The Effect of Magnesium Halides on the Reaction of Phosphonates with Phenylmagnesium Bromide

H. R. HAYS

The Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239

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The effect of magnesium chloride and bromide on the rate of reaction of diethyl phenylphosphonate with phenylmagnesium bromide has been investigated in diethyl ether, tetrahydrofuran, and benzene. Contrary to previous reports the reaction is not accelerated but is retarded by the addition of these magnesium halides. Possible explanations for these results are presented.

The reaction of diethyl phenylphosphonate with phenylmagnesium bromide has been reported to be accelerated by the addition of magnesium bromide.[1] On the basis of this report it was proposed that the magnesium bromide and the diethyl phenylphosphonate formed an activated complex in which the phosphoryl group was coordinated to the magnesium through the oxygen atom. Similar reasoning was used to explain the facile formation of triphenylphosphine oxide from diethyl phosphorochloridate and phenylmagnesium bromide in diethyl ether. Subsequently, several authors have cited this work as evidence for the proposal that increasing the positive character of the phosphorus atom increases its susceptibility to nucleophilic attack.[2] Although this concept seems highly reasonable, recent evidence concerning the substitution reactions of phosphoryl halides suggests the opposite may be true.[3] Furthermore, the fact that trimethylaluminum, a relatively good Lewis Acid, failed to give substitution reactions with dialkyl alkylphosphonates[4] was puzzling in view of the reported effect of magnesium halides on the substitution reactions of phosphorus esters. In an attempt to resolve this matter and to answer several questions raised in an earlier study,[5] the effect of magnesium halides on the reaction rate of diethyl phenylphosphonate with phenylmagnesium bromide was reinvestigated.

Results

The reaction of diethyl phenylphosphonate with phenylmagnesium bromide in the absence and in the presence of magnesium halides was investigated in tetrahydrofuran (THF), diethyl ether, and benzene. The principal part of our study was carried out using THF as the solvent since the reaction is homogeneous and can be followed quite nicely by gas chromatographic analysis of hydrolyzed aliquots taken at time intervals. In contrast, the reactions in diethyl ether and benzene became heterogeneous. In all cases, however, control reactions of diethyl phenylphosphonate with phenylmagnesium bromide were run under the same conditions as the reactions with added magnesium halides. Furthermore, the triphenylphosphine oxide was isolated in several cases, and the relative yields were found to be directionally consistent with the gas chromatographic analyses. Results of analysis of ^{31}P nmr spectra were also directionally consistent, although two of the signals overlapped, making quantitative analysis by this method difficult. Additional confirmation of our results was made in several cases by titration of the remaining phenylmagnesium bromide. (See the Experimental Section and ref 16).

The effect of 1 equiv of added magnesium halide on the rate of reaction of phenylmagnesium bromide with diethyl phenylphosphonate in THF at 68° is illustrated in Figure 1 which shows the percentage of phenylmagnesium bromide reacted as a function of time. Figures 2–4 merely exemplify the effect of 1 equiv of magnesium halide on the percentages of starting diethyl phenylphosphonate, the intermediate ethyl diphenylphosphinate, and the triphenylphosphine oxide, respectively, in THF at 68°. In all cases the data for $MgClBr$ were intermediate between $MgBr_2$ and $MgCl_2$; consequently, for simplicity these data are recorded in the Experimental Section. The isolated yields of triphenylphosphine oxide after 6 hr were 55–59% in the absence of magnesium halides and 19–25% in the presence of magnesium halides.

Essentially the same effect was observed when the reactions were carried out in diethyl ether at 34°, although the over-all reaction is much slower than in THF at 68°. This is illustrated in Figure 5. At some point between 22 and 90 hr the reaction mixture became heterogeneous. The final analysis was therefore made on the total hydrolysis products. For simplicity the different percentages of starting material, intermediate, and product are given in the tables in the Experimental Section.

In benzene at 72° the reaction of diethyl phenylphosphonate with phenylmagnesium bromide became heterogeneous in a short time and could not be followed as in THF or diethyl ether. Under the conditions used by Burger and Dawson,[1] but in the absence of added magnesium bromide, a mixture of 9.8% diethyl phenylphosphonate, 11.8% ethyl diphenylphosphinate, and 78.4% triphenylphosphine oxide was obtained. In contrast, under the same conditions in the presence of magnesium bromide, a mixture of 23.4% diethyl phenylphosphonate, 21.6% ethyl diphenylphosphinate, and 55% triphenylphosphine oxide was obtained. The isolated yields of triphenylphosphine oxide from the two experiments were 58 and 30%, respectively.

