The Chemistry of Diphosphine Disulfides. III. Influence of Structure on the Course of Phosphinothioic Halide–Grignard Reactions[1]

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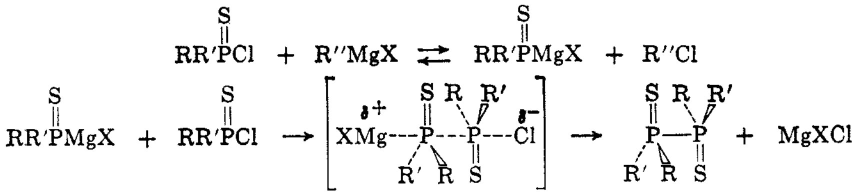
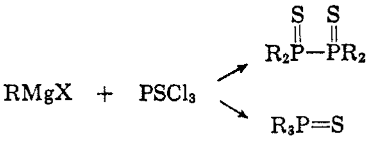
Reactions of dimethyl-, diethyl-, or di(*n*-propyl)phosphinothioic halides with Grignard reagents give trisubstituted phosphine sulfides in high yield. In conflict with results reported by Bogolyubov, it was not possible to obtain diphosphine disulfides from these reactions. Methylphenylphosphinothioic chloride reacts with aliphatic or aromatic Grignard reagents to yield both trisubstituted phosphine sulfides and *meso*-1,2-dimethyl-1,2-diphenyldiphosphine disulfide. Diphenylphosphinothioic chloride reacts with aliphatic Grignard reagents to yield tetraphenyldiphosphine disulfide, but it reacts with aromatic Grignard reagents to yield trisubstituted phosphine sulfides. These results indicate that metal–halogen exchange processes precede the P–P coupling step involved in diphosphine disulfide formation. The high stereoselectivity of the coupling step can be explained by the mechanism



$$RR'\overset{S}{\overset{\|}{P}}Cl + R''MgX \rightleftarrows RR'\overset{S}{\overset{\|}{P}}MgX + R''Cl$$

The reactions of Grignard reagents with thiophosphorus halides can take several courses, depending on the structures of the thiophosphorus halide and the Grignard reagent.[2–6] Thiophosphoryl chloride reacts with simple aliphatic Grignard reagents to yield diphosphine disulfides in high yield, but this reagent reacts with acetylenic,[7] vinyl,[5] aromatic,[10] benzyl,[10] or hindered[5] alkyl Grignard reagents to yield trisubstituted phosphine sulfides primarily.



$$RMgX + PSCl_3 \rightarrow R_2\overset{S}{\overset{\|}{P}}-\overset{S}{\overset{\|}{P}}R_2 \text{ or } R_3P{=}S$$

It is interesting to note that those Grignard reagents which yield phosphine sulfides when treated with $PSCl_3$ are also the Grignard reagents which are initiators for the stereospecific polymerization of methyl methacrylate.[8] The parallelism noted for the behavior of various Grignard reagents in these two widely different reactions is extremely good.

The behavior of Grignard reagents toward alkyl- or arylphosphonothioic dihalides parallels, in general, their behavior toward $PSCl_3$, except that diphosphine disulfides (instead of trisubstituted phosphine sulfides) have been obtained from the reactions of alkylphosphonothioic dihalides with aromatic and benzyl Grignard reagents.[9,10] Racemic and *meso* forms of dialkyldiaryldiphosphine disulfides have been obtained by these latter reactions. Interestingly, alkynyl Grignard reagents[11,12] yield only phosphine sulfides in these reactions.

Harwood and Pollart[13] observed that disubstituted phosphinothioic halides, in contrast to thiophosphoryl halides or substituted phosphonothioic halides, yield only phosphine sulfides when treated with Grignard reagents. On the basis of this observation, these workers concluded that either reduction or metal–halogen exchange processes precede the P–P coupling step involved in diphosphine disulfide formation. Recently, however, Bogolyubov[14] obtained results which are inconsistent with such an interpretation; he reported isolating tetraethyldiphosphine disulfide in 50% yield and tetra-*n*-propyldiphosphine disulfide in 24% yield from reactions of the corresponding phosphinothioic chlorides with Grignard reagents.

In order to resolve the conflicting results obtained by Bogolyubov and by Harwood and Pollart, to define better the scope of the stepwise phosphine sulfide synthesis outlined by the latter workers, and to obtain additional information related to the mechanism of the reaction yielding diphosphine disulfide derivatives, the reactions of a series of substituted phosphinothioic halides with Grignard reagents were investigated in the present study.

