., Int. Ed. Engl.*, **11**, 298 (1972); (b) S. V. McKinley and J. W. Rakshys, Jr., *J. Chem. Soc., Chem. Commun.*, 134 (1972); (c) F. Camps, J. Castells, J. Font, and F. Vela, *Tetrahedron Lett.*, 1715 (1971).

(2) (a) J. P. Collman, L. S. Hegedus, M. P. Cooke, J. R. Norton, G. Dolcetti, and D. N. Marquardt, *J. Amer. Chem. Soc.*, **94**, 1789 (1972); (b) R. H. Grubbs, L. C. Kroll, and E. M. Sweet, Abstracts of Papers, 164th National Meeting of the American Chemical Society, New York, N. Y., Sept 1972, No. POLY-46; (c) R. H. Grubbs and L. C. Kroll, *J. Amer. Chem. Soc.*, **93**, 3062 (1971); (d) M. Capka, P. Svoboda, M. Cerny, and J. Hetflejš, *Tetrahedron Lett.*, 4787 (1971); (e) P. L. Ragg, British Patent 1,249,033 (1971); (f) J. Manassen, *Isr. J. Chem. Suppl. Proc. Isr. Chem. Soc.*, **8**, 5 (1970); (g) K. G. Allum, R. D. Hancock,

and P. J. Robinson, German Patent 1,948,987 (1970); U. S. Patent 3,652,778 (1972); (h) K. G. Allum and R. D. Hancock, German Patent 1,948,988 (1970); U. S. Patent 3,658,884 (1972).

(3) These transformations proceed analogously to similar reactions using triphenylphosphine dichloride. In effect, the latter reagent and the polymeric phosphine dichlorides behave like mild forms of PCl_5 . See, for example, (a) G. A. Wiley, R. L. Hershkovitz, B. M. Rein, and B. C. Chung, *J. Amer. Chem. Soc.*, **86**, 964 (1964); (b) L. Horner, H. Oediger, and H. Hoffmann, *Justus Liebigs Ann. Chem.*, **626**, 26 (1959); (c) H. M. Relles, U. S. Patent 3,715,407 (1973); (d) H. M. Relles, unpublished results.

these transformations, which simultaneously leads to the corresponding polymeric phosphine oxides, allows one to continually reuse the polymeric reagents. That is, by analogy with the reported⁴ conversion of triphenylphosphine oxide to triphenylphosphine dichloride (eq 1), the recovered polymeric phosphine oxides

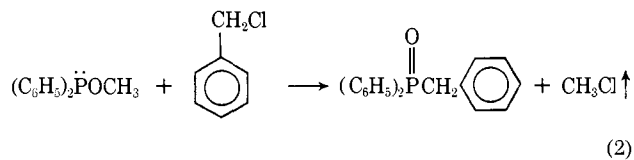


can be reconverted to the reactive polymeric phosphine dichlorides on treatment with phosgene.

Synthetic Procedures

The key to success in carrying out chemical reactions, and especially organometallic reactions, with solvent-swallowable, cross-linked polystyrene beads lies in the finding that, before the reactions are attempted, the beads must be pretreated so as to remove surface impurities remaining from the emulsion polymerization reactions in which they were produced. Commonly used in these emulsion polymerizations are suspension and stabilizing agents such as hydrated colloidal alumina ($\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$), Fuller's earth, carboxymethylcellulose, stearic acid, sodium lauryl sulfate, and sodium polyacrylamide.⁵ Attempting to carry out chemical reactions with organometallic reagents on solvent-swollen beads with such surface contaminants would lead to the formation of ions on the surface of the beads which could prevent further penetration of the reagents into them. Indeed, we found that chloromethylated or brominated beads which had only been washed initially with organic solvents prior to use gave little or no reaction with lithium diphenylphosphide, lithium biphenyl, or butyllithium.^{3d} On the other hand, if the beads were initially washed with aqueous HCl at 60°, aqueous NaOH at 60°, and then with organic solvents,⁽¹⁾ they could then be used with great success in a variety of organometallic reactions. (One piece of confirmatory evidence for this explanation lies in the finding that improperly washed beads contained 70 ppm of aluminum, while properly washed beads contained only 40 ppm, the latter presumably being well distributed throughout the interior of the beads.)

Arbuzov Reaction Route. Cross-linked polystyrene beads were chloromethylated⁶ with chloromethyl methyl ether and BF_3 to give beads **2** containing $-\text{CH}_2\text{Cl}$ groups on *ca.* 100% of the rings. After appropriate experimental conditions for conducting an Arbuzov reaction between benzyl chloride and methyl diphenylphosphinite (eq 2) had been established (which also provided



for the volatilization of most of the CH_3Cl), the same reaction was allowed to proceed on the chloromethylated polymer beads. This reaction was monitored by ^1H nmr spectroscopy using an internal standard and observing the loss of the phosphinite from the

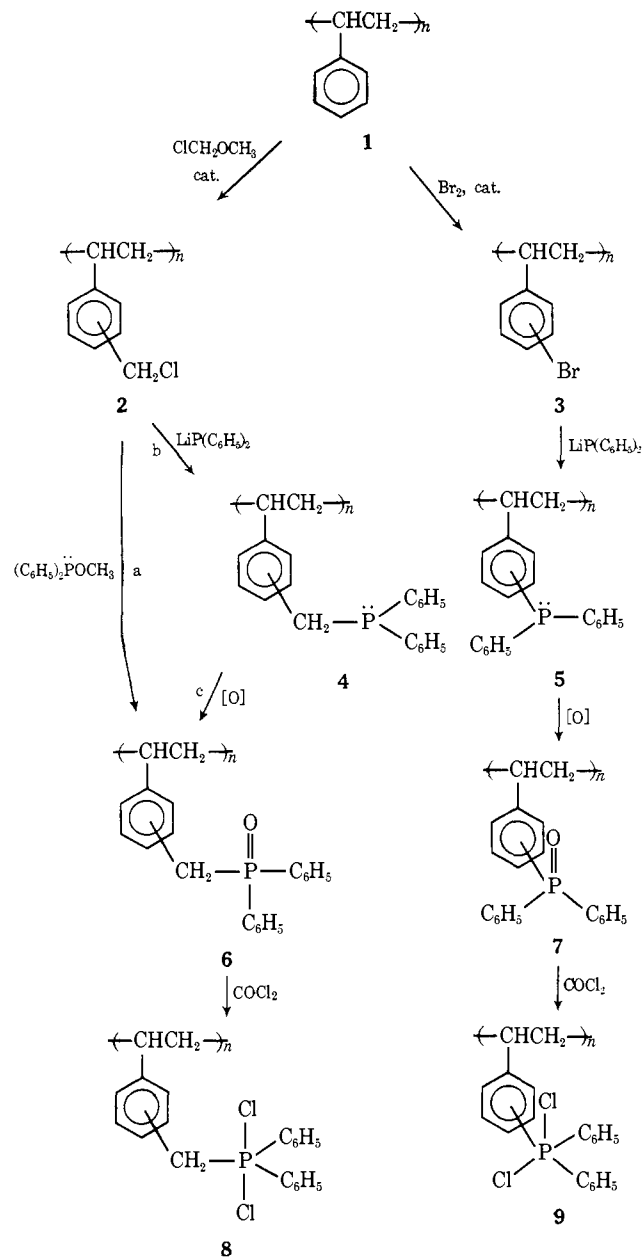
(4) R. Appel and W. Heinzelmann, German Patent 1,192,205 (1966).

