

washed, dried and evaporated. The residue was dissolved in cyclohexane and passed through a short column of alumina to remove tarry impurities.

The eluate on evaporation to dryness left yellow crystals, m.p. 161°. Recrystallization from acetone gave the pure 1,1'-dibenzhydrylferrocene as yellow needles, m.p. 162-163°.

Anal. Calcd. for $C_{36}H_{30}Fe$: C, 83.4; H, 5.8. Found: C, 83.7; H, 5.8.

This product was indistinguishable in melting point, mixed melting point and infrared spectrum (determined in carbon tetrachloride solution with a Baird double beam spectrophotometer, Fig. 2e) from a sample supplied by Dr. E. Csendes.¹³

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CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, VICTOR CHEMICAL WORKS]

Allyl Esters of Phosphonic Acids. III. Influence of Substituents on Polymerization Characteristics¹

BY A. D. F. TOY AND ROBERT S. COOPER

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It is well-known that diallyl esters of organic dibasic acids will undergo polymerization to form cross-linked types of glassy resins. It has been shown that the diallyl esters of the arylphosphonic acids undergo polymerization to produce hard, transparent solids which are flame resistant. Further studies covering more than thirty allyl esters of phosphonic acids and other phosphorus-containing allyl derivatives have shown that glassy polymers are not obtained in all cases. The following factors are among those which appear to govern the polymerization characteristics of these compounds: (1) steric hindrance as determined by the size of the substituent group; (2) electrical character of the substituent group and (3) presence or absence of inhibitory groups. The dimethallyl esters polymerize faster than the corresponding diallyl esters. The degree of flame resistance of these phosphorus-containing polymers seems to depend upon their thermal stability rather than upon the phosphorus content of the monomers.

It is well-known that the diallyl esters of dibasic acids, such as diallyl phthalate^{2,3} and diethylene glycol bis-(allylcarbonate)⁴ will undergo polymerization to form cross-linked glassy solids. In previous papers^{5,6} of this series, it has been shown that the diallyl esters of arylphosphonic acids also undergo similar polymerization reactions to form hard transparent resins. A unique property of these arylphosphonate polymers is their flame resistance, that is, they are self-extinguishing when removed from a flame. This self-extinguishing characteristic is even retained in copolymers produced by copolymerization with other compatible monomers. It had been assumed that the observed polymerization tendencies of these substances are typical of all diallyl esters and that the self-extinguishing characteristic is due to the phosphorus content. However, further studies in this Laboratory have shown that these generalizations do not always hold. Differences in the polymerization and flame resistant characteristics have been observed among the allyl esters of various phosphonic acids.

This paper constitutes a preliminary report on the influence of substituents on the polymerization characteristics and other properties of the allyl esters of some phosphonic acids and some allyl derivatives of other phosphorus-containing acids.⁷

The diallyl and dimethallyl esters of a series of al-

kenyl- and alkylphosphonic acids, as well as some derivatives of compounds containing phosphorus-oxygen, phosphorus-sulfur and phosphorus-nitrogen bonds have been studied.

Experimental

The allyl and methallyl esters were prepared by the interaction of the acid chlorides and the alcohols in the presence of a tertiary amine as the condensation agent.^{8,9} The alkylphosphonic dichlorides were prepared using the Woodstock method⁹ which involves the action of phosphorus(V) oxide on the addition compound of phosphorus pentachloride and the desired olefin.¹⁰ The alkylphosphonic dichlorides were prepared: (a) by the action of phosphorus pentachloride on the alkylphosphonic acids which in turn were prepared by the hydrolysis of the dialkyl alkylphosphonates obtained by the action of sodium dialkyl phosphites¹¹ on the alkyl halides¹²; (b) by the hydrolysis of the complex formed by the action of phosphorus trichloride and aluminum chloride and alkyl halide as reported by Clay,¹³ and by Kinnear and Perren¹⁴; and (c) by the action of oxygen on a mixture of phosphorus trichloride and the hydrocarbon as reported by Clayton and Jensen.¹⁵ Other acid chlorides necessary for the preparation of the allyl derivatives of various miscellaneous phosphorus-containing acids were prepared by standard procedures involving the action of phos-

(8) A. D. F. Toy, U. S. Patent 2,425,766 (1947).