Results

Aliphatic Grignard–Dialkylphosphinothioic Halide Reactions.—Because of its significance to previous interpretations of the mechanism and scope of Grignard–thiophosphoryl halide reactions, it seemed important to check Bogolyubov's claim that some dialkylphosphinothioic chlorides react with alkyl Grignard reagents to yield diphosphine disulfides. When reactions of di-

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[1] Presented before the Division of Organic Chemistry at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

[2] A. H. Cowley, *Chem. Rev.*, **65**, 617 (1965).

[3] K. D. Berlin, T. H. Austin, M. Peterson, and M. Nagabhushnam, *Topics Phosphorus Chem.*, **1**, 17 (1964).

[4] L. Maier, *Progr. Inorg. Chem.*, **5**, 27 (1963).

[5] H. Niebergall and B. Langenfeld, *Chem. Ber.*, **95**, 64 (1962).

[6] L. Maier, *Topics Phosphorus Chem.*, **2**, 43 (1965).

[7] G. M. Bogolyubov and A. A. Petrov, *Zh. Obshch. Khim.*, **35**, 704 (1965); *Chem. Abstr.*, **63**, 4430 (1965); *J. Gen. Chem. USSR*, **35**, 705 (1965).

[8] A. Nishioka, H. Watanake, K. Abe, and Y. Sono, *J. Polymer Sci.*, **48**, 241 (1960).

[9] L. Maier, *Chem. Ber.*, **94**, 3043 (1961).

[10] P. C. Crofts and K. Gosling, *J. Chem. Soc.*, 2486 (1964).

[11] G. M. Bogolyubov and A. A. Petrov, *Zh. Obshch. Khim.*, **35**, 988 (1965); *Chem. Abstr.*, **63**, 9981*h* (1965); *J. Gen. Chem. USSR*, **35**, 994 (1965).

[12] G. M. Bogolyubov, K. S. Mingaleva, and A. A. Petrov, *Zh. Obshch. Khim.*, **35**, 1566 (1965); *Chem. Abstr.*, **63**, 17860*c* (1965); *J. Gen. Chem. USSR*, **35**, 1570 (1965).

[13] H. J. Harwood and K. A. Pollart, *J. Org. Chem.*, **28**, 3430 (1963).

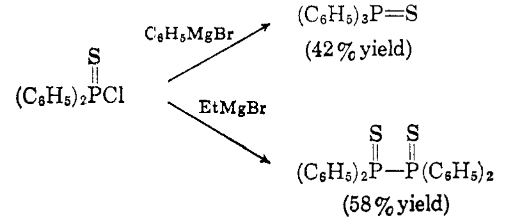
[14] G. M. Bogolyubov, *Zh. Obshch. Khim.*, **35**, 754 (1965); *Chem. Abstr.*, **63**, 4327 (1965); *J. Gen. Chem. USSR*, **35**, 755 (1965).

ethylphosphinothioic chlroide with ethylmagnesium bromide (or chloride) were conducted in the present study, triethylphosphine sulfide was obtained in yields ranging from 70 to 90%, and there was no indication that any diphosphine disulfide derivatives were present among the reaction products. Since Bogolyubov's paper did not provide specific reaction conditions, we varied our conditions extensively in an effort to obtain results similar to his. Reaction temperature, reagent concentrations, and order of addition were changed, but in no instance was any tetraethyldiphosphine disulfide obtained. Excess magnesium, in various forms, was added to some of the reaction systems, but the reaction course was not changed.

Similarly, we obtained tri(*n*-propyl)phosphine sulfide in 73% yield from the reaction of dipropylphosphinothioic chloride with propylmagnesium chloride, and found no evidence for the presence of tetrapropyldiphosphine disulfide in the reaction mixture. In addition, the reactions of dimethylphosphinothioic bromide, diethylphosphinothioic bromide, or di(*n*-propyl)phosphinothioic bromide with methyl-, ethyl-, or *n*-propylmagnesium bromide produced trisubstituted phosphine sulfides in yields ranging from 44 to 77% (*cf.* Table I). No diphosphine disulfide derivatives were obtained from these reactions, although their properties are such that they should be easily isolated.

We are unable to explain the results of Bogolyubov at this point and believe that *the general course of dialkylphosphinothioic halide–Grignard reactions leads to trisubstituted phosphine sulfides*[13] *and not to diphosphine disulfide derivatives.*[14]

Grignard Reactions Involving Alkylaryl- or Diarylphosphinothioic Halides.—In contrast to the results described above, we obtained *both* diphosphine disulfide derivatives and trisubstituted phosphine sulfides from the reactions of Grignard reagents with aryl-substituted phosphinothioic halides. The relative yields of these products seem to depend on the structures of the reactants. For example, diphenylphosphinothioic chloride reacted with phenylmagnesium bromide to yield only[15] triphenylphosphine sulfide, whereas the corresponding reaction with ethylmagnesium bromide yielded only[15] the diphosphine disulfide derivative. The reactions of methylphenylphosphinothioic chloride with ethyl- or phenylmagnesium bromide, however, yielded both types of products, the phosphine sulfide derivative predominating in both cases. It is important to note that only[16] the *meso* form of 1,2-dimethyl-1,2-diphenyldiphosphine disulfide was obtained from these latter reactions. The results obtained in these studies cast considerable light on the mechanism of the reaction yielding diphosphine disulfide derivatives, as will be discussed next.

