C. Stability of 12.—A solution of **12** in acetonitrile was heated for 3 hr. Distillation of the solvent plus possible volatile components gave a distillate which was only acetonitrile by vpc. The residue was heated at reflux in fresh acetonitrile for 24 hr and evaporated to leave a new residue with an nmr spectrum which was identical with that of **12**.

The Reaction of α-Chloroisobutyrophenone with Triphenylphosphine. A. In Benzene or Xylene.—A mixture of **8** and triphenylphosphine (0.028 mol each) in benzene (25 ml) was heated at reflux for 12 days to give 2-benzoylpropyltriphenylphosphonium chloride **10b** (0.305 g, 0.0006 mol, 2%): mp 229–232°; ir (CH_2Cl_2), very similar to that of the corresponding bromide **10a**. The remaining solution contained starting compounds and triphenylphosphine oxide (by tlc). A mixture of **8** and triphenylphosphine (0.0158 mol each) in xylene (15 ml) was heated at reflux for 40 hr to give **10b** (5.64 g, 0.0126 mol, 80%), ir and nmr spectra as above. Addition of mercuric chloride in ethanol to the residual solution gave $(C_6H_5)_3P\cdot HgCl_2$ (1.56 g, 0.03 mol, 19%).

B. In Methanol.—A mixture of **8** and triphenylphosphine (0.021 mol each) in methanol (40 ml) was heated at reflux for 3 days to give no **10b** nor isobutyrophenone. Much triphenylphosphine was left (precipitate with mercuric chloride).

The Reaction of α-Mesyloxyisobutyrophenone 9 with Triphenylphosphine.—A solution of mesyloxyisobutyrophenone[24b] (1.51 g, 0.0062 mol) and triphenylphosphine (1.61 g, 0.0062 mol) in dry glyme (25 ml, distilled from $LiAlH_4$) was heated at reflux for 6 days. Triphenylphosphine was now absent (negative mercuric chloride test). 2-Benzoylpropyltriphenylphosphonium mesylate was formed as an insoluble precipitate (2.41 g, 0.0048 mol, 77%), mp 178.5–179.5° (recrystallized from glyme). The ir spectrum (CH_2Cl_2) exhibited peaks at 5.92 (C=O) and 8.2–8.4 μ (mesylate anion). The nmr spectrum ($CDCl_3$) exhibited peaks as those for **10a** (above) and a singlet at τ 7.32 (OSO_2CH_3).

Control Experiments. A. The Stability of α-Bromoisobutyrophenone.—No methacrylophenone was formed, and **7** was recovered unchanged (by tlc) after it was heated at reflux in acetonitrile solution (24 hr), in benzene–methanol solution (5:1 v/v, 24 hr), or in a solution of triphenylphosphine oxide in 5:1 benzene–methanol (24 hr).

B. 2-Benzoylpropyltriphenylphosphonium Bromide.—A solution of **10a** (0.502 g) in methanol (10 ml) was heated at reflux for 24 hr. No compounds other than **10a** were detected by tlc. Evaporation of the solvent left a solid (0.51 g), mp 217–224°, whose ir (CH_2Cl_2) spectrum was identical with that of genuine **10a**.

Registry No.—Triphenylphosphine, 603-35-0; **9**, 17231-17-3; **10a**, 17730-94-8; **10c**, 17730-97-1; **11**, 769-60-8; **12a**, 17730-95-9; **12b**, 17730-96-0; **13**, 611-70-1.

The Reaction of Diethyl Phosphonate with Methyl and Ethyl Grignard Reagents

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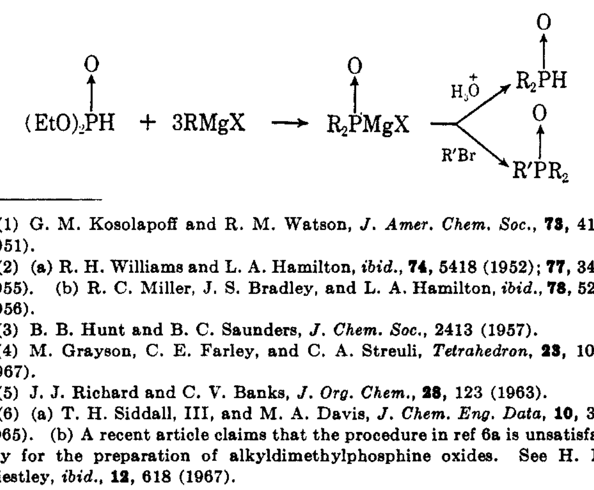
The reaction of diethyl phosphonate with methyl and ethyl Grignard reagents has been investigated. Chemical and physical evidence suggest that the intermediate (I) is not a diethoxyphosphinylmagnesium halide [$(RO)_2P(\rightarrow O)MgX$] but is a trivalent phosphorus species [$(RO)_2\ddot{P}OMgX$]. The latter undergoes rapid substitution with methyl Grignard reagent at 25° to give the halomagnesium dimethyl- and diethylphosphinites ($R_2\ddot{P}OMgX$), II and III, respectively. Phosphorus nmr spectra suggest that the phosphorus atom in the phosphinites (II and III) is also best represented as a trivalent species. Hydrolysis of the phosphinites (II and III) with aqueous potassium carbonate gave aqueous solutions of the hitherto unknown dimethylphosphine oxide and diethylphosphine oxide, respectively. Contrary to previous reports, these secondary phosphine oxides are sufficiently stable to be isolated in good yields by careful distillation. Their structures were confirmed by infrared and proton and phosphorus nmr spectra, and by several of their reactions. Alkylation of the phosphinites (II and III) in tetrahydrofuran produced tertiary phosphine oxides in good yields. These findings demonstrate that the reaction of diethyl phosphonate with Grignard reagents is a useful and general synthesis of both secondary and tertiary phosphine oxides.