Discussion

From these results it is readily obvious that the reaction of diethyl phenylphosphonate with phenylmag-

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

(2) (a) K. D. Berlin and G. B. Butler, *Chem. Rev.*, **60**, 243 (1960); (b) K. D. Berlin, T. H. Austin, and K. L. Stone, *J. Amer. Chem. Soc.*, **86**, 1787 (1964); (c) K. D. Berlin and M. E. Peterson, *J. Org. Chem.*, **32**, 125 (1967); (d) K. D. Berlin and R. U. Pagilagan, *ibid.*, **32**, 129 (1967).

(3) R. S. Drago, V. A. Mode, J. G. Kay, and D. L. Lydy, *J. Amer. Chem. Soc.*, **87**, 5010 (1965).

(4) H. R. Hays, unpublished results. Upon heating mixtures of trimethylaluminum and dialkyl alkylphosphonates elimination of olefin and formation of methane and aluminum phosphonates were observed. For further details see the Experimental Section.

(5) H. R. Hays, *J. Org. Chem.*, submitted for publication.

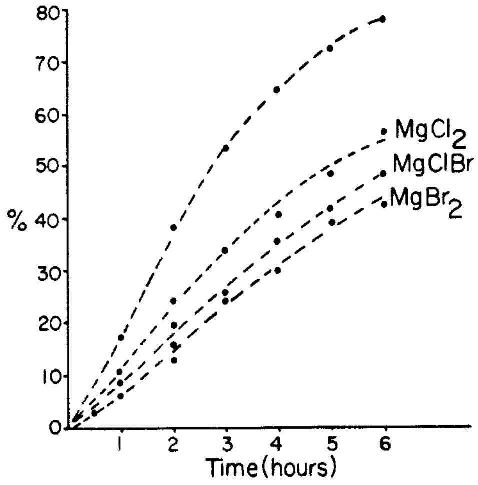

Figure 1.—The effect of MgX_2 on the percentage of C_6H_5MgBr reacted vs. time: $C_6H_5\overset{\overset{O}{\uparrow}}{P}(OEt)_2 + 2C_6H_5MgBr$, THF, 68°.

$$\% \; C_6H_5MgBr = \frac{\% \; (C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}OEt + 2 \times \% \; (C_6H_5)_3\overset{\overset{O}{\uparrow}}{P}}{2}$$

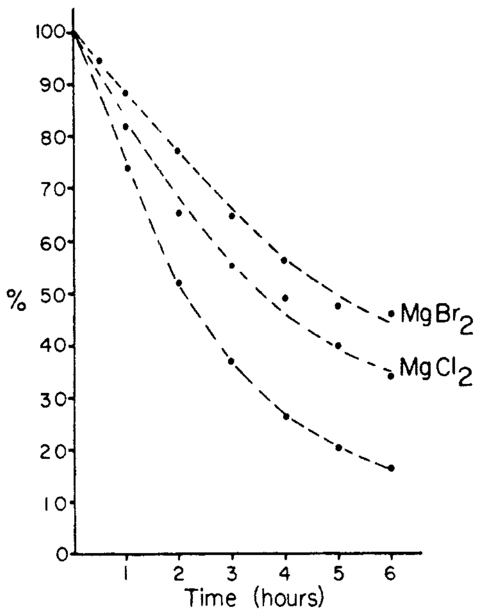

Figure 2.—The effect of MgX_2 on the percentage of $C_6H_5\overset{\overset{O}{\uparrow}}{P}(OEt)_2$ not reacted vs. time: $C_6H_5\overset{\overset{O}{\uparrow}}{P}(OEt)_2 + 2C_6H_5MgBr$, THF, 68°.

