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Nucleophilic Displacement Reactions on Organophosphorus Esters by Grignard Reagents. I¹BY K. DARRELL BERLIN, T. HOWARD AUSTIN,² AND KIRBY L. STONE³

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Careful examination by gas chromatography of the various reaction mixtures from the condensation of trimethyl phosphite with the phenyl Grignard reagent under nitrogen revealed only trivalent phosphorus compounds. In no instance were products detected which suggested the occurrence of a Michaelis-Arbuzov rearrangement *in situ*; thus, previously reported data are repudiated. A mechanism is postulated for the stepwise displacement of methoxy groups in which the initial Grignard-phosphite complex is attacked by the Grignard reagent. With a 1:1 ratio of phosphite to Grignard reagent, considerable methyl diphenylphosphinite was observed; this is in contrast to other reports. An explanation of the observed products is postulated to involve equilibria between complexes of Grignard reagent and intermediate esters.

Displacement reactions of Grignard reagents on phosphorus esters have been known for some time,⁴⁻⁹ but no report has appeared which describes a systematic study. Preliminary data concerning the reactivity of trivalent phosphorus esters have been recorded,⁸⁻¹¹ but a careful product determination by gas chromatography was lacking. The process has been assumed to involve stepwise displacement of alkoxy groups, although insufficient evidence has heretofore prevented a mechanistic evaluation. We intended to examine the reaction mixtures from the condensation of trimethyl phosphite with the phenyl Grignard reagent, the concentration of the latter to be varied over a wide range. Comparison of mole ratios of reactants to moles of products should provide a basis for critical appraisal of the displacement sequence. It also seemed possible to clarify the long-standing enigma which centered upon the observation that diphenylmethylphosphine oxide resulted from a classical Michaelis-Arbuzov rearrangement of an intermediate phosphinite.⁹ Detection and authentication of products were made by injection of known samples of pure compounds into a gas chromatography unit with a hydrogen flame detection cell. Accurately weighed samples of triphenylphosphine, dimethyl phenylphosphonite, and methyl diphenylphosphinite were dissolved in a known volume of ether and standard area/mole ratios were determined from the average of many injections. It was noted that the area/mole ratio was essentially unchanged with ether or benzene as solvent, although fluctuations in retention time were noted with different sized injections. Consequently, from a large number of injections, average values for the molar ratios of products were calculated from the ratios of peak areas.

With a ratio greater than three (Grignard reagent to phosphite), triphenylphosphine was produced in nearly quantitative yield (Table I).¹² At all concentra-

tions of the Grignard reagent, a white, finely divided, insoluble material formed immediately by an exothermic process.¹³ With an exact 3:1 ratio of Grignard reagent to phosphite, triphenylphosphine, traces of methyl diphenylphosphinite, and starting material were obtained. An average yield of the tertiary phosphine was 63% after heating the reaction mixture for long periods. It is apparent from several experiments with this ratio of reactants (3:1) that the Grignard reagent is complexed and not available for the displacement step to convert all of the phosphite to triphenylphosphine.

The rate of addition altered the ratio of products sharply even at 0° with a 1:1 ratio of reactants (phosphite added to the Grignard reagent). With a 0.5-hr. addition time as a standard for comparison, the mole ratio of triphenylphosphine to dimethyl phenylphosphonite to methyl diphenylphosphinite averaged 2:2.5:1. Our results were reproducible in many experiments. The compounds cited have been suggested as products by others,^{8-10,23} but were usually isolated as the acids in varying yields. When the addition time was increased to 3.5 hr., triphenylphosphine and trimethyl phosphite were isolated in nearly equivalent amounts. Only trace quantities of the phosphonite ester and the phosphinite ester could be found by gas chromatography. In both examples the concentrations of reagents were constant, and the mixtures were held at 55° for an equivalent length of time. This information suggests that the initial complex formed must react immediately with the Grignard reagent.¹⁴ Most probably, coordination of Grignard reagent with the phosphorus ester precedes the displacement reaction. In order to activate the ester for the displacement step in the series of compounds listed below, it is postulated that a complex must form. In excess Grignard reagent, the complexes generated from the phosphonite ester or phosphinite ester, respectively, condense rapidly with the Grignard reagent in the sequence depicted since high yields of triphenylphosphine were observed.

phosphine oxide, dimethyl phenylphosphonate, methyl diphenylphosphinate, and trimethyl phosphite were formed in abundance. Methyl diphenylphosphinate was synthesized since it was apparently unknown.