Diethyl phosphonate and alkyl or aryl Grignard reagents have been used extensively to prepare secondary phosphine oxides[1-4] and unsymmetrical tertiary phosphine oxides.[5-7] However, attempts to prepare the lower molecular weight dialkylphosphine oxides (C_1–C_4) by this procedure were unsuccessful, reportedly because of their instability.[2] Possibly for this reason only higher alkyl Grignard reagents have been used in the synthesis of trialkylphosphine oxides.[6] To determine the generality of this route to secondary and tertiary phosphine oxides, the reaction of diethyl phosphonate with methyl and ethyl Grignard reagents was investigated.



$$(EtO)_2\overset{O\uparrow}{P}H + 3RMgX \longrightarrow R_2\overset{O\uparrow}{P}MgX \begin{cases} \xrightarrow{H_3O^+} R_2\overset{O\uparrow}{P}H \\ \xrightarrow{R'Br} R'\overset{O\uparrow}{P}R_2 \end{cases}$$

Results

The over-all reaction of diethyl phosphonate with 3 equiv of methylmagnesium chloride is rapid and quite exothermic. An ice bath is required to maintain a temperature of 25–30°. That the reaction is relatively fast is evident from the fact that reaction times longer than 1–2 hr did not significantly increase the yield of dimethylphosphine oxide (Table I). Furthermore, only 30–34% yields of methane were obtained when 1 equiv of diethyl phosphonate was added to methylmagnesium chloride in tetrahydrofuran (THF).[8] In the latter case a 62% yield of dimethyl-

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(1) G. M. Kosolapoff and R. M. Watson, *J. Amer. Chem. Soc.*, **73**, 4101 (1951).

(2) (a) R. H. Williams and L. A. Hamilton, *ibid.*, **74**, 5418 (1952); **77**, 3411 (1955). (b) R. C. Miller, J. S. Bradley, and L. A. Hamilton, *ibid.*, **78**, 5299 (1956).

(3) B. B. Hunt and B. C. Saunders, *J. Chem. Soc.*, 2413 (1957).

(4) M. Grayson, C. E. Farley, and C. A. Streuli, *Tetrahedron*, **23**, 1065 (1967).

(5) J. J. Richard and C. V. Banks, *J. Org. Chem.*, **28**, 123 (1963).

(6) (a) T. H. Siddall, III, and M. A. Davis, *J. Chem. Eng. Data*, **10**, 303 (1965). (b) A recent article claims that the procedure in ref 6a is unsatisfactory for the preparation of alkyldimethylphosphine oxides. See H. M. Priestley, *ibid.*, **12**, 618 (1967).

(7) I. M. Downie and G. Morris, *J. Chem. Soc.*, 5771 (1965).

(8) A. N. Pudovik, *Zh. Obshch. Khim.*, **22**, 109 (1952); *Chem. Abstr.*, **46**, 11099 (1952). Ethane was obtained in 30–32% yields upon straight addition of diethyl phosphonate to ethylmagnesium bromide.

TABLE I

DIMETHYLPHOSPHINE OXIDE PREPARATIONS

Preparation[a]	Reactant ratio	Reaction Temp, °C	Time, hr	$(\mathrm{CH_3})_2\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{P}}\mathrm{H}$ yield, %
1–5	3:1	25 ± 5	1–2	56–63
6	3.4:1	25 ± 5	1	34[b]
7	4:1	25 ± 5	1	61
8	3:1	Reflux	1	48[c]
9	3:1	25 ± 5	5	43
10[d]	3:1	25 ± 5	0.5	89 (crude)[e] (>90% CH_4)
11[f]	1:1	25 ± 5	0.5	62[g] (30% CH_4)
12[f]	1:1	25 ± 5	0.5	*g* (34% CH_4)

