other evidence substantiates its participation.[1,4,8,10-13] Evaluation of the data obtained on product yield indicates clearly that the conversion into the displacement products depends on the relative concentration of reactants.

Comparison of yields of displacement products indicates that 1 is less reactive than trimethyl phosphite[1b] toward 2. The comparison is interesting since identical leaving groups are being displaced on phosphorus. Whether the complexing ability or the geometric features of the two esters (O–P–O angle in 1 is $\sim$109° compared with $\sim$100° for the O–P–O angle in trimethyl phosphite)[21] governs the course of the reaction is problematical. Formation of the Grignard complex of the phosphite has been postulated to enhance reactivity by increasing the partial positive charge on phosphorus and by reducing steric hindrance of backside attack through an increase in the O–P–O bond angle.[7] Such hybridization on phosphorus may not be necessary in phosphate complex formation. Though the formation of the complex of 1 undoubtedly increases the partial positive charge on phosphorus, the effect is certainly less than with the phosphite.

Experimental Section

Starting Materials.—Trimethyl phosphate (1, Ethyl Corp.), triethyl phosphate (Matheson Coleman and Bell), diphenyl phenylphosphonate and triphenyl phosphate (6, Victor Chemical), phenyl Grignard reagent (2), ethyl Grignard reagent and methyl Grignard reagent (Arapahoe Chemical), triethylamine (Eastman), and tris(2,6-dimethylphenyl) phosphate (Aldrich) were obtained from commercial sources. Methyl diphenylphosphinate (4) and triphenylphosphine oxide (5) were generously supplied by T. H. Austin. All of the liquids were distilled and the center cuts, as examined for purity by gas chromatography with the Hy-Fi Aerograph A-550 hydrogen flame chromatograph, showed only a single peak.[6] All of the solids were recrystallized and each showed one peak by gas chromatography.

Dimethyl Phenylphosphonate (3).—Phenylphosphonic dichloride, (76.80 g, 0.39 mole), was dissolved in 0.3 l. of absolute ether in a 1-l. flask equipped with a stirrer, a condenser, thermometer, and a pressure-equalizing addition funnel charged with triethylamine (95.75 g, 0.94 mole). The entire system was swept with anhydrous nitrogen. After the dropwise addition of the amine was completed (30 min), the flask was immersed in an ice bath and the temperature was adjusted to 10°. Methanol (28.85 g, 0.882 mole) was added dropwise with the temperature maintained below 16°. Ethyl ether (100 ml) was added to the white slurry to facilitate stirring. The reaction was then heated under reflux for 45 min, cooled, and filtered to remove the white solid. The liquid residue was dried over anhydrous magnesium sulfate, concentrated to 80–100 ml of dark red liquid, and vacuum distilled (53.45 g, 72.9%), bp 79–80° (2.0 mm) [lit.[23] bp 103° (4 mm)].

Reaction of 1 with 2.—The following procedure is typical of the method used. Commercial 2 ($\sim$3 *N*) was added to 200 ml of anhydrous ether under a blanket of nitrogen. Concentration of the reagent was determined by removing several 1.0-ml aliquots, quenching in 0.1027 *N* hydrochloric acid, boiling, and back titrating the excess acid with 0.1028 *N* sodium hydroxide.[1b]

A solution of 1 (13.73 g, 0.0980 mole) in 50 ml of anhydrous benzene was added dropwise at room temperature with stirring to 0.2941 mole of the Grignard reagent in 300 ml of ether. The reaction temperature rose 2° during the period of addition (45 min). An additional 150 ml of dry benzene was added and the mixture was then heated rapidly to 60°.

The mixture was held at reflux for 1 hr at 60–63° during which time a syrupy solid appeared on the walls of the flask. The mixture was cooled to 3° and hydrolyzed with cold 15% ammonium chloride (400 ml). During addition of the first 25 ml, the reaction was exothermic necessitating cooling and dropwise addition to maintain the temperature below 15°. The remainder was then added rapidly and the mixture was allowed to come to room temperature. Because of slow decomposition of the solid in the aqueous layer, stirring was continued for 3 hr. The organic layer was decanted and the aqueous layer was extracted with three 100-ml quantities of ether. The original organic layer and the extracts were dried ($MgSO_4$), combined, and concentrated to 30 ml. The concentrate was diluted to exactly 100 ml with ether for gc analysis.[24] In this experiment 4, 5, toluene, and biphenyl were identified as major products. No dimethyl phenylphosphonate (3) was detected.