(5) G. R. Stark, "Biochemical Aspects of Reactions on Solid Supports," Academic Press, New York, N. Y., 1971, pp 197-198.

(6) R. B. Merrifield, *J. Amer. Chem. Soc.*, **85**, 2149 (1963); K. W. Pepper, H. M. Paisley, and M. A. Young, *J. Chem. Soc.*, 4097 (1953).

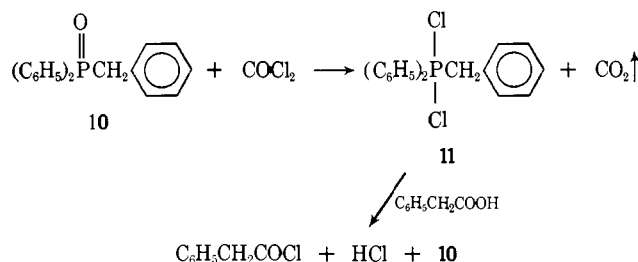
solution. According to this analysis, the reaction proceeded to *ca.* 90% of theory presumably to give **6** (Scheme I, path a). This structure could be inferred

Scheme I. Synthetic Sequences

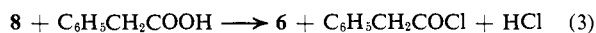


from the corresponding model reaction, and elemental analysis tended to support it. However, relatively firm structural evidence was not provided until the chemical behavior of this material was examined. Namely, while suspended in CH_3CN or CH_2Cl_2 , it underwent a characteristic reaction with phosgene in which vigorous gas evolution was observed. This behavior was identical with that observed for benzyl diphenylphosphine oxide (Scheme II) and triphenylphosphine oxide.^{3d,4} Nmr evidence was obtained for benzyl diphenylphosphine dichloride (**11**), and this material *quantitatively* converted phenylacetic acid to phenylacetyl chloride, simultaneously regenerating **10**. The use of phosphine dichlorides for preparing acid chlorides is well known.^{3b} The phosgenated polymer,

Scheme II



whose structure would be expected to be **8**, was similarly effective in converting phenylacetic acid to phenylacetyl chloride (eq 3). In fact, the use of this reaction and a



simple ^1H nmr integration of the reaction solution to determine the extent of conversion of the acid to the acid chloride proved to be the most convenient method for analyzing the activity of **8**, prepared by this method (path a) and by another method (paths b and c; *vide infra*), and polymer **9** (*vide infra*) which had similar reactivity.⁷

In the present case, this analysis indicated that polymer **8** contained reactive $-\text{CH}_2\text{P}(\text{Cl})_2(\text{C}_6\text{H}_5)_2$ groups on ca. 95% of the rings. This high value is perhaps not so surprising when one considers the nature of the reactions involved and the bead microstructure. In the first place, the Arbuzov reaction had proceeded to ca. 90% of theory. Secondly, most of the $-\text{CH}_2\text{PO}(\text{C}_6\text{H}_5)_2$ ring substituents would be in the sterically most accessible position para to the main polymer chain since the initial chloromethylation would certainly have occurred there predominantly. Thirdly, according to molecular models, even the ring position ortho to the main chain offers little additional steric hindrance to attack of phosgene on the $-\text{CH}_2\text{PO}(\text{C}_6\text{H}_5)_2$ group or of phenylacetic acid on the $-\text{CH}_2\text{P}(\text{Cl})_2(\text{C}_6\text{H}_5)_2$ group by comparison with the corresponding reactions of benzyl-diphenylphosphine oxide and benzyl-diphenylphosphine dichloride. Fourthly, the latter two reactions were found to occur quantitatively. Finally, since these beads are relatively lightly cross-linked (2%) and appear to swell two to three times their dry volume in various solvents, we feel that they can be pictured for the most part simply as highly concentrated solutions of linear polymer chains on which chemical reactions can proceed in much the same way as with nonpolymeric molecules in solution.

Since the presence of residual phosgene would make the analysis of reactive groups high by reconvertng some phosphine oxide groups, regenerated by reaction with the phenylacetic acid, back to phosphine dichloride groups which could undergo additional reaction, an exhaustive effort was made to remove all of the excess phosgene after **6** had been converted to **8**.

(7) Implicit in this analytical method is the assumption that concentrations of reagents in the solutions were the same inside and outside of the swollen polymer beads. The facts that (1) comparable analyses were obtained on single batches of beads using widely differing solvents (CH_3CN and CH_2Cl_2) and (2) total separations of soluble reaction products from spent beads were achieved by simple filtration and sometimes washing with a small amount of fresh solvent, implying facile transfer of reagents in and out of the swollen beads, lends credence to this assumption.

Lithium Diphenylphosphide-Chloromethyl Route. By analogy with previous reports using alkali metal diphenylphosphides,^{1a, 2b, g, h} it was our intention to displace the chlorines of **2** with lithium diphenylphosphide in THF to obtain $-\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ groups in the beads. Since lithium diphenylphosphide is extremely air and moisture sensitive, performing it and subsequently adding chloromethylated beads which could contain entrapped air and moisture were not desirable. Furthermore, the manipulations which would be required in carrying out an air- and moisture-free inverse addition⁸ of the preformed lithium diphenylphosphide in THF to THF-swelled beads under N_2 were unnecessary since it seemed appropriate to make use of the fact that the solid swollen beads and solid metallic lithium, being two nonhomogeneous phases, could be cosuspended in THF under N_2 without reacting with each other. (In contrast, one would expect soluble chloromethylated polystyrene or, for that matter, benzyl chloride, to react rapidly in THF with suspended lithium metal to produce $-\text{CH}_2\text{Li}$ groups on the polymer, which could then react further with $-\text{CH}_2\text{Cl}$ groups to give $-\text{CH}_2\text{CH}_2-$ linkages + LiCl .) If chlorodiphenylphosphine were then added to the solution, it would react with the metallic lithium to give soluble lithium diphenylphosphide, and the latter could migrate into the solvent-swollen beads and react with the $-\text{CH}_2\text{Cl}$ groups.