(13) It has been noted that upon addition of a portion of the trimethyl phosphite to *p*-tolyl Grignard reagent (1:3 ratio of phosphite to Grignard reagent) heat is evolved. Additional ester introduced did not result in a change in temperature of the mixture; see P. W. Morgan and B. C. Herr, *J. Am. Chem. Soc.*, **74**, 4526 (1952). In our case, rapid addition of approximately one-half of the phosphite to Grignard reagent (1:1 ratio) occurred exothermically, and the remaining phosphite could be added with little temperature change.

(14) It is recorded (ref. 13) that trimethyl phosphite and the *p*-tolyl Grignard reagent afforded tri-*p*-tolylphosphine (37.4%) after 3 hr. with a 1:3 ratio of ester to Grignard reagent.

(1) We gratefully acknowledge the support of this research by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under grant AF-AFOSR-132-63. This work was presented in part at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(2) Predoctoral candidate, 1962-.

(3) National Science Foundation Undergraduate Trainee, Summer, 1962.

(4) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, Chapters 6 and 7.

(5) K. D. Berlin and G. B. Butler, *Chem. Rev.*, **60**, 243 (1960).

(6) K. D. Berlin and G. B. Butler, *J. Am. Chem. Soc.*, **82**, 2712 (1960).

(7) K. D. Berlin and G. B. Butler, *J. Org. Chem.*, **25**, 2006 (1960).

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

(9) H. Gilman and J. D. Robinson, *Rec. trav. chim.*, **48**, 328 (1929).

(10) H. M. Maguire and G. Shaw, *J. Chem. Soc.*, 2039 (1955).

(11) (a) M. Sander, *Chem. Ber.*, **93**, 1220 (1960); (b) *ibid.*, **95**, 473 (1962).

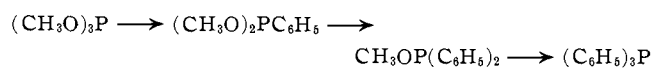
(12) Unless the nitrogen used was deoxygenated, tetravalent phosphorus compounds could be found in the reaction mixtures. Specifically, triphenyl-

TABLE I

RMgX (CH ₃ O) ₃ P	Temp., ^a °C.	Time, hr.		Ratio ^b of compounds present			
		Addn.	Reacn.	(CH ₃ O) ₃ P	(CH ₃ O) ₂ PC ₆ H ₅	CH ₃ OP(C ₆ H ₅) ₂	(C ₆ H ₅) ₃ P
1:1	55	0.5	10	Present ^c	2.5	1	2
1:1	55 ^d	3.5	7.5	1	Trace	Trace	1
1:1 ^e	55	0.5	10	1.5 ^f	1 ^f	Trace	..
3:1	55	.5	10	1 ^g	...	Trace ^g	2 ^g
4:1	55	.75	10	Quant.
7:1	55	1.5	3	Quant.

^a Represents temperature at which reaction was held during time specified as reaction time. ^b Ratios are given as mole ratios. ^c Amount of (CH₃O)₃P was in excess of 40%. ^d Addition was slow and hence not much evolution of heat; to get a comparison with other experiments, the temperature was held at 55° during addition-reaction sequence. ^e Inverse addition. ^f Dimethyl phenylphosphonite was formed in 42% yield with less than 2% methyl diphenylphosphinite as the only other product. ^g Triphenylphosphine was formed in 63% yield with 3% of methyl diphenylphosphinite as the only other product.

Competition for the Grignard reagent is apparently



operative with all intermediate esters. The supporting analogy is found in the work of Sander,¹¹ who determined the order of decreasing stability in the complexes from magnesium chloride to be phosphine > phosphinite > phosphonite > phosphite. Thus, all trimethyl phosphite may complex with the Grignard reagent initially, particularly upon rapid mixing. However, an equilibrium is predictable in which the phosphonite ester (and in turn the phosphinite ester) competes with trimethyl phosphite for the Grignard reagent. Because the reaction with the phosphite was so rapid even at 0°, it was not possible to determine the ratio of phosphite to Grignard reagent in the initial complex.

