

By suitable manipulation of the algebraic equivalents of the preceding paragraph it is readily seen that the most stable hydrocarbon of type B will have a  $4n + 2$  central ring flanked by two rings, the sum of whose sizes is  $4n'$ . In addition the flanking rings will be fused to the central rings so as to form even bridges, which for a central benzene ring means *meta* fusion.

The group of molecules of type C in Chart V can be seen to be incapable of having a zero HMO level because only one of the coefficients is odd and must enter as  $\pm 3$  to the final value of  $\pi_e$ . It might be supposed that the least stable molecules would occur when the first two terms of eq 8 had one sign and the last two terms have the opposite sign ( $\pi_e = \pm 1$ ). It is demonstrated in the Appendix that this situation is topologically impossible. The most stable molecule should occur when all of the terms in eq 8 have the same sign ( $\pi_e = +9$ ). Using the same method applied above and described in the Appendix it is possible to show that this maximum value is also topologically impossible. Accordingly, neither of the extreme values are represented by real molecules.

**Acknowledgment.** The support of the National Science Foundation is gratefully acknowledged.

### Appendix

The total number of  $\pi$  atoms in a molecule of type C of Chart V is  $(M + N + P - 4)$  and the total number of double bonds in the molecule is  $(M + N + P - 4)/2$ . For the case where  $M$ ,  $N$ , and  $P$  are all odd the number of double bonds in each is  $(M - 1)/2$ ,  $(N - 1)/2$ , and  $(P - 1)/2$ , respectively. If the total number of double bonds and the number of double bonds in one ring, say  $M$ , are to be even it follows that  $[(M + N + P - 4)/2] - [(M - 1)/2] = \text{even} - \text{even} = \text{even}$  so that  $N + P - 3$  must also be even. This is clearly impossible for odd  $N$  and  $P$  and no cases of type C with a  $|\pi_e|$  of 1 can exist with an even total number of double bonds. If the total number of double bonds and the number of double bonds in one ring, say  $M$ , are to be odd it follows that  $N + P - 3$  must be even. Again this is impossible and no examples of type C with  $\pi_e = \pm 1$  can exist.

## The Kinetics of the Reaction of Ethyl Diphenylphosphinate with Phenylmagnesium Bromide

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**Abstract:** The reaction of ethyl diphenylphosphinate and phenylmagnesium bromide has been investigated in tetrahydrofuran (THF). Infrared and phosphorus nmr spectral evidence has been obtained for the rapid formation of a moderately strong 1:1 complex between the phosphoryl oxygen atom of the phosphinate and the magnesium atom of the Grignard reagent. The  $K_{eq}$  for the formation of this complex is estimated to be about  $6 \times 10^3$  l. mole<sup>-1</sup> or greater. The exchange of ethyl diphenylphosphinate in the complex is fast on the nmr time scale. Subsequent slow reorganization of this complex to product has been found to follow first-order kinetics and to be concentration independent over the range that was investigated (0.03–0.5 *M*). Below 0.03 *M* the results suggest that dissociation of the complex becomes appreciable. The  $E_a$  (13.4 kcal/mole) and  $\Delta S^\ddagger$  (–33.2 eu) for the reorganization of the complex to product were calculated from the average first-order rate constants obtained at four temperatures. The phosphorus nmr spectrum of the product of the reorganization step indicates a relatively strong complex between the phosphoryl oxygen atom of triphenylphosphine oxide and magnesium bromoethoxide and not a pentacoordinate phosphorane as has been suggested. Tributylphosphine oxide accelerates the rate of reaction of ethyl diphenylphosphinate with phenylmagnesium bromide, whereas magnesium bromoethoxide retards the reaction. Phosphorus nmr spectral evidence for complex formation is presented. The rate of reaction of ethyl diphenylphosphinate with phenylmagnesium bromide in THF is about five times that in diethyl ether. All of these observations appear consistent with the proposed mechanism. Spectral and kinetic data have been obtained for the more complex reaction of diphenylmagnesium with ethyl diphenylphosphinate.

The kinetics and mechanisms of reactions of Grignard reagents with ketones have been studied extensively.<sup>1</sup> In contrast, the kinetics of the reactions of phosphorus esters with Grignard reagents have received little atten-

tion. This may be due in part to the ensuing controversy over the nature of the Grignard reagent and its role in the mechanism of reaction with ketones. Another factor may be that many of the reaction mixtures of phosphorus esters and Grignard reagents become heterogeneous in diethyl ether alone or in benzene–ether mixtures.<sup>2</sup>

During the investigation of the reactions of phosphorus

(1) For recent pertinent reviews of this work see: (a) E. C. Ashby, *Quart. Rev.* (London), **2**, 259 (1967), and E. C. Ashby, R. B. Duke, and H. M. Neumann, *J. Amer. Chem. Soc.*, **89**, 1964 (1967); (b) S. G. Smith and J. Billet, *ibid.*, **89**, 6948 (1967); (c) S. G. Smith and G. Su, *ibid.*, **88**, 3995 (1966); (d) H. O. House and J. E. Oliver, *J. Org. Chem.*, **33**, 929 (1968); (e) G. E. Coates, M. L. H. Green, and K. Wade in "Organometallic Compounds, Vol. I, The Main Group Elements," G. E. Coates and K. Wade, Eds., Methuen and Co., Ltd., London, EC4, 1967, pp 76–103.

(2) This has been recognized as a complicating factor in rate studies of the reactions of alkyl diphenylphosphinates and methylmagnesium iodide: K. D. Berlin and R. U. Pagilagan, *J. Org. Chem.*, **32**, 129 (1967).

Table I. Phosphorus Nmr Data<sup>a</sup>

	Nmr, ppm	$\Delta$ , ppm
Ph <sub>2</sub> P(O)OEt	-28.2	
+0.5 PhMgBr	-31.4	3.2
+1.0 PhMgBr	-34.4	6.2
+2.0 PhMgBr	-34.5	6.3
+1.0 MgBrOEt	-32.3	4.1
+1.0 Ph <sub>2</sub> Mg	-31.7	3.5
+1.0 MgBr <sub>2</sub>	-30.0	1.8
Ph <sub>3</sub> PO	-23.5	
+1.0 PhMgBr	-36.2	12.7
+1.0 MgBrOEt	-33.8	10.3
Bu <sub>3</sub> PO	-41.7	
+0.5 PhMgBr	-59.6	17.9
+1.0 PhMgBr	-60.6	18.9
+2.0 PhMgBr	-60.5	18.8
Bu <sub>3</sub> PO		
+1 Ph <sub>2</sub> P(O)OEt	-59.6	17.9
+1.0 PhMgBr	-31.8	3.5

<sup>a</sup> All spectra were recorded in THF at 0.8 M concentration of phosphorus compound on a Varian HR-60 at 24.3 MHz (reference 85% H<sub>3</sub>PO<sub>4</sub>).

esters with Grignard reagents<sup>3</sup> several unique properties of the ethyl diphenylphosphinate-phenylmagnesium bromide-THF system became readily apparent. The combination of these properties, described below, makes this system particularly suitable for further study. The reaction is homogeneous under the conditions studied. The phenylmagnesium bromide is largely monomeric over a broad concentration range.<sup>1a</sup> Both the starting material and the product after hydrolysis are readily analyzed by gas chromatography. There are no complicating intermediates capable of reaction with phenylmagnesium bromide as there are in the reactions of triethyl phosphate and diethyl phenylphosphonate with phenylmagnesium bromide. Finally, the rate of reaction is sufficiently slow for convenient study, yet fast enough for study over a relatively wide temperature range. Further studies of this system are described in the present paper. The results are believed to be indicative of the reactive species in the Grignard reagent and the mechanism of the reaction of phosphorus esters with Grignard reagents and to be relatable to certain observations made about the reactions of ketones with Grignard reagents.

## Results

The phosphorus nmr spectra of ethyl diphenylphosphinate, triphenylphosphine oxide, and tributylphosphine oxide in THF are recorded in Table I along with the changes in the chemical shifts resulting from the presence of phenylmagnesium bromide, diphenylmagnesium bromide, and magnesium bromoethoxide.

The infrared phosphoryl frequency of ethyl diphenylphosphinate (6% in THF), recorded with a Perkin-Elmer Model 21 spectrophotometer, appeared at 1236 cm<sup>-1</sup> and was shifted to 1208 cm<sup>-1</sup> in the presence of 1 equiv of phenylmagnesium bromide.

The results of one set of gas chromatographic analyses of aliquots taken from the reaction of ethyl diphenylphosphinate and phenylmagnesium bromide are shown in Table II. (See the Experimental Section for an

Table II. Gas Chromatograph Analysis of the Reaction of Ethyl Diphenylphosphinate and Phenylmagnesium Bromide<sup>a</sup>

Time, min	% Ph <sub>2</sub> P(O)OEt	Concn, M
10	89	0.509
20	77	0.440
30	64	0.366
40	54	0.309
50	45	0.257
60	40	0.229
70	34	0.194
80	29	0.166
90	25	0.143
100	22	0.126
120	15	0.086

<sup>a</sup> Table III, expt 14, in THF at 67.8°; C<sub>0</sub> = 0.572 M in both reactants.

indication of the accuracy of this method.) Figure 1 illustrates a first-order plot of the data given in Table II. Reasonably good agreement with first-order kinetics was observed over 85% of the reaction, whereas a second-order plot of 1/C vs. t for this same run gave a curve which was evident after 35% reaction. In four similar experiments (0.572 M and 67.8°) good agreement with first-order kinetics was observed over 75, 76, 81, and 86% of the reactions. Beyond these points the reactions slowed very slightly, then more appreciably at about 90-95% reaction. The reactions *did* go to completion upon further heating overnight. Similarly, in experiments using 0.2 M concentrations at 67.8°, excellent agreement with first-order kinetics was observed over 76-83% of the reactions. Worthy of note is the fact that in the latter stages of the reaction the actual increment of change becomes relatively small compared to the error in measurement. This results in a greater degree of scatter or uncertainty in the final analyses than in the initial analyses. This problem is obviously minimized at the higher temperatures. At 0.03 M concentrations of reactants, excellent agreement with first-order kinetics was observed over 52-55% of the reactions, beyond which a decrease in the reaction rate was observed. The rate constants in Table III determined over the initial 52-53% of the reactions agreed with those obtained at higher concentrations. In two experiments with 0.01 M reactants, plots of log C vs. t gave distinct curves, the initial slopes of which were about one-half of those at higher concentrations.

The rate constants for the reaction of ethyl diphenylphosphinate with phenylmagnesium bromide determined by a least-squares treatment of data similar to that described above and obtained at four different temperatures are given in Table III. Also included in Table III are the initial concentrations of reactants (C<sub>0</sub>), the percentages of the reactions followed, and the number of analyses (n) made in each experiment.

Three experiments using 2:1 ratios of phenylmagnesium bromide:ethyl diphenylphosphinate were carried out simultaneously with three control reactions (1:1 ratios). First-order kinetics were observed in all cases and the rate constants were found to be nearly comparable. Second-order plots (1/C vs. t) and third-order plots (1/2C<sup>2</sup> vs. t) of the same data became distinct curves after about 25-35% reaction. Significantly, the rate of reaction was not increased by 100% excess phenyl-

(3) (a) H. R. Hays, *J. Org. Chem.*, **33**, 3690 (1968); (b) *ibid.*, **33**, 4201 (1968); (c) *ibid.*, in press.

Table III. Kinetic Data for the Reaction of Ethyl Diphenylphosphinate and Phenylmagnesium Bromide<sup>a</sup>

Expt	Temp, °C	C <sub>0</sub> , M	% reaction	n	k, sec <sup>-1</sup>	k <sub>av</sub> , sec <sup>-1</sup>
1	50.0 ± 0.01	0.433	27	6	8.99 × 10 <sup>-5</sup>	8.59 × 10 <sup>-5</sup>
2	50.0 ± 0.01	0.500	62	19	8.54 × 10 <sup>-5</sup>	
3	50.0 ± 0.01	0.500	58	9	8.13 × 10 <sup>-5</sup>	
4	50.0 ± 0.01	0.100	38	10	8.06 × 10 <sup>-5</sup>	
5	50.0 ± 0.01	0.100	50	14	8.33 × 10 <sup>-5</sup>	
6	50.0 ± 0.01	0.030	52	7	9.17 × 10 <sup>-5</sup>	
7	50.0 ± 0.01	0.030	53	6	8.90 × 10 <sup>-5</sup>	1.51 × 10 <sup>-5</sup>
8	25.0 ± 0.01	0.382	25	6	1.30 × 10 <sup>-5</sup>	
9	25.0 ± 0.01	0.200	28	6	1.63 × 10 <sup>-5</sup>	
10	25.0 ± 0.01	0.200	28	6	1.60 × 10 <sup>-5</sup>	6.04 × 10 <sup>-6</sup>
11	14.2 ± 0.1	0.097	63	13	5.92 × 10 <sup>-6</sup>	
12	14.2 ± 0.1	0.195	16	8	6.19 × 10 <sup>-6</sup>	
13	14.2 ± 0.1	0.100	44	16	6.00 × 10 <sup>-6</sup>	2.55 × 10 <sup>-4</sup>
14	67.8 ± 0.3	0.572	85	11	2.66 × 10 <sup>-4</sup>	
15	67.8 ± 0.3	0.091	67	6	2.57 × 10 <sup>-4</sup>	
16	67.8 ± 0.3	0.203	61	6	2.70 × 10 <sup>-4</sup>	
17	67.8 ± 0.3	0.103 <sup>b</sup>	60	6	2.40 × 10 <sup>-4</sup>	
18	67.8 ± 0.3	0.433	76	10	2.43 × 10 <sup>-4</sup>	
19	67.8 ± 0.3	0.200	83	11	2.49 × 10 <sup>-4</sup>	2.10 × 10 <sup>-4</sup>
20	67.8 ± 0.3	0.200 <sup>c</sup>	78	11	2.10 × 10 <sup>-4</sup>	
21	67.0 ± 0.3	0.121	69	10	1.98 × 10 <sup>-4</sup>	
22	67.0 ± 0.3	0.472 <sup>d</sup>	60	7	1.93 × 10 <sup>-4</sup>	
23	67.0 ± 0.3	0.572	81	12	2.19 × 10 <sup>-4</sup>	

<sup>a</sup> In THF, C<sub>0</sub> of ethyl diphenylphosphinate = C<sub>0</sub> of phenylmagnesium bromide. <sup>b</sup> C<sub>0</sub> of phenylmagnesium bromide = 0.206 M. <sup>c</sup> C<sub>0</sub> of phenylmagnesium bromide = 0.400 M. <sup>d</sup> C<sub>0</sub> of phenylmagnesium bromide = 0.572 M.

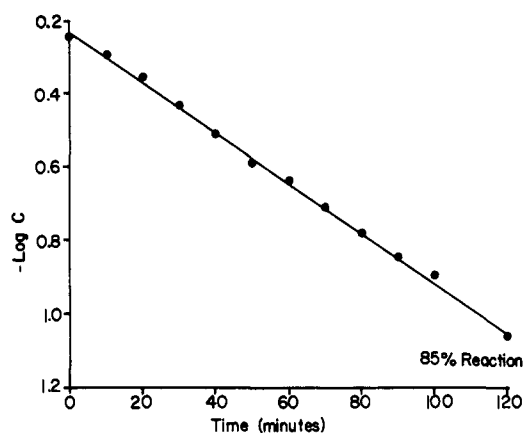
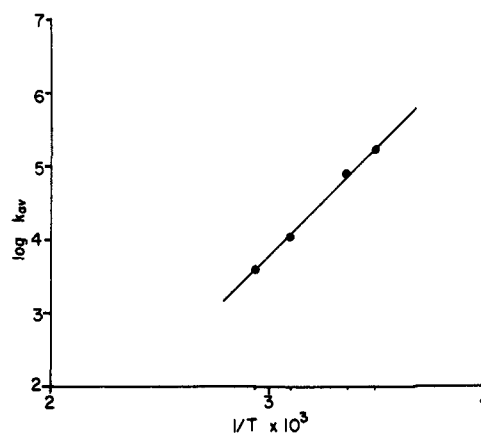


Figure 1. First-order plot of the kinetic data in Table II.

Figure 2. Arrhenius plot of log k<sub>av</sub> vs. 1/T.

magnesium bromide. Instead a very slight decrease in the reaction rate of the 2:1 experiments relative to the 1:1 experiments was observed. For example, after 2 hr at 67.8° with 0.2 M ethyl diphenylphosphinate, 83 and 78% conversions to triphenylphosphine oxide were observed for 1:1 and 2:1 experiments, respectively.

The average values of the rate constants in Table III were used in the Arrhenius plot of log k vs. 1/T and illustrated in Figure 2. Least-squares treatment of this data gave E<sub>a</sub> and ΔS<sup>‡</sup> as 13.4 kcal/mole and -33.2 eu, respectively.

The effect of diethyl ether as solvent on the rate of reaction of ethyl diphenylphosphinate and phenylmagnesium bromide was found to be negative with respect to THF. The magnitude of this solvent effect is illustrated in Figure 3.

Figure 4 illustrates the opposing effects of 1 equiv of each of magnesium bromoethoxide and tributylphosphine

oxide on the reaction rate of ethyl diphenylphosphinate and phenylmagnesium bromide. Phosphorus nmr spectral evidence for the formation of the ethyl diphenylphosphinate-magnesium bromoethoxide, the tributylphosphine oxide-phenylmagnesium bromide, and the ethyl diphenylphosphinate-tributylphosphine oxide-phenylmagnesium bromide complexes is recorded in Table I.

Ethyl diphenylphosphinate formed a weaker complex with diphenylmagnesium (Table I) than with phenylmagnesium bromide. Subsequent reorganization of the phosphinate-diphenylmagnesium complex to product was found to be significantly faster than the rate of reaction of the analogous phenylmagnesium bromide complex (see Figure 5). In addition, the over-all reaction was found to be complex. After about 20% reaction a noticeable acceleration in the rate of formation of triphenylphosphine oxide was observed. As a result the analytical data gave a sharp curve when log C

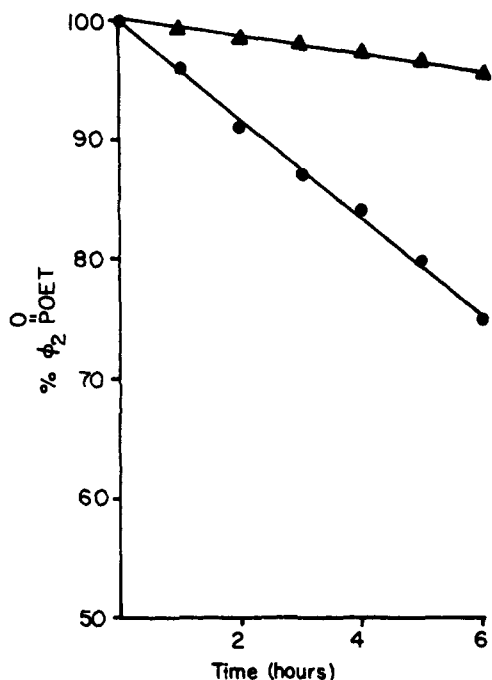


Figure 3. The effect of solvent on the reaction of ethyl diphenylphosphinate with phenylmagnesium bromide at 25°:  $\circ$ , in THF;  $\Delta$ , in diethyl ether.

was plotted vs.  $t$ . Deviation from a straight line was even more pronounced when a second-order plot of  $1/C$  vs.  $t$  was made.

The phosphorus nmr spectrum of the magnesium bromide complex (Table I) with ethyl diphenylphosphinate indicates a weaker complex than either of the diphenylmagnesium or phenylmagnesium bromide complexes with ethyl diphenylphosphinate.

#### Discussion

The fact that the phosphorus nmr chemical shift of ethyl diphenylphosphinate in THF is significantly different (6.2 ppm) than in the presence of 1 equiv of phenylmagnesium bromide is indicative of complex formation. Furthermore, the variations in chemical shift with varying amounts of phenylmagnesium bromide are consistent with a 1:1 complex in which the ethyl diphenylphosphinate and the Grignard reagent are completely associated at concentrations of 0.8  $M$  in each reactant. With lower ratios than 1:1 of phenylmagnesium bromide:phosphinate the observance of a time-averaged chemical shift indicates that the complexed ethyl diphenylphosphinate is undergoing rapid exchange relative to the nmr time scale with the phosphorus ester in solution. The direction and the magnitude of the changes in chemical shifts are similar to those observed in hydrogen-bonding studies.<sup>4</sup> For example, the chemical shift of triphenylphosphine oxide varies from  $-24.8$  ppm in dioxane<sup>4</sup> to  $-29.8$  ppm ( $\Delta$  5.0 ppm) in 2-propanol to  $-32.6$  ppm ( $\Delta$  7.8 ppm) in methanol. All of these data are consistent with an interaction of the order of several kilocalories between the phosphoryl oxygen and the magnesium atoms.

(4) G. E. Maciel and R. V. James, *Inorg. Chem.*, **3**, 1650 (1964).

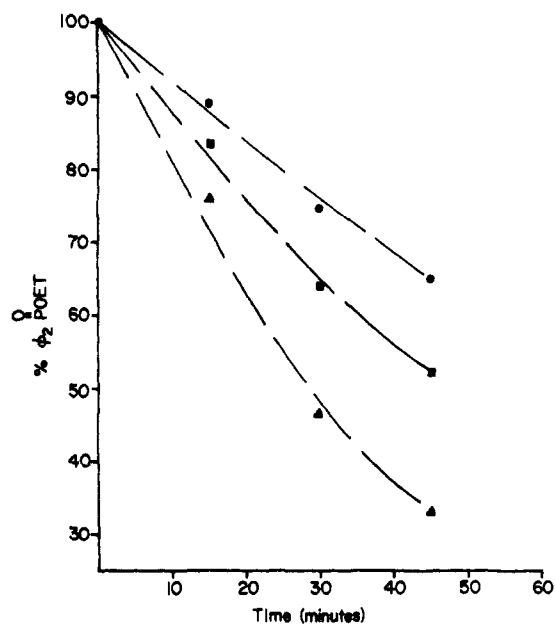


Figure 4. The effect of added  $\text{MgBrOEt}$  ( $\circ$ ) and tributylphosphine oxide ( $\Delta$ ) on the reaction of ethyl diphenylphosphinate and phenylmagnesium bromide in THF at 67.8° (control  $\square$ ).

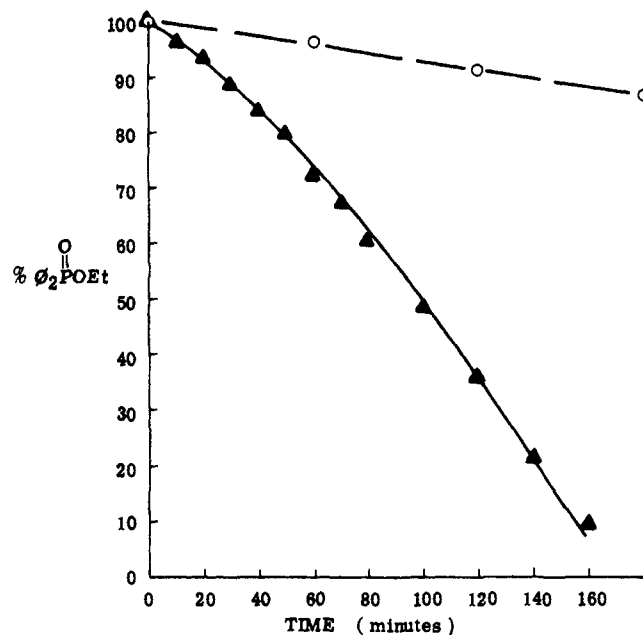


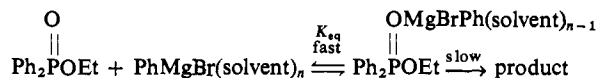
Figure 5. The rate of reaction of  $\text{Ph}_2\text{P}(\text{O})\text{OEt}$  with  $\text{Ph}_2\text{Mg}$  ( $\Delta$ ) vs.  $\text{PhMgBr}$  ( $\circ$ ) in THF (0.3  $M$  in each reactant) at 25°.

The observation that the phosphoryl infrared absorption frequency decreases by  $28\text{ cm}^{-1}$  when 1 equiv of phenylmagnesium bromide is added to ethyl diphenylphosphinate in THF is also consistent with complex formation. Berlin and Pagilagan<sup>5</sup> observed a  $14\text{-cm}^{-1}$  decrease in the phosphoryl frequency of the well-characterized 3:1 complex of ethyl diphenylphosphinate and magnesium iodide. A similar decrease of about  $0.2\ \mu$  in the phosphoryl frequency of triphenylphosphine oxide

(5) K. D. Berlin and R. U. Pagilagan, *Chem. Commun.*, **19**, 687 (1966).

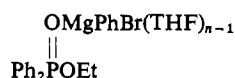
was observed on addition of phenol.<sup>6</sup> In this case the association constant has been shown to be 1055 l. mole<sup>-1</sup> in carbon tetrachloride at 20°. These data in conjunction with the nmr data suggest that the interaction between ethyl diphenylphosphinate and phenylmagnesium bromide is at least of the order of a moderately strong hydrogen bond.

The fact that first-order kinetics were observed over a large part of the reaction of ethyl diphenylphosphinate and phenylmagnesium bromide suggests a number of points. First, these results along with the spectral data are entirely consistent with the following mechanism involving the rapid formation of a 1:1 complex followed by a relatively slow reorganization to products. Recent

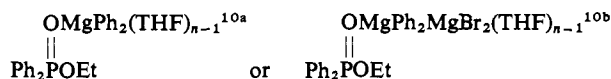


spectroscopic and kinetic evidence strongly indicates that the reaction of 2,4-dimethyl-4-methylmercaptobenzophenone and methylmagnesium bromide follows the same reaction scheme.<sup>1b,c</sup> Unlike the ketone-Grignard reaction, however, the kinetics of the reaction of ethyl diphenylphosphinate and phenylmagnesium bromide appears concentration independent over the range of 0.03–0.5 M. This suggests that  $K_{\text{eq}}$  is considerably larger for the phosphorus ester-Grignard reagent complex than the  $K_{\text{eq}}$  for the ketone-Grignard reagent complex (6 l. mole<sup>-1</sup>).<sup>1b,c</sup> Comparison of the basicities of several phosphoryl compounds with those of ketones lends support to this idea.<sup>8</sup> For example, the  $\text{p}K_{\text{BH}^+}$  of diphenylmethylphosphine oxide and dimethylphenylphosphine oxide are –3.20 and –2.09, respectively, as compared to the  $\text{p}K_{\text{BH}^+}$  of –6.45 for acetophenone. If  $K_{\text{eq}}$  is assumed to be about  $6 \times 10^3$  l. mole<sup>-1</sup> or greater ( $\Delta F \geq -5.1$  kcal),<sup>9</sup> then the degree of association for ethyl diphenylphosphinate and phenylmagnesium bromide in THF should be 98.2% at 0.5 M, 96.1% at 0.1 M, and 93% at 0.03 M or greater. Thus the observation of first-order kinetics over this concentration range with change in the order of reaction at lower concentrations does not seem unreasonable.

The observation of first-order kinetics in experiments with 1:1 as well as 2:1 reactant ratios and the spectral data constitute strong evidence that the reactive species is



and not



or a combination of these possible complexes. Contributions from either of the latter two complexes should

(6) J. V. Bell, J. Heisler, H. Tannenbaum, and J. Goldenson, *J. Amer. Chem. Soc.*, **76**, 5185 (1954).

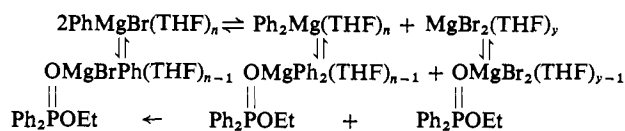
(7) G. Aksnes and T. Gramstad, *Acta Chem. Scand.*, **14**, 1485 (1960).

(8) P. Haake, R. D. Cook, and G. H. Hurst, *J. Amer. Chem. Soc.*, **89**, 2650 (1967).

(9) Energetically this is comparable to a moderately strong hydrogen bond.

(10) (a) Dialkylmagnesium compounds are known to be more reactive than alkylmagnesium halides and have been thought by some to be the reactive species in Grignard reactions; see ref 1d. (b) The termolecular mechanism recently proposed by K. D. Berlin and M. E. Peterson, *J. Org. Chem.*, **32**, 127 (1967), for the reactions of phosphorus esters with Grignard reagents is also excluded for the same reasons.

result in more complex kinetic schemes. These conclusions are further supported by the facts that the reaction of ethyl diphenylphosphinate is significantly faster with diphenylmagnesium than with phenylmagnesium bromide and that the reaction is not a simple first-order process. Phosphorus nmr spectra of the individual complexes are also consistent with the above interpretation in that the phenylmagnesium bromide complex with the phosphinate is considerably stronger than either the analogous diphenylmagnesium or magnesium bromide complexes (Table I).<sup>11</sup> Therein probably lies the driving force for displacement of the initial phenylmagnesium bromide, diphenylmagnesium, magnesium bromide equilibrium<sup>11</sup> in THF to essentially the single complex as shown below. From a kinetic and



spectral standpoint, if an equilibrium exists in the bottom equation, the amount of the complexes present on the right appear insignificant.

The negative effect of diethyl ether on the rate of reaction of ethyl diphenylphosphinate and phenylmagnesium bromide as compared to THF at 25° may result from one of two or a combination of both factors. The first may be the lesser reactivity of the dimeric and higher associated species of phenylmagnesium bromide that are known to exist in diethyl ether, as compared to the monomeric phenylmagnesium bromide in THF.<sup>1a</sup> The other possibility is that in reactions involving solvated organometallics the basicity of the solvent will affect the reactivity of the organometallic either negatively or positively depending upon whether the displacement of a solvent molecule from the solvated organometallic by the reacting species is either the slow step or precedes the slow step.<sup>1e</sup> In the case of ethyl diphenylphosphinate and phenylmagnesium bromide, complex formation is fast. Accordingly, the reaction should be faster in the more basic THF solvent as a result of the THF imparting more carbanionic character to the phenylmagnesium bromide than does diethyl ether.

The thermodynamic values obtained in this study ( $E_a = 13.4$  kcal/mole and  $\Delta S^\ddagger = -33.2$  eu) appear to be comparable with those obtained for other bimolecular substitutions on a tetrahedral phosphorus.<sup>12</sup> These reactions are characterized by large negative entropy changes ranging from –10 to –34 eu. For example, the activation energy and entropy of activation for the basic hydrolysis of diethyl methylphosphonate have been found to be 13.4 kcal/mole and –33.7 eu, respectively.<sup>13</sup>

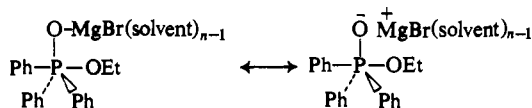
The nature of the transition state between the ethyl diphenylphosphinate-phenylmagnesium bromide complex and the product is also of interest. The results of

(11) The relative instability of the phosphinate-magnesium bromide complex compared to the other complexes is not surprising since magnesium bromide has a higher coordination number for THF ( $\nu = n + 2$  or 4) than either phenylmagnesium bromide or diphenylmagnesium ( $n$  is believed to be 2); see M. B. Smith and W. E. Becker, *Tetrahedron*, **23**, 4215 (1967).

(12) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus (Reaction Mechanisms in Organic Chemistry, Monograph 5)," C. Eaborn and N. B. Chapman, Ed., Elsevier Publishing Co., New York, N. Y., 1967, pp 302, 313, 314.

(13) G. Aksnes and J. Songstad, *Acta Chem. Scand.*, **19**, 893 (1965).

this study as well as those of related studies<sup>3c,14-16</sup> are believed to be consistent with the pentacovalent phosphorane shown below. A similar pentacovalent struc-



ture has been proposed for the alkaline hydrolysis of phosphoryl halides.<sup>14</sup> That the reaction is not a simple nucleophilic displacement in which the phosphoryl group is unperturbed appears evident from the kinetic data and the spectral data. The latter indicate that a considerable amount of polarization of the phosphoryl bond occurs in the complex. In addition, the inverse relationship of the reactivity of phosphorus esters in reactions with phenylmagnesium bromide to the degree of P=O p $\pi$ -d $\pi$  bonding has been recognized.<sup>3c</sup> Further indirect support for such a transition state appears in the recent report concerning the preparation and stability of triphenyldiethoxyphosphorane,<sup>15</sup> although the latter is expected to be much more stable than the analogous magnesium compound. The recent observation that inversion of configuration occurs in the reaction of methyl phenylpropylphosphinate with methylmagnesium chloride<sup>16</sup> suggests that backside attack may also occur in this case.

That the product of the reaction of ethyl diphenylphosphinate and phenylmagnesium bromide is a fairly strong complex of triphenylphosphine oxide and magnesium bromoethoxide and not the phosphorane described above<sup>17</sup> is evident from a consideration of the following variations in the phosphorus nmr spectra of triphenylphosphine oxide: -23.5 ppm in THF, -29.8 ppm in *i*-PrOH,<sup>4</sup> -32.6 ppm in CH<sub>3</sub>OH;<sup>4</sup> Ph<sub>3</sub>P<sup>+</sup>OH HSO<sub>4</sub><sup>-</sup>, -59.8 ppm in H<sub>2</sub>SO<sub>4</sub>,<sup>4</sup> and Ph<sub>3</sub>P<sup>+</sup>OEtBF<sub>4</sub><sup>-</sup>, -62 ppm.<sup>15</sup> The phosphorus nmr spectrum of the product (-34.2 ppm in THF) and that of a mixture of triphenylphosphine oxide and magnesium bromoethoxide (-33.8 ppm) are consistent with a complex in which the phosphoryl group of triphenylphosphine oxide is highly polarized by complexation with the magnesium bromoethoxide. If the product were a pentacovalent phosphorane a much more positive chemical shift would be expected.<sup>18</sup> Triphenyldiethoxyphosphorane, for example, has a phosphorus chemical shift of +55 ppm.<sup>15</sup> The effect on the chemical shift of replacing an ethyl group by MgBr(solvent)<sub>n-1</sub> is not expected to be great in view of the chemical shifts of (C<sub>2</sub>H<sub>5</sub>O)<sub>3</sub>P (-139 ppm) and (C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>POMgX (-137 ppm).<sup>3a</sup>

The negative effect of magnesium bromoethoxide on the rate of reaction of ethyl diphenylphosphinate with phenylmagnesium bromide is reminiscent of the negative effects of magnesium halides on the reaction of diethyl phenylphosphonate and phenylmagnesium bromide.<sup>3b</sup> This negative effect may be due to complex formation

(14) R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, New York, N. Y., 1965, p 254.

(15) D. B. Denney, D. Z. Denney, and L. A. Wilson, *Tetrahedron Lett.*, 85 (1968).

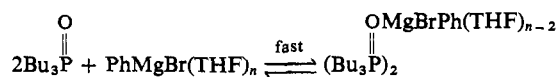
(16) O. Korpium and K. Mislow, *J. Amer. Chem. Soc.*, **89**, 4784 (1967).

(17) Similar pentacovalent phosphoranes were recently proposed as products of the reactions of phosphorus esters with Grignard reagents: R. S. Edmundson and J. O. L. Wrigley, *Tetrahedron*, **23**, 283 (1967).

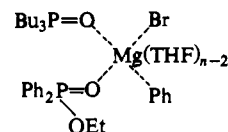
(18) F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968).

between ethyl diphenylphosphinate and the magnesium bromoethoxide (which is sterically hindered with respect to the solvated Grignard reagent), or the complex (see Table I) may have to dissociate prior to complexation and reaction with the Grignard reagent. An alternative possibility is that the reactivity of the phenylmagnesium bromide is decreased by complexation with the magnesium bromoethoxide.<sup>3b</sup>

The positive effect of tributylphosphine oxide on the reaction rate of ethyl diphenylphosphinate appears reasonable in view of the following facts. Alkyl diphenylphosphinates and magnesium iodide are known to form 3:1 complexes.<sup>5</sup> The phosphorus nmr spectral data in Table I suggest the rapid formation of a strong 2:1 complex between tributylphosphine oxide and phenylmagnesium bromide. Accordingly, the observed



chemical shifts for 1:1:1 mixtures of tributylphosphine oxide:ethyl diphenylphosphinate:phenylmagnesium bromide are suggestive of rapid formation of the following complex. This complex should reorganize to products



at a faster rate than the Ph<sub>2</sub>P(OEt)=OMgBrPh(THF)<sub>n-1</sub> complex for the same reason that the latter is expected to reorganize faster than the Ph<sub>2</sub>P(OEt)=OMgBrPh(Et<sub>2</sub>O)<sub>n-1</sub> complex.<sup>1e</sup> That is, the more basic the complexing agent or solvent the more carbanionic and thus the more reactive is the phenylmagnesium bromide. If displacement of the solvent or complexing agent from the phenylmagnesium bromide were the slow step, exactly the opposite order of reactivity would be expected.<sup>1e</sup>

The fact that the reaction of ethyl diphenylphosphinate with phenylmagnesium bromide follows first-order kinetics over a larger portion of the reaction at higher concentrations is undoubtedly due to the higher degree of association at higher concentrations. Below 0.03 M concentrations of reactants the results suggest that dissociation does become significant. That the decrease in rate during the final stages of the reaction is due to a decrease in the degree of association and not due to the formation of an "inactive complex" is further suggested by three additional observations. The triphenylphosphine oxide-magnesium bromoethoxide complex is considerably stronger than the starting complex. Accordingly, there should be very little if any free magnesium bromoethoxide present to retard the reaction. In addition, a decrease in rate brought about by any magnesium bromoethoxide available for complexation may be compensated for by the increase in reaction rate due to the corresponding amount of available triphenylphosphine oxide, that is, if triphenylphosphine oxide behaves analogously to tributylphosphine oxide and is capable of accelerating the rate of reaction. Certainly triphenylphosphine oxide is more basic than THF and does form a relatively strong complex with phenylmagnesium bromide (see Table I). Thus, in the absence

Table IV

Calcd	% Ph <sub>2</sub> P(O)OEt	Gc analysis
21.5		22.4
38.8		39.9
50.0		50.0
56.6		57.8
81.2		81.5
92.8		91.1
98.5		98.4

of any steric factors triphenylphosphine oxide would also be expected to accelerate the rate of reaction of ethyl diphenylphosphinate with phenylmagnesium bromide. Finally, the reactions with higher concentrations of reactants (1:1 reactant ratios) were observed to go to completion if given sufficient time.

### Experimental Section

All solvents were freshly distilled over lithium aluminum hydride under a dry argon atmosphere prior to their use. All operations were carried out under argon.

**Materials.** Ethyl diphenylphosphinate was prepared by the hydrogen peroxide oxidation of ethyl diphenylphosphinite. The latter was prepared from commercially available diphenylchlorophosphine, ethanol, and triethylamine in diethyl ether. The purity of the ethyl diphenylphosphinate was confirmed by elemental analysis, infrared, phosphorus nmr, and proton nmr spectra.

Phenylmagnesium bromide was prepared from magnesium turnings and also from singly sublimed magnesium obtained from the Dow Chemical Co.<sup>19</sup> To prepare the phenylmagnesium bromide 1 mole of freshly distilled bromobenzene in about 800 ml of THF was added dropwise to 2 g-atoms of washed and dried magnesium turnings in 200 ml of THF. External cooling was used to maintain the temperature at 20–30°. After stirring overnight the THF solution was refluxed 1 hr, then filtered twice through sintered-glass filters. Triple analysis of samples of the Grignard reagent by the double titration procedure of Vlismas and Parker<sup>20</sup> indicated a total base strength of 0.97 *M* with the Grignard con-

centration being 0.95 *M*. The Grignard solution from the magnesium turnings was relatively dark, whereas that from the singly sublimed magnesium was clear with a slight yellow tint.

**Kinetic Procedure.** All glassware was dried in an oven, then flame dried while flushing with dry argon. The desired amount of freshly distilled THF was then placed *via* syringe in the flask immersed in the constant-temperature bath. To this the desired amount of Grignard reagent was added *via* syringe and the solution was allowed to equilibrate for 45 min. At this time the desired amount of ethyl diphenylphosphinate was added *via* syringe either in the molten state or as a 1 *M* solution in THF. At the proper intervals 3-ml samples of the reaction mixture were removed *via* syringe and injected into 6 ml of nearly saturated ammonium chloride solution. After agitation and quick separation the THF layer was dried over Linde 4A Molecular Sieves for 1 hr. The samples were then carefully analyzed by gas chromatography on a 5-ft column of SE-30 on Chromosorb W, programmed over the temperature ranges of 120 or 130 to 250°. Under these conditions ethyl diphenylphosphinate and triphenylphosphine oxide had retention times of about 6–5 and 10–9 min, respectively. An indication of the accuracy of the gas chromatographic analyses can be seen in the analysis in Table IV of samples of ethyl diphenylphosphinate and triphenylphosphine oxide in THF that were made up by volumetric dilution of samples of more concentrated solutions. Least-squares treatment of the data obtained in this manner gave the rate data summarized in Table III. Experiments 13, 16, and 17 were carried out using the phenylmagnesium bromide prepared from the singly sublimed magnesium. There does not appear to be any significant difference in the rate constants obtained using either type of magnesium.

In studying the effects of diethyl ether as solvent, a control experiment was carried out simultaneously. In studying the effects of magnesium bromoethoxide and tributylphosphine oxide, both reactions were carried out simultaneously with a control reaction.

Diphenylmagnesium was prepared in diethyl ether by the dioxane procedure after which the diethyl ether was displaced by THF.<sup>21</sup> The diphenylmagnesium was then analyzed by the same procedure as the phenylmagnesium bromide.<sup>20</sup>

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(21) R. M. Salinger and H. S. Mosher, *J. Amer. Chem. Soc.*, **86**, 1782 (1964).

(19) We are indebted to the Dow Chemical Co. for supplying the singly sublimed magnesium used in these studies.

(20) T. Vlismas and R. D. Parker, *J. Organometal. Chem.*, **10**, 193 (1967).