Indeed, cosuspending the chloromethylated beads and lithium metal under N_2 in a THF solution of chlorodiphenylphosphine at $\sim 25^\circ$ for 18 hr led to nearly complete displacement of the chlorines by diphenylphosphide ions. The resulting polymer beads **4** (according to chlorine analysis, phosphorus analysis, and the observed weight increase) contained $-\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ groups on approximately 90% of the rings. These phosphine-containing beads were readily oxidized with peracetic acid to the phosphine oxide form **6** whose structure was again substantiated by its reaction with phosgene to give **8**. Analysis using the phenylacetic acid reaction method indicated that 77% of the rings contained reactive $-\text{CH}_2\text{P}(\text{Cl})_2(\text{C}_6\text{H}_5)_2$ sites. After these beads were used for a series of three reactions (*vide infra*), another analysis indicated this value to be 76%.

Lithium Diphenylphosphide-Bromine Route. While conducting the various steps in the synthetic sequence leading to 2% cross-linked polystyrene beads **9**, a parallel series was carried out on linear, soluble polystyrene itself. In the cross-linked sequence, elemental analysis indicated that bromination occurred to give a material **3** containing bromines on 89% of the rings; in the soluble sequence, this value was 92%.

The reactions of the two brominated materials with lithium diphenylphosphide had to be carried out in different ways. The cross-linked beads were conveniently cosuspended with lithium metal in a THF solution containing chlorodiphenylphosphine, whereas the lithium diphenylphosphide had to be preformed in order to avoid reaction of the metal with the soluble brominated polystyrene. In the former case, cross-linked **5** was produced which contained $-\text{P}(\text{C}_6\text{H}_5)_2$ groups on approximately 85% of the rings. In the latter case, the ^1H nmr spectrum of the isolated soluble **5** agreed

(8) A. M. Aguiar, H. J. Greenberg, and K. E. Rubenstein, *J. Org. Chem.*, **28**, 2091 (1963).

Table I. Chemical Transformations Using Cross-Linked Polymeric Phosphine Dichlorides^a

Phosphine dichloride structure	Solvent	Reactant	Product	Yield, ^b %
8	CH ₂ Cl ₂	C ₆ H ₅ CH ₂ COOH	C ₆ H ₅ CH ₂ COCl	100
8	CH ₂ Cl ₂	CH ₃ C ₆ H ₄ COOH (<i>p</i>)	CH ₃ C ₆ H ₄ COCl (<i>p</i>)	98
8	CH ₂ Cl ₂	HOOC ₆ H ₄ COOH (<i>p</i>)	ClOCC ₆ H ₄ COCl (<i>p</i>)	91 ^c
9	CH ₂ Cl ₂	HOOC ₆ H ₄ COOH (<i>p</i>)	ClOCC ₆ H ₄ COCl (<i>p</i>)	95 ^d
9	CH ₃ CN	HOOC ₆ H ₄ COOH (<i>p</i>)	ClOCC ₆ H ₄ COCl (<i>p</i>)	98
9	CH ₃ CN	HOOC ₆ H ₄ COOH (<i>m</i>)	ClOCC ₆ H ₄ COCl (<i>m</i>)	87
9	CH ₃ CN	C ₆ H ₅ CONHC ₆ H ₅	C ₆ H ₅ C(Cl)=NC ₆ H ₅	93
8	CH ₂ Cl ₂	C ₆ H ₅ CONH ₂	C ₆ H ₅ C=N	78 ^e
9	CH ₃ CN	C ₆ H ₅ CH ₂ OH	C ₆ H ₅ CH ₂ Cl	88
9	CH ₃ CN	C ₆ H ₅ COCH ₃	C ₆ H ₅ C(Cl)=CH ₂	75

^a These reactions were performed using an excess of the polymeric phosphine dichloride **8** or **9**, unless stated otherwise. ^b Based on the reactant unless otherwise noted. ^c Excess terephthalic acid was used; this yield is based on the moles of reactive $-\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ groups present in **8**. ^d This is the zero-order kinetic run discussed in the text. ^e Some benzonitrile was lost by solvent removal during the work-up.

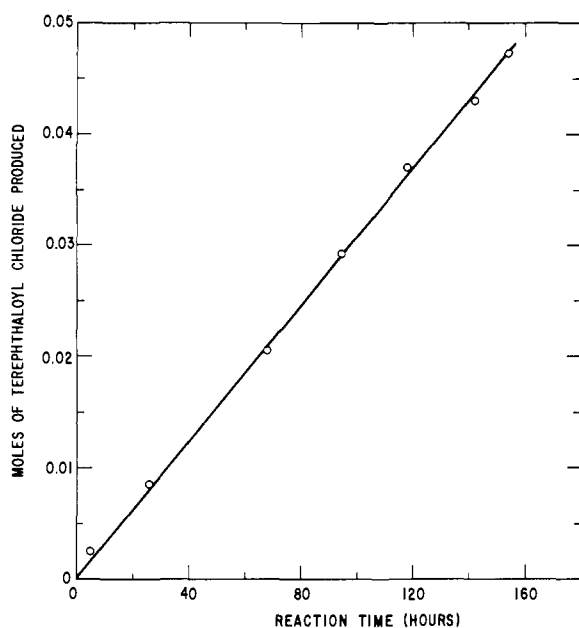


Figure 1. Rate of conversion of terephthalic acid to terephthaloyl chloride in CH₂Cl₂.

fairly well with the proposed structure and indicated that approximately 90% of the rings contained $-\text{P}(\text{C}_6\text{H}_5)_2$ groups. (Polymer fractionation may have occurred, however, during isolation.)

Oxidations of cross-linked and soluble **5** were achieved readily with peracetic acid in CH₂Cl₂-acetic acid and with a CH₂Cl₂-aqueous H₂O₂ two-phased system, respectively. Evidence for the structure of the resulting soluble phosphine oxide polymer **7** was obtained through its reaction with phosgene-producing soluble **9** and the use of this reagent to convert a sample of terephthalic acid to terephthaloyl chloride. The cross-linked phosphine oxide polymer **7** was similarly treated with phosgene to produce cross-linked **9**. The reactivity of the latter material was carefully determined by the phenylacetic acid reaction method; two separately synthesized batches of cross-linked **9** contained reactive $-\text{P}(\text{C}_6\text{H}_5)_2$ groups on $87 \pm 3\%$ of the rings.

Chemical Conversions

All of the reactions described below were carried out with cross-linked beads depicted by structures **8** or **9**.