A 1:1 ratio of butyl Grignard reagent to tributyl phosphite was reported to produce the corresponding phosphonite (69%).^{11a} Under nearly identical conditions we found trimethyl phosphite with the phenyl Grignard reagent gave a mixture of the corresponding phosphonite, phosphinite, and tertiary phosphine. This seems to verify the suggestion of Sander that the displacement process is markedly dependent upon the nature of the Grignard reagent.^{11a} Even with the addition of phosphite to Grignard reagent in a 1:1 ratio, an excess of the latter is present during most of the addition. Consequently, in the slow addition experiment the intermediate phosphonite and phosphinite react to give triphenylphosphine thus removing the Grignard reagent. This is supported by the observation that addition of the last one-half mole of phosphite (approximately) occurred without the evolution of heat. In agreement also is the recovery of trimethyl phosphite in a 50% yield.

Several carefully controlled reactions involving an inverse addition sequence (Grignard reagent added to phosphite) were investigated. Rapid increase in temperature and formation of a precipitate were noted immediately upon contact of the reagents. The temperature rose throughout the entire addition in contrast to the temperature change during the normal addition. Moderate yields (41%) of dimethyl phenylphosphonite were reproducible from several runs. Sander was able to obtain fair yields of dialkyl alkylphosphonites by the regular addition process.^{11a} It seems logical from the data published that the displacement reactions of OR groups on phosphorus esters are dependent upon the relative concentrations of reagents. Small quantities of phosphinite were detected in the inverse reaction

mixture, but triphenylphosphine was surprisingly absent. Trimethyl phosphite and a few trace materials completed the analysis of the reaction mixture. In view of the postulated equilibrium the low yield of methyl diphenylphosphinite was unexpected. However, in the inverse reaction the phenyl Grignard reagent is not in excess and it is possible that the unreacted one-half mole is heavily complexed. The order of complexing may be the reverse of that found by Sander.¹¹ Since aryl groups are attached to phosphorus in our series, stability of complexes may vary in the series: (CH₃O)₃P > (CH₃O)₂PC₆H₅ > CH₃OP(C₆H₅)₂ > (C₆H₅)₃P. Complex formation between the electron pair on phosphorus and magnesium of the Grignard reagent is predictable. Resonance delocalization of the electron pair should be more appreciable with an increase in the number of attached phenyl substituents. Interaction between the electron pair on phosphorus and the benzene rings in triphenylphosphine is indicated from its ultraviolet spectrum.^{15,16}

Filtration of a reaction mixture (1:1 ratio, normal addition, addition time of 0.5 hr., and 1-hr. reaction time) was accomplished under anhydrous conditions. Since the solid material was very finely divided, the filtration required a considerably long time to perform using gravity flow techniques. It was also necessary to wash the precipitate many times to remove all traces of the filtrate since the reaction was carried out using benzene and it was desired to test the solid for the presence of benzene after hydrolysis. It was impossible under the conditions employed to keep the system free of oxygen, and since the oxidation of the trivalent compounds is very facile in solution,^{17,18} it was possible for the reaction mixture to undergo oxidation during filtration. We have found that triphenylphosphine in benzene solutions of our reaction mixtures undergoes autoxidation rapidly in contact with air. This rate is greatly increased above room temperature. The solid material was dried after filtration and subsequently hydrolyzed with aqueous ammonium chloride in an extremely exothermic process. Triphenylphosphine oxide and methyl diphenylphosphinate were the major products in an approximate ratio of 1.86:1. Benzene, traces of methyl phenylmethylphosphinate, and diphenylmethylphosphine oxide were also present. It will be recalled that hydrolysis of the total reaction mixture under nitrogen revealed only trivalent phosphorus esters. It should

(15) H. H. Jaffé, *J. Chem. Phys.*, **22**, 1430 (1954).

(16) H. H. Jaffé and L. D. Freedman, *J. Am. Chem. Soc.*, **74**, 1069 (1952).

(17) S. A. Buckler, *ibid.*, **84**, 3093 (1962).

(18) W. P. Jorissen, *Ber.*, **29**, 1707 (1896).

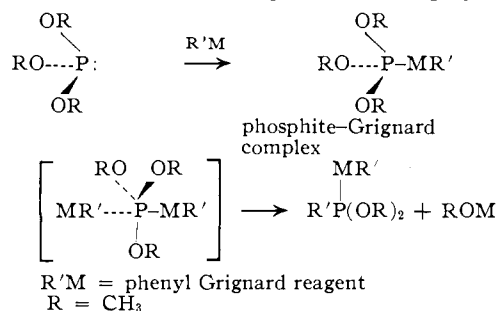
also be noted that under regular work-up conditions, no products were detected which could have been formed by a Michaelis-Arbuzov rearrangement.

Hydrolysis of the clear supernatant liquid and analysis of the organic layer revealed triphenylphosphine and methyl diphenylphosphinate as major products. Partial oxidation of the phosphine occurred also and the total yield was based on triphenylphosphine and triphenylphosphine oxide.

It is our contention that the displacement of OR groups by the Grignard reagent is a very rapid and exothermic reaction. It appears reasonable that the white material which precipitates is probably a magnesium salt. This material is formed in the reaction under anhydrous conditions, and the heat of solution of this material would account for the extremely exothermic process which occurs upon hydrolysis of the solid material.¹⁹ The white solid is present in each reaction mixture in fairly large quantities (it begins forming within the first minute of addition). Analysis of the solid and the filtrate showed that very little of the total amount of phosphorus compounds was actually in the solid phase, the great majority being found in the filtrate. Apparently, oxidation occurred during the work-up and the oxidized compounds were precipitated by the magnesium salt as adducts. This seems reasonable since no trivalent material was found in analysis of the solid. This type of adduct has been reported to be insoluble.²⁰ In support of this hypothesis it was found that when triphenylphosphine was added to a solution of phenyl Grignard reagent in ether and benzene, no precipitate formed under conditions similar to those used for the reactions. In contrast, triphenylphosphine oxide did form a white, insoluble complex with the phenyl Grignard reagent in ether-benzene at room temperature.

Another relevant precedent is the observation that sufficient Grignard reagent must be present to complex with phosphonates to give moderate yields of phosphine oxides.²¹ Similarly, Dawson and Burger noted that magnesium bromide complexed with diethyl phenylphosphonate, and the complex condensed exothermically with the phenyl Grignard reagent to give triphenylphosphine oxide (55%).²⁰ In all of these condensations in ether, the reaction most probably involves an equilibrium between ester and ester-Grignard complex.

Examination of molecular models indicates the back side of trimethyl phosphite to be highly hindered



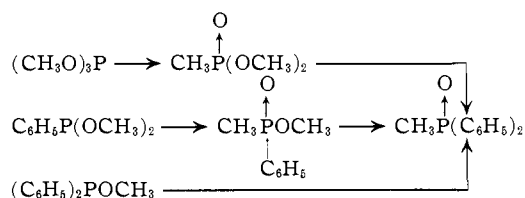
(19) Thermodynamic data show the heat of solution of anhydrous magnesium bromide to be extremely high (43.24 kcal./mole), and, for example, in the hydrolysis of anhydrous magnesium bromomethoxide, one would expect a similar exotherm: N. N. Beketoff, *Bull. Acad. Sci. U.S.S.R.*, **34**, 291 (1892); "International Critical Tables," Vol. 5, 1929, p. 195.

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

(21) For a discussion of this, see ref. 5, pp. 244-245.

to attack. However, if the trigonal configuration of the phosphorus atom is altered to a near tetragonal arrangement in the complex, opportunity for displacement appears markedly improved from steric considerations alone.^{22,23} Expansion of the valence shell on phosphorus to accommodate ten electrons is permitted since 3d-orbitals are available. This postulate finds its analogy in the decomposition of methylethylphenylbenzylphosphonium iodide with sodium butoxide.²⁴ Attack of butoxide ion was presumed to occur on the tetravalent phosphorus to give pentavalent phosphorus-containing intermediates. Perhaps more related is the elegant data published recently concerning exchange of methoxide ion with a methoxy function (isotopically labeled) in a phosphinate. An SN2 type process was envisioned with a transition state reminiscent of a bipyramidal arrangement of the atoms.²⁵ Although we have schematically shown the postulated mechanism of displacement to involve a 90° angle between the attacking and leaving groups, the other possibility cannot be discounted that the displacement may occur by a classical SN2 process in which there is a 180° angle between the attacking and leaving groups.