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[23] C. E. Griffin and N. T. Castellucci, *J. Org. Chem.*, **26**, 629 (1961).

[24] Gc analyses were obtained using an Aerograph Hy-Fi A550 and an Aerograph 1520B equipped with hydrogen flame detectors. Analyses were obtained on the following columns; silicone rubber (5% on acid-washed, DMCS-treated Chromosorb G, 60–80 mesh, 6 ft × $^1/_8$ in.) and Silicone 30 (6% on acid-washed, DMCS-treated Chromosorb G, 80–100 mesh, 6 ft × $^1/_8$ in.). Since it was not possible to separate biphenyl and 3 on the above columns, all analyses for 3 were obtained using an SE-30 column (5% on Chromosorb W 60–80 mesh, 5 ft × $^1/_8$ in.).

Nucleophilic Displacement Reactions on Organophosphorus Esters by Grignard Reagents. III. The Reaction of Alkyl Diphenylphosphinates with Alkyl Grignards[1]

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The relative reactivities of *n*-propyl, isobutyl, and neopentyl diphenylphosphinates with methyl-, *n*-propyl-, and *sec*-butylmagnesium iodide were evaluated. The order of reactivity of the phosphinates for certain Grignard reagents is *n*-propyl > isobutyl > neopentyl; the order of the Grignard reagent for a specific phosphinate is methyl > *n*-propyl > *sec*-butyl. The order of reactivity of the phosphinates was observed to parallel the ability of these compounds to complex with anhydrous magnesium iodide. A mechanism is postulated wherein facile coordination of the Grignard reagent with the phosphinate is a requisite for reaction to occur.

The preparation of tertiary phosphine oxides *via* the reaction of Grignard reagents with phosphorus esters has been known for sometime. However, the available data at present do not permit evaluation of the importance of the different factors involved in these reactions.[3-5] Burger and Dawson prepared tertiary phosphine oxides from dialkyl phosphorochloridates and Grignard reagents.[6] With *o*-anisyl Grignard reagent, in a 1:1 mole ratio of reactants, it was possible to

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[1] (a) We gratefully acknowledge support by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Grant AF-AFOSR-132-65. (b) For the preceding paper see, K. D. Berlin and M. E. Peterson, *J. Org. Chem.*, **32**, 125 (1967).

[2] Postdoctoral Research Associate, 1965–1966.

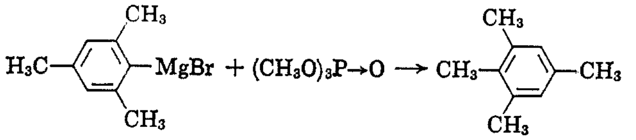
[3] K. D. Berlin and G. B. Butler, *Chem. Rev.*, **60**, 243 (1960).

[4] K. D. Berlin, T. H. Austin, M. Peterson, and M. Nagabhushanam in "Topics in Phosphorus Chemistry," Vol. I, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, Chapter 2.

[5] L. D. Friedman and G. O. Doak, *Chem. Rev.*, **57**, 479 (1957).

[6] A. Burger and N. D. Dawson, *J. Org. Chem.*, **16**, 1250 (1951).

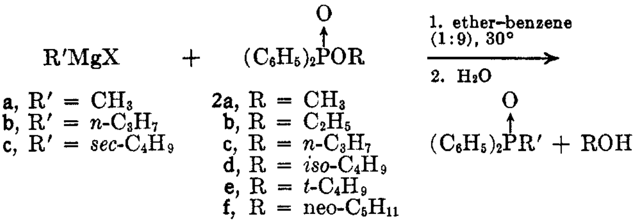
obtain a good yield of the corresponding dialkyl *o*-anisylphosphonate. It was suggested that a steric effect created by the *ortho* substituent in the Grignard reagent retarded further reaction of the intermediate phosphonate under the conditions of the reaction. Gilman[7] did not report that mesityl Grignard reagent attacked the phosphorus in trimethyl phosphate, but it was demonstrated that C alkylation by the Grignard reagent took place. Steric hindrance to approach of the Grignard reagent was suggested to accommodate this observation.[7] Indeed, tri-*n*-butyl phosphate failed to react with mesityl Grignard in ether or tetrahydrofuran.