[a] All reactions were carried out using methylmagnesium chloride in THF with the exception of 6 in which methylmagnesium bromide was used in diethyl ether. [b] A 4% yield of dimethylphosphinic acid was also isolated. [c] A 7% yield of dimethylphosphinic acid was isolated along with 8% dimethylphosphine. [d] In this preparation 1 equiv of methylmagnesium chloride was added to the diethyl phosphonate. Over a 90% yield of methane was obtained. The resulting solution was then added to 2 equiv of methylmagnesium chloride. [e] The proton nmr spectrum of the neat product indicated that the dimethylphosphine oxide was contaminated with about 3% water. [f] The diethyl phosphonate was added to the Grignard reagent in THF. [g] Unreacted diethyl phosphonate was observed in run 11, whereas in run 12 diethyl phosphonate was recovered to the extent of 44% of the starting material. In the latter case the dimethylphosphine oxide was observed but not isolated.

phosphine oxide[9] was obtained along with a 44% recovery of unreacted diethyl phosphonate.

In spite of the over-all rapidity of the reaction inverse addition of 1 equiv of methylmagnesium chloride to the diethyl phosphonate gave greater than 90% yields of methane[10] and a solution of the intermediate I $[(\mathrm{RO})_2\ddot{\mathrm{P}}\mathrm{OMgX}]$. The latter had the following properties. First, the phosphorus nmr spectrum of the solution of I consisted of a singlet at −137 ppm. Second, upon addition of an additional 2 equiv of methylmagnesium chloride, a fast and exothermic reaction occurred to produce the II $[(\mathrm{CH_3})_2\ddot{\mathrm{P}}\mathrm{OMgX}]$. As might be expected, this stage of the reaction was not quite so exothermic as the over-all reaction. Attempts to record the phosphorus nmr spectrum of II were unsuccessful, presumably owing to its insolubility. However, the phosphorus nmr spectrum of the analogous diethyl intermediate III $[(\mathrm{C_2H_5})_2\ddot{\mathrm{P}}\mathrm{OMgX}]$ consisted of a singlet at −108 ppm. Further reaction of II with methylmagnesium chloride in refluxing THF to produce trimethylphosphine occurred, but only to a small extent (1.5%).

Hydrolysis of II with aqueous potassium carbonate, followed by removal of the water from the aqueous phase and careful distillation, gave crystalline dimethylphosphine oxide in the yields shown in Table I. The structure of the highly hygroscopic product was confirmed by a first-order analysis of the infrared and proton and phosphorus nmr spectral data given in the Experimental Section and by its addition to 1-dodecene to give the known dimethyldodecylphosphine oxide.

The yields of crude dimethylphosphine oxide prior to distillation were generally 74–89%. Proton nmr spectra of the crude products indicated about 2% an impurity. The final distilled yields of dimethylphosphine oxide shown in Table I depended largely upon the care with which it was distilled. Prolonged distillation at 70–75° or distillation at elevated temperatures gave lower yields of dimethylphosphine oxide along with small amounts of the disproportionation products, dimethylphosphine and dimethylphosphinic acid. The yields of dimethylphosphine oxide were not increased by refluxing, use of longer reaction times, or use of a reactant ratio above 3:1 of methylmagnesium chloride to diethyl phosphonate.

Alkylation of II in refluxing tetrahydrofuran, followed by hydrolysis and work-up of the products, gave the alkyldimethylphosphine oxides shown in Table II. The yields of alkyldimethylphosphine oxides were decreased when reactant ratios above 3:1 of methylmagnesium chloride to diethyl phosphonate were used. When 4:1 reactant ratios were used, a considerable amount of residual material remained after distillation of the alkyldimethylphosphine oxide. Attempts to alkylate II with long-chain bromides in refluxing diethyl ether gave less than 10% yields of dimethyldodecylphosphine oxide.

TABLE II

ALKYLDIMETHYLPHOSPHINE OXIDE PREPARATIONS

Preparation[a]	Reactant ratio[b]	Alkyl group	$\mathrm{R}\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{P}}(\mathrm{CH_3})_2$ yield, %
1 and 2	3:1:1	$C_{12}H_{25}$	*c*
3 and 4	4:1:1.6	$C_{12}H_{25}$	65–67[d]
5 and 6	3:1:1.2	$C_{12}H_{25}$	71–85[d]
7	4:1:1.6	$C_{14}H_{29}$	68[d]

[a] All preparations except 1 and 2 were made in THF. [b] Ratio of $CH_3MgCl/(C_2H_5O)_2P(\rightarrow O)H/RBr$. [c] Diethyl ether was used as a solvent. In both cases work-up yielded only a very small amount of the phosphine oxide and alkyltrimethylphosphonium salt. See R. G. Laughlin, *J. Org. Chem.*, **30**, 1322 (1965), for the properties of these alkyldimethyl- and alkyldiethylphosphine oxides. [d] Some alkyltrimethylphosphonium salt was formed.

The over-all reaction of diethyl phosphonate with ethylmagnesium bromide to produce III was exothermic and relatively fast but somewhat slower than with methylmagnesium chloride. Hydrolysis of III and work-up in the manner described for dimethylphosphine oxide gave the yields of diethylphosphine oxide shown in Table III. As in the case of dimethylphosphine oxide, longer reaction times, refluxing, or reactant ratios greater than 3:1 did not significantly increase the yields of diethylphosphine oxide.

TABLE III

DIETHYLPHOSPHINE OXIDE PREPARATIONS

Preparation[a]	Reactant ratio	Reaction temp, °C	Time, hr	$(\mathrm{C_2H_5})_2\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{P}}\mathrm{H}$ yield, %
1–3	3:1	25 ± 5	16	52–58
4	4:1	25 ± 5	2.5	56
5	3:1	Reflux	1	35[b]
6	4:1	25	20	55

[a] All preparations except 1 were made using ethylmagnesium bromide in THF. Preparation 1 was made in diethyl ether–THF. [b] A 12% yield of diethylphosphinic acid was also isolated.

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(9) Based upon the amount of Grignard reagent that was used.

(10) O. Gawron, C. Grelecki, W. Reilly, and J. Sands, *J. Amer. Chem. Soc.*, **75**, 3591 (1953). Ethane was obtained in nearly quantitative yield from diethyl phosphonate and ethyl Grignard reagent.

Diethylphosphine oxide was considerably more stable than dimethylphosphine oxide. Upon the rapid heating of neat samples, dimethylphosphine oxide decomposed slowly at 100–120°, whereas diethylphosphine oxide did not decompose at a comparable rate until 180–200° was reached. Qualitatively the disproportionation of dimethylphosphine oxide to dimethylphosphine and dimethylphosphinic acid appeared to have an induction period, suggesting that the decomposition is acid catalyzed. The fact that only the disproportionation products[2] were obtained from the acid-catalyzed hydrolysis of II lends further support to the idea that disproportionation is acid catalyzed.

Alkylation of III with alkyl bromides in refluxing tetrahydrofuran gave the alkyldiethylphosphine oxides in the yields shown in Table IV. In contrast to the alkyldimethylphosphine oxides, the yields of alkyldiethylphosphine oxides were not affected by excess ethylmagnesium bromide. In addition, slightly higher yields of the alkyldiethylphosphine oxides were generally isolated.

TABLE IV

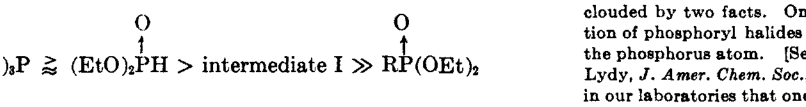
ALKYLDIETHYLPHOSPHINE OXIDE PREPARATIONS

Preparation[a]	Reactant[b] ratio	Alkyl group	$R\overset{O}{\overset{\uparrow}{P}}(C_2H_5)_2$ yield, %
1 and 2	3.6:1:1.6	$C_{12}H_{25}$	88–89[c]
3	3.6:1:1.6	$C_{14}H_{29}$	72[c]
4	3.6:1:1.6	$C_{16}H_{33}$	91[c]
5	3.6:1:1.6	$C_{18}H_{37}$	89[c]

[a] All preparations were made in THF. [b] Ratio of $C_2H_5MgBr/C_2H_5O)_2P(\rightarrow O)H/RBr$. [c] See Table II, footnote *c*.

Reaction of II with a variety of other alkylating agents gave a number of different tertiary phosphine oxides. Thus epoxides with II gave the β-hydroxyalkyldimethylphosphine oxides in 38–71% yields. Use of 1,2-dichlorobutane produced a 30% yield of 1,2-bis(dimethylphosphinyl)butane. The latter was also obtained in 49% yield by the addition of II to α,β-butenyldimethylphosphine oxide. In addition, chloromethyl alkyl ethers and chloromethyl alkyl sulfides and II also gave the corresponding phosphine oxides in good yields.

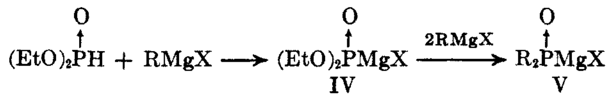
For comparison purposes, reactions of methylmagnesium chloride with triethyl phosphite and diethyl alkylphosphonates ($R = C_2H_5$ and $C_{12}H_{25}$) were carried out under the same conditions as were the reactions of methylmagnesium chloride with diethyl phosphonate and with intermediate I. The reaction of methylmagnesium chloride with triethyl phosphite was fast and very exothermic, whereas the diethyl alkylphosphonates did not react appreciably, if at all (less than 1% after 1 hr at 25°) until the THF was refluxed. Based upon these facts the qualitative order of reactivity of the various phosphorus esters to methylmagnesium chloride in THF was determined to be



$$(EtO)_3P \gtrapprox (EtO)_2\overset{O}{\overset{\uparrow}{P}}H > \text{intermediate I} \gg R\overset{O}{\overset{\uparrow}{P}}(OEt)_2$$

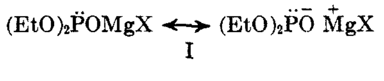
Discussion

The reaction of dialkyl phosphonates with Grignard reagents has long been visualized as proceeding *via* a dialkoxyphosphinylmagnesium halide (IV).[3,6,8,10,11] Substitution on IV by the Grignard reagent to produce the dialkylphosphinylmagnesium halide (V) was believed to proceed analogously to the reaction of dialkyl alkylphosphonates with Grignard reagents. By analogy with Grignard reagents it is assumed that IV and V were resonance hybrids of covalent and ionic forms in which the phosphorus atom possessed a high degree of negative charge. The results of our investigation do not support this picture. For example, reaction of the intermediate IV with a carbanionic species such as Grignard reagents would be expected to proceed much slower than the reaction of diethyl alkylphosphonates with Grignard reagents.[12] Actually, the opposite is true. Diethyl phosphonate and the intermediate I react rapidly with methylmagnesium chloride under conditions where diethyl alkylphosphonates do not even react.



$$(EtO)_2\overset{O}{\overset{\uparrow}{P}}H + RMgX \longrightarrow \underset{\text{IV}}{(EtO)_2\overset{O}{\overset{\uparrow}{P}}MgX} \xrightarrow{2RMgX} \underset{\text{V}}{R_2\overset{O}{\overset{\uparrow}{P}}MgX}$$

Insight into the nature of I was obtained from its phosphorus nmr spectrum of −137 ppm. Such a large negative chemical shift is not characteristic of phosphoryl compounds, which generally possess chemical shifts in the range of 0 to −60 ppm. In contrast trivalent phosphorus compounds are characterized by large negative chemical shifts. For example, the chemical shift of triethyl phosphite (−139 ppm) is very close to that of I. Similarly, the large negative chemical shifts of alkali metal diethyl phosphites has been attributed to their trivalent character.[13] Thus the reactive intermediate I in the reaction of diethyl phosphonate with Grignard reagents would seem best represented as a hybrid of the structures shown below, in which the negative charge resides largely on the oxygen atom. That the reactive intermediate I does possess trivalent character is further supported by the fact that the trivalent ester, triethyl phosphite, also reacts vigorously and exothermically with methylmagnesium chloride. This is not to say that some delocalization of the negative charge from the oxygen atom to the phosphorus atom does not occur in I. To the contrary some delocalization would explain the fact that I reacts somewhat less readily with methylmagnesium chloride than does triethyl phosphite.



$$(EtO)_2\ddot{P}OMgX \longleftrightarrow \underset{\text{I}}{(EtO)_2\ddot{P}\ddot{O}\ \overset{+}{M}gX}$$

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(11) (a) K. Sasse in "Methode der organischen Chemie (Houben-Weyl)," Organische Phosphorverbindungen, part 1, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1963, p 197; (b) K. D. Berlin, T. H. Austin, M. Peterson, and M. Nagabhushanam in "Topics in Phosphorus Chemistry," Vol. I, M. Grayson and E. J. Griffith, Ed., John Wiley & Sons, Inc., New York, N. Y., 1964, pp 41, 42.

(12) This is assuming that the rate of substitution of phosphorus esters is faster when the phosphorus atom possesses a greater positive charge [see ref 11b, p 40]. Although highly reasonable, the validity of this proposal is clouded by two facts. One is a report that claims that the rate of substitution of phosphoryl halides is not directly related to the positive charge on the phosphorus atom. [See R. S. Drago, V. A. Mode, J. G. Kay, and D. L. Lydy, *J. Amer. Chem. Soc.*, **87**, 5010 (1965).] The other is the recent finding in our laboratories that one of the principal pieces of evidence offered to support the proposal is incorrect. [See N. D. Dawson and A. A. Burger, *J. Org. Chem.*, **18**, 207 (1953).] That is, contrary to the literature, magnesium halides do not activate diethyl phenylphosphonate to phenylmagnesium bromide. Further details of these findings will be presented at a later date.

(13) K. Moedritzer, *J. Inorg. Nucl. Chem.*, **22**, 19 (1961).

Finally, the trivalent nature of the products II and III is supported by the large negative chemical shift of III (−108 ppm). As in I some delocalization of the negative charge from the oxygen to the phosphorus atom in II and III would be expected, although possibly to a lesser degree than in I.

$$R_2\ddot{P}OMgX \longleftrightarrow R_2\ddot{P}\overset{-}{O}\ \overset{+}{M}gX$$

II, R = CH_3
III, R = Et

Structures I, II, and III are also consistent with the fact that under certain unusual conditions O alkylation of similar intermediates has been observed.[14] As in our case, however, hydrolysis or alkylation of such intermediates generally produces the thermodynamically more stable phosphoryl compounds by either protonation or alkylation on phosphorus.

The question of whether an inactive complex is formed in THF from I or II and methylmagnesium chloride is of interest, particularly since such an explanation has been recently proposed[11b] to explain the results of Pudovik,[8] and the fact that the yields of triphenylphosphine from trimethyl phosphite and phenylmagnesium bromide in diethyl ether are reportedly increased to nearly quantitative yields by the use of excess Grignard reagent.[15] Our results suggest that this is not the case, at least in the preparation of dimethylphosphine oxide in THF. The yields of dimethylphosphine oxide were not increased when a 4:1 reactant ratio of methylmagnesium chloride to diethyl phosphonate was used. A more likely explanation for the less than quantitative yields of dimethylphosphine oxide is a partial loss during work-up. In view of the fact that other Lewis bases enhance the activity of other organometallic reagents,[16] further investigation of this area would seem worthwhile.

With regard to synthetic utility the reaction of diethyl phosphonate with Grignard reagents followed by hydrolysis or alkylation now appears to constitute a general and very versatile synthesis of secondary or tertiary phosphine oxides. In addition to the simple aliphatic cases, the preparation of β-hydroxyalkyldimethylphosphine oxides and 1,2-bis(dimethylphosphinyl)alkanes in moderate to good yields from reactions of II with epoxides or 1,2-dichloroalkanes or α,α-butenyldimethylphosphine oxide, respectively, attests to the versatility of this synthesis. However, different isolation procedures appear necessary dependent upon whether the phosphine oxide has a low molecular weight (highly water soluble) or a high molecular weight. Furthermore, although diethyl ether could be used as solvent in the preparation of dimethylphosphine oxide, its use in the alkylation of II with dodecyl bromide was totally unsatisfactory, presumably owing to the heterogeneity of the system. Consequently THF was generally used as the solvent in these reactions.

Experimental Section

All reactions and operations were carried out under argon in a well-ventilated hood.

Dimethylphoshine Oxide.—Freshly distilled diethyl phosphonate (138 g, 1.0 mol) was added to 1 l. of 3 *M* methylmagnesium chloride in THF at such a rate that with ice bath cooling the temperature was maintained at 20–30°. After stirring at room temperature for 1 hr the mixture was hydrolyzed by mixing with an ice-cold aqueous solution of potassium carbonate (414 g, 3 mol) in 500 ml of water). At this point the odor of dimethyl- or trimethylphosphine was detectable. After filtering and washing the magnesium carbonate four times with 250 ml of ethanol, most of the ethanol and water filtrate was removed on a rotary evaporator under reduced pressure and a bath temperature of 48° to give 99 g of crude product. The remainder of the water was removed by shaking with Linde Type 4A molecular sieves in chloroform. Subsequent distillation gave 2.6 g of dimethylphosphine oxide, bp 60–65° (6 mm), contaminated with about 5% water, 49 g (63%) of dimethylphosphine oxide, bp 65–67° (6 mm), mp 39–41°, and 3.5 g of residual dimethylphosphinic acid. The product as such possessed a dimethylphosphine odor and was contaminated with approximately 2% unidentified impurity. Further purification was accomplished by vacuum sublimation. The infrared spectrum[17] of a molten sample of dimethylphosphine oxide consisted of a very intense phosphoryl absorption at 8.48 μ, a medium PH band at 4.34 μ, and a strong PCH_3 band at 7.75 μ, along with strong absorptions at 9.75, 10.70, 11.62, and 13.37 μ. Weaker absorptions at 3.40, 3.48, 7.07, and 14.47 μ were also observed. The phosphorus nmr spectrum[18] of a 50% solution consisted of a pair of septuplets centered at −18.6 (in dioxane, J_{PH} = 456 cps, J_{PCH} = 14 cps) and −33 ppm (in D_2O). Upon standing in D_2O the spectrum changed to a 1:1:1 trio of septuplets (J_{PD} = 74.6 cps). The proton nmr spectrum[19] of a 50% solution of dimethylphosphine oxide in D_2O consisted of two widely spaced septuplets centered at τ 2.5 (J_{PH} = 490 cps, J_{PHCH} = 3.5 cps) and two doublets centered at τ 7.89 (J_{PCH} = 14 cps, J_{PHCH} = 3.5 cps) in the ratio 1:6, respectively. Upon standing in D_2O, exchange of the PH proton occurred. Dimethylphosphine oxide (3.4 g, 0.044 mol), dodecene (20 g, 0.119 mol), and 0.3 g of azobisisobutylonitrile (ABN) were heated at 70° for 24 hr. An additional 0.3 g of ABN was added after 6 hr of heating. The dimethyldodecylphosphine oxide (8.1 g, 76%) was then isolated by distillation.

Decomposition of Dimethylphosphine Oxide.—No evidence of decomposition was observed in the phosphorus nmr spectra of a 50% aqueous solution heated at 90° for 36 hr. Less than 3% decomposition was observed in dioxane under the same conditions. Decomposition of 7.8-g samples of neat dimethylphosphine oxide appeared to be slow at 100°, reaching completion after about 1 hr at 120°. At 160–170° the decomposition to dimethylphosphinic acid[20] and dimethylphosphine was complete in less than 10 min. The yields of dimethylphosphinic acid and dimethylphosphine (characterized as trimethylphosphonium iodide[21]) were 96–100% and 91–92%, respectively.

Diethylphosphine Oxide.—Using the procedure described above with the exception that ethylmagnesium bromide was used, 55 g (52%) of diethylphosphine oxide, bp 53–55° (0.6 mm) [lit. bp 52–53° (1.5 mm)],[22] was obtained. In general the diethylphosphine oxide was more stable than the dimethylphosphine oxide; consequently, the product was free of any diethylphosphine or diethylphosphinic acid. The infrared spectrum of diethylphosphine oxide consisted of a strong phosphoryl band at 8.50 μ and medium intensity bands at 3.32, 4.32, 6.86, 7.12, 7.92, 9.56, 10.56, 11.19, 13.12, and 13.67 μ. The phosphorus nmr spectrum consisted of two complex multiplets centered at −47.7 (J_{PH} = 463 cps in water, 50%), −41 (in $CHCl_3$, 50%), and −37 ppm (neat). The proton nmr spectrum run immediately in D_2O consisted of two widely spaced pentuplets centered at τ 2.85 (J_{PH} = 468 cps, J_{CHPH} = 3.5 cps), a complex multiplet at τ 7.64, and two triplets centered at τ 8.36 (J_{PCCH} = 18.8 cps, J_{CHCH} = 7.5 cps), in the ratio 1:4:6. Upon standing the

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PH proton underwent deuterium exchange and the complex multiplet at λ 7.64 became two partially overlapping quartets with $J_{\mathrm{PCH}} = 12.5$ cps.

Decomposition of Diethylphosphine Oxide.—Upon heating of neat samples of diethylphosphine oxide, slow decomposition to diethylphosphine and diethylphosphinic acid occurred at about 180–200°. At 225°, decomposition was complete in a few minutes. Both diethylphosphine and diethylphosphinic acid, identified by their boiling point and proton and phosphorus nmr spectra,[20,23] were obtained in nearly quantitative yields.

Alkyldimethyl and Alkyldiethylphosphine Oxides.—The procedure was the same as for the dimethylphosphine oxide except for the following. Alkyl bromide (1.2 mol) was added prior to hydrolysis, and the reaction mixture was refluxed for 4–8 hr. Hydrolysis was effected by pouring into a mixture of 300 ml of concentrated hydrochloric acid and 2 l. of ice. This mixture was then extracted with diethyl ether, which was removed on a rotary evaporator. Attempted distillation led to decomposition at elevated temperatures. Consequently the product was dissolved in chloroform and water washed, then distilled. In subsequent preparations, after hydrolysis, water was added, and the THF was removed by distillation. Then all but 1–3% of the dimethyldodecylphosphine oxide was separated from the aqueous phase by one extraction with 250 ml of chloroform. Very little, if any (<3%), magnesium salts were partitioned into the chloroform layer. Removal of the chloroform and distillation gave the phosphine oxides in Tables II and IV.

β-Hydroxybutyldimethylphosphine Oxide.—1,2-Epoxybutane (10% excess) was used in place of the alkyl bromide. After refluxing 4 hr the mixture was hydrolyzed with aqueous potassium carbonate and worked up in the manner described for dimethylphosphine oxide. Distillation gave 38–52% yields of β-hydroxybutyldimethylphosphine oxide, bp 104–108° (0.01–0.02 mm). The infrared spectrum of a mineral oil mull showed intense bands at 8.73 (P→O), and 3.40 μ (OH), medium bands at 7.72 and 7.76 μ (P–CH_3) and at 10.62 μ, and weak bands at 8.12, 8.89, 9.58, 9.83, 10.26, 11.46, 11.63, and 13.49 μ. The phosphorus nmr spectrum in benzene consisted of a complex multiplet at −41 ppm. The proton nmr spectrum in $CHCl_3$ consisted of a doublet at τ 4.59 τ ($J_{\mathrm{CHOH}} = 5$ cps), a multiplet at τ 6.05 (CHO), a multiplet at 8.09 (CCH_2P), a pair of doublets at τ 8.38 and 8.45 ($J_{\mathrm{P-CH_3}} = 13$ cps), and a triplet at τ 9.06 ($J_{\mathrm{CH_3CH_2}} = 7$ cps) in the ratio 1:1:2:8:3.

Anal. Calcd for $C_6H_{15}PO_2$: C, 48.0; H, 10.1; P, 20.6; Found: C, 47.8; H, 10.0; P, 20.8.

β-Hydroxydodecyldimethylphosphine Oxide.—1,2-Epoxydodecane (10% excess) and the same general procedure as with the alkyldimethylphosphine oxides were used. The β-hydroxydodecyldimethylphosphine oxide, mp 76–76.5°, was not distilled but was recrystallized twice from hexane to give a 71% yield. The spectral properties were in agreement with those of β-hydroxybutyldimethylphosphine oxide.

Anal. Calcd for $C_{14}H_{31}PO_2$: C, 64.1; H, 11.9; P, 11.8. Found: C, 63.9; H, 11.7; P, 11.5.

1,2-Bis(dimethylphosphinyl)butane. A.—Use of 1,2-dichlorobutane as the alkylating agent for II and the aqueous K_2CO_3 hydrolysis procedure gave a 30% yield of 1,2-bis(dimethylphosphinyl)butane, bp 172–175° (0.5 mm). The phosphorus nmr spectrum in benzene consisted of two complex multiplets at −41.7 and −48.3 ppm with equal areas. The proton nmr spectrum in $CHCl_3$ was very complex consisting of a CH_2CH_3 triplet at τ 8.88 ($J_{\mathrm{CH_3-CH}} = 7.5$ cps), a P–CH_3 doublet at τ 8.44 ($J_{\mathrm{PCH_3}} = 12$ cps), and a pair of PCH_3 doublets at τ 8.46 ($J_{\mathrm{PCH_3}} = 11$ cps), and τ 8.50 ($J_{\mathrm{PCH_3}} = 11$ cps), superimposed on complex multiplets over the range τ 7.70–8.65. The 1,2-bis(dimethylphosphinyl)butane obtained in this manner was identical in all aspects with the product obtained below in B.

Anal. Calcd for $C_8H_{20}P_2O_2$: C, 45.6; H, 9.6; P, 29.4. Found: C, 45.4; H, 9.7; P, 29.1.

B.—α,β-Butenyldimethylphosphine oxide, bp 78–82° (0.1 mm) (P^{31} nmr spectrum −26 ppm in benzene), obtained in 70% yield from the pyrolysis at 235–245° of β-acetoxybutyldimethylphosphine oxide, bp 103–116° (0.1–0.6 mm), was added to II and refluxed 4 hr. Work-up of the product gave a 49% yield of 1,2-bis(dimethylphosphinyl)butane. Worthy of note with regard to the pyrolysis of the β-acetoxyphosphine oxide is the fact that heating the α,β-butenyldimethylphosphine oxide at elevated temperatures for several hours resulted in isomerization to a mixture of 13% α,β-butenyldimethylphosphine oxide–87% β,γ-butenyldimethylphosphine oxide. The latter gives a phosphorous nmr spectrum of −37 ppm. Consequently the pyrolysis time was kept at 1.5 hr to minimize isomerization.

Decoxymethyldimethylphosphine Oxide.—Chloromethyldodecyl ether (10% excess) was added to II. Following refluxing for 4 hr and work-up the product, bp 152–154° (1.0 mm), was isolated in 65% yield by distillation.

Anal. Calcd for $C_{13}H_{29}PO_2$: C, 62.9; H, 11.9; P, 12.5; Found: C, 63.0; H, 12.1; P, 12.3.

Decylthiomethyldimethylphosphine Oxide.—Chloromethyl dodecyl sulfide (10% excess) was added to II. The product, bp 170–179° (3–4 mm), was isolated in 66% yield.

Anal. Calcd for $C_{13}H_{29}POS$: C, 59.1; H, 11.1; P, 11.7. Found: C, 59.3; H, 11.0; P, 11.9.

Registry No.—Diethyl phosphonate, 762-04-9; dimethylphosphine oxide, 7211-39-4; diethylphosphine oxide, 7215-33-0; β-hydroxybutyldimethylphosphine oxide, 17193-99-6; β-hydroxydodecyldimethylphosphine oxide, 17190-96-4; 1,2-bis(dimethylphosphinyl)butane, 17190-97-5; decyloxymethyldimethylphosphine oxide, 17190-98-6; decylthiomethyldimethylphosphine oxide, 17190-99-7.

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