During each transformation, structures **6** or **7**, respectively, were regenerated so that after isolation and rephosgenation, **8** or **9** was again available for further use. In some cases, excess phosgene was deliberately *not* removed from the suspension of **8** or **9** so that it could continually reconvert phosphine oxide groups, generated during reactions, back to phosphine dichloride groups for further reaction. In a sense then, **8** and **9** could be considered as catalysts for effecting chemical transformations using phosgene, although in reality the reactions proceed by interaction of the reagents, specifically with **8** or **9**.

The variety of reactions which have been carried out using **8** or **9** are summarized in Table I. Each of these reactions can also be achieved³ using triphenylphosphine dichloride, but the simplicity of the present systems is evidenced by the fact that only phosgene is consumed, and work-up consists of filtration and solvent removal. In general, the reaction products were obtained in very high yield and purity.

The behavior in the reaction of terephthalic acid with **9** in CH₂Cl₂ showed some interesting features. First, it was *much* slower than the same reaction in CH₃CN. Secondly, under conditions where the activity of **9** was kept at its maximum by the presence of a large excess of phosgene, the rate of appearance (as determined by ¹H nmr spectroscopy using an internal standard) of terephthaloyl chloride varied linearly with time (Figure 1). Since the reaction of a *soluble* acid (such as phenylacetic acid) with **9** was rapid and complete in a few minutes under the same conditions, we suggest that the apparent zero-order rate behavior arose because the rate-limiting aspect of this reaction system was simply the rate at which the very insoluble terephthalic acid dissolved.⁹

Experimental Section

General Comments. Tetrahydrofuran (THF), used in the experiments below, was purified under N₂ by stirring with and distilling from lithium biphenyl and then stored continuously under nitrogen. Methylene chloride was dried with MgSO₄ and filtered. Acetonitrile was dried by distillation from P₂O₅. Chlorobenzene was distilled and stored over CaH₂. The 2% cross-linked polystyrene beads, **1**, were obtained from Eastman or Dow Chemical Co. Before they were used for our sequences of chemical reactions, it was necessary to wash them thoroughly to remove surface impuri-

(9) We cannot, of course, rule out another potential zero-order rate-limiting component, namely, the rate of penetration of terephthalic acid into the beads, but based on our experience this appears unlikely.⁷

ties.¹⁰ The solutions and conditions used for washings, in the order in which they were used, were: 1 N NaOH, 60°; 1 N HCl, 60°; 1 N NaOH, 60°; 1 N HCl, 60°; H₂O, 25°; DMF, 40°; 1 N HCl, 60°; H₂O, 60°; CH₃OH; 2:3 (v/v) CH₂Cl₂-CH₃OH; 3:1 CH₂Cl₂-CH₃OH; 9:1 CH₂Cl₂-CH₃OH; pure CH₂Cl₂. Following the washing procedure, the beads were freed of all solvent to constant weight at 100° *in vacuo* (first ~10 mm overnight and then ~0.1 mm for several hours). Chlorodiphenylphosphine (Aldrich reagent) was redistilled before use: bp 115–120° (0.1 mm). ¹H nmr spectra were recorded with a Varian Associates T-60 spectrometer using external TMS as standard unless otherwise stated. Useful markers calibrated against external TMS were the upfield ¹³C side band of CH₂Cl₂ (δ 3.78) and the downfield ¹³C side band of CH₃CN (δ 3.18). Infrared spectra were taken in chloroform solution. Vpc analyses were performed using a 10% silicone gum (SE-30) column.

Elemental analyses were obtained on the beads at various stages of the synthetic sequences. These data were only used qualitatively as an indication of the success of various reactions.¹¹ The actual activity of each batch of beads, in terms of the number of reactive R-PCl₂(C₆H₅)₂ groups, was determined by converting the phosphine oxide form to the R-PCl₂(C₆H₅)₂ form with phosgene, exhaustively removing the excess phosgene, adding a known excess of phenylacetic acid to the suspension of beads in an appropriate solvent (CH₂Cl₂ or CH₃CN), and then determining the relative molar amounts of phenylacetyl chloride produced and phenylacetic acid left unreacted in the solution⁷ by ¹H nmr spectroscopy. This was accomplished conveniently by integration of the corresponding methylene proton singlets: phenylacetyl chloride, δ 4.11 (CH₂Cl₂), 4.30 (CH₃CN); phenylacetic acid, δ 3.63 (CH₂Cl₂), 3.70 (CH₃CN). Control experiments showed that (a) phenylacetyl chloride and phenylacetic acid did *not* cocondense to form phenylacetic anhydride (δ 3.88 (CH₃CN), -CH₂-s) under the conditions employed for the bead analyses, and (b) a large excess of phosgene alone in CH₃CN or CH₂Cl₂ was capable of converting only *ca.* 25% (4 hr) or 10% (64 hr), respectively, of phenylacetic acid to phenylacetyl chloride at *ca.* 25°, whereas this conversion was complete (100%) under similar conditions (solvent, phenylacetic acid concentration, and temperature) with a small excess of R-PCl₂(C₆H₅)₂ beads after only 30 min (*vide infra*).¹²

Chloromethylation of 2% Cross-Linked Polystyrene Beads. Preparation of 2. A 20.92-g sample (0.20 mol of repeating units) of 2% cross-linked polystyrene beads (200–400 mesh) was allowed to swell and stirred with 175 ml of chloromethyl methyl ether. The system was then saturated with BF₃, allowed to stir at ~25–40° for 2 hr, and then filtered. The beads were washed with 2:3, 3:1, and 9:1 CH₂Cl₂-CH₃OH, with pure CH₂Cl₂, and then freed of traces of solvent overnight at 90° *in vacuo*. The yield was 30.15 g.

Anal. Calcd for -CH₂Cl group on 100% of the rings: Cl, 23.2. Found: Cl, 23.0.

Reaction of Methyl Diphenylphosphinite with 2. Preparation of 6 (Path a). A 12.60-g sample of 2 from the previous experiment (0.084 mol of repeating units, ~0.084 mol of -CH₂Cl groups) and 70 ml of dry chlorobenzene were stirred under dry nitrogen for 15 min, and then 23.4 g (0.108 mol) of methyl diphenylphosphinite was added; 2.16 g (0.018 mol) of mesitylene was also added as an internal standard (methyl peak) for monitoring the diminution of methyl diphenylphosphinite by ¹H nmr integration of samples of the solution (see the related experimental details in the corresponding model reactions). The suspension was heated at reflux under nitrogen. ¹H nmr data indicated that the reaction had proceeded to *ca.* 90% of theory after 4 hr., *i.e.*, (0.90)(0.084) = 0.076 mol of the phosphorus reagent had been removed from the solution by reaction. The system was allowed to cool to room temperature.