Several workers have reported that good yields of tertiary phosphine oxides could be obtained by using an excess of the Grignard reagent with the required tetrasubstituted ester.[8-11] In several investigations[12-14] concerned with this type of displacement reaction on esters of phosphorus acids, it is likely that failure to obtain good yields of the tertiary phosphine oxides was due to the low molar ratio of Grignard reagent to that of the phosphorus ester.[3] Dawson and Burger[15] presented evidence that addition of magnesium bromide to a phosphonate, prior to reaction with the Grignard reagent, increased the yield of the expected tertiary phosphine oxide. An activated complex, in which the phosphoryl oxygen was coordinated with the magnesium, was the explanation offered for this observation. It seems likely that the attack of the nucleophile on the phosphorus was made more facile through coordination of the phosphoryl oxygen with the magnesium.[3] That the nature of the leaving group influences the facility with which these reactions occur has been indicated by the relative ease of displacement of the phenoxy group over that of the ethoxy moiety.[3,4,8]

We have investigated the reaction of a series of alkyl diphenylphosphinates with alkyl Grignard reagents (Scheme I). The size of R and R′ was varied to study the effect on the rate and over-all nature of the reaction. The use of the phosphinates precludes the ambiguity that can possibly arise from the formation of the intermediate esters which are capable of further reaction with the Grignard reagent.

SCHEME I



$$R'MgX + (C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}OR \xrightarrow[2.\ H_2O]{1.\ \text{ether-benzene } (1:9),\ 30°} (C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}R' + ROH$$

1a, $R' = CH_3$
b, $R' = n\text{-}C_3H_7$
c, $R' = sec\text{-}C_4H_9$

2a, $R = CH_3$
b, $R = C_2H_5$
c, $R = n\text{-}C_3H_7$
d, $R = iso\text{-}C_4H_9$
e, $R = t\text{-}C_4H_9$
f, $R = \text{neo-}C_5H_{11}$

Results

Reaction of Phosphinates with Grignard Reagents.—The constituents of the reaction mixture of the phosphinate and Grignard reagent were observed to be dependent on the nature of the alkyl substituent in the phosphinate and the type of Grignard reagent. For example, methyl (**2a**) and ethyl diphenylphosphinates (**2b**) form a turbid mixture upon the rapid addition of approximately 25% of the methylmagnesium iodide (1:1 molar ratio of ester to Grignard reagent) with the subsequent separation of a syrupy substance[16] after a reaction period of 15–20 min. With *n*-propyl (**1c**) and isobutyl diphenylphosphinates (**2d**), turbidity occurred upon addition of about 50% of the Grignard reagent. The turbidity disappeared on further addition of the methylmagnesium iodide (**1a**). Separation of a syrupy material resulted after 8–12 hr of reaction with *n*-propyl diphenylphosphinate and 20 hr in the case of isobutyl diphenylphosphinate. In contrast, no turbidity was observed with neopentyl diphenylphosphinate (**2f**) and **1a**, but separation of a syrupy material took place after 20–24 hr of reaction. Formation of all the oils was found to depend also on the molar ratio of phosphinate to Grignard reagent. For example, when a 2:1 molar ratio of methylmagnesium iodide and the phosphinate, respectively, was used, the oil was not observed even after 48 hr. The formation of the oils with 1:1 molar ratio of esters to Grignard reagents is considered to result from the low solubility of the complexed ester. In the presence of excess methyl Grignard reagent, the complex ester is consumed rapidly and no oil is observed.

Similarly, the occurrence of turbidity in the reaction mixture has been observed with *n*-propyl (**1b**) or *sec*-butyl Grignard reagent (**1c**) when allowed to react with **2a**, **2b**, or **2c**. In contrast, highly branched alkyl phosphinates such as isobutyl and neopentyl diphenylphosphinates did not form turbid solutions at any molar ratio. This behavior is apparently true with higher alkyl Grignard reagents and branched alkyl diphenylphosphinates.

The syrupy precipitate was isolated from the reaction of phosphinates with methylmagnesium iodide and was analyzed for phosphorus and magnesium ion content. Table I summarizes the results. The relative

TABLE I

ANALYSES OF THE PRECIPITATES FROM THE REACTION OF METHYLMAGNESIUM IODIDE AND ALKYL DIPHENYLPHOSPHINATES $[(C_6H_5)_2P(O)(OR)]$

R	Time of sample withdrawal, hr[a]	Relative amounts: Phosphinate	Relative amounts: Phosphine oxide	Relative amounts: Mg	Total P cpd/ Mg ion
2c	2.3	1	1.10	2.3	1:1.09
	5.0	1	1.10	2.4	1:1.14
2d	2.2	1	0.77	3.8	1:1.65
	2.2	1	1.40	3.5	1:1.46
2f	5.0	1	0.94	5.43	1:2.8
	14.0	1	0.95	5.87	1:3.0

[a] Time of sample withdrawal has reference to the time of initial separation of the oil.

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(7) H. Gilman and B. J. Gaj, *J. Am. Chem. Soc.*, **82**, 6326 (1960).

(8) K. D. Berlin and M. Nagabhushanam, *Chem. Ind.* (London), 974 (1964).

(9) P. W. Morgan and B. C. Herr, *J. Am. Chem. Soc.*, **74**, 4526 (1952).

(10) K. D. Berlin and G. B. Butler, *J. Org. Chem.*, **25**, 2006 (1960).

(11) K. D. Berlin and G. B. Butler, *J. Am. Chem. Soc.*, **82**, 2712 (1960).

(12) H. Gilman and J. Robinson, *Rec. Trav. Chim.*, **48**, 328 (1929).

(13) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **72**, 5508 (1950).

(14) M. H. Maguire and G. Shaw, *J. Chem. Soc.*, 2039 (1955).

(15) N. D. Dawson and A. Burger, *J. Org. Chem.*, **18**, 207 (1953).

(16) (a) An analogous situation has been found with ketones and Grignard reagents; see P. Pfeiffer and H. Blank, *J. Prakt. Chem.*, **153**, 242 (1939). These investigators actually isolated coordination compounds between Grignard reagents and ketones as solids or oily liquids; treatment with water regenerated the ketone. (b) R. N. Lewis and J. R. Wright, *J. Am. Chem. Soc.*, **74**, 1253 (1952). Complexation of ketones with Grignard reagents and solvent effects were evaluated by these workers.

amounts of the phosphinate to phosphine oxide, in this precipitate, for a particular reaction vary little with time, but the ratio of the total phosphorus compounds to magnesium ion is not constant and changes with a change in the alkyl diphenylphosphinate. Because of the many species present in the reaction mixture, it is difficult to speculate on the exact nature of this complex. It is of interest to note that Pickard and Kenyon[17] reported isolation of the complex of methylmagnesium iodide and tribenzylphosphine oxide. This complex was apparently stable and analyzed to have a formula of $3(C_6H_5CH_2)_3P\rightarrow O\cdot Mg(CH_3)I$.

A series of experiments was conducted wherein the changes in concentration of phosphinate and phosphine oxide formed were determined as a function of time. Efforts to fit the data to a simple kinetic order (first, second, or third) did not give linear plots. However, a typical plot of the concentration of phosphinate *vs.* time is shown in Figure 1. The curves representing the reaction with a 1:1 molar ratio of reactants are characterized by two inflection points. The first one can be attributed to a concentration of phosphine oxide which has an inhibitory effect on the rate of reaction of phosphinate. The second inflection point is due to the separation of the syrupy oil containing phosphinate and phosphine oxide.

In order to evaluate the effect of structure of both the reactants on the rates of reaction, a series of runs was made using a variety of phosphinates and alkyl Grignard reagents. Tables II and III summarize the results. It is noteworthy that the reactivity decreases with branching of the alkyl substituent in the phosphinate and also in the organometallic reagent. The change in the reactivity was much more apparent when bulky Grignard reagents were employed. In the case of *t*-butyl diphenylphosphinate (**2c**), the predominant course of the reaction was elimination. The formation of isobutylene was proven by isolation of the olefin and identification by its infrared spectrum. Diphenylphosphinic acid was also isolated and characterized.

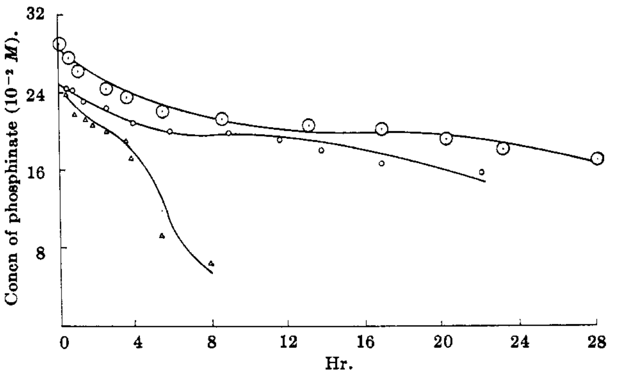


Figure 1.—Reaction of alkyl diphenylphosphinate and methylmagnesium iodide with a 1:1 mole ratio of reactants: △, *n*-propyl; ○, isobutyl; ⊙, neopentyl.

TABLE II

REACTION OF METHYLMAGNESIUM IODIDE WITH ALKYL DIPHENYLPHOSPHINATES IN BENZENE–ETHER (9:1) AT 30°[a]

Alkyl group	Ratio of $(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}OR/RMgX$	Fraction reacted after 60 min, %	Remarks
	1:1	13.4	
2c	1:1	6.6	With 9.2% $(C_6H_5)_2P(O)CH_3$ added
	2:1	23.9	
2d	1:1	7.1	
	2:1	12.9	
2f	1:1	4.8	
2e	2:1	8.9	
	1:1		86% elimination giving isobutylene, only 14% displacement on phosphorus

[a] The data pertain to analysis of the reaction solution before precipitation.

TABLE III

REACTION OF ALKYL DIPHENYLPHOSPHINATES WITH *n*-PROPYL- AND *sec*-BUTYLMAGNESIUM IODIDE IN BENZENE–ETHER (9:1) AT 30.0°

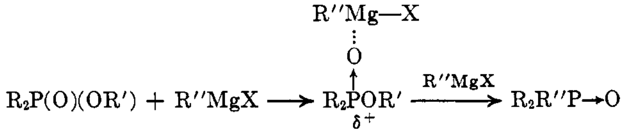
		1b		1c	
	Ratio	Fraction reacted after 60 min, %	Fraction reacted after 24 hr, %	Fraction reacted after 60 min, %	Fraction reacted after 24 hr, %
2c	1:1	Trace	6.35	0	1.44
2d	1:1	0	0.24	0	0[b]
2f	1:1	*a*		0	0[b]

[a] Oxide could not be resolved from the phosphinate. [b] No oxide detected even after 59 hr of reaction.

Complex Formation with MgI₂.—A careful study of the complexing ability of alkyl diphenylphosphinates with magnesium iodide as a function of the alkyl substituent has been made using infrared spectroscopy.[18] The order of decreasing ability of MgI_2 to complex with the esters of diphenylphosphinic acid is methyl > *n*-propyl > isobutyl > isopropyl ~ neopentyl.

Discussion

On the basis of the catalytic action of magnesium bromide and the increased yields of phosphine oxide when excess Grignard reagent was used in the reaction of phosphorus esters, Burger and Dawson[15] proposed a gross mechanism which can be illustrated with a phosphinate. One can surmise that on the basis of



$$R_2P(O)(OR') + R''MgX \longrightarrow \underset{\delta^+}{R_2\overset{\overset{\overset{\delta^-}{R''Mg{-}X}}{\vdots}}{\overset{O}{\overset{\uparrow}{P}}}OR'} \xrightarrow{R''MgX} R_2R''P\rightarrow O$$

this proposal, several parameters, in addition to the basicity of the leaving group, could conceivably influence the mode of the reaction. It is likely that structural and solvent changes[19] and the presence of any species which could affect the complex formation might be very influential in regard to the rate of reaction as well as to the nature of the products.