(9) W. H. Woodstock, U. S. Patent 2,471,472 (1949).

(10) Commercial grades of isobutylene and diisobutylene were used. In the case of isobutenylphosphonic dichloride, the chlorine content was always found to be 2 to 3% higher than the calculated value; this finding may be attributed to contamination with isochlorobutylphosphonic dichloride. The contaminant may be dehydrochlorinated, however, by heating the crude mixture under reflux until no more hydrogen chloride is evolved; the resulting product is purified by distillation.

(11) A convenient method for the preparation of sodium dialkylphosphite entails the addition of dialkylphosphite to metallic sodium dissolved in liquid ammonia. The completion of the reaction is indicated by the disappearance of the blue color. This reaction has been found to be applicable with diethyl, dibutyl and dioctylphosphites, but not with diallyl phosphite.

(12) G. Kosolapoff, *THIS JOURNAL*, **67**, 1180 (1945).

(13) J. P. Clay, *J. Org. Chem.*, **16**, 892 (1951).

(14) A. M. Kinnear and E. A. Perren, *J. Chem. Soc.*, 3437 (1952).

(15) J. O. Clayton and W. L. Jensen, *THIS JOURNAL*, **70**, 3880 (1948).

(1) Presented in part before the Division of Organic Chemistry at the 122nd Meeting of the American Chemical Society, Atlantic City, N. J., September, 1952.

(2) D. A. Kardashev, N. S. Leznov and V. P. Nuzhdina, *Khimicheskaya Prom.*, No. 2, 5 (1945).

(3) W. Simpson, *J. Soc. Chem. Ind.*, **65**, 107 (1946).

(4) I. E. Muskat and F. Strain, U. S. Patent 2,370,565 (1945).

(5) A. D. F. Toy, *THIS JOURNAL*, **70**, 186 (1948).

(6) A. D. F. Toy and L. Brown, *Ind. Eng. Chem.*, **40**, 2276 (1948).

(7) Since the presentation of this paper, G. Kamai and V. A. Kukhtin, *Doklady Akad. Nauk. SSSR*, **89**, 309 (1953), have reported the synthesis and polymerization of several unsaturated phosphonates. They have also observed that certain groups attached to the phosphorus atom activate the polymerizability of some allyl phosphonates.

TABLE I
 COMPOUNDS YIELDING HARD GLASSY SOLIDS ON POLYMERIZATION

Compounds	Yield, %	°C.	B.P. Mm.	d^{25}_{25}	n^{25}_D	Analyses, Calcd.	P. % Found
$\text{HP}(\text{OCH}_2\text{CH}=\text{CH}_2)_{16,17}$		-61	1	1.078	1.4459	19.1	19.0
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3 \\ \diagdown \\ \text{C}=\text{CH}-\text{P}(\text{OCH}_2\text{CH}=\text{CH}_2)_2 \\ \diagup \\ \text{CH}_3 \end{array}$	69	87-91	0.5	1.0485	1.4670	14.3	14.0
$\begin{array}{c} \text{O} \quad \text{CH}_3 \\ \quad \\ \text{CH}_3 \\ \diagdown \\ \text{C}=\text{CH}-\text{P}(\text{OCH}_2\text{C}=\text{CH}_2)_2^a \\ \diagup \\ \text{CH}_3 \end{array}$	64.3	108-115	2	1.0091	1.4668	12.7	12.6
$\text{C}_6\text{H}_5\text{P}(\text{OCH}_2\text{CH}=\text{CH}_2)_2^5$							
$\begin{array}{c} \text{O} \\ \\ \text{C}_6\text{H}_5\text{OP}(\text{OCH}_2\text{CH}=\text{CH}_2)_2 \end{array}$	64	102	0.5	1.142	1.4957	12.2	12.3
$\begin{array}{c} \text{O} \\ \\ \text{C}_6\text{H}_5\text{CH}_2\text{P}(\text{OCH}_2\text{CH}=\text{CH}_2)_2^{18} \end{array}$	79.4	141-143	1.5	1.099	1.5113	12.3	12.3
$\begin{array}{c} \text{O} \quad \text{CH}_3 \\ \quad \\ \text{C}_6\text{H}_5\text{CH}_2\text{P}(\text{OCH}_2\text{C}=\text{CH}_2)_2 \end{array}$..	158-163	2	1.0630	1.5053	11.06	11.0