A thorough search of the products in our reaction did not reveal the presence of dimethyl methylphosphonate, but a trace of diphenylmethylphosphine oxide was detected along with a trace of methyl phenylmethylphosphinate in the hydrolysate of the solid material. The purity of all starting materials was checked by gas chromatography prior to each experiment. Theoretically, it is possible that trimethyl phosphite could undergo an intramolecular rearrangement (Michaelis-Arbuzov) to give dimethyl methylphosphonate which could then be converted to the unsymmetrical phosphine oxide.²⁶ Also, dimethyl methylphosphonate could rearrange to methyl phenylmethylphosphinate²⁷ which is capable of producing diphenylmethylphosphine oxide. Similarly methyl di-



phenylphosphinite could yield the unsymmetrical phosphine oxide directly by rearrangement.²⁸ Since diphenylmethylphosphine oxide was not found, it must be concluded that the previously recorded⁹ results were obtained because of an impurity in trimethyl phosphite, probably dimethyl methylphosphonate. In our hands conversion of the latter was facile with the phenyl Grignard reagent to give the unsym-

(22) The action of lithium reagents might be compared and it would be expected that the increased reactivity might offset the decreased coordination ability. This is the case as indicated in a lone report: J. L. Willans, *Chem. Ind. (London)*, 235 (1957).

(23) G. F. Wright in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 8.

(24) C. B. Parisek, W. E. McEwen, and C. A. VanderWerf, *J. Am. Chem. Soc.*, **82**, 5503 (1960).

(25) M. Green and R. F. Hudson, *J. Chem. Soc.*, 540 (1963).

(26) See ref. 4, Chapter 6.

(27) We thank Dr. H. J. Harwood, Department of Chemistry, University of Akron, who supplied an authentic sample of this ester.

(28) For a recent summary of the Michaelis-Arbuzov rearrangement, see K. D. Berlin, C. Hildebrand, A. South, D. M. Hellwege, E. A. Pier, and J. G. Verkade, *Tetrahedron*, **20**, 323 (1964).

metrical phosphine oxide in quantitative yield. Furthermore, methyl diphenylphosphinite reacted with the phenyl Grignard reagent to give only triphenylphosphine, quantitatively. Since traces of methyl phenylmethylphosphinate and diphenylmethylphosphine oxide were found only in the hydrolysis mixture of the dried, solid precipitate, they may result from thermal rearrangement of dimethyl phenylphosphonite and methyl diphenylphosphinite, respectively, in the highly exothermic decomposition. Hydrolysis of the reaction mixtures in the regular manner did not produce the phosphinate or the unsymmetrical phosphine oxide.

Experimental²⁹

Starting Materials.—The following compounds were prepared by methods already in the literature: dimethyl phenylphosphonite,³⁰ methyl diphenylphosphinite,³¹ dimethyl phenylphosphonate,³² triphenylphosphine oxide,³³ and diphenylmethylphosphine oxide.⁴ Trimethyl phosphite (Victor Chemical), dimethyl methylphosphonate (Victor Chemical), triphenylphosphine (Eastman Kodak), and trimethyl phosphate (Ethyl Corporation) were obtained from commercial sources. All of the liquid compounds 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 one peak. All of the solids were recrystallized and each showed one peak by gas chromatography.

Methyl Diphenylphosphinite.—Methyl diphenylphosphinite (13.97 g., 0.06459 mole) dissolved in 250 ml. of anhydrous ether was placed in a 500-ml. flask equipped with a stirrer, a reflux condenser, and a pressure equalizing addition funnel charged with 20 ml. of 30% hydrogen peroxide diluted to 100 ml. with water. The entire system was swept with anhydrous, deoxygenated nitrogen. The extremely exothermic addition was controlled by rapid stirring with the reaction pot in an ice-salt bath. After the addition was complete (30 min.), the mixture was allowed to come to room temperature with stirring. The mixture was then boiled 1 hr. with stirring. The organic phase was dried over magnesium sulfate and distilled (11.87 g., 78.6%); b.p. 139–140° (0.34 mm.); $\lambda_{\text{max}}^{\text{KBr}}$ 6.92 ($\text{C}_6\text{H}_5\text{-P}$), 8.12, 8.81, 9.61 (P-O-alkyl), 12.5, 13.25, 13.68, and 14.33 μ .

Anal. Calcd. for $\text{C}_{12}\text{H}_{18}\text{O}_2\text{P}$: C, 67.24; H, 5.64; P, 13.24. Found: C, 67.84; H, 5.69; P, 13.71.

Reaction of Trimethyl Phosphite with the Phenyl Grignard Reagent.—The following procedure is typical of the condensations performed. The Grignard reagent of bromobenzene was prepared in ether under nitrogen from the following reagents: 30.00 g. (1.25 g.-atoms) of magnesium turnings, 176.02 g. (1.07 moles) of distilled bromobenzene, and 200 ml. of anhydrous ether. In all cases concentration of reagent was determined by quenching 2-ml. aliquots with 50 ml. of 0.1018 *N* hydrochloric acid (boiled for 10 min.) followed by back titration of excess acid with 0.0977 *N* sodium hydroxide. Enough aliquots were withdrawn to es-

tablish an average figure for the concentration of the Grignard reagent.