From consideration of our results, it seems that, when such displacements on phosphorus esters are complicated by the presence of phosphine oxide, complexation of the Grignard reagent with the oxide can occur and retard the entire chemical transformation. Table II shows a significant decrease in the relative rate of reaction of **2c** and **1a** in the presence of added

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(17) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **89**, 262 (1906).

(18) K. D. Berlin and R. U. Pagilagan, *Chem. Commun.* (London), 687 (1966).

(19) R. G. Laughlin, *J. Org. Chem.*, **30**, 1322 (1965).

TABLE IV

PHYSICAL PROPERTIES OF THE ALKYL DIPHENYLPHOSPHINATES [$(C_6H_5)_2P(O)(OR)$]

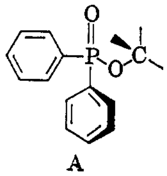
		Anal, %						Infrared,[a] cm^{-1}		Nmr[b]			
		Calcd			Found								
R	Mp, °C	C	H	P	C	H	P	P–O–C	P→O	CH_3	OCCH	OCH_2	Aryl H
n-C_3H_7	89.5–91.0	69.22	6.51	11.90	69.40	6.48	12.09	1000	1222	1.00 t	2.00 m	4.05 q	7.25–8.30 m
i-C_4H_9	79.3–80.5	70.06	6.98	11.30	69.94	7.05	11.45	1020	1221	1.00 d	2.45 m	3.93 q	7.25–8.25 m
neo-C_5H_{11}	86.5–87.5	70.82	7.34	10.74	70.84	7.36	10.80	1025	1227	1.00 s		3.75 d	7.35–8.05 m

[a] Spectra taken in KBr pellet using a Beckman infrared spectrophotometer (IR-5a). [b] Nmr spectra taken in 10% CCl_4 solution using a Varian Associate Model A-60; the symbols s, d, t, q, and m represent singlet, doublet, triplet, quartet, and multiplet, respectively.

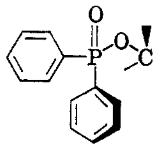
methyldiphenylphosphine oxide. Furthermore, the appearance of a syrupy precipitate, which normally occurs between 8 and 12 hr with a 1:1 molar ratio of reactants, was expedited by the presence of added phosphine oxide to 4.5 hr (essentially the same concentration and mole ratio of reactants were used). Thus, in order to obtain good yields of the phosphine oxide in these reactions, it is apparent that the necessity of using excess Grignard reagent is to compensate for the competition between the phosphine oxide and the ester for complexation with the organometallic reagent.[11,17,18] That this complexation does indeed occur in the reaction is indicated by the inhibitory effect of added phosphine oxide and the isolation and analyses of the syrupy precipitate from the reaction mixture (Tables I and II). It is interesting to note that the ratio of the total phosphorus compounds to that of magnesium ion in these precipitates increases with branching in the alkyl group of the phosphinate. It is difficult to speculate on the nature of this complex as one would expect the presence of several species in the reaction mixture. Nevertheless, the complex formation between the phosphinate and the Grignard reagent is further substantiated by the formation of turbidity upon mixing of the solution of the phosphorus ester with that of the organometallic reactant. The occurrence of turbidity could not be due to concentration differences as the range of concentration used in these experiments is far below the maximum value for insolubility of phosphinate or phosphine oxide (all phosphinates and phosphine oxides are soluble in ether–benzene to the extent that 0.5 M solutions were easily prepared; the kinetic runs did not contain solutions of ester or oxide in excess of 0.36 M). The obvious explanation is that the complexation is quite dependent on the steric requirement of the Grignard reagent and phosphinate. For example, there was no turbidity with **1a** or **1b** and **2f**. Similarly, the same behavior has been observed with **2d** or **2f** when treated with *sec*-butylmagnesium iodide (**1c**).[18] Thus complex formation is inhibited by the steric requirements of the alkyl group in both the Grignard and phosphinate. This result is in agreement with an observation on the complexing ability of these phosphinates with anhydrous magnesium iodide.[18]

From the relative reactivities of the phosphinates (Tables II and III) it appears that there is more sensitivity to a change in the structure of the Grignard reagent that there is in the phosphinate itself. Table II shows less alteration in the relative reactivity as the branching in the alkyl group of the phosphinate is increased. The observed decrease in reactivity could be due, in part, to the increasing basicity of the leaving group as methyl groups are successively introduced at the β-carbon atom. This, however, is in extreme contrast when such a change in structure is manifested in the Grignard reagent. After 24 hr of reaction, only 1.44% of **2c** had reacted with **1c** and no phosphine oxide was detected from the reaction of **1c** with **2d** or **2f**. As one would expect, the relative reactivity of these esters with n-propylmagnesium iodide lies between the methyl and *sec*-butyl Grignard reagents.

Siddall and Prohaska[20,21] have postulated the existence of rotamers in several phosphorus esters. Of the two energetically possible conformations (structure A and B), structure A is favored over that of B as there is considerable steric interaction between the phenyl and alkyl groups in B.[18] In structure A the phosphoryl group is partially screened by the alkyl group and approach by a reactant is made difficult. In any event as R increases in size, ease of complex formation should decrease. Although the nmr data for the esters do not infer a high population of preferred conformation (by virtue of nonequivalence of protons in the alcohol portion), the complex (ester–Grignard) may indeed assume a rigid geometric configuration.



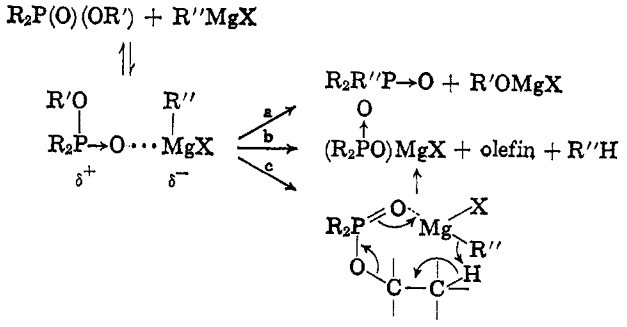
A



B

In phosphinate esters with alkyl groups having relatively high steric requirements, such as **2e**, the attack on phosphorus is apparently unfavorable (models also suggest this is true) and the mode of reaction is essentially a β-elimination process. This behavior of **2e** has been observed also with the reaction of this phosphinate with anhydrous magnesium iodide giving isobutylene and the diphenylphosphinic acid magnesium salt.[18]

A unified mechanism can, thus, be proposed to accommodate the observed results. It is not possible to



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(20) T. H. Siddall, III, and C. A. Prohaska, *J. Am. Chem. Soc.*, **84**, 2502 (1962).

(21) T. H. Siddall, III, and C. A. Prohaska, *ibid.*, **84**, 3467 (1962).

distinguish at present between mechanistic pathway b or c.

It does seem reasonable that the decrease in reactivity in the series of phosphinates for a particular Grignard reagent could be attributed in part to some steric interference in the formation of the complex. This contention is made more convincing if one takes into consideration the drastic change in reactivity of a phosphinate with **1a**, **1b**, or **1c**. In this case, the basicity of the alkoxy leaving group is not changed and furthermore, the basicity of the organometallic reagent would be expected to increase in the series due to the inductive electron-donating ability of alkyl groups. Actually, one would expect the order of increasing reactivity of the Grignard reagent to be methyl < *n*-propyl < *sec*-butyl on the basis of inductive effects alone.

The small differences in reactivity of the series of alkyl phosphinates for methylmagnesium iodide could be due mostly to the increasing basicity of the leaving group. It is conceivable that because the methyl Grignard reagent has small steric requirements, complexation is not greatly affected even in the case of neopentyl diphenylphosphinate. With *t*-butyl diphenylphosphinate wherein the alkyl groups are attached to the α carbon, the attack on phosphorus becomes very prohibitive and the predominant pathway of reaction is elimination. As one would predict, only elimination products were detected in the reaction of **2e** with bulky Grignard reagents such as **1b** and **1c**.