^a This polymer is a hard, but opaque solid.

phorus trichloride on the corresponding alcohols, phenols or amines.

The properties of the various allyl esters are summarized in Tables I, II and III. Reported yields were calculated on the basis of the quantity of acid chloride used.

The polymerization study was carried out for the purpose of obtaining comparative data on the general polymerization characteristics of each compound. The compounds (5-g. samples) were heated under a nitrogen atmosphere at 87-88° in an oil-bath for 18 hours in the presence of 3% benzoyl peroxide catalyst. Diallyl phosphite should be polymerized with only 2% benzoyl peroxide since 3% or more sometimes causes violent decomposition. Under these particular conditions, the diallyl esters of arylphosphonic acids polymerized into hard glassy solids. The results of this study showed that the greatest differences in the polymerization characteristics arise with variations in the nature of the substituent groups attached to the phosphorus atom and are less influenced by changing from the allyl to the methallyl esters.

The compounds may be divided into three general classes according to the nature of the polymer formed: (a) those which polymerize into hard glassy solids are listed in Table I, (b) those which polymerize into moderately hard and flexible solids, artgum-like materials or very soft gels are given in Table II and (c) compounds which remain fluid after the polymerization test are presented in Table III. All of the monomers were subjected to purification by distillation by conventional means before the polymerization test with the exception of the styrylphosphonates which had to be purified by molecular distillation. Diallyl phenylphosphonate is included in Table I so that the effect of variation in structure among the different compounds may be evaluated. The compounds are arranged only roughly in order of the hardness of the polymer produced. The hardness of polymers was determined only in a qualitative manner; the first four compounds in Table I are about equally hard

(16) W. E. Craig and W. F. Hester, U. S. Patent 2,495,958 (Jan. 31, 1950), describe diallyl phosphite as a yellow oil which was not distillable, as it decomposed when subjected to elevated temperatures. Later, Walter, *et al.*,¹⁷ reported the synthesis of the diallyl phosphite in high yield and found it to be distillable with b.p. 80° (2 mm.). No other physical constants or analyses were given.

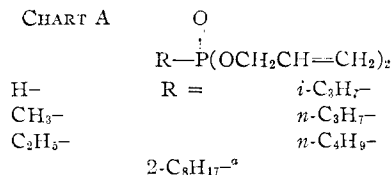
(17) G. E. Walter, I. Hornstein and G. M. Steinberg, U. S. Patent 2,574,516 (Nov. 13, 1951).

(18) D. Harman and A. R. Stiles, U. S. Patent 2,601,520 (June 24, 1952), reported the synthesis of diallyl benzylphosphonate and diallyl *n*-butylphosphonate by the Arbuzov rearrangement, *i.e.*, by the action of benzylchloride or *n*-butyl chloride on triallyl phosphite. The reported indices of refraction were n^{20}_D 1.5132 and 1.4553, respectively.

while the last two on the same table are only slightly harder than those listed among the harder polymers in Table II.