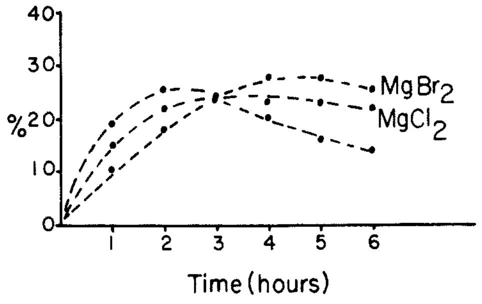

Figure 3.—The effect of MgX_2 on the percentage of $(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}OEt$ vs. time: $C_6H_5\overset{\overset{O}{\uparrow}}{P}(OEt)_2 + 2C_6H_5MgBr$, THF, 68°.

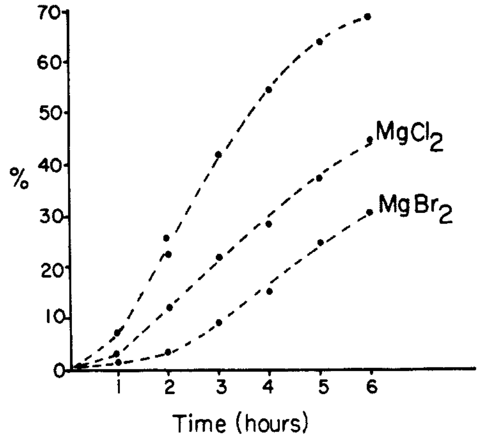

Figure 4.—The effect of MgX_2 on the percentage of $(C_6H_5)_3\overset{\overset{O}{\uparrow}}{P}$ formed vs. time: $C_6H_5\overset{\overset{O}{\uparrow}}{P}(OEt)_2 + 2C_6H_5MgBr$, THF, 68°.

nesium bromide is not accelerated but is retarded by the addition of magnesium chloride or bromide. Several possible explanations of the data have been considered.[6] For example, preliminary results of a related study of substituted phosphonate esters and phenylmagnesium bromide show that their reactivity is increased by electron-withdrawing substituents attached to the phosphorus atom.[7] That is, in a series of phosphorus esters with nearly the same P→O bond strengths and ground-state energies, the pentacovalent transition state is stabilized by electrophilic substituents. Thus the fact that magnesium halides retard the reaction under study is not due to electronic destabilization of the transition state as a result of polarization of the phosphoryl bond by the magnesium halide.

Conceivably, the complex of diethyl phenylphosphonate with the magnesium halide, if formed,[8] might be sterically hindered to attack by the solvated Grignard reagent. That is, a bimolecular, rather than a termolecular, mechanism may be involved in the latter case. Smith and coworkers[9] have recently reported evidence that methylmagnesium bromide and 2,4-dimethyl-4′-methylmercaptobenzophenone react by a bimolecular mechanism rather than the termolecular mechanism reported for benzophenone.[10]

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[6] Worthy of note is the fact that magnesium bromide also retards the addition of methylmagnesium bromide to pinacolone and suppresses the tendency of magnesium alkoxides to give enolization of ketones. See H. O. House and D. D. Traficante, *J. Org. Chem.*, **28**, 355 (1963).

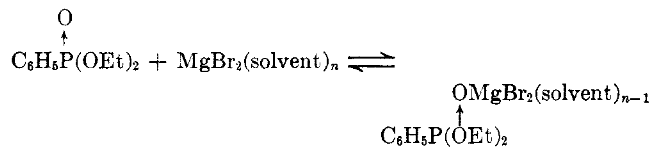
[7] H. R. Hays, to be submitted for publication.

[8] This is not meant to imply that diethyl phenylphosphonate and magnesium halides as such do not form complexes. The question is whether such complexes are formed in the presence of phenylmagnesium bromide, which may also be capable of complexing with magnesium halides. See the following discussion.

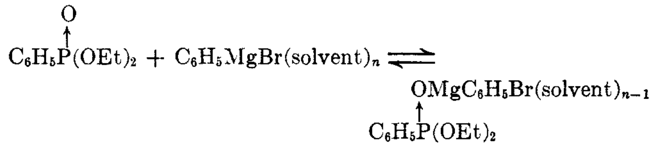
[9] (a) S. G. Smith and G. Su, *J. Amer. Chem. Soc.*, **88**, 3995 (1966); S. G. Smith and J. Billet, *ibid.*, **89**, 6948 (1967); (b) H. R. Hays, *ibid.*, submitted for publication. Preliminary kinetic data on the reaction of ethyl diphenylphosphinate and phenylmagnesium bromide are consistent with the rapid formation of a bimolecular complex which then proceeds to products by a first-order process. Thus the magnesium halide could be competing with the phenylmagnesium bromide for the phosphonate ester.

[10] E. C. Ashby, R. B. Duke, and H. M. Neumann, *ibid.*, **89**, 1964 (1967).

In an attempt to gain information about complex formation, the phosphorus nmr spectra of diethyl phenylphosphonate with magnesium bromide and diethyl phenylphosphonate with phenylmagnesium bromide were recorded in THF and diethyl ether. Aside from a slight broadening of the phosphorus signals and small differences in the chemical shifts (less than 1-2 ppm), the spectra were essentially the same as that of diethyl phenylphosphonate. These results coupled with the results of a recent study of the basicity of various phosphoryl compounds[11] and the pK_B's of THF[12] and diethyl ether[12] suggest that the diethyl phenylphosphonate complexes shown below are relatively weak complexes.



$$C_6H_5\overset{\overset{O}{\uparrow}}{P}(OEt)_2 + MgBr_2(\text{solvent})_n \rightleftharpoons C_6H_5\overset{\overset{OMgBr_2(\text{solvent})_{n-1}}{\uparrow}}{P}(OEt)_2$$



$$C_6H_5\overset{\overset{O}{\uparrow}}{P}(OEt)_2 + C_6H_5MgBr(\text{solvent})_n \rightleftharpoons C_6H_5\overset{\overset{OMgC_6H_5Br(\text{solvent})_{n-1}}{\uparrow}}{P}(OEt)_2$$

Another possibility may be that the magnesium halide forms a complex with the phenylmagnesium bromide thus deactivating the Grignard reagent. Ashby and coworkers have isolated the related complex $EtMg_2Cl_3$ by fractional crystallization from THF.[13] In addition a similar complex between magnesium bromide and magnesium alkoxides has been proposed to explain the negative effect of magnesium bromide on the enolization of ketones.[6] Whether or not such a complex possesses a structure bridged through the halogen atoms or is ionic in nature appears speculative at this time.[14]

Several other possible explanations of the results were considered. These are repression of the Schlenck equilibrium (*i.e.*, diphenylmagnesium concentration), a medium effect, and the possibility that diethyl phenylphosphonate might react with the magnesium halide.[15] All of these are believed unlikely for the following reasons. First, kinetic evidence regarding the reaction of ethyl diphenylphosphinate with phenylmagnesium bromide[9b] indicates the reactive species is phenylmagnesium bromide and not diphenylmagnesium. The fact that complex formation is also shown to be important suggests the negative effect of magnesium halides is not due to a medium effect. Second, no evidence of reaction was observed when diethyl phenylphosphonate and magnesium bromide were heated in refluxing THF for 6 hr. No ethyl bromide or ethylene could be detected in the ir spectra of the THF vapors, and 67% of the diethyl phenylphosphonate was recovered. This is in contrast to diethyl phenylphosphonate and magnesium iodide which did react upon heating in refluxing THF.

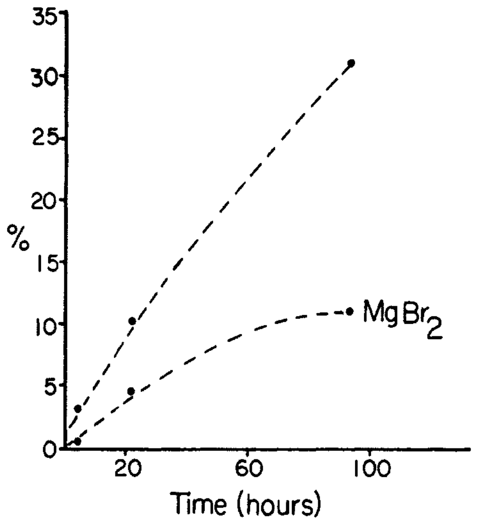


Figure 5.—The effect of $MgBr_2$ on the percentage of C_6H_5MgBr reacted *vs.* time: $C_6H_5\overset{\overset{O}{\uparrow}}{P}(OEt)_2 + 2C_6H_5MgBr$, Et_2O, 34°.

The findings of this study indicate that another explanation is required for the fact that diethyl phosphorochloridate reacts so readily with phenylmagnesium bromide in diethyl ether to produce triphenylphosphine oxide.[1] An investigation of this reaction is presently underway.

Experimental Section

Materials.—Diethyl phenylphosphonate was prepared from commercial phenylphosphonyl chloride, ethanol, and triethylamine in ether. Ethyl diphenylphosphinate was prepared by oxidation of ethyl diphenylphosphinite, obtained from commercial diphenylchlorophosphine, ethanol, and triethylamine in ether. Reference triphenylphosphine oxide was obtained by the oxidation of commercial triphenylphosphine with hydrogen peroxide. The purity of the products was confirmed by gas chromatography and by their infrared and proton and phosphorus nmr spectra.

Phenylmagnesium bromide in ether was obtained from a commercial source. Upon displacement of the diethyl ether with THF and subsequent refluxing, the percentage of biphenyl impurity increased, presumably as a result of the coupling of phenylmagnesium bromide with bromobenzene impurity. Consequently, phenylmagnesium bromide was prepared in THF using 100% excess magnesium and reaction temperatures of 30–40°. When prepared in this manner and using the procedure recently reported by Watson and Eastham, the phenylmagnesium bromide titration showed a nearly quantitative yield.[16] Only a trace of biphenyl was observed in the gas chromatograms.

Magnesium bromide and magnesium chlorobromide were prepared by the addition of dibromoethane and 1-bromo-2-chloroethane, respectively, to magnesium in diethyl ether. Magnesium chloride was obtained commercially.

All solvents were freshly distilled over lithium aluminum hydride.

Reaction of Diethyl Phenylphosphonate with Phenylmagnesium Bromide. A. In THF.—To the magnesium halide (0.1 mol) under argon 70 ml of tetrahydrofuran was added. Upon addition of 21.4 g of diethyl phenylphosphonate (0.1 mol) small heat effects resulted in a temperature rise of a few degrees. Surprisingly in the case of magnesium bromide, a secondary factor, perhaps a negative heat of solution, resulted in a slower over-all temperature drop of a few degrees. Both the magnesium bromide and the chloro bromide dissolved upon subsequent stirring, whereas a part of the magnesium chloride remained insoluble. Upon addition of 84 ml of warm 2.4 *M* phenylmagnesium bromide,

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

[12] E. M. Arnett in "Progress in Physical Organic Chemistry," Vol. 1, S. G. Cohen, A. Streitwieser, and R. W. Taft, Ed., Interscience Publishers, New York, N. Y., 1963, p 325.

[13] E. C. Ashby and W. E. Becker, *J. Amer. Chem. Soc.*, **85**, 119 (1963).

[14] E. C. Ashby, *Quart. Rev.* (London), **21**, 259 (1967).

[15] The complex of methyl diphenylphosphinate and magnesium iodide is known to readily form methyl iodide and the magnesium salt of diphenylphosphinic acid. See K. D. Berlin and R. U. Pagilagan, *Chem. Commun.*, **19**, 687 (1966).

[16] S. C. Watson and J. F. Eastham, *J. Organometal. Chem.*, **9**, 165 (1967).

the reaction vessel and control experiment were placed in an oil bath preheated to 68–70°. (The phenylmagnesium bromide crystallizes from a 2.4 *M* solution upon cooling to room temperature.) In the control experiments 84 ml of 2.4 *M* phenylmagnesium bromide in warm THF was added to the 70 ml of THF followed by the addition of 21.4 g of the diethyl phenylphosphonate (0.1 mol). As in the case of the magnesium halides a slight temperature rise was observed; however, the only differences in the phosphorus nmr spectrum were less than 1–2 ppm differences in the chemical shifts and a slight broadening of the diethyl phenylphosphonate signal. Diethyl phenylphosphonate (25% in THF) for example, had a phosphorus chemical shift of −17.3 ppm *vs.* −17.7 ppm in the presence of an equivalent amount of phenylmagnesium bromide and −17.3 ppm in the presence of magnesium bromide. Likewise, no significant difference was observed in the phosphorus nmr spectrum in diethyl ether of diethyl phenylphosphonate (−17.5 ppm) and magnesium bromide (−18.3 ppm).[17] After heating for the times shown in Tables I, II, III, and IV, 5-ml samples were removed and hydrolyzed with an equivalent amount of cold ammonium chloride solution. The resultant organic phases were separated, dried over molecular sieves, and analyzed as quickly as possible by gas chromatography to give the percentage compositions shown in Tables I, II, III, and IV. A 5 ft column of 10% SE 30 on Chromosorb W was used over the temperatures 130–250°. The percentage of phenylmagnesium bromide reacted was taken as one-half of the sum of the ethyl diphenylphosphinate and twice the amount of triphenylphosphine oxide. That this is a close approximation was shown by the agreement with the percentage of remaining phenylmagnesium bromide as determined by the titration procedure of Watson and Eastham.[16] Phosphorus nmr spectral analysis of the mixtures were also in good agreement with the results shown except that low percentages of ethyl diphenylphosphinate were not observed. In addition, work-up of several of the reactions listed in Tables I and II (magnesium halide) by hydrolysis with ammonium chloride solution, followed by removal of the THF and digestion with diethyl ether, gave 55–59% of triphenylphosphine oxide (Table I) and 19–25% of triphenylphosphine oxide (Table II) after 6 hr. After 23 hr at 68°, yields of 41 and 12% of crystalline triphenylphosphine oxide, mp 152–153°, were obtained in the absence and presence of added magnesium bromide, respectively. To check the possibility of side reactions, 21.4 g of diethyl phenylphosphonate, magnesium bromide (0.1 mol), and 70 ml of THF were heated at 68° for 6 hr using a 45° condenser with a subsequent Dry Ice trap. No evidence of ethyl bromide formation was observed in the ir spectrum of a small amount of diethyl ether, and THF collected in the Dry Ice trap. Upon work-up 67% of the diethyl phenylphosphonate was recovered. Very little if any C alkylation of the phenylmagnesium bromide to give ethylbenzene was observed in the reaction of diethyl phenylphosphonate with phenylmagnesium bromide in the presence of magnesium bromide at 68° in THF.

B. In Diethyl Ether.—Essentially the same procedure as in A was followed with the exception that the oil bath was preheated to 34°. At some point between 22 and 94 hr the control reaction became heterogeneous, necessitating work-up at that point. The results obtained from this study are given in Tables V and VI.

TABLE I

$C_6H_5\overset{\overset{O}{\uparrow}}{P}(OEt)_2 + 2C_6H_5MgBr$, THF, 68°

Time, hr	$C_6H_5\overset{\overset{O}{\uparrow}}{P}(OEt)_2$, %	$(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}OEt$, %	$(C_6H_5)_3\overset{\overset{O}{\uparrow}}{P}$, %	C_6H_5MgBr reacted, %
1	74.5	19.5	6	15.7
2	52.5	25.1	22.4	35.0
3	33.2	23.8	43.0	54.9
4	25.1	21.7	53.2	64.0
5	21.4	15.6	63.0	70.8
6	20.1	13.4	66.5	73.2
23	2.2	4.6	93.1	94.3

TABLE II

$C_6H_5\overset{\overset{O}{\uparrow}}{P}(OEt)_2 + 2C_6H_5MgBr + MgBr_2$, THF, 68°

Time, hr	$C_6H_5\overset{\overset{O}{\uparrow}}{P}(OEt)_2$, %	$(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}OEt$, %	$(C_6H_5)_3\overset{\overset{O}{\uparrow}}{P}$, %	C_6H_5MgBr reacted, %
1	88.0	10.6	1.4	6.7
2	79.0	16.8	4.2	12.6
3	64.1	23.6	12.3	24.1
4	56.1	29.0	14.9	29.4
5	45.9	29.0	24.8	39.4
6	46.3	23.6	30.1	41.9
23	24.8	18.7	56.5	63.8

TABLE III

$C_6H_5\overset{\overset{O}{\uparrow}}{P}(OEt)_2 + 2C_6H_5MgBr + MgClBr$, THF, 68°

Time, hr	$C_6H_5\overset{\overset{O}{\uparrow}}{P}(OEt)_2$, %	$(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}OEt$, %	$(C_6H_5)_3\overset{\overset{O}{\uparrow}}{P}$, %	C_6H_5MgBr reacted, %
1	83.3	14.5	2.2	9.4
2	70.1	21.4	8.5	19.2
3	65.1	20.6	14.3	24.6
4	49.9	26.4	23.7	36.9
5	41.8	25.0	33.2	40.7
6	39.4	22.8	37.8	49.2

TABLE IV

$C_6H_5\overset{\overset{O}{\uparrow}}{P}(OEt)_2 + 2C_6H_5MgBr + MgCl_2$, THF, 68°

Time, hr	$C_6H_5\overset{\overset{O}{\uparrow}}{P}(OEt)_2$, %	$(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}OEt$, %	$(C_6H_5)_3\overset{\overset{O}{\uparrow}}{P}$, %	C_6H_5MgBr reacted, %
1	82.2	14.7	3.1	10.4
2	64.8	22.4	12.8	24.0
3	54.7	23.5	21.8	33.5
4	49.0	23.0	28.0	39.5
5	40.3	23.0	36.7	48.2
6	32.8	22.4	44.8	56.0

TABLE V

$C_6H_5\overset{\overset{O}{\uparrow}}{P}(OEt)_2 + 2C_6H_5MgBr, Et_2O$, 34°

Time, hr	$C_6H_5\overset{\overset{O}{\uparrow}}{P}(OEt)_2$, %	$(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}OEt$, %	$(C_6H_5)_3\overset{\overset{O}{\uparrow}}{P}$, %	C_6H_5MgBr reacted, %
1.5	98.2	1.8	...	0.9
4.5	94.0	5.5	0.5	3.0
22	83.0	13.7	3.3	10.1
94	56.7	23.7	19.55	31.4

TABLE VI

$C_6H_5\overset{\overset{O}{\uparrow}}{P}(OEt)_2 + 2C_6H_5MgBr + MgBr_2, Et_2O$, 34°

Time, hr	$C_6H_5\overset{\overset{O}{\uparrow}}{P}(OEt)_2$, %	$(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}OEt$, %	$(C_6H_5)_3\overset{\overset{O}{\uparrow}}{P}$, %	C_6H_5MgBr reacted, %
1.5	99.6	0.4	...	0.2
4.5	98.9	1.1	...	0.6
22	91.5	7.9	0.6	4.5
94	81.7	14.3	4.0	11.1

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(17) Significant differences were observed in the nmr spectra of the more basic phosphoryl compounds: $(C_6H_5)_3PO$ in THF −23.5 ppm, + MgBrOEt −33.8 ppm; $(C_6H_5)_2O{=}POEt$ in THF −28.2 ppm, + $MgBr_2$ −30.0 ppm; $(C_6H_5)_2O{=}POEt$ in THF + $(C_6H_5)MgBr$ −34.4 ppm.

C. In Benzene.—The procedure of Burger and Dawson (MgBr$_2$) was repeated with a control experiment. In the latter case the reaction became heterogeneous in about 2 hr. After 6 hr in benzene (oil bath temperature of 73°) the reactions were worked up to give 24.5 and 24 g of crude material, respectively. Gas chromatographic analysis indicated 23.4% diethyl phenylphosphonate, 21.6% ethyl diphenylphosphinate, and 55% triphenylphosphine oxide from Burger and Dawson's conditions with MgBr$_2$ and 9.8% diethyl phenylphosphonate, 11.8% ethyl diphenylphosphinate, and 78.4% triphenylphosphine oxide from the control experiment. Following digestion with diethyl ether, 30 and 58% yields of triphenylphosphine oxide were isolated from the run containing magnesium bromide and the control experiment, respectively.

Reactions of Trimethylaluminum. A. With Dodecylphosphonyl Dichloride.—To 14.5 g of trimethylaluminum (0.2 mol) under argon was added *very slowly* 28 g of dodecylphosphonyl dichloride (0.1 mol). Care was required during the addition to keep the temperature below 45° as several of these reactions blew up. After stirring overnight and heating slowly to 130° over a period of 8 hr, the mixture was cooled and solvolyzed cautiously with 50 ml of ethanol. Addition of ice-cold 1:1 hydrochloric acid gave a solution which was extracted with diethyl ether. Following removal of the ether, dissolution in chloroform, and water washing, distillation gave 17 g (71%) of dimethyldodecylphosphine oxide, mp 83-84°. Use of 0.2 mol of trimethylaluminum to 0.3 mol of dodecylphosphonyl dichloride gave a mixture of largely diethyl dodecylphosphonate and ethyl dodecylmethylphosphinate in about a 2:1 ratio.

B. With Dialkyl Alkylphosphonates.—Upon adding 16.5 g of trimethylaluminum to 200 ml of THF considerable heat was evolved. Addition of 30.6 g of diethyl dodecylphosphonate gave a relatively small heat effect. After refluxing 3.5 hr work-up as above gave 88% recovered diethyl dodecylphosphonate. No evidence of substitution products could be detected in the gas chromatograph or the phosphorus nmr spectrum of the crude product.

Addition of 30.6 g of diethyl dodecylphosphonate to 16.5 g of trimethylaluminum at 10° resulted in considerable heat evolution. Upon heating slowly to 70° for 3 hr, 100° for 1 hr, and reflux for 8 hr, (130-135°) ethylene and methane gas were evolved. Work-up in the manner as above gave a solid that was insoluble in water and diethyl ether. Recrystallization from acetone gave 12.3 g (43%) of aluminum tris(ethyl dodecylphosphonate).

Anal. Calcd for $C_{42}H_{90}P_3O_9Al$: C, 58.8; H, 10.6; Al, 3.1. Found: C, 59.2; H, 10.6; Al, 2.8.

Again no substitution products were detected in the crude products.

Phosphorus nmr spectra of a 3:1 mixture of diethyl ethylphosphonate-trimethylaluminum showed a signal at -32.2 ppm with a shoulder at -35.2 ppm.

In THF diethyl ethylphosphonate (-32.5 ppm) and trimethylaluminum (1:1) gave only one signal at -33.5 ppm.

Registry No.—Phenylmagnesium bromide, 100-58-3; magnesium chloride, 7786-30-3; magnesium bromide, 7789-48-2; diethyl phenylphosphonate, 1754-49-0; diethyl ethylphosphonate, 78-38-6; trimethylaluminum 75-24-1; dimethyldodecylphosphine, 871-95-4; aluminum tris(ethyl dodecylphosphonate), 17448-03-2.

Acknowledgments.—The author wishes to thank Mr. Bruce Banker for his excellent technical assistance and Dr. D. J. Peterson, Dr. C. D. Broaddus, Dr. R. G. Laughlin, and Dr. T. J. Logan for their helpful discussions.

Synthesis and Acetolysis of Mixed Trialkyl Phosphites

EARL S. HUYSER AND JERRY A. DIETER[1]

Department of Chemistry, University of Kansas, Lawrence, Kansas 66044

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A number of mixed trialkyl phosphites were prepared by reaction of the appropriate mono- or dialkyl chlorophosphite and alcohol in an inert solvent in the presence of N,N-dimethylaniline. Reaction of these mixed trialkyl phosphites with acetic acid at 125° resulted in formation of a mixture of acetate esters and dialkyl phosphites. Analysis of the acetate esters produced in this manner served as a means of determining the nature of the acetolysis of various alkyl groups from trialkyl phosphites.

The dealkylation reactions of phosphite esters with hydrogen halides yielding an alkyl halide and a phosphite ester with one less alkyl group have been extensively studied by Gerrard and his coworkers.[2] They found that (1) the reactions of trialkyl phosphites with a hydrogen halide were faster than those of dialkyl phosphites and monoalkyl phosphites; (2) the removal of the alkyl group occurred with inversion of configuration in the trialkyl and dialkyl phosphites, whereas extensive racemization was observed in the reactions of monoalkyl phosphites having an optically active alkyl group; and (3) the order of reactivity of the hydrogen halides with a given trialkyl halide was HI > HBr > HCl. Reactions of trialkyl phosphites with sulfuric acid yielding sulfate esters have been reported.[3] Similarly, reactions of trialkyl phosphites with mono- and dialkyl phosphates yielding the trialkyl phosphates are known.[4] Carboxylic acids have been reported to react at elevated temperatures (110-170°) with equivalent amounts of triethyl phosphite yielding the ethyl carboxylate and diethyl phosphite.[5] Esterification of furylacrylic acid was accomplished by heating the acid for 3 hr at 150-160° with triethyl phosphite.[6] Reactions of dialkyl phosphites with carboxylic acids are also known but occur more slowly at the conditions used for the reactions with trialkyl phosphites.[7]

The work described in this article is concerned with the acetolysis reactions of several mixed trialkyl phosphites. The purpose of this study was to determine

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