Experimental Section[22]

Grignard Reagents.—The methylmagnesium iodide was obtained from the Arapahoe Chemical Co., Boulder, Colo. The *n*-propyl- (**1b**) and *sec*-butylmagnesium iodide (**1c**) were prepared by standard procedures. The Grignard solutions used in the experiments were in 1:1 benzene–ether and titrated immediately before use.

Preparation of Alkyl Diphenylphosphinates.—The alkyl diphenylphosphinates were prepared by methods already in the literature.[23] The structures of these compounds are substantiated by infrared, nmr, and elemental analyses; the latter was carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. Table IV gives the properties of and results of elemental analyses on the new esters.

Measurement of the Relative Reactivities of the Phosphinates with Grignard Reagents.—The following is typical of the procedures used.

A solution of 8.00 ml (0.3528 *M*) of *n*-propyl diphenylphosphinate in anhydrous benzene, as measured by a buret, was introduced into a glass bulb equipped with two openings. One opening was connected to a nitrogen gas ballast and the other was fitted with a neoprene rubber cap. To this was added rapidly 2.00 ml of 1.4114 *M* solution of methylmagnesium iodide. The mixture was agitated vigorously for 30 sec and placed in an oil bath maintained at a temperature of 30.0 ± 0.2°. At selected time intervals, a 0.4-ml aliquot portion of the reaction mixture was withdrawn by means of a syringe and hydrolyzed with 2.0 ml of 17% aqueous ammonium chloride solution. The mixture was allowed to stand for 1 hr at room temperature and the concentrations of the *n*-propyl diphenylphosphinate and methyldiphenylphosphine oxide were determined by gc.[24]

Reaction of Grignard Reagents with *t*-Butyl Diphenylphosphinate (2e).—A solution of methylmagnesium iodide in 1:1 benzene–ether containing 0.01 mole of the Grignard reagent was placed in a 100-ml, two-necked flask fitted with a gas-equilibrating dropping funnel and a condenser. At the end of the condenser was attached drying tubes (NaOH and a molecular sieve) from which a line led to a gas buret. A solution of 2.74 g (0.01 mole) of **2e** in 40 ml of anhydrous benzene, contained in the addition funnel, was added dropwise within a period of 15 min. The reaction mixture was allowed to react for 16 hr after which time the gas buret was disconnected and the reaction mixture was cooled and hydrolyzed with 100 ml of 17% ammonium chloride solution. The infrared spectrum of the gaseous product was taken and found to be identical with that of isobutylene. The organic layer was analyzed by gc and showed the presence of only diphenylmethylphosphine oxide and a trace of **2e**.

The aqueous layer was made strongly acid, pH ~1, with 6 *N* HCl solution and allowed to stand at room temperature for 6 hr. The white solid that formed was filtered off and washed in sequence with 5 ml of distilled water and finally with 10 ml of benzene. This compound was identified as the diphenylphosphinic acid by mixture melting point determination with an authentic sample and infrared analysis. The yield of diphenylphosphinic acid was 30% and the phosphine oxide was 5% based on the phosphinate.

Analyses of the Precipitate.—The syrupy material from the reaction of methylmagnesium iodide with either **2c**, **2d**, or **2f**, was withdrawn by means of a syringe and made up to a volume of 1.0 ml with anhydrous benzene. The solution was then hydrolyzed with 2.00 ml of 17% aqueous ammonium chloride solution. The organic layer was separated and analyzed by gc.

The magnesium ion content of the aqueous layer was determined by titration with EDTA.[25]

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[22] All melting points are corrected. Solvents used were all anhydrous and all reactions and manipulations were carried out under N_2 unless stated otherwise.

[23] K. D. Berlin, T. H. Austin, and M. Nagabhushanam, *J. Org. Chem.*, **30**, 1267 (1965).

[24] K. D. Berlin, T. H. Austin, M. Nagabhushanam, M. Peterson, J. Calvert, L. A. Wilson, and D. Hopper, *J. Gas Chromatog.*, **3**, 256 (1965).

[25] C. N. Reilly and D. T. Sawyer, "Experiments for Instrumental Methods," McGraw-Hill Book Co., Inc., New York, N. Y., 1961, pp 260–267.