Discussion

Differences in the polymerization characteristics were first observed among the diallyl esters of the alkenylphosphonic acids. It was assumed that steric factors due to differences in the size of the alkenyl radicals were responsible for the observation that the isobutenyl derivatives form hard solids, whereas the isoocetenyl derivatives form only slightly viscous liquids. Such an assumption is not out of line since a similar behavior has been reported for the polymers of the esters of methacrylic acids. Within a certain limit, as the size of the alkyl groups in the methacrylates is increased, the softening points of the resulting polymers decrease. The polymer of the methyl ester has a softening point of 125° while the polymer of the octyl ester has a softening point below room temperature.¹⁹ In order to demonstrate the validity of such a hypothesis, the polymerization characteristics of a series of diallyl alkylphosphonates were studied (Chart A). The diallyl phosphite was included as first member of this series, since structurally speaking it may be considered as the diallyl ester of the



^a For this compound the methallyl ester was used.

hypothetical phosphonic acid. The hydrogen attached to the phosphorus atom should offer the minimum of steric interference; the next member, the diallyl methylphosphonate should also offer

(19) E. I. du Pont de Nemours and Co., Inc., *Ind. Eng. Chem.*, **28**, 1160 (1936).

TABLE II
 COMPOUNDS POLYMERIZED INTO MODERATELY HARD AND FLEXIBLE-TO-SOFT ARTGUM SOLIDS OR RUBBERY GELS

Compounds	Yield, %	B.P. °C.	Mm.	d^{25}_4	n^{25}_D	Analyses, P, % Calcd.	Found	Ref.
$\text{Cyclo-C}_6\text{H}_{11}-\text{P}(\text{O})(\text{CH}_3)(\text{OCH}_2\text{C}=\text{CH}_2)_2$	73	94-98	0.5	1.027	1.4738	11.4	11.4	
$\text{Cyclo-C}_6\text{H}_{11}-\text{P}(\text{O})(\text{OCH}_2\text{CH}=\text{CH}_2)_2$	74.6	100-103	0.5	1.0485	1.4734	12.7	12.8	20
$\text{CH}_3-\text{P}(\text{O})(\text{OCH}_2\text{C}=\text{CH}_2)_2$	69.5	95	1	1.024	1.4491	15.2	15.1	
$\text{CH}_3-\text{P}(\text{O})(\text{OCH}_2\text{CH}=\text{CH}_2)_2$	47	77-85	0.5	1.044	1.4468	17.6	17.5	21 ^c
$\text{C}_2\text{H}_5-\text{P}(\text{O})(\text{OCH}_2\text{C}=\text{CH}_2)_2$	76.8	93-95	1	1.006	1.4502	14.2	14.2	
$\text{C}_2\text{H}_5-\text{P}(\text{O})(\text{OCH}_2\text{CH}=\text{CH}_2)_2$	65.8	73-78	0.5	0.9963	1.4470	16.3	16.3	^c
<i>iso</i> - $\text{C}_3\text{H}_7-\text{P}(\text{O})(\text{OCH}_2\text{C}=\text{CH}_2)_2$	60	106-108	2	0.990	1.4490	13.4	13.5	
<i>iso</i> - $\text{C}_3\text{H}_7-\text{P}(\text{O})(\text{OCH}_2\text{CH}=\text{CH}_2)_2$	60.8	52	0.5	1.0166	1.4459	15.2	15.4	
<i>n</i> - $\text{C}_3\text{H}_7-\text{P}(\text{O})(\text{OCH}_2\text{C}=\text{CH}_2)_2$	84	107-112	1-2	0.9909	1.4512	13.4	13.2	
<i>n</i> - $\text{C}_3\text{H}_7-\text{P}(\text{O})(\text{OCH}_2\text{CH}=\text{CH}_2)_2$	63.3	91	1	1.021	1.4472	15.2	15.1	
<i>n</i> - $\text{C}_4\text{H}_9-\text{P}(\text{O})(\text{OCH}_2\text{C}=\text{CH}_2)_2$	85.4	104-106	1	0.9789	1.4519	12.6	12.8	
<i>n</i> - $\text{C}_4\text{H}_9-\text{P}(\text{O})(\text{OCH}_2\text{CH}=\text{CH}_2)_2$	74	75-81	0.5	1.002	1.4478	14.2	14.2	18
<i>iso</i> - $\text{C}_4\text{H}_9-\text{P}(\text{O})(\text{OCH}_2\text{CH}=\text{CH}_2)_2$	79.2	65-67	0.5	1.005	1.4456	14.2	14.0	
$2-\text{C}_8\text{H}_{17}-\text{P}(\text{O})(\text{OCH}_2\text{C}=\text{CH}_2)_2$	59.5	125	0.5	0.947	1.4543	10.3	10.4	
$\text{C}_6\text{H}_5\text{CH}=\text{CH}-\text{P}(\text{O})(\text{OCH}_2\text{C}=\text{CH}_2)_2$	77.4	^a		1.0692	1.5360	10.6	10.4	
$\text{C}_6\text{H}_5\text{CH}=\text{CH}-\text{P}(\text{O})(\text{OCH}_2\text{CH}=\text{CH}_2)_2$	70.0	^b		1.0996	1.5445	11.7	11.4	
$(\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{CH}_3)-\text{CH}_2-\text{P}(\text{O})(\text{OCH}_2\text{CH}=\text{CH}_2)_2$	84	92	0.5	0.9641	1.4489	11.3	11.3	

