Anal. Calcd for $C_{13}H_{16}FeO$: C, 63.96; H, 6.61. Found: C, 63.68; H, 6.41.

Reaction of Lithioferrocene with Styrene Oxide.—This followed the same procedure as in the case of ethylene oxide. There was obtained 1.5 g (23% of theory) of **2-ferrocenyl-1-phenyl-1-ethanol** which melted at 82–84° after crystallization from a mixture of petroleum ether and ethyl ether. The infrared spectrum (Nujol mull) showed absorption bands at 3225, 1110, 1045, 1005, 820, 810, 775, 755, and 700 cm^{-1}; nmr ($\nu_{max}^{DCCl_3}$) δ 7.45 (singlet, five protons, C_6H_5), 4.8 (poorly defined multiplet, one proton, CHOH), 4.18 (singlet, nine protons, ferrocene ring protons), 2.80 (doublet, J = 8 cps, two protons, $FcCH_2$), and 2.18 (poorly defined singlet, one proton, CHOH).

Anal. Calcd for $C_{18}H_{18}FeO$: C, 70.61; H, 5.92. Found: C, 70.32; H, 5.97.

Ferrocenylmagnesium Bromide.—Lithioferrocene (0.021 mole) was prepared as described above and to it was added rapidly under a dry, oxygen-free nitrogen atmosphere an ether solution of 0.025 mole of magnesium bromide from 6 g of magnesium turnings and 4.7 g of ethylene dibromide. The magnesium bromide ether "solution" was actually composed of two layers: a brown lower layer and a milky-white upper layer. Both layers were added rapidly to the stirred solution of the lithioferrocene. The color changed immediately from red to yellow-orange. The reaction mixture was stirred for 15 min at room temperature before using.

Carbonation of the Grignard reagent with excess Dry Ice yielded the known **ferrocenecarboxylic acid**, mp 195–205° dec, in 72% yield after recrystallization from a mixture of petroleum ether and ethyl ether.

Acknowledgment.—The financial support provided by the American Cyanamid Company is deeply appreciated.

Nucleophilic Displacement Reactions on Organophosphorus Esters by Grignard Reagents. II. Evidence for Competitive Displacement on Carbon and Phosphorus in the Reaction of Grignard Reagents with Simple Phosphates[1]

K. DARRELL BERLIN AND MELBERT E. PETERSON[2]

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma

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In the reaction of trimethyl phosphate (**1**) with phenyl Grignard reagent (**2**) all products of displacement reactions, namely, dimethyl phenylphosphonate (**3**), methyl diphenylphosphinate (**4**), and triphenylphosphine oxide (**5**), were not found. Surprisingly, careful investigation of various reaction mixtures have revealed only the presence of **4** and **5**. In no case was **3** detected. Interestingly, with the comparatively small Grignard reagent, the C-alkylation product, toluene, was detected in all condensations of **1** and **2**. In addition small amounts of ethylbenzene were found when triethyl phosphate was treated with **2**. A reaction mechanism is proposed for both C alkylation and displacement on phosphorus.

Several instances of reaction of trialkyl and triaryl phosphorus esters with Grignard reagents have appeared in the literature. Gilman and Vernon[3] reported that triphenylphosphine oxide (**5**) and phenol were produced from triphenyl phosphate (**6**) when treated with phenyl Grignard reagent (**2**) (4:1 mole ratio of reactants). Reaction of the propyl Grignard reagent with triphenyl phosphite at 95° gave tri-*n*-propylphosphine.

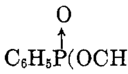
Condensation of triethyl phosphate with **2** was reported to yield diethyl phenylphosphonate (16%) and diphenylphosphinic acid (17%).[4] Reaction of *n*-propyl Grignard reagent with **6** (4:1 mole ratio) in boiling ether for 6 hr gave no reaction, whereas apparently some of the expected phosphine oxide was obtained when the above mixture was heated in ether–toluene at 95°.[3] Tri-*p*-tolyl phosphate reacted with **2** at 105° for 5 hr to give **3** (50%).[3] Treatment of **1** with the bulky mesityl Grignard reagent led to C alkylation rather than attack on phosphorus.[5] This result has been attributed to the bulkiness of the Grignard reagent which retarded approach of the reagent to phosphorus.