(10) Successful chloromethylation was achieved with 2% cross-linked polystyrene beads which had been washed only with 9:1 CH₂Cl₂:CH₃OH and pure CH₂Cl₂ and dried at 100° *in vacuo*, but a subsequent reaction with lithium biphenyl complex in THF (followed by treatment with chlorodiphenylphosphine) failed to significantly alter the halogen content of the beads: 26.7% Cl → 25.5% Cl, 0.9% P. Similarly washed and dried and then chloromethylated or brominated 8% cross-linked beads underwent a small amount of reduction and almost no phosphorus incorporation on treatment with lithium diphenylphosphide in THF; chloromethylated case: 18.5% Cl → 15.5% Cl, 0.5% P; brominated case: 38.6% Br → 33.6% Br, 1.1% P. These results may be attributed to residual coatings on the bead surfaces which prevented penetration of the organometallic reagents (see Discussion section).

(11) Phosphorus analyses especially were usually high and nonreproducible.

(12) See paragraph at the end of the paper concerning the availability of supplementary material.

The beads were filtered, washed thoroughly with four 100-ml portions of CH₂Cl₂, and then stored *in vacuo* at 95° overnight. The beads 6 thus obtained weighed 24.97 g.

Anal. Found: C, 78.3; H, 6.2; Cl, 1.2; P, 9.8. 11.2.¹¹

Reaction of 6 (from Path a) with Phosgene to Give 8. Determination of the Amount of Reactive Phosphine Dichloride Sites in 8. A. Acetonitrile. Excess phosgene was added slowly to a suspension of 24.70 g (0.083 mol of repeating units) of 6, from the previous experiment, in 50 ml of CH₃CN under dry nitrogen. Gas evolution became somewhat vigorous, as the phosphine oxide groups were converted to phosphine dichloride groups, gradually subsided, and then stopped after *ca.* 15 min (total). The system was heated at reflux (condenser water temperature was 15°) for 4 hr to eliminate excess phosgene and then cooled to *ca.* 25°. Exactly 21.76 g (0.160 mol) of phenylacetic acid was added to the suspension of 8, and the system was stirred for 30 min. ¹H nmr analysis of a sample of the solution indicated the presence of 0.078 mol of phenylacetyl chloride and 0.082 mol of phenylacetic acid. Thus, out of 0.083 mol of repeating units, there was 0.078 mol of reactive -CH₂PCL₂(C₆H₅)₂ sites (equivalent to a reactive site on 94% of the rings).

The beads were filtered thoroughly, washed with the CH₃OH-CH₂Cl₂ series, and stored *in vacuo* at 100°; 24.58 g of 6 was recovered.

B. Methylene Chloride. Analysis was repeated on 24.30 g of these beads 6 by the same method as used in A except that the solvent was methylene chloride. The ¹H nmr results indicated that out of 0.082 mol of repeating units, there was 0.080 mol of reactive -CH₂PCL₂(C₆H₅)₂ sites (97% of the rings).

Following this determination, excess phosgene was again added, and the system was then refluxed for 3.5 hr. After this treatment, phenylacetyl chloride was the only component in the solution (¹H nmr); no phenylacetic acid remained. The beads were isolated as usual, 24.20 g recovered.

Anal. Found: P, 10.5, 12.2.¹¹

Reaction of 8 with Terephthalic Acid. A 24.00-g sample of 6 (path a) (0.081 mol of repeating units), recovered from the previous two analysis experiments, was suspended in 100 ml of CH₂Cl₂ and converted to 8 with phosgene. Excess phosgene was removed by allowing the system to reflux (condenser at 15°) for 3.5 hr. According to the previous analyses, this would contain 0.077 mol (average value) of reactive -CH₂PCL₂(C₆H₅)₂ sites. Terephthalic acid,¹³ 13.28 g (0.080 mol, 0.160 mol of carboxylic acid), and 4.80 g (0.040 mol) of mesitylene (¹H nmr internal standard: δ 2.25, methyl, s, 9; 6.73, aromatic, s, 3) were added, and the system was heated at reflux for 16 hr.¹⁴ At this point, ¹H nmr analysis indicated that the solution contained 0.035 mol of terephthaloyl chloride (δ 8.18, aromatic singlet). Thus, at least 0.070 mol of the 0.077 mol of -CH₂PCL₂(C₆H₅)₂ sites accessible to phenylacetic acid were also accessible to the very slowly dissolving terephthalic acid. (A similar experiment which included isolation of the terephthaloyl chloride was also performed (*vide infra*).)

These beads were recovered by filtering and washing with CH₃OH-CH₂Cl₂, then with three 200-ml portions of warm DMF (to move any entrapped terephthalic acid), and then with the usual CH₃OH-CH₂Cl₂ series. After storing *in vacuo* at 100° overnight, the recovered beads weighed 23.81 g.

Reaction of Chlorodiphenylphosphine and Lithium with 2. Preparation of 4 (Path b). A 17.13-g sample of 2 (*vide supra*) (0.114 mol of repeating units, ~0.114 mol of -CH₂Cl groups) and 400 ml of THF were stirred under a nitrogen stream for 2 hr. Chlorodiphenylphosphine, 49.0 g (0.222 mol), in 200 ml of THF was then added, followed by 3.6 g (0.52 mol) of lithium wire (cleaned under hexane and cut into ~1/8 in. lengths). The system was stirred at ~25°, with some initial external cooling, for 18 hr. The excess lithium wire was removed and some methanol was added to destroy the excess diphenylphosphide ions. The beads were filtered, washed with 2:3, 3:1, and 9:1, chloroform-CH₃OH and pure chloroform, and then stored *in vacuo*, under N₂, at 100° until constant weight was achieved. The beads thus obtained weighed 33.24 g.

Anal. Found: C, 80.5; H, 6.2; Cl, 1.3; P, 13.3.¹¹

Oxidation of 4 with Peracetic Acid. Preparation of 6 (Path c). A solution of peracetic acid in acetic acid was prepared by slightly warming 11.0 g of 30% H₂O₂ with 53.5 g of acetic anhydride until the two phases became homogeneous; this solution now contained 0.097 mol of peracetic acid. This solution was added to 18.05 g of 4

(13) The solubility of terephthalic acid in CH₂Cl₂ is extremely low. None could be observed in a single scan ¹H nmr spectrum (Varian Associates T-60 instrument) of a saturated solution.

(14) Control experiments showed that terephthalic acid does not react with phosgene alone in methylene chloride or in acetonitrile.

from the previous experiment (0.062 mol of repeating units), 75 ml of CH_2Cl_2 , and 50 ml of acetic acid. An exotherm was observed which caused the CH_2Cl_2 to boil. After the initial exotherm, the system cooled back to $\sim 25^\circ$ and was then stirred at $\sim 25^\circ$ overnight. The beads were filtered, washed, and dried as described for 4. The yield of **6** was 18.30 g.

Anal. Found: C, 77.7; H, 6.0; Cl, 1.2; P, 11.2.¹¹

Reaction of 6 (from Path c) with Phosgene to Give 8. Determination of the Amount of Active Phosphine Dichloride Sites in 8. A suspension of 18.20 g of **6** from the previous experiment (0.062 mol of repeating units) and 100 ml of CH_2Cl_2 was stirred at $\sim 25^\circ$, and excess phosgene gas was passed in until CO_2 evolution was no longer observed. The resulting beads **8** were filtered in a dry atmosphere and washed five times with 50-ml portions of dry CH_2Cl_2 to remove excess phosgene.

To these beads was added a solution of 13.6 g (0.100 mol) of phenylacetic acid in 100 ml of CH_2Cl_2 . The resulting suspension was stirred at $\sim 25^\circ$ for 1 hr, and then a sample of the solution was analyzed by ^1H nmr. It showed 0.048 mol of phenylacetyl chloride and 0.052 mol of phenylacetic acid. Thus, out of 0.062 mol of repeating units, 0.048 mol contained reactive $-\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ sites ($\sim 77\%$ of the rings).

Reaction of 8 with Phenylacetic Acid. Isolation of Phenylacetyl Chloride. After the beads used in the previous experiment were thoroughly washed, rephosgenated, and then treated to remove excess phosgene, they (0.048 mol of reactive $-\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ sites) were suspended in 50 ml of dry CH_2Cl_2 containing 5.44 g (0.040 mol) of phenylacetic acid. Analysis by ^1H nmr of a sample of the solution removed after 30 min showed that the only material present was phenylacetyl chloride, δ 4.11 and 7.20. The system was filtered to remove the beads. Methylene chloride was removed from the filtrate *in vacuo* to give 6.13 g (100% yield) of phenylacetyl chloride which was unequivocally identified by comparison of its ^1H nmr and ir spectra with those of an authentic sample: ^1H nmr (CDCl_3 , internal TMS) δ 4.00 (methylene, s, 2), 7.16 (aryl, broad s, 5); ir 1800 cm^{-1} , C=O (no carboxylic acid C=O or OH).

Bromination of 2% Cross-Linked Polystyrene Beads. Preparation of 3. A suspension of 83.68 g (0.800 mol of repeating units) of 2% cross-linked polystyrene (16–25 mesh) in 500 ml of nitromethane containing 56 g (0.8 mol) of BF_3 was stirred at $\sim 25^\circ$ in the dark, while 256 g (1.60 mol) of Br_2 was added dropwise during 0.5 hr (external cooling required). Vigorous HBr evolution was observed during the addition. The system was stirred for an additional 18 hr at $\sim 25^\circ$, and the beads were then filtered. They were washed with 9:1, 3:1, 2:3, 3:1, and 9:1 CH_2Cl_2 : CH_3OH and pure CH_2Cl_2 , and then stored *in vacuo* at $\sim 100^\circ$ until all excess solvent had been removed. The yield was 147.70 g. Elemental analysis indicated that 89% of the rings contained bromine.

Anal. Found: Br, 40.4.

Reaction of Chlorodiphenylphosphine and Lithium with 3. Preparation of 5. Exactly 36.92 g (0.200 mol of repeating units) of **3**, from the previous experiment, was stirred for 1 hr under nitrogen with 900 ml of THF. A solution of 88 g (0.40 mol) of chlorodiphenylphosphine in 300 ml of THF was added, followed by 6.4 g (0.93 mol) of lithium metal (wire cut into $\sim 1/8$ in. lengths under hexane just before adding to the reaction mixture). The system was stirred at $\sim 25^\circ$ (some external cooling required initially) for 18 hr, the excess pieces of lithium were carefully removed under nitrogen, and the solution was then heated under nitrogen at reflux for 4.5 hr. Some methanol was then added; the beads were filtered, washed with 2:3, 3:1, and 9:1 $-\text{CH}_2\text{Cl}_2$: CH_3OH and pure CH_2Cl_2 , and freed of solvent *in vacuo* at $\sim 100^\circ$ overnight. The yield was 53.55 g.

Anal. Found: C, 81.8; H, 6.1; Br, 1.4; P, 11.6.¹¹

Oxidation of 5 with Peracetic Acid. Preparation of 7. A suspension of 53.45 g (0.200 mol of repeating units) of **5**, prepared in the previous experiment, in 50 ml of CH_2Cl_2 and 50 ml of acetic acid was stirred at $\sim 25^\circ$ in a water bath while 70 ml of 40% peracetic acid in acetic acid was added slowly (exothermic oxidation). After the system was stirred at $\sim 25^\circ$ for 3 hr, the beads were filtered, washed with the usual CH_2Cl_2 : CH_3OH series and then with pure CH_2Cl_2 , and freed of solvents *in vacuo* overnight at $\sim 100^\circ$. The material obtained weighed 57.60 g.

Anal. Found: C, 77.3; H, 5.9; P, 11.3.¹¹

Reaction of 7 with Phosgene to Give 9. Determination of the Amount of Active Phosphine Dichloride Sites in 9. Exactly 14.40 g (0.050 mol of repeating units) of **7**, prepared in the experiment above, was stirred in 100 ml of CH_2Cl_2 as excess phosgene was admitted to the solution. Vigorous evolution of CO_2 ensued and the system was allowed to stir at $\sim 25^\circ$ for 1 hr. Excess phosgene was re-

moved by filtering the beads and then washing them five times with 50-ml portions of dry CH_2Cl_2 .

Then a solution of 13.6 g (0.100 mol) of phenylacetic acid in 75 ml of CH_2Cl_2 was added, and the system was stirred at $\sim 25^\circ$. Analysis of the solution by nmr after 20 min indicated the presence of 0.0425 mol of phenylacetyl chloride. Another analysis after 60 min gave a value of 0.0460 mol. Average: 0.0443 mol of phenylacetyl chloride, *i.e.*, 0.0443 mol of reactive $-\text{P}(\text{C}_6\text{H}_5)_2$ sites in 0.050 mol of repeating units; $\sim 89\%$ of the rings contain reactive $-\text{P}(\text{C}_6\text{H}_5)_2$ sites.

More phosgene was admitted to the above solution to reconvert the re-formed phosphine oxide beads **7** back to the phosphine dichloride beads **9** so that further reaction with the rest of the phenylacetic acid could occur. Indeed, after an additional 45 min, a total of 0.060 mol of phenylacetyl chloride was present; after 1.5 hr, 0.0715 mol was present; and after 16 hr, 0.100 mol was present.

The beads were recovered in the phosphine oxide form **7** by filtering, washing with the usual CH_2Cl_2 : CH_3OH series and then with pure CH_2Cl_2 , and freeing of solvent as usual, yield 14.15 g.

Reaction of 9 with Terephthalic Acid in Methylene Chloride. A suspension of 13.40 g (0.0465 mol of repeating units) of **7**, from the previous experiment, 8.3 g (0.050 mol) of terephthalic acid, and 2.4 g (0.020 mol) of mesitylene (an internal nmr standard) in 100 ml of CH_2Cl_2 was stirred at $\sim 25^\circ$ and then saturated with phosgene; much CO_2 evolution was noted. According to the previous experiment, 0.0413 mol of reactive $-\text{P}(\text{C}_6\text{H}_5)_2$ sites would have been produced at this point; the excess phosgene was allowed to remain in order to reconvert $-\text{PO}(\text{C}_6\text{H}_5)_2$ sites, regenerated through reaction with the terephthalic acid, back to reactive $-\text{P}(\text{C}_6\text{H}_5)_2$ sites. Plotting the amount of terephthaloyl chloride produced (as determined by nmr analysis) *vs.* time gave a straight line (see Figure 1). In this system, ~ 0.0206 mol (*i.e.*, $\sim 0.0413/2$) of terephthaloyl chloride was produced in 68 hr and ~ 0.050 mol in 163 hr. The overall rate of this conversion was greatly increased by using a better solvent and high temperatures (*vide infra*).

Reaction of 9 with Terephthalic Acid in Acetonitrile. A suspension of 15.70 g (0.0600 mol of repeating units) of another batch of **7** in 100 ml of CH_3CN was saturated with phosgene to convert the $-\text{PO}(\text{C}_6\text{H}_5)_2$ groups to $-\text{P}(\text{C}_6\text{H}_5)_2$ groups; much CO_2 evolution was observed. According to a previous analysis, ~ 0.0503 mol of reactive $-\text{P}(\text{C}_6\text{H}_5)_2$ sites would have been produced by this treatment. Excess phosgene was then removed by refluxing the system ($\sim 82^\circ$) for 5 hr.

Then, 3.32 g (0.020 mol) of terephthalic acid was added and refluxing was continued. ^1H nmr analysis indicated that the reaction was complete in less than 2 hr; *i.e.*, the amount of terephthaloyl chloride was the same after 2 and 4 hr of reflux. The system was cooled; the beads were filtered and washed with 25 ml of CH_2Cl_2 . The combined filtrates gave, after solvent removal, 3.98 g (98% yield) of terephthaloyl chloride, mp $79\text{--}80.5^\circ$ (lit.¹⁵ mp $80\text{--}82^\circ$), which displayed an appropriate ^1H nmr aromatic singlet at δ 8.20 (CDCl_3 , internal TMS).

The beads were washed thoroughly with the CH_3OH : $-\text{CH}_2\text{Cl}_2$ series, CH_2Cl_2 , and CH_3CN . They were then reused in other experiments.¹²

Bromination of Polystyrene. Formation of Soluble 3. To a solution of 10.5 g (0.1 mol) of polystyrene and 13.6 g (0.1 mol) of ZnCl_2 in 150 ml of chloroform and 100 ml of acetic acid was added 17.0 g (0.106 mol) of Br_2 in the dark. After the solution had stirred for 95 hr at room temperature, another 17.0 g of Br_2 was added and stirring was continued for another 24 hr. The polymer was precipitated by adding the system to methanol, reprecipitated from methylene chloride by adding to methanol, and then dried *in vacuo* at 70° overnight, yield 14.7 g. Elemental analysis of this material corresponded to polystyrene containing a bromine on 92% of the repeating units.

Anal. Found: C, 54.9; H, 4.1; Br, 41.7.

Reaction of Lithium Diphenylphosphide with Soluble 3. Formation of Soluble 5. A solution of 11.0 g (0.050 mol) of chlorodiphenylphosphine in 150 ml of THF was stirred at room temperature under N_2 for 19 hr¹⁷ with 0.75 g (0.109 mol) of lithium. The excess lithium was removed and 6.0 g of brominated polystyrene from the previous experiment in 50 ml of THF was added under N_2 . After the reaction mixture was allowed to reflux for 2 hr, it was added to

(15) N. Rabjohn, U. S. Patent 2,525,722 (1950).

(16) The methanol would also convert residual $-\text{P}(\text{C}_6\text{H}_5)_2$ groups to $-\text{PO}(\text{C}_6\text{H}_5)_2$ groups.^{3a}

(17) Essentially no chlorodiphenylphosphine remained after 5 hr (vpc).

1000 ml of methanol and 400 ml of hexane. The precipitated polymer was filtered, washed with solvent, and dried. The isolated polymer, 7.30 g, displayed a ^1H nmr spectrum (CDCl_3) in good agreement with structure 5: δ 0.06–2.7 (alkyl, broadened m, 3.2), 6.0–7.6 (aromatic, broadened, m, 14.0).

Anal. Found: C, 83.1; H, 7.0; Br, 2.2; P, 6.4.

Oxidation of Soluble 5. Formation of Soluble 7. A solution of 3.60 g of diphenylphosphinated polystyrene, from the previous experiment, in 30 ml of CH_2Cl_2 was stirred with 40 ml of 3% H_2O_2 for 2 hr at room temperature. The methylene chloride layer was separated, dried (MgSO_4), and then added to 900 ml of hexane. The precipitated polymer was filtered, washed, and dried; 2.82 g was obtained.

Reaction of Soluble 7 with Phosgene. Formation of Soluble 9 and Its Reaction with Terephthalic Acid. A 0.48-g sample of the phosphine oxide polymer, from the previous experiment, was stirred with 10 ml of CH_3CN (not soluble).¹⁸ Phosgene was passed over the solution for 10 min. During this time, vigorous evolution of gas was noted, and the polymer completely dissolved.¹⁸ Terephthalic acid (0.11 g) was added (not soluble), and the system was refluxed for 0.5 hr (then all soluble). The nmr spectrum showed only the polymer and terephthaloyl chloride: δ 8.16 (aromatic, s).

Preparation of Benzylidiphenylphosphine Oxide. A deep red solution of lithium diphenylphosphide was prepared under nitrogen from 11.0 g (0.050 mol) of chlorodiphenylphosphine, 0.80 g (0.12 mol) of lithium (wire, cut into *ca.* 0.25-in. lengths), and 150 ml of THF by stirring for 21 hr at *ca.* 25°. The excess lithium metal was removed, and then 6.3 g (0.050 mol) of benzyl chloride was added dropwise with some external cooling; the red color was completely discharged just as the last few drops were added. The solution was stirred at *ca.* 25° for an additional 1 hr, and then all of the solvent was removed *in vacuo*. The residue was stirred with CH_2Cl_2 , the insoluble lithium chloride was removed by filtration, and the filtrate was freed of solvent. The ^1H nmr spectrum (CDCl_3 internal TMS) of this residue was in agreement with the expected product, benzylidiphenylphosphine: δ 3.39 [CH_2 , very slightly broadened singlet ($J_{\text{P-H}} \approx 0$ Hz),¹⁹ 2], 6.85–7.62 (aryl, m, 15).

Exactly 8.00 g of this product was dissolved in 50 ml of CH_2Cl_2 , and this solution was vigorously stirred overnight with 75 ml of 3% aqueous H_2O_2 . The layers were separated, the CH_2Cl_2 solution was dried with MgSO_4 , and the solvent was removed *in vacuo*. The residue, after recrystallization from benzene, gave 6.1 g (72%) of benzylidiphenylphosphine oxide, mp 192–193° (lit.²⁰ mp 191–192°). The ^1H nmr spectrum (CDCl_3) was also characteristic: δ 3.64 (CH_2 , d, $J_{\text{P-H}} = 14$ Hz, 2), 7.10–8.05 (aryl, m, 15).

Reaction of Benzylidiphenylphosphine Oxide with Phosgene and the Reaction of the Product Therefrom with Phenylacetic Acid. Phosgene gas was passed over a suspension of 8.76 g (0.0300 mol) of benzylidiphenylphosphine oxide in 75 ml of CH_3CN . Vigorous gas evolution and dissolution of some additional material ensued. The system was then heated at reflux (condenser at *ca.* 15°) for 3 hr to drive off the excess phosgene. A sample of the solution portion of the resulting suspension was examined by ^1H nmr spectroscopy and showed peaks at δ 5.05 (CH_2 , d, $J_{\text{P-H}} = 11$ Hz, 2) and 7.10–8.41 (aryl, m, 15); no starting material remained. This spectrum agreed with the expected product, benzylidiphenylphosphine dichloride. This nmr sample was carefully returned to the main portion of the reaction.

Then, 4.08 g (0.0300 mol) of phenylacetic acid was added. The resulting homogeneous²¹ solution, by ^1H nmr analysis, contained

(18) This physical behavior is exactly analogous to that observed in the reaction of triphenylphosphine oxide with phosgene in this solvent.

(19) This value is in line with those for other alkyl phosphines; see G. Mavel, *Progr. Nucl. Magn. Resonance Spectrosc.*, 1, 261, 266 (1966), and references cited therein.

(20) A. M. Aguiar, J. Beisler, and A. Mills, *J. Org. Chem.*, 27, 1001 (1962).

only phenylacetyl chloride [δ 4.40 (CH_2 , s) + aryl] and benzylidiphenylphosphine oxide²¹ [δ 4.20 (CH_2 , d, $J_{\text{P-H}} = 14$ Hz) + aryl] in a 1:1 mole ratio; neither phenylacetic acid nor benzylidiphenylphosphine dichloride could be detected.

The reaction mixture was neutralized by stirring with aqueous NaHCO_3 . The precipitate which then appeared was filtered, washed with some water, and dried. In this way, 8.10 g (92%) of pure benzylidiphenylphosphine oxide was recovered: mp 191–192°; ^1H nmr (CDCl_3) identical with that observed previously.

Preparation of Methyl Diphenylphosphinite.²² To a stirred solution of 32.0 g (1.00 mol) of anhydrous methanol and 79.0 g (1.00 mol) of pyridine (Karl Fischer reagent grade) in 2000 ml of Et_2O (freshly distilled from CaH_2) was added dropwise during 1 hr at 0° a second solution of 220.0 g (1.00 mol) of chlorodiphenylphosphine in 200 ml of Et_2O . After the addition was complete, the system was allowed to warm to *ca.* 25°, and the insoluble pyridine hydrochloride was removed by filtration. The Et_2O was removed and the product distilled, bp 93° (0.1 mm) (lit.²² 151–152° (10 mm)) to give 170.3 g (79%) of methyl diphenylphosphinite: ^1H nmr (CDCl_3) δ 3.56 (OCH_3 , d, $J_{\text{P-H}} = 14$ Hz, 3), 7.13–7.76 (aryl, m, 10).

Reaction of Methyl Diphenylphosphinite with Benzyl Chloride. Route to Benzylidiphenylphosphine Oxide via an Arbuzov Reaction. A solution of 1.26 g (0.010 mol) of benzyl chloride and 2.16 g (0.010 mol) of methyl diphenylphosphinite in 5 ml of dry chlorobenzene was refluxed under nitrogen. The reaction was monitored by removing small samples, diluting with CDCl_3 , and examining the ^1H nmr spectrum. In this way, the disappearance of the starting materials ($-\text{CH}_2\text{Cl}$, δ 4.63, s; $\text{P}-\text{OCH}_3$; 3.77, d, $J = 14$ Hz) and the simultaneous appearance of benzylidiphenylphosphine oxide ($\text{P}-\text{CH}_2$, 3.75, d, $J = 14$ Hz) was observed; the CH_2 doublet for the latter in these chlorobenzene- CDCl_3 solutions was only ~ 0.02 ppm upfield from that of the CH_3O doublet of the starting material, and the $J_{\text{P-H}}$ was essentially the same. Some buildup of methyl chloride in the early part of the reaction was noted (δ 3.00), but it was readily lost from the refluxing (condenser at 15°) reaction mixture because of its volatility; only a trace of diphenylmethylphosphine oxide, resulting from a side-Arbuzov reaction with methyl chloride, was detected ($\text{P}-\text{CH}_3$, δ 2.09, d, $J = 13$ Hz). The reaction was complete after 6 hr at reflux, and the product recrystallized out on cooling. In this way, 2.08 g of benzylidiphenylphosphine oxide, mp 192–193°, was obtained; its ^1H nmr (CDCl_3) spectrum was identical with that found previously (*vide supra*).

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Supplementary Material Available. Additional experimental procedures will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-6469.

(21) The phosphine oxide was not very soluble in acetonitrile. This solution was homogeneous, probably because the HCl produced by the reaction formed a hydrochloride salt with the phosphine oxide which was soluble. The relatively large downfield shift of the $\text{P}-\text{CH}_2$ protons in this solution from that reported above for the pure phosphine oxide (in CDCl_3) is also suggestive of salt formation as is the observed precipitation of the phosphine oxide when the system was neutralized.

(22) Modification of the method of A. E. Arbuzov and K. V. Nikonov, *Zh. Obshch. Khim.*, 18, 2008 (1948); *Chem. Abstr.*, 43, 3801 (1949).