The purity of trimethyl phosphite was checked immediately prior to the Grignard reaction by injection on the v.p.c. unit on silicone rubber (10% on Chromosorb W), Apiezon L (10% on Chromosorb W), and Apiezon K (10% on Fluoropak 90). Only one peak was observed. All columns and packings were obtained from the Wilkens Instrument and Research, Inc., Walnut Creek, Calif. The v.p.c. instrument used was a Hy Fi 550 with hydrogen flame detector. Authentic samples of pure compounds were always injected during the same period that the reaction mixture was being examined. Under a nitrogen blanket the solution of phosphite (18.6615 g., 0.150 mole) in 176 ml. of anhydrous benzene was added dropwise at room temperature, with stirring, to 1.065 moles of the Grignard reagent in 400 ml. of anhydrous ether. Although highly exothermic (30 ml. of solution added over 5 min. caused a 20° rise), the addition was controllable and required 1.5 hr. to complete in this experiment.

The reaction did not appear to be exothermic after initial complex formation. Consequently, addition of the remaining phosphite solution was performed at room temperature and no further precipitation was noticed. The mixture was then held at reflux for 3 hr. after which it was cooled to 0° with ice and decomposed by slow addition of 400 ml. of 20% aqueous ammonium chloride. The organic layer was decanted and the aqueous portion was allowed to stand overnight, since decomposition in the mixture appeared to be slow. Extraction of the water layer was made with three 100-ml. quantities of benzene. The original organic layer and the extracts were dried over magnesium sulfate and combined. One-half of the sample was used for analysis by v.p.c. and the remaining portion was distilled. Column chromatography of the fractions and residue verified the presence of the compounds detected by v.p.c. when percentages were greater than 2%. In this example triphenylphosphine was isolated (18.91 g., 95.8%) and a trace of biphenyl. If the nitrogen was not deoxygenated with a chromic sulfate-sulfuric acid solution in contact with amalgamated zinc, small amounts of the corresponding phosphonate and phosphinate esters could be found in the mixtures along with some triphenylphosphine oxide. The procedure for the inverse-addition experiment was essentially the same as described for the normal addition reaction.

Reaction of Dimethyl Methylphosphonate with the Phenyl Grignard Reagent.—Under an atmosphere of nitrogen a solution of dimethyl methylphosphonate (16.39 g., 0.132 mole) in 50 ml. of anhydrous benzene was added dropwise with stirring to 0.396 mole of the phenyl Grignard reagent in 150 ml. of ether. No change in appearance of the solutions was noted during the addition period of 0.5 hr. The solution was then heated to reflux at 50–55°, and after 15 min. the sudden appearance of a heavy viscous precipitate was noted. After 5 min. no further precipitation occurred and the mixture was heated at reflux for an additional 15 hr. The decomposition and work-up procedures were as described previously. Analysis by v.p.c. revealed diphenylmethylphosphine oxide as the only product. Isolation by column chromatography on alumina and authentication with a pure sample verified the v.p.c. data.

Reaction of Methyl Diphenylphosphinite with the Phenyl Grignard Reagent.—Distilled methyl diphenylphosphinite (13.600 g., 0.0629 mole) in 100 ml. of anhydrous benzene was added to 0.1887 mole of the phenyl Grignard reagent in 250 ml. of ether. The addition was highly exothermic and a heavy precipitate was deposited upon contact of the reagents. After 8 hr. at 55°, the mixture was cooled to 0° and decomposed as outlined previously. Triphenylphosphine was formed in quantitative yield as substantiated by v.p.c. and infrared analysis.

(29) All melting points are corrected. All boiling points are uncorrected.

(30) H. J. Harwood and D. W. Grisley, Jr., *J. Am. Chem. Soc.*, **82**, 425 (1960).

(31) B. A. Arbuzov and N. P. Grechkin, *Zh. Obshchei Khim.*, **20**, 107 (1950); *Chem. Abstr.*, **44**, 5832 (1950).

(32) C. E. Griffin and N. T. Castellucci, *J. Org. Chem.*, **26**, 629 (1961).

(33) For a general procedure for the oxidation of triphenylphosphine to triphenylphosphine oxide, see our previous report: K. D. Berlin and G. B. Butler, *ibid.*, **26**, 2537 (1961).