^a Purified in a Hickman still; bath temperature 135-142° (0.003 mm.); rate, drop/2-3 sec. ^b Purified in a Hickmans till; bath temperature 130-140° (0.007 mm.); rate, drop/2-4 sec. ^c These compounds are quite soluble in water but not in saturated sodium chloride solution.

little steric hindrance by the methyl radical. The results of the polymerization tests showed that diallyl phosphite polymerizes to a hard and glassy solid while the diallyl methylphosphonate yields only a moderately hard and somewhat flexible solid. As the size of the alkyl group is increased, there is a tendency for the polymerized product to become an artgum to soft gel-like material; the dimethylallyl 2-octylphosphonate still yielded a tough rubbery

(20) A. J. Castro and W. E. Elwell, *THIS JOURNAL*, **72**, 2275 (1950), reported the synthesis of this compound by the same method.

(21) Reference was made to this compound by Kamai and Kukhtin.⁷

gel instead of an oil. From the nature of the polymers obtained in this series of alkylphosphonates, it is apparent that the size of the alkyl group has some effect. However, inasmuch as the 2-octyl group should be comparable in size to the isoöctenyl group, the steric factor alone does not explain why the diallyl and dimethylallyl isoöctenylphosphonates do not polymerize beyond the oily stage.

No complete theory has yet been formulated to explain the differences in the polymerization characteristics of various diallyl organic phosphonates. However, it is significant that glassy solids (Table

TABLE III
 COMPOUNDS REMAINING AS LIQUIDS AFTER THE POLYMERIZATION TEST

Compounds	Yield, %	B.P. °C.	Mm.	d_{25}^{25}	n_D^{25}	Calcd.	Analyses, %	Found
$ \begin{array}{c} \text{CH}_3 \quad \text{O} \quad \text{CH}_3 \\ \quad \quad \\ (\text{CH}_3)_3\text{CCH}_2\text{C}=\text{CH}-\text{P}(\text{OCH}_2\text{C}=\text{CH}_2)_2 \end{array} $	82.8	121-125	1	0.9638	1.4668	P, 10.3		P, 10.4
$ \begin{array}{c} \text{CH}_3 \quad \text{O} \\ \quad \\ (\text{CH}_3)_3\text{CCH}_2\text{C}=\text{CH}-\text{P}(\text{OCH}_2\text{CH}=\text{CH}_2)_2 \end{array} $	87.5	124-125	2	0.9795	1.4660	P, 11.4		P, 11.4
$ \begin{array}{c} \text{S} \\ \\ \text{C}_6\text{H}_5\text{P}(\text{OCH}_2\text{CH}=\text{CH}_2)_2 \end{array} $	64.5	126-129	1	1.115	1.5508	P, 12.2; S, 12.6		P, 12.4; S, 12.9
$ \begin{array}{c} \text{O} \quad \text{H} \quad \text{CH}_3 \\ \quad \quad \\ \text{C}_6\text{H}_5\text{P}(\text{NCH}_2\text{C}=\text{CH}_2)_2 \end{array} $	55.8	M.p. 88-89					P, 11.7; N, 10.6	P, 11.7; N, 10.3
$ \begin{array}{c} \text{O} \\ \\ (\text{CH}_3)_2\text{N}-\text{P}(\text{OCH}_2\text{CH}=\text{CH}_2)_2^a \end{array} $	71.4	75	0.5	1.0561	1.4465	P, 15.2; N, 6.9		P, 15.2; N, 6.8
$ \begin{array}{c} \text{O} \\ \\ (\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{N}(\text{CH}_2\text{CH}=\text{CH}_2)_2)^b \end{array} $	72.0	77-81	1	1.013	1.4430	P, 13.3; N, 6.0		P, 13.1; N, 5.8
$ \begin{array}{c} \text{O} \quad \text{H} \quad \text{CH}_3 \\ \quad \quad \\ (\text{C}_2\text{H}_5\text{O})_2\text{PN}-\text{CH}_2\text{C}=\text{CH}_2 \end{array} $	81.3	96	0.5	1.124	1.4412	P, 15.0; N, 6.8		P, 15.0; N, 6.6
$ \begin{array}{c} \text{O} \\ \\ (\text{C}_2\text{H}_5\text{O})_2\text{POCH}_2\text{CH}=\text{CH}_2 \end{array} $	72.5	63	0.5	1.073	1.4216	P, 16.0		P, 16.1

^a Original viscosity = 2.3 centipoises. Polymerized sample, viscosity = 26 centipoises. 55.8% of the original monomer recovered unchanged by distillation at 0.5 mm. ^b Original viscosity = 2.8 centipoises. Polymerized sample, viscosity = 5.2 centipoises. 84% of the original monomer was recovered unchanged from the polymerized sample by distillation at 0.5 mm.

I) are obtained where the substituent attached to the phosphorus atom is more electro-negative than the methyl group, whereas only moderately hard solids or flexible artgum to soft rubbery gels (Table II) characterize the polymers formed when the organic substituent attached to the phosphorus atom is in general approximately as electropositive, or more so, than the methyl radical.²² A more direct comparison is that between the isobutenyl and isobutylphosphonate. The more electronegative unsaturated isobutenyl derivative polymerizes into a hard glassy solid while the more electropositive isobutyl derivative produced only a moderately hard artgum-like solid. The above results showed that besides the steric factor, the electrical character of the substituent group has a definite influence on the polymerization characteristic of the compound even though such a substituent group is rather far removed from the double bonds of the allyl groups.

The reason for the failure of some of the compounds listed in Table III to polymerize beyond the oily stage is obvious only in some cases. It is a well-known fact in polymer chemistry that some sulfur-containing compounds inhibit the peroxide catalyst type of polymerization, thus diallyl phenylthionophosphonate does not polymerize. The inability of diallyl dimethylamido phosphate to polymerize to a solid was unexpected, since amido groups, in general, are not recognized as inhibitors in the addition type of polymerization. However, since dimethylallyl phenylphosphonamide and diethyl diallylamido phosphate were found also not to

be polymerizable to solids under the conditions used, it is probable that the presence of the phosphorus-amido group exercises some inhibitory action on the polymerization. In order to check such a possibility, controlled polymerization studies were carried out using diallyl phenylphosphonate and diallyl phthalate. Since both of these monomers will polymerize into hard, strong solids when heated individually in the presence of benzoyl peroxide catalyst a number of tests were performed by polymerizing each of them individually in the presence of 5% of the following compounds: hexamethyl phosphoramidate, diallyl dimethylamido phosphate, diethyl diallylamido phosphate, phosphoric trianilide, phosphoric triamide and triethyl phosphate. These experiments showed that the addition of 5% of compounds containing the phosphorus-amido group resulted in the formation of liquids, soft gels and hard artgum-like materials, whereