

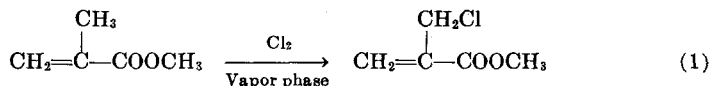
Phosphorus Derivatives of Methyl 2-(Chloromethyl)acrylate*

ALLAN E. SHERR† and HARVEY G. KLEIN,‡ *Central Research Division,
American Cyanamid Company, Stamford, Connecticut*

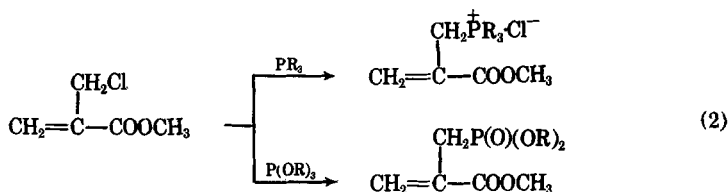
Synopsis

Several phosphorus derivatives of methyl 2-(chloromethyl)acrylate, including three phosphonium salts and one phosphonate ester have been prepared. A brief study was made of their polymerization characteristics under free-radical conditions. Several factors were noted which prevented the synthesis of methyl 2-[(diethoxyphosphinyl)-methyl]acrylate in high yields in initial experiments. Homopolymerization of these phosphorus derivatives does not take place readily in the presence of free-radical initiators.

The attractiveness of methyl 2-(chloromethyl)acrylate as a potential low-cost vinyl monomer, led us to a brief investigation into the synthesis of phosphorus-containing derivatives of this compound.



High yields of the starting material, methyl 2-(chloromethyl)acrylate, were obtained by the vapor-phase chlorination of methyl methacrylate [eq. (1)].¹ We then considered which phosphorus derivatives to prepare, particularly from the standpoint of availability of the organophosphorus reactants. We chose to prepare several phosphonium salts and one phosphonate ester derivative of methyl 2-(chloromethyl)acrylate, by treatment with tertiary phosphines and trialkyl phosphites [eq. (2)]. The three tertiary phosphines, triphenyl, tributyl, and tris(2-cyanoethyl) were



* Presented in part at the 152nd National Meeting of the American Chemical Society, New York, New York, September 1966.

† Present address: American Cyanamid Company, Bound Brook, New Jersey 08805.

‡ Present address: American Cyanamid Company, Washington, D. C.

readily available, the first two commercially, and the latter prepared in high yields in our laboratory from acrylonitrile and phosphine. Triethyl phosphite which was used to prepare the diethyl phosphonate, methyl 2-[(diethoxyphosphinyl)methyl]acrylate, is also commercially available. Another phase of this work was a study of the polymerization characteristics of the phosphorus compounds.

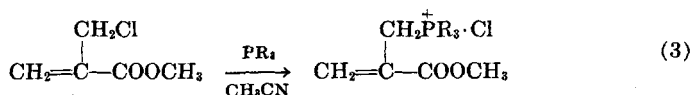
Preparation and Properties of Phosphonium Derivatives of Methyl 2-(Chloromethyl)acrylate

Since the replaceable chlorine in methyl 2-(chloromethyl)acrylate was allylic, replacement by nucleophilic reagents, such as phosphines, was expected without difficulty under relatively mild conditions (Table I). Addi-

TABLE I
Phosphonium Derivatives of Methyl 2-(chloromethyl)acrylate [Eq. (3)]

R	Yield, %	M.p., °C.
-C ₆ H ₅	97	140-144 (dec.)
-(CH ₂) ₃ CH ₃	74	Oil
-CH ₂ CH ₂ CN	73	151-154 (dec.)

tion of tris(2-cyanoethyl)phosphine to methyl 2-(chloromethyl)acrylate in acetonitrile solvent gave a vigorous exothermic reaction accompanied by precipitation of the product. A 73% yield of tris(2-cyanoethyl)(2-methoxycarbonylallyl)phosphonium chloride was obtained. The product gave an analysis and infrared spectrum consistent with the structure shown. A band in the infrared assigned to the CH=CH₂ group, indicated that the vinyl group was unaffected. The product, as expected for phosphonium salts, was soluble in water.



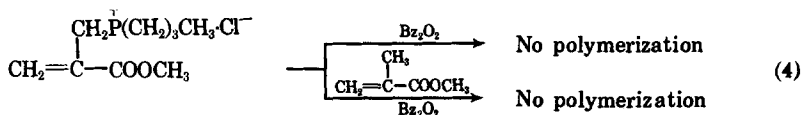
Tributyl(2-methoxycarbonylallyl)phosphonium chloride was prepared in a 74% yield in the same manner as the aforementioned tris(2-cyanoethyl) derivative. In contrast, this phosphonium salt was a hygroscopic oil, as is true of many tributylphosphonium salts. Isolation of this material was carried out by evaporation of the solvent and purification of the residual oil by washing with selective solvents to remove unreacted starting materials.

Treatment of methyl 2-(chloromethyl)acrylate with triphenylphosphine was not visibly exothermic as was observed with the two previous phosphonium salt preparations. Isolation of the solid product was effected by solvent evaporation and washing of the oily residue with diethyl ether. Better than a 90% yield of the desired compound was obtained.

From this and previous work on phosphonium salts, it was found that an excellent procedure for carrying out these reactions is to use acetonitrile as the solvent, assuming the reactants are soluble in this solvent, and if the product is soluble in the reaction solvent, to isolate the product by solvent evaporation and washing of the residue with diethyl ether. In most cases, the residual oil yields a solid product.

We have found, qualitatively, that the displacement of chlorine from methyl 2-(chloromethyl)acrylate by tris(2-cyanoethyl), tributyl, and triphenyl phosphines, takes place under more mild conditions than from propyl chloride, or in general, from long chain alkyl chlorides.

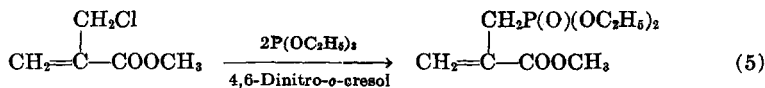
Since tributyl(2-methoxycarbonylallyl)phosphonium chloride was a liquid, we attempted to homopolymerize this compound in bulk in the presence of free-radical initiators, but without success. Heating this salt with methyl methacrylate, in a sealed tube under a nitrogen atmosphere with benzoyl peroxide catalyst, did not give rise to polymer as shown by no viscosity increase during the reaction.



We propose two plausible explanations for the lack of polymerization of this phosphonium salt. First, the strongly electron-withdrawing positive phosphorus atom deactivates the double bond toward free-radical polymerization. Secondly, the phosphonium salt monomer reacts with the peroxide catalyst. Rabinowitz et al.² have shown that peroxide catalysts react with phosphonium salts to liberate free halogen. Thus, the formation of halogen would occur in preference to polymerization. Although no visible evidence of halogen formation was noted, any halogen formed probably would have reacted *in situ* immediately with methyl methacrylate.

Preparation of Phosphonate Ester, Methyl 2-[(Diethoxyphosphinyl)methyl]-Acrylate

Phosphonates can readily be prepared by treating alkyl halides with trialkyl phosphites. When triethyl phosphite was added to methyl 2-(chloromethyl)acrylate, a vigorous exothermic reaction took place. Only polymer was isolated. Since we believed that either the starting material, methyl 2-(chloromethyl)acrylate, or the expected product had polymerized, we carried out further reactions in the presence of free-radical inhibitors. We met with limited success when the reaction was carried out in the presence of hydroquinone. Yields of less than 5% of the desired compounds were obtained in addition to low molecular weight polymer. Some of the high-boiling fractions contained mixtures of monomer and low molecular weight polymer. There was evidence from spectral data that the hydroquinone inhibitor may have reacted with the starting material, methyl 2-(chloromethyl)acrylate.



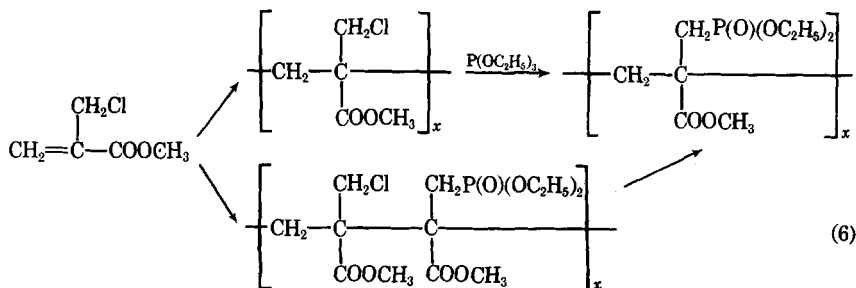
77% Yield; b.p. 86–89.5°C./0.15 mm.

Finally, we worked out the conditions to obtain good yields of the desired product by minimizing polymerization. (1) The exothermic reaction on addition of triethyl phosphite had to be moderated by providing external cooling. (2) The inhibitor, 4,6-dinitro-*o*-cresol, was effective in preventing polymerization. About 4% based on the weight of methyl 2-(chloromethyl)acrylate was used. (3) The overall reaction temperature was kept as low as possible. The temperature was kept below about 90°C. during the reaction.

Under these conditions, a 77% yield of the desired compound was obtained. The product had a boiling point of 86–89.5°C. at 0.15 mm. pressure and could be redistilled in the absence of inhibitor without any noticeable polymerization taking place.

The ineffectiveness of hydroquinone in contrast to 4,6-dinitro-*o*-cresol might be explained by the anticipated lower reactivity of the hindered phenol with alkyl halides. Therefore, a sufficient quantity of 4,6-dinitro-*o*-cresol remained unreacted so that it could prevent polymerization from taking place.

In the early experiments in which polymer was obtained, we postulate two reaction paths which would account for this occurrence [eq. (6)]

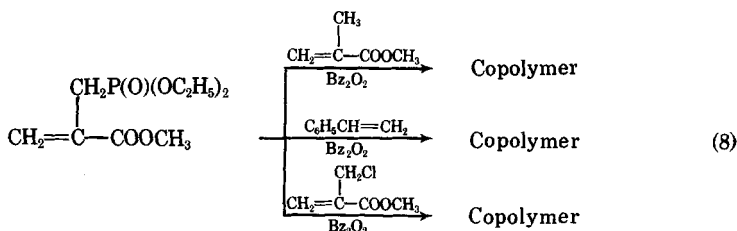
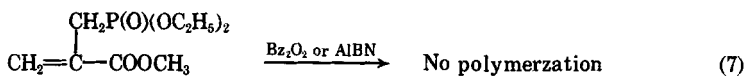


The starting material, methyl 2-(chloromethyl)acrylate, may have homopolymerized and then reacted with triethyl phosphite; alternatively, methyl 2-(chloromethyl)acrylate may have copolymerized with the product, methyl 2-[(diethoxyphosphinyl)methyl]acrylate, which then reacted with triethyl phosphite to give the polymer as indicated in eq. (6).

Polymerization Study with the Phosphonate Ester

It was decided to try to polymerize this material in the presence of free-radical initiators. For example, when the phosphonate ester was heated with 2% by weight of benzoyl peroxide for 48 hr. at 85°C. in a sealed tube under nitrogen, no polymer was obtained, as indicated by the absence of a molecular weight increase or viscosity increase [eq. (7)].

Based on the lack of success with the polymerization of the phosphonate ester under free radical conditions, not much success was expected in copolymerizing this compound with other vinyl monomers, such as methyl methacrylate, methyl 2-(chloromethyl) acrylate, or styrene. However, copolymerization did occur in each case [eq. (8)].



Copolymerization of methyl 2-[(diethoxyphosphinyl)methyl]acrylate with methyl methacrylate for 18 hr. at 90°C. in a sealed tube under nitrogen in the presence of benzoyl peroxide, gave a hard, clear, yellowish polymer.

Copolymerization of the phosphonate ester with styrene in a 1:3 by weight ratio in the presence of benzoyl peroxide at 80–85°C. for 22 hr., gave a soft, translucent, polymeric material.

Finally, polymerization with methyl 2-(chloromethyl)acrylate gave a clear, colorless polymer.

From the lack of success with the homopolymerization of methyl 2-[(diethoxyphosphinyl)methyl]acrylate and tributyl(2-methoxycarbonylallyl)phosphonium chloride, and the fact that both methyl 2-(chloromethyl)acrylate and methyl methacrylate can be polymerized under free-radical conditions, we can establish, at least qualitatively, the following order of reactivity, $\text{H} > \text{Cl} > \text{P}^+$ and phosphonate, in which the hydrogen on methyl methacrylate is successively replaced by these groups. These results can be explained by a decrease in activity with increase in electronegativity of the group.

EXPERIMENTAL

Melting points were determined in a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Tris(2-cyanoethyl)(2-methoxycarbonylallyl)phosphonium Chloride. Methyl 2-(chloromethyl)acrylate (19.4 g., 0.14 mole) was dissolved in 40 ml. of acetonitrile. Tris(2-cyanoethyl) phosphine³ (27 g., 0.14 mole) was added. A vigorous exothermic reaction occurred and a solid precipitated. The reaction mixture was kept in a nitrogen atmosphere for 2 hr. The solid was removed by filtration, washed with acetonitrile, with anhydrous ether, and dried in vacuum to give 34 g. (73% yield) of a white solid, m.p.

151–154°C. (dec.). The solid was water-soluble but was insoluble in hot methyl methacrylate; thus, bulk polymerization was not tried.

ANAL. Calcd. for $C_{14}H_{19}ClN_3O_2P$: P, 9.45%; Cl, 10.82%. Found: P, 9.54%; Cl, 10.74%.

The infrared spectrum (mull in mineral oil) showed a carbonyl band at 1707 cm^{-1} , a $H_2C=CH$ band at 1630 cm^{-1} , and C—O bands at 1225 and 1132 cm^{-1} .

(2-Methoxycarbonylallyl)triphenylphosphonium Chloride. Triphenyl phosphine (26 g., 0.1 mole) was dissolved in 200 ml. of acetonitrile by heating to 33°C. This solution was added dropwise over 30 min. to a solution of 13 g. (0.1 mole) of methyl 2-(chloromethyl)acrylate dissolved in 75 ml. of acetonitrile. The mixture was refluxed with stirring in a nitrogen atmosphere for 2.5 hr., cooled, and the solvent removed by distillation under vacuum. The viscous oily residue was washed several times with anhydrous ether until the residue solidified. The solid was filtered and dried *in vacuo* to give 38 g. (97% yield) of a hydrated solid, m.p. 132–140°C. A sample dried in an oven for 5 hr. at 110°C. had a melting point of 140–144°C. (dec.). The compound was insoluble in hot methyl methacrylate but was soluble in water.

In KBr the infrared spectrum showed a carbonyl band at 1722 cm^{-1} , a $H_2C=CH$ band at 1628 cm^{-1} , and C—O bands at 1207 and 1137 cm^{-1} .

Tributyl(2-methoxycarbonylallyl)phosphonium Chloride. This compound was prepared similarly to the tris (cyanoethyl) compound. The yield was 23 g. (74%). The compound was soluble in water and in methyl methacrylate, but no viscosity increase was observed during an attempt at bulk polymerization with a benzoyl peroxide catalyst.

In KBr the infrared spectrum showed a carbonyl band at 1717 cm^{-1} , a $H_2C=CH$ band at 1628 cm^{-1} , and C—O bands at 1215 and 1138 cm^{-1} .

Methyl 2-[(Diethoxyphosphinyl)methyl]acrylate. A procedure similar to that of Saunders⁴ was used to prepare the phosphonate. Triethyl phosphite (34 g., 0.2 mole) was added dropwise to a stirred mixture of methyl 2-(chloromethyl)acrylate (13 g., 0.1 mole) and 4,6-dinitro-*o*-cresol (0.5 g., 0.0025 mole) in a nitrogen atmosphere. The temperature was maintained below 10°C. The reaction mixture was stirred 5 min. after the addition was complete and allowed to warm to room temperature. An exotherm was observed. The temperature was kept below 35°C. by cooling until the exotherm subsided. The mixture was heated at $90 \pm 2^\circ C.$ for 5 hr., then cooled to room temperature and allowed to stand overnight. Excess triethyl phosphite was distilled off *in vacuo*, and the residue distilled to give 18.1 g. of material, b.p. 80–91°C./0.025 mm., a 76.6% yield of crude products. Redistillation through a short Vigreux column gave a major fraction, b.p. 86–89.5°C./0.15 mm.

ANAL. Calcd. for $C_8H_{17}O_5P$: C, 45.77%; P, 13.11%; H, 7.25%. Found: C, 45.84%; P, 13.17%; H, 7.60%.

Polymerization of Methyl 2-[(Diethoxyphosphinyl)methyl]acrylate. Methyl 2-[(diethoxyphosphinyl)methyl]acrylate was copolymerized with methyl methacrylate (MMA) in bulk in the presence of benzoyl peroxide by heating at 90°C. for 18 hr. in a test tube sealed under N₂. The results are summarized in Table II.

TABLE II

Monomer			Polymer		
Phosphonate ester, g.	Methyl methacrylate, g.	Benzoyl peroxide, %	Residual methyl methacrylate, %	Intrinsic viscosity ^a	Physical state
1	4	0.05	7.65	1.1	Hard, clear, yellow
1.5	4.5	0.06	11.6	0.27	Hard, clear, yellow

^a in DMF, 0.5 g./100 ml.

Summary

Several phosphorus derivatives of methyl 2-(chloromethyl)acrylate, including three phosphonium salts and one phosphonate ester, have been prepared. A brief study was made of their polymerization characteristics under free radical conditions. Several factors were noted which prevented the synthesis of methyl 2-[(diethoxyphosphinyl)methyl]acrylate in high yields in initial experiments. Homopolymerization of these phosphorus derivatives does not take place readily in the presence of free-radical initiators.

The infrared spectra were interpreted by N. B. Colthup, microanalyses were performed in the General Analytical Group of the Stamford Laboratories, and methyl 2-(chloromethyl)acrylate was prepared by F. Walrond. The assistance of these people is gratefully acknowledged.

References

1. D. S. Hoffenberg and L. M. Zaccardo, U. S. Pat. 3,213,072 (1965).
2. R. Rabinowitz, A. C. Henry, and R. Marcus, *J. Polymer Sci. A*, **3**, 2055 (1965).
3. M. M. Rauhut, I. Heckenbleikner, H. A. Currier, F. C. Schaeffer, and V. P. Wystrach, *J. Am. Chem. Soc.*, **81**, 1103 (1959).
4. B. C. Saunders, G. J. Stacey, F. Wild, and I. G. E. Wilding, *J. Chem. Soc.*, **1943**, 699.

Résumé

De nombreux dérivés phosphorés de l'acrylate de méthyle-2-chlorométhylè y compris trois sels de phosphonium et un ester phosphonique ont été préparés. Une étude brève a été faite concernant les caractéristiques de polymérisation par radicaux libres. De

nombreux facteurs ont été notés qui empêchent la synthèse de l'acrylate de méthyle-2-diéthoxyphosphénylméthyle avec des rendements élevés dans les expériences initiales. L'homopolymérisation de ce dérivé phosphoré n'a pas lieu facilement en présence d'initiateurs par radicaux libres.

Zusammenfassung

Einige Phosphorderivate von Methyl-2-(chloromethyl)-acrylat, nämlich drei Phosphoniumsalze und ein Phosphonatester, wurden dargestellt. Eine kurze Untersuchung ihres Polymerisationsverhaltens bei radikalischer Anregung wurde durchgeführt. Mehrere Faktoren, welche eine hohe Ausbeute bei der Synthese von Methyl-2[(di-äthoxyphosphinyl)-methyl]-acrylat in den Anfangsversuchen verhinderten, wurden festgestellt. Homopolymerisation dieser Phosphorderivate in Gegenwart radikalischer Starter verläuft nur schwierig.

Received November 21, 1966

Prod. No. 1535