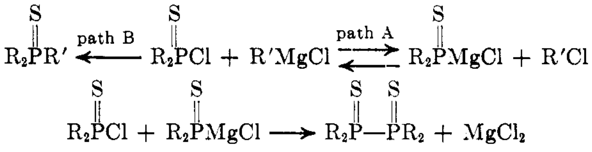


$$(C_6H_5)_2\overset{S}{\overset{\|}{P}}Cl \xrightarrow{C_6H_5MgBr} (C_6H_5)_3P{=}S \ (42\%\ \text{yield})$$

$$(C_6H_5)_2\overset{S}{\overset{\|}{P}}Cl \xrightarrow{EtMgBr} (C_6H_5)_2\overset{S}{\overset{\|}{P}}-\overset{S}{\overset{\|}{P}}(C_6H_5)_2 \ (58\%\ \text{yield})$$

Discussion

In an earlier paper,[13] we concluded that the P–P coupling step in reactions yielding diphosphine disulfides is preceded either by a reduction step yielding an RP=S-type intermediate or else by a metal–halogen exchange reaction. Either process was consistent with the observation that thiophosphorus compounds containing two or more phosphorus–halogen bonds tend to yield diphosphine disulfide when treated with Grignard reagents, whereas other thiophosphorus compounds usually yield phosphine sulfides in such reactions. Since several phosphinothioic halides were noted in the present study to yield diphosphine disulfides when treated with Grignard reagents, it is no longer necessary to require the participation of a reduced intermediate, such as RP=S, in the P–P coupling process. Instead, it seems much more likely that a metal–halogen exchange process precedes the coupling step.



$$R_2\overset{S}{\overset{\|}{P}}R' \xleftarrow{\text{path B}} R_2\overset{S}{\overset{\|}{P}}Cl + R'MgCl \overset{\text{path A}}{\rightleftharpoons} R_2\overset{S}{\overset{\|}{P}}MgCl + R'Cl$$

$$R_2\overset{S}{\overset{\|}{P}}Cl + R_2\overset{S}{\overset{\|}{P}}MgCl \longrightarrow R_2\overset{S}{\overset{\|}{P}}-\overset{S}{\overset{\|}{P}}R_2 + MgCl_2$$

Evidence that metal–halogen processes occur during these reactions was obtained by submitting the reaction mixtures to gas–liquid partition chromatographic analysis. We observed that ethyl chloride is formed in the initial stages of ethylmagnesium bromide–diphenylphosphinothioic chloride reactions. Once formed, ethyl chloride rapidly disappears, presumably owing to subsequent reaction with ethylmagnesium bromide.

If one assumes that metal–halogen exchange must be favorable, both kinetically and thermodynamically, for diphosphine disulfide formation to take place, then the results obtained in previously reported thiophosphorus halide–Grignard reactions can be explained. Metal–halogen exchange[17,18] between a Grignard reagent and a phosphorus halide should be favored thermodynamically when electronegative atoms or groups (phenyl, vinyl, alkynyl) are attached to the phosphorus atom and when alkyl Grignard reagents are employed. Aromatic, alkenyl, and alkynyl Grignard reagents should be less likely to exchange with a given thiophosphoryl halide than alkyl Grignard reagents, and the tendency of thiophosphoryl halides to exchange with a given Grignard reagent should decrease according to the series[20] thiophosphoryl chloride, arylthiophosphonic dichloride, diarylthiophosphinic

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(15) The crystallization characteristics of these two products are considerably different, and it is a simple matter to detect one product in the presence of the other.

(16) Our work on phenylphosphonothioic chloride–Grignard reactions has provided us with experience in the separation of the *meso* and racemic forms of this product. We are confident that the *meso* product is the only one formed in this reaction.

(17) (a) R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 339 (1951); (b) E. A. Braude, *Progr. Org. Chem.*, **3**, 172 (1955); (c) H. G. Viehe, *Chem. Ber.*, **92**, 3064 (1959), and references therein.

(18) The operation of metal–halogen exchange processes during reactions yielding tetrasubstituted diphosphines seems to be well established.[2,19]

(19) (a) K. Issleib and B. Walker, *Chem. Ber.*, **97**, 3424 (1964); (b) K. Issleib and G. Harzfeld, *ibid.*, **95**, 268 (1962); (c) K. Issleib and D. Jacob, *ibid.*, **94**, 107 (1961); (d) K. Issleib and D. Müller, *ibid.*, **92**, 3175 (1959), and other references in this series; (e) F. Glockling, *Quart. Rev.* (London), **20**, 46 (1966).

(20) This series is believed to be arranged in order of decreasing electronegativity of the phosphorus atom, but some inversions may be necessary when quantitative information about R₂PSCl–metal alkyl exchange processes becomes available.

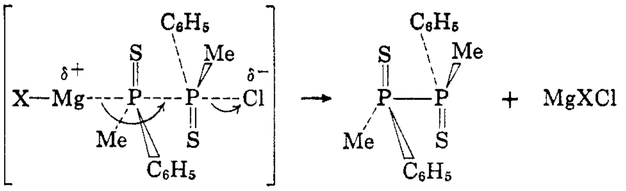
chloride, alkylphosphonothioic dichloride, alkylarylphosphinothioic chloride, and dialkylphosphinothioic chloride.

If metal–halogen exchange must precede the P–P coupling step leading to diphosphine disulfide formation, the expectations outlined above are consistent with the general behavior of thiophosphoryl halide–Grignard reactions: (a) thiophosphoryl bromide usually yields phosphine sulfides when treated with aliphatic Grignard reagents, but thiophosphoryl chloride usually yields diphosphine disulfide derivatives in analogous reactions; (b) most alkyl Grignard reagents react with thiophosphoryl chloride to yield diphosphine disulfides, but aryl, alkenyl, and alkynyl Grignard reagents yield only phosphine sulfides in such reactions; (c) dialkylphosphinothioic chlorides react with both alkyl and aryl Grignard reagents to yield only phosphine sulfides, whereas diarylphosphinothioic chlorides yield diphosphine disulfides with alkyl Grignard reagents, although they yield phosphine sulfides when treated with aromatic Grignard reagents; and (d) both types of products result from reactions involving alkylarylphosphinothioic halides.[21]

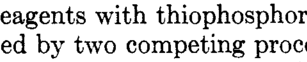
Phosphine sulfides are obtained as the principal products of some reactions in which metal–halogen interchange should be thermodynamically favorable and diphosphine disulfide formation should be expected. Typical of such cases are the reactions of cycloalkyl, secondary, and higher alkyl Grignard reagents with $PSCl_3$. In such cases, metal–halogen exchange is probably unfavorable kinetically, owing to steric effects. According to the scheme outlined above, metal–halogen exchange (path A) competes with a substitution reaction (path B) leading to phosphine sulfide. Since metal–halogen exchange probably involves a four-center transition state, it should be more sensitive to steric effects than the substitution (displacement) reaction. Grignard reagents having large steric requirements should thus prefer to engage in displacement reactions rather than in metal–halogen exchange reactions, and they should yield phosphine sulfides in these reactions rather than diphosphine disulfides.[22] Steric effects are probably also responsible for the stereoregulating influence of secondary and higher alkyl Grignard reagents on some vinyl polymerizations.[8] The parallel effects shown by such reagents in their behavior toward $PSCl_3$ or vinyl monomers are thus understandable.

Also related to the kinetic aspects of these reactions is the rate of the competing displacement process (path B). Any factors which would enhance the rate of this process relative to the metal–halogen exchange reaction would favor phosphine sulfide formation. Since charge separation is undoubtedly much greater in the transition state for path B than it is for metal–halogen exchange, the use of solvents with high dielectric constants should favor the displacement reaction, and phosphine sulfide formation should prevail. This factor may explain why appreciable phosphine sulfide formation is observed when reactions are conducted in tetrahydrofuran. Also, diphosphine dioxide formation does not occur when phosphoryl halides are allowed to react with Grignard reagents; this may be a result of the ease with which phosphoryl halides participate in nucleophilic displacement reactions.

Finally, the stereochemistry of these reactions will be considered. Previously alkylphosphonothioic dihalides were reported[9,13] to react with alkyl or aryl Grignard reagents to yield *meso-* and *dl*-diphosphine disulfide derivatives. Similar results were obtained in the present study; phenylphosphonothioic dichloride formed *meso-* and *dl*-1,2-dimethyl-1,2-diphenyldiphosphine disulfide when allowed to react with methylmagnesium bromide. However, when methylphenylphosphinothioic chloride was treated with ethyl- or phenylmagnesium bromide, only *meso*-dimethyldiphenyldiphosphine disulfide and phosphine sulfides were recovered from these reactions. Formation of the *meso* product can be explained by a transition state such as the following, where the displacing $[C_6H_5MeP{=}S]^-$ ion may be separated from its MgX^+ counterpart at the start of reaction. Should the $[C_6H_5MeP{=}S]^-$ ion be independent of MgX^+, it would be a planar ion; the configuration that its phosphorus atom adopted in the product would be determined by the configuration of the phosphorus atom undergoing displacement. The latter should suffer inversion, as is common[23] for nucleophilic displacement reactions involving pentavalent phosphorus compounds. The transition state depicted above is the most energetically favorable one of its type that can be drawn; similar structures leading to the *dl* product would be much more sterically hindered.



The formation of both *dl-* and *meso*-diphosphine disulfide derivatives in the reactions of Grignard reagents with $RPSCl_2$-type compounds is probably due to epimerization of *meso* coupled products of the type shown.



$$\mathrm{ClR\overset{\overset{S}{\|}}{P}{-}\overset{\overset{S}{\|}}{P}RCl} \quad \text{and} \quad \mathrm{ClR\overset{\overset{S}{\|}}{P}{-}\overset{\overset{S}{\|}}{P}R_2}$$

The facile racemization of phosphoryl and thiophosphoryl halides in the presence of halide salts is well known.[23] Alternatively, the *dl* and *meso* products may result from the reaction of an intermediate such as $RP{=}S$ with R_2PSCl or $RPSCl_2$. Clearly, more work needs to be done in this area.

In summary, the products obtained in the reactions of Grignard reagents with thiophosphoryl halides seem to be controlled by two competing processes: a metal–halogen exchange reaction (which leads ultimately to P–P coupling) and a displacement reaction (which yields

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[21] Not in accord with expectation is the relative behavior of reactions involving aromatic Grignard reagents and thiophosphoryl chloride or alkylphosphonothioic dihalides. Although tetrasubstituted diphosphine disulfides result from aryl Grignard–alkylphosphonothioic dihalide reactions, only triarylphosphine sulfides result from aryl Grignard–$PSCl_3$ reactions. This anomaly can be explained by the fact that tetraaryldiphosphine disulfides react with aryl Grignard reagents to form triarylphosphine sulfides and other products. Presumably, tetraaryldiphosphine disulfides can form in aryl Grignard–$PSCl_3$ reactions, but such products are not stable in the reaction system.

[22] It should be noted at this point, however, that both processes are subject to steric inhibition. We thus failed in several attempts to effect any reaction between *t*-butylmagnesium chloride and methylphenylphosphinothioic chloride.

[23] R. F. Hudson, *Advan. Inorg. Chem. Radiochem.*, **5**, 347 (1963).

TABLE I

PRODUCTS OBTAINED FROM THE REACTIONS OF DISUBSTITUTED PHOSPHINOTHIOIC HALIDES WITH GRIGNARD REAGENTS

		Phosphine sulfide identification				Diphosphine disulfide identification	
Phosphinothioic halide	Grignard	Bp, °C (mm)	Mp, °C	Registry no.	Yield, %	Mp, °C	Yield, %
$(CH_3)_2P(=S)Br$	C_2H_5MgBr		103.5–105[a]	4319-0-88	69		
	C_3H_7MgBr		89–90[b]	13639-66-2	Low		
$(C_2H_5)_2P(=S)Br$	CH_3MgBr		64–66[c]	1706-98-5	59		
	C_2H_5MgBr		94–96[d]	597-51-3	76.5		
	C_3H_7MgBr		47–49[e]	13639-69-5	44		
$(C_2H_5)_2P(=S)Cl$	C_2H_5MgBr		94–96[d]		82		
$(C_3H_7)_2P(=S)Cl$	CH_3MgBr	106–109 (1.5)	55–57[f]	13639-70-8	69		
	C_2H_5MgBr	113–116 (0.7)	*g*	13639-71-9	86		
	C_3H_7MgBr	108–110 (1.0)	*h*	13639-72-0	73		
$C_6H_5(CH_3)P(=S)Cl$	$(CH_3)_3CMgCl$			No reaction			
	C_2H_5MgBr	156–158 (6)	30–33[i]		64	217–219[j]	10
	C_6H_5MgBr	202–204 (1.0)	66–67[k]	13639-74-2	52	217–219[j]	13
$(C_6H_5)_2P(=S)Cl$	CH_3MgBr					170–172[l]	54
	C_2H_5MgBr					170–172[l]	58
	C_6H_5MgBr		161–162[m]	3878-45-3	42		

[a] A melting point for this compound is not given in the literature. See L. Maier, *J. Inorg. Nucl. Chem.*, **24**, 1073 (1962). This material is difficult to crystallize when small amounts of disubstituted phosphinothioic halides or other impurities are present. *Anal.* Calcd for $C_4H_{11}PS$: C, 39.25; H, 9.02; P, 25.41; S, 26.20. Found: C, 39.49; H, 9.19; P, 25.49; S, 26.36. [b] The low yield is attributed to the strong tendency of this material to sublime. *Anal.* Calcd for $C_5H_{13}PS$: C, 44.10; H, 9.55; P, 22.80; S, 23.52. Found: C, 44.25; H, 9.61; P, 23.02; S, 23.78. [c] Lit.[9] mp 66°. [d] Lit.[24] mp 94°. [e] *Anal.* Calcd for $C_7H_{17}PS$: C, 51.22; H, 10.37; P, 18.90; S, 19.52. Found: C, 51.32; H, 10.26; P, 18.94; S, 19.70. [f] *Anal.* Calcd for $C_7H_{17}PS$: C, 51.22; H, 10.37; P, 18.90; S, 19.52. Found: C, 51.03; H, 10.33; P, 18.79; S, 19.35. [g] *Anal.* Calcd for $C_8H_{19}PS$: C, 53.90; H, 10.70; P, 17.45; S, 17.95. Found: C, 53.63; H, 10.82; P, 17.38; S, 18.20. [h] R. A. Zingaro and R. E. McGlothlin, *J. Chem. Eng. Data*, **8**, 226 (1963), gave bp 112° (1.1 mm). [i] Lit.[13] bp 103–105° (0.04 mm), mp 33–34°. [j] Lit.[9] mp 206–208°. [k] L. Maier, *Helv. Chim. Acta*, **47**, 120 (1964), gave bp 157–159° (0.1 mm). This material is difficult to crystallize when small amounts of disubstituted phosphinothioic halides or other impurities are present. [l] Maier (footnote *k*) gave mp 168–169°. [m] W. Strecker and C. Grossmann, *Ber.*, **49**, 63 (1916), gave mp 161°.

phosphine sulfide derivatives). The former process is favored when phosphorus derivatives containing electronegative substituents and when electropositive Grignard reagents are reactants; the latter process is favored when sterically hindered reactants are employed and when the reactions are conducted in highly polar solvents. The process establishing P–P bonds seems to be a nucleophilic displacement by a thiophosphorus anion on a thiophosphoryl halide.

Experimental Section

Dialkylphosphinothioic Halides.—Dimethylphosphinothioic chloride (bp 76–78° (15 mm)), diethylphosphinothioic chloride, (bp 80–85° (1.0 mm)), di(*n*-propyl)phosphinothioic chloride, (bp 100–102° (3 mm)), diethylphosphinothioic bromide (bp 108–110° (7 mm)), and methylphenylphosphinothioic chloride (bp 124–126° (3 mm)) were prepared by adding slightly less than a stoichiometric amount of the halogen to a solution or suspension of the appropriate diphosphine disulfide at temperatures below 10°. Dimethylphosphinothioic chloride could only be prepared at room temperature, however. The products were isolated by distillation and the yields ranged from 78 to 85%.

Diphenylphosphinothioic Chloride.—A mixture of sulfur (10.0 g, excess) and chlorodiphenylphosphine (55.3 g, 0.25 mole) in 125 ml of carbon disulfide was refluxed (40–50°), with stirring, for 12 hr. Carbon disulfide was then distilled off, excess sulfur was separated from the residue by filtration, and the residual liquid was distilled under reduced pressure. Diphenylphosphinothioic chloride (53.0 g, 85%) was collected at 186–200° (1.5 mm), (lit.[24] bp 275–280° (15 mm)).

Phenylphosphonothioic Dichloride.—A mixture of dichlorophenylphosphine (90 g, 0.5 mole) and excess thiophosphoryl chloride was refluxed for 3 hr at 115°. Phosphorus trichloride which formed in the reaction was removed by distillation and the heavy, oily residue was distilled. Phenylphosphonothioic dichloride was collected at 110° (4 mm) (lit.[24] bp 270° (1 atm)). The yield was 80 g (76%).

Reaction of Phenylphosphonothioic Dichloride with Methylmagnesium Bromide.—Methylmagnesium bromide (0.75 mole) was prepared from magnesium turnings (18.24 g, 0.75 g-atom) and excess methyl bromide in ether at 0–5°. A solution of phenylphosphonothioic dichloride (52.7 g, 0.25 mole) in ether was then added dropwise to the stirred Grignard solution at such a rate that the reaction mixture could be maintained at 0–5° by ice cooling. When the addition was complete, the mixture was refluxed for about an hour. The mixture was again cooled in an ice bath and dilute hydrochloric acid was added slowly to the reaction mixture. After this treatment, ether, aqueous, and solid phases were present in the reaction vessel. The ether phase was separated and the solid phase (12.8 g) was separated from the aqueous phase. The latter was extracted with fresh ether and the ether phases were combined, dried, and evaporated to obtain an additional 12.5 g of solid material. Both solids proved to be mixtures of *dl*- and *meso*-dimethyldiphenyldiphosphine disulfide. The products were separated by fractional crystallization from ethanol and (later) chloroform. The *dl* product melted at 144–146° (lit.[9] mp 145–146°) and the *meso* product melted at 216–218° (lit.[9] mp 206–208°). The combined yield of recrystallized products was 62%.

Reactions of Disubstituted Phosphinothioic Halides with Grignard Reagents. General Procedure.—A solution of phosphinothioic halide (0.035 mole) in 20 ml of dry ether was added to a solution of 0.06 mole of Grignard reagent at such a rate that the stirred reaction mixture could be maintained at 0–5° by an ice bath. After the addition was complete, the reaction mixture was allowed to warm to room temperature and was refluxed for 3 hr. The reaction mixture was then cooled in an ice bath and excess Grignard reagent was decomposed by the addition of an aqueous ammonium chloride solution. The ether phase present in the reaction mixture was separated and the aqueous phase was extracted with fresh ether. The combined ether phases were dried and the ether was evaporated to obtain products. These were separated or purified by either fractional crystallization or distillation. Phosphine sulfide derivatives were usually recrystallized from cyclohexane or ethanol, whereas diphosphine disulfide derivatives were recrystallized from ethanol. Table I summarizes the results obtained from these experiments.

Reactions of Diethylphosphinothioic Chloride with Ethylmagnesium Bromide. Reverse Addition Technique.—A solution of ethylmagnesium bromide (0.043 mole) in ether was added to a stirred solution of diethylphosphinothioic chloride (4.0 g, 0.025 mole) in ether (30 ml) at such a rate that the reaction mixture could be maintained at 0–5° by an ice bath. After the addition was complete, the mixture was brought to room temperature and refluxed for about 2 hr. After recooling, the mixture was treated with ammonium chloride to hydrolyze excess Grignard reagent. The ether layer was then separated from the aqueous layer and the latter was extracted at least three times with fresh ether. The combined ether layers were dried over $MgSO_4$ and the ether was evaporated to obtain a white solid.

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[24] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950.

This material proved to be triethylphosphine sulfide. The yield of product, after recrystallization from cyclohexane, was 3.4 g (90%), mp 93–96°. No diphosphine disulfide derivative was isolated or detected.

Reaction at Elevated Temperatures.—The reaction was conducted according to the general procedure (conventional order of addition) described above, except that the addition reaction occurred while the ether solution was maintained at reflux. Using the general work-up procedure, triethylphosphine sulfide was obtained in 70% yield. No tetraethyldiphosphine disulfide was found.

Reaction at Low Temperature.—Following the general procedure, a solution of diethylphosphinothioic chloride in ether was added, with stirring, to a solution of ethylmagnesium bromide in ether, the temperature being maintained between −10° and −5°. Work-up of the reaction mixture after 12 hr of stirring yielded 70% triethylphosphine sulfide, but no tetraethyldiphosphine disulfide was found.

Effect of Excess Magnesium.—Ethylmagnesium bromide was prepared by treating ethyl bromide (0.04 mole) with 0.044 g-atom of magnesium and then with 0.016 mole of diethylphosphinothioic chloride. No diphosphine disulfide resulted from this reaction, but triethylphosphine sulfide was obtained in 89% yield. In another experiment, ethyl bromide (0.0045 mole) was allowed to react with 0.04 g-atom of magnesium turnings and the reaction mixture was further treated with 0.02 mole of diethylphosphinothioic chloride. The reaction mixture was refluxed for 24 hr and then worked up. Unreacted diethylphosphinothioic chloride (60%) and triethylphosphine oxide,[25] mp 43–45°, were the only products isolated. No tetraethyldiphosphine disulfide was evident. A similar result was obtained when magnesium powder was used instead of magnesium turnings.

Reaction of Diphenylphosphinothioic Chloride with Ethylmagnesium Bromide.—A solution of diphenylphosphinothioic chloride (11.5 g, 0.045 mole) in ether was added dropwise to a stirred solution of ethylmagnesium bromide (0.025 mole) in ether at 5°. When addition was complete, the mixture was warmed to room temperature and stirred for 10 min. Gas–liquid partition chromatographic examination of the reaction mixture indicated the presence of ethyl chloride. After another 30-min stirring, however, the ethyl chloride had disappeared. Work-up of the reaction mixture yielded tetraphenyldiphosphine disulfide, 0.78 g (9%), unreacted diphenylphosphinothioic chloride, 6.3 g (56%), and diphenylphosphinic acid, 1.5 g (15.5%), mp and mmp 190–192°. When this reaction was conducted with an excess (0.067 mole) of ethylmagnesium bromide, the yield of tetraphenyldiphosphine disulfide was 58%.

Reaction of Tetraphenyldiphosphine Disulfide with Phenylmagnesium Bromide.—A solution of tetraphenyldiphosphine disulfide, 1.8 g (0.0040 mole), in tetrahydrofuran (20 ml) was added slowly, with stirring, to a solution of phenylmagnesium bromide (0.050 mole) in ether at room temperature. The reaction mixture was stirred for another 12 hr and was then worked up in the standard way. No tetraphenyldiphosphine disulfide was recovered. Instead, triphenylphosphine sulfide, 0.386 g (35%), mp and mmp 160–162° (lit.[29] mp 161°), and an unidentified liquid were obtained.

Reaction of Methylphenylphosphinothioic Chloride with Ethylmagnesium Bromide.—Methylphenylphosphinothioic chloride (3.80 g, 0.02 mole) was added dropwise to a well-stirred solution of ethylmagnesium bromide (0.035 mole) in ether at 10°. After the addition was complete, the mixture was warmed and refluxed for 2 hr. After being cooled to room temperature, the mixture was treated with dilute H_2SO_4. The solid which separated was filtered and the ether and water phases present in the filtrate were separated. The aqueous phase was extracted three times with ether and discarded. The combined ether portions were dried over $MgSO_4$ and concentrated. The concentrate consisted of an oil and a suspended solid. This solid was identical with the solid recovered from the reaction mixture.

The solid fractions were combined and recrystallized from chloroform to obtain shining crystals of *meso*-1,2-dimethyl-1,2-diphenyldiphosphine disulfide, 0.30 g (10%), mp 220° (lit.[22] mp 206–208°).

Anal. Calcd for $C_{14}H_{16}P_2S_2$ (310.4): C, 54.20; H, 5.15; P, 20.00; S, 20.60. Found: C, 54.26; H, 5.25; P, 19.89; S, 20.51.

The oil was distilled to obtain methylethylphenylphosphine sulfide, bp 156–158° (6 mm), 2.8 g (64%) (lit.[13] bp 103–105° (0.04 mm)). After reaction with thionyl chloride in benzene, the corresponding oxide was obtained, bp 112–115° (0.3 mm).

Reaction of Methylphenylphosphinothioic Chloride with Phenylmagnesium Chloride.—This reaction was conducted in exactly the same manner as was the reaction of ethylmagnesium bromide with methylphenylphosphinothioic chloride. The yield of 1,2-dimethyl-1,2-diphenyldiphosphine disulfide obtained was 13%, mp 217–219°. The principal product of the reaction was methyldiphenylphosphine sulfide (52%), bp 210–220° (6 mm) (lit.[27] bp 157–159° (0.1 mm)). This product reacted with thionyl chloride in benzene to form methyldiphenylphosphine oxide, mp 112–115° (lit.[26] mp 108–109°).

Registry No.—Dimethylphosphinothioic chloride, 993-12-4; diethylphosphinothioic chloride, 3982-89-6; di(*n*-propyl)phosphinothioic chloride, 2524-18-7; diethylphosphinothioic bromide, 3981-46-2; methylphenylphosphinothioic chloride, 13639-62-8; diphenylphosphinothioic chloride, 1015-37-8; phenylphosphinothioic dichloride, 3497-00-5; $(CH_3)_2PSBr$, 6839-93-6; methylmagnesium bromide, 75-16-1; ethyl magnesium bromide, 925-90-6; C_3H_7MgBr, 927-77-5; phenylmagnesium bromide, 100-58-3; phenylmagnesium chloride, 100-59-4; methylethylphenylphosphine sulfide, 13639-73-1; *dl*-dimethyldiphenyldiphosphine disulfide, 13639-75-3; *meso*-dimethyldiphenyldiphosphine disulfide, 13639-76-4; tetraphenyldiphosphine disulfide, 1054-60-0.

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[25] This product probably resulted from the reaction of diethylphosphinic chloride with the Grignard reagent. The phosphinic chloride seems to result from a reaction involving the thiophosphinic halide and a partially oxidized magnesium surface.

[26] A. E. Arbuzov and K. V. Nikonorov, *Zh. Obshch. Khim.*, **18**, 2008 (1948).