$(CH_3O)_3P \rightarrow O$

1

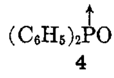
C_6H_5MgBr

2



$C_6H_5\overset{\overset{O}{\uparrow}}{P}(OCH_3)_2$

3



$(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}OCH_3$

4

$(C_6H_5)_3P \rightarrow O$

5

$(C_6H_5O)_3P \rightarrow O$

6

In the above-cited examples no systematic study was made of the effects of varying concentration of the Grignard reagent with respect to the ester. In addition no detailed analysis with gas chromatography was reported. A meticulous examination was made recently on the reaction of Grignard reagents on phosphites.[1b] We now report an extensive related study with organic phosphates.

We have examined the reaction of **1** with controlled amounts of **2** (Table I). We had anticipated that information concerning the mechanism of this displacement reaction would be revealed by careful analysis of the relative amounts of mono, di, and tri displacement products. Analysis of the reaction mixture was accomplished by gas chromatography (gc) in a manner analogous to that reported earlier.[1b,6]

In several respects the reaction of the phosphate **1** was quite different from that of trimethyl phosphite as reported previously.[1b] When **2** was treated with **1** (1:4 mole ratio) in ether–benzene at 60° for 1 hr, **5** was obtained in low yield (10%) in contrast with the quantitative yield of triphenylphosphine realized from the phosphite.[1b] It should be noted that under com-

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(1) (a) We gratefully acknowledge support by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-132-65. (b) For the preceeding paper, see K. D. Berlin, T. H. Austin, and K. L. Stone, *J. Am. Chem. Soc.*, **86**, 1787 (1964).

(2) National Science Foundation Faculty Fellow, 1964–1965; National Science Foundation Cooperative Fellow, 1965–1966.

(3) H. Gilman and C. C. Vernon, *J. Am. Chem. Soc.*, **48**, 1063 (1926).

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

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

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

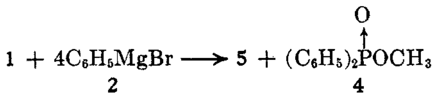
TABLE I

DATA ON REACTIONS OF **1** WITH **2**

		Temp,[a]	Time, hr		Relative ratio[b] of compounds present		
Expt	**2**:**1**	°C	Addn	Reacn	**4**	**5**	Toluene
1	1:1	60	0.5	1	3.15 (0.97)[f]	1.00 (0.81)	8.82 (0.69)[h]
2	1:1	60	0.5	1	2.63 (1.00)	1.00 (1.00)	10.2 (1.00)
3	1:1[c]	60	0.5	1	34.0 (0.12)	1.00 (0.01)	4.00 (0.37)
4	1:1[c]	60	1.25	1	8.5 (1.68)	1.00 (0.52)	8.74 (0.44)
5	1:1[c]	60	1.75	1	1.43 (0.71)	1.00 (1.31)	5.23 (0.66)
6	3:1	60	0.5	1	0.58 (0.56)	1.00 (2.53)	4.84 (1.19)
7	3:1	70	0.5	1	0.16 (0.40)	1.00 (6.82)	1.13 (0.75)
8	3:1[d]	60	0.5	1	1.75 (0.08)	1.00 (0.11)	156.0 (1.75)
9	4:1	60	0.5	1	1.47 (2.29)	1.00 (4.10)	0.75 (0.30)
10	3:1[e]	90	0.5		...	5.9[g] (14.92)	...

[a] Represents temperature at which reaction was held during period specified as reaction time. [b] The actual per cent yields of **4**, **5**, and toluene were based on trimethyl phosphate. A minimum of two runs was performed for each set of conditions. [c] Inverse addition. [d] Ether–benzene solvent system replaced with ether–tetrahydrofuran. [e] Anisole used as solvent. [f] The numbers not in parentheses which pertain to relative ratios of **4**, **5**, and toluene can be compared horizontally for each run (except run 10) with **5** as the standard. All numbers in parentheses in the three vertical columns correspond to relative ratios of **4**, **5**, and toluene and can be compared to run 2 as the standard (=1.00). [g] Based on 3:1 60° run. [h] Total conversion of **1** was achieved in all reactions with **2**:**1** greater than 1:1. In the 1:1 reactions conversion was greater than 75%.

parable conditions with **2** and **6** (4:1 mole ratio) the oxide **5** could be isolated in high yield (95%). Whereas trimethyl phosphite immediately produced a fine, white precipitate in a vigorous exothermic reaction when added to **2**,[1b] regardless of the mole ratio of **2** to **1** there was only a small increase in temperature (1–2°). With completion of addition, a layer of gummy material was observed on the sides of the flask.



$$\mathbf{1} + \underset{\mathbf{2}}{4C_6H_5MgBr} \longrightarrow \mathbf{5} + \underset{\mathbf{4}}{(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}OCH_3}$$

One of the most surprising results of the work was the absence of detectable amounts of the monodisplacement product, dimethyl phenylphosphonate (**3**), from all reactions regardless of the concentration of **2** to **1**. This is in contrast to the reported results from triethyl phosphate and **2**.[4] An inverse addition was performed (1:1 mole ratio) in an effort to "trap" the phosphonate by minimizing the possibility of the reaction with excess **2**. Also, a reaction was run at 30° (3:1 mole ratio), and, although phosphinate and phosphine oxide were detected in both cases, no **3** was found in any of the experiments. It was observed, however, that the inverse addition led to decreased yields of **5** and methyl diphenylphosphinate (**4**) (compare runs 2 and 3 in Table I). As was found with the trimethyl phosphite,[1b] the rate of addition had a pronounced effect on the yield and ratio of products in the present work. In two inverse addition reactions (identical except for rate of addition of Grignard reagent), increasing the addition time from 30 to 105 min led to a sixfold increase in **4** and a 100-fold increase in **5**.

The displacement reaction of alkoxy (or aryloxy) groups from phosphate esters has been suggested to occur in a stepwise manner.[7] The Grignard reagent is visualized as reversibly complexing with the phosphoryl oxygen (Chart I) thus increasing the positive character of phosphorus and making it more susceptible to the attacking Grignard reagent.[7,8] Displacement of an alkoxide ion yields the phosphonate and repetition of the process leads to formation of the phosphinate and phosphine oxide, all presumably in complexed form. Hydrolysis then converts each complex into the respective displacement product.

Initial formation of the complex between the magnesium of the Grignard reagent and the phosphoryl oxygen atom, thus tying up 1 mole of the reagent, has been postulated to account for several observations. For example, Kosolapoff[9] did not find **5** when diethyl phenylphosphonate was treated with 2 moles of **2** under strenuous conditions (85–95°, 8 hr in toluene). Only diphenylphosphinic acid (32%) was obtained. Presumably the failure to obtain **5** may be attributed to the absence of excess Grignard reagent. When allyl Grignard reagent was allowed to condense with diphenyl phenylphosphonate, diallylphenylphosphine oxide was obtained in yield greater than 50%.[10] Diphenyl phenylphosphonate has been employed as a source for unsymmetrical tertiary phosphine oxides.[11] Condensation of diphenyl methylphosphonate with *p*-tolyl Grignard reagent resulted in 60% of the theoretical amount of di(*p*-tolyl)methylphosphine oxide.[12] In each of the above examples a 1-mole excess of Grignard reagent was used. Dimethyl- and diethylalkylphosphine oxides are readily available from diphenyl alkylphosphonates and the methyl or ethyl Grignard reagents in tetrahydrofuran (4:1 mole ratio of Grignard reagent to ester).[13]

It appears that the reactivity of the phosphate is much less than that of the phosphite with the same Grignard reagent. Notably, the vigorous complex formation with trimethyl phosphite[1b] (as evidenced by the highly exothermic addition reaction) and the

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[7] See, for example, K. D. Berlin and G. B. Butler, *Chem. Rev.*, **60**, 243 (1960).

[8] Pertinent to the discussion are several facts established by others. A complex of tribenzylphosphine oxide and methylmagnesium iodide has been isolated: see R. H. Pritchard and J. Kenyon, *J. Chem. Soc.*, **89**, 262 (1906). Mixing magnesium bromide with diethyl phenylphosphonate gave a solid complex which, when treated with **2**, led to an improved yield of **5**: N. D. Dawson and A. Burger, *J. Org. Chem.*, **18**, 207 (1953). A series of complexes of alkyl phosphinates with magnesium iodide has been isolated in our laboratory. The formation of a ester–Grignard reagent complex has been used to account for the observed reaction of trimethyl phosphite and **2**.[1b] Triphenylphosphine oxide has been found to complex with **2** in ether giving an insoluble complex in our laboratory.

[9] G. M. Kosolapoff, *J. Am. Chem. Soc.*, **72**, 5508 (1950).

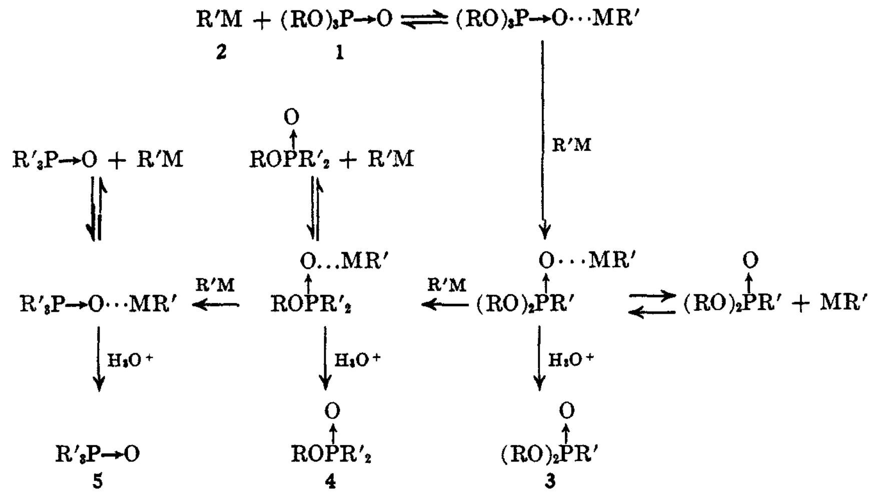
[10] K. D. Berlin and G. B. Butler, *ibid.*, **82**, 2712 (1960).

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

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

[13] R. G. Laughlin, *J. Org. Chem.*, **30**, 1322 (1965).

CHART I

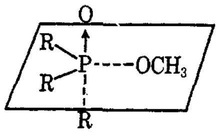


$R'M = C_6H_5MgBr$
$R = CH_3$
$R' = C_6H_5$

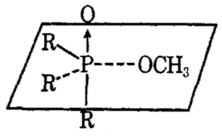
formation of precipitate is not observed in the phosphate series at 60° in ether–benzene. In addition, low conversion in the phosphate series results in markedly lower yields of the displacement products. It seems likely that a phosphate complex would be less favored because of the decreased basicity of the phosphoryl group of the phosphate in comparison with the unshared electron pair on phosphorus in the phosphite.

Since no phosphonate was isolated in any of the reaction mixtures from 1 and 2 it appears that the postulated Grignard complex might be highly reactive when formed. Models indicate the ester oxygen atoms in 1 screen the phosphorus atom well and probably retard approach of the attacking Grignard reagent. It may be noted that although the alkoxy groups are more electronegative than the aryl groups[14] (the phosphate would be expected to be most reactive species), p_π–d_π bonding in the transition state between the alkoxy oxygen and phosphorus apparently diminishes the positive charge on phosphorus.[15] In agreement with our data involving 1 and 2, 1 has already been observed to be much less reactive to alkaline hydrolysis than dimethyl ethylphosphonate and methyl diethylphosphinate.[16] In a related series, PO_4^{3-}, $CH_3PO_3^{2-}$, $(CH_3)_2PO_2^-$, and $(CH_3)_3P{\rightarrow}O$, the positive charge on phosphorus is found to increase in the order shown.[17] In contrast to the influence of the alkyl group, the presence of the phenyl group would be expected to enhance the positive charge on phosphorus and thus increase its reactivity. In a study of the rate of chloride exchange for a series of compounds $[RP(O)Cl_2]$, the order was found to be $R = C_6H_5 > CH_3 > OCH_3 > Cl > OC_6H_5$.[15] Examination of the donor or base strength of a similar series was made by measurement of OH stretching frequency in the infrared which shifted in the adduct. The order of decreasing shift was found to be $R = C_6H_5 > CH_3 > OCH_3 > OC_6H_5 > Cl$.[15]

Justification for the isolation of the phosphinate is difficult although models imply that the increased number of phenyl groups in 4 may reduce the effective coordination between the P→O group and magnesium halide. The phenyl groups could also block attack at either the apical (a) or basal (b) positions.



a



b

Low yields of the displacement products can in part be attributed to slight solubility of one or more of the complexed species present. We postulate the existence of an equilibrium between the free and the complexed esters in solution. However, because of continual reaction of each complex with 2 it was not feasible to obtain solubility data on the various complexes.

When the addition of esters 1, 3, or 4 to the Grignard reagent 2 in reactions run at 30° was complete (Table II), two distinct organic layers were observable. The dark brown lower layer was hydrolyzed in a very exothermic reaction which could result from the presence of unreacted Grignard reagent or magnesium salts. Gc analysis proved the presence of the displacement products 4 and 5 and the absence of 3.

Analyses of the hydrolyzed upper and lower layers respectively, have been combined in Table II. Acidification of the aqueous layer to pH 1 resulted in the precipitation of diphenylphosphinic acid. The acid which has been included in the tables as 4 is presumably formed by hydrolysis of the phosphinate 4. Attack of the Grignard reagent on the methyl carbon atom of the phosphinate (C alkylation) could also serve as a source of the acid. This seems unlikely, however, in view of the very low yield of toluene from 4 (see Table II) in comparison to that from 1 and 3.

Surprisingly, the C-alkylation product toluene was detected in all reaction mixtures of 1 and 2. Some

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[14] E. A. C. Lucken and M. A. Whitehead, *J. Chem. Soc.*, 2459 (1961).

[15] R. S. Drago, V. A. Mode, J. G. Kay, and D. L. Lydy, *J. Am. Chem. Soc.*, **87**, 5010 (1965).

[16] R. F. Hudson and D. C. Harper, *J. Chem. Soc.*, 1356 (1958).

[17] H. Gerding, J. W. Maarsen, and D. H. Zijp, *Rec. Trav. Chim.*, **77**, 361 (1958).

TABLE II

DATA ON REACTION OF **1**, **3** AND **4** WITH **2** AT 30°

Expt	Ester	**2**:ester	Time, hr		Relative ratio[a] of compounds present		
			Addn	Reacn	**4**	**5**	Toluene
1	**1**	4:1	0.5	1	3.58(1.00)[b]	1.00(1.00)	22.9 (1.00)
2	**3**	3:1	0.5	1	2.19(8.97)	1.00(14.7)	0.55 (0.35)
3	**4**	2:1	0.5	1	...	1.00(26.2)	0.037(0.042)

[a] The actual per cent yields of products were based on trimethyl phosphate used. A minimum of two runs was performed for each set of conditions. [b] All numbers not in parentheses pertain to relative yields of **4**, **5**, and toluene and can be compared horizontally for each run with **5** as the standard. All numbers in parentheses in the vertical columns correspond to relative ratios of **4**, **5**, and toluene based on yields from **1** as the standard (1.00).

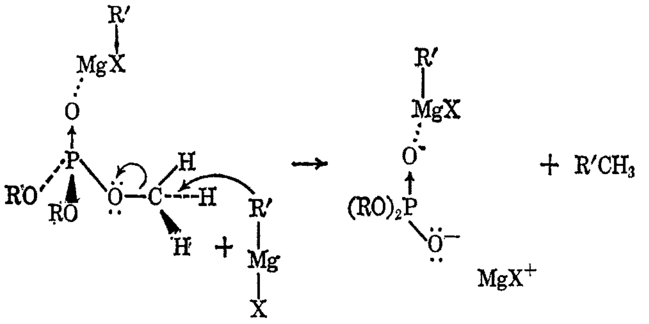
analogous situations have been observed.[18] Gilman and Gaj found that the use of certain hindered Grignard reagents with **1** led to C alkylation.[5] Trimethyl phosphate and mesityl Grignard reagent led to 1,2,3,5-tetramethylbenzene. 1,1,1-Triphenylethane formed (77%) when trityl Grignard reagent was employed. In apparently related cases the bulky lithium reagents, diphenylmethyllithium and triphenylsilyllithium, produced C-alkylation products in major amounts when allowed to react with phosphates.[19] No data was presented which was explicable by attack on phosphorus.

In ether–benzene the yield of toluene based on **1** (10% with 3:1 mole ratio of **2** to **1**) was found to decrease slightly as the molar ratio of **2** to **1** increased from 1:1 to 4:1. A correspondingly small increase in yields of displacement products was always noted and was reproducible. Increase in time of addition and reaction temperature led to higher yields of toluene. When the ether–benzene solvent was replaced with boiling tetrahydrofuran, the yield increased to 18% whereas the yield of **4** and **5** was reduced approximately sevenfold.[20] It is noteworthy that with **1** both C alkylation and attack on phosphorus were observed with **2** which is generally not considered a bulky Grignard reagent.

To examine the scope of the C-alkylation process we investigated the reaction of **2** and triethyl phosphate (4:1 mole ratio). Ethylbenzene (<1%) was detected from a reaction mixture which had been heated at 60° for 4 hr. It should be noted that mesityl Grignard reagent gave no reaction with tri-*n*-butyl phosphate in ether or tetrahydrofuran.[5] Thus the ester as well as the Grignard reagent is important in determining the over-all rate of alkoxy displacement.[5,21]

In the reaction of **2** and triethyl phosphate (4:1 mole ratio) both diethyl phenylphosphonate and ethyl diphenylphosphinate were identified in the reaction mixture by gc. In similar reactions of **6** and diphenyl phenylphosphonate with ethyl Grignard reagent (1 mole excess) only traces of ethylbenzene were found. No evidence of C alkylation was obtained on analysis of the reaction of methyl Grignard reagent (under nearly identical conditions as were described previously) with tris(4-chlorophenyl) phosphate and with tris(2,6-dimethylphenyl) phosphate. These results leave some doubt as to the nature of the attack on carbon. The Grignard–solvent aggregate likely differs markedly in ability to coordinate with the P→O group in each ester and consequently the rates of attack on phosphorus also vary.[22]

The formation of C alkylation products is thought to occur *via* an SN2-type displacement on carbon of the activated complex by the attacking Grignard reagent. That triethyl phosphate is less reactive compared to **1** toward **2** may be rationalized on an increased steric hindrance at the α carbon. In addition the electron density on the α-carbon atom in **1** is possibly less than in triethyl phosphate based on hyperconjugation considerations. Consequently reported inertness of tri-*n*-butyl phosphate toward mesityl Grignard reagent is understandable. As Table II indicates, the major source of the C-alkylation product in the condensation of **1** and **2** is apparently the phosphate ester complex.



On the basis of our experimental data it is evident that the nucleophilic displacement of methoxy groups from **1** is a stepwise process. Although the postulated intermediate dimethyl phenylphosphate (**3**) was not detected in any reaction mixture obtained from **1**,

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(18) Some alkylating properties of phosphates with related systems have been studied to a limited extent. For example, trialkyl phosphates have been reported to serve as alkylating agents for the O alkylation of phenols [C. R. Noller and G. R. Dutton, *J. Am. Chem. Soc.*, **55**, 424 (1933)] and alcohols [A. D. Toy, *ibid.*, **66**, 499 (1944)], the S alkylation of mercaptans [R. G. Harvey and E. V. Jensen, *J. Org. Chem.*, **28**, 470 (1963)], and the N alkylation of thiourea [J. B. Parker and T. D. Smith, *J. Chem. Soc.*, 442 (1961)] and arylamines [J. H. Billman, *J. Am. Chem. Soc.*, **64**, 2977 (1942); *ibid.*, **68**, 895 (1946)]. Recently, use has been made of **1** with arylamines to produce both N- and C-alkylation products [F. W. Jones, G. O. Osborne, G. J. Sutherland, R. D. Topsom, and J. Vaughan, *Chem. Commun.* (London), 18 (1966)]. The N alkylation of 4-nitrophthalimide by **1** has also been reported: J. H. Billman and R. V. Cash, *Proc. Indiana Acad. Sci.*, **63**, 108 (1953). Dimethyl sulfate has been extensively used as an efficient alkylating agent; see for example, C. M. Suter, "Tetravalent Sulfur Compounds," John Wiley and Sons, Inc., New York, N. Y., 1944, p 58–60. Khotinsky and Melamed reported the formation of toluene in the reaction of trimethyl borate and **1**: E. Khotinsky and M. Melamed, *Ber.*, **42**, 3090 (1909). Gilman and Vernon[8] were unable to reproduce this result, however.

(19) H. Gilman and B. J. Gaj, *J. Org. Chem.*, **26**, 2471 (1961).

(20) The apparent lack of reaction between diphenyl dodecylphosphonate and isopropyl Grignard reagent in boiling tetrahydrofuran has been attributed to the deactivating effect of tetrahydrofuran on the Grignard reagent due to its greater basicity; see ref 13 and R. N. Lewis and J. R. Wright, *J. Am. Chem. Soc.*, **74**, 1253 (1952). It appears more likely in both cases that steric hindrance due to bulkiness of the solvated Grignard reagent is a major factor.

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

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

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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(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]

K. DARRELL BERLIN AND ROLANDO U. PAGILAGAN[2]

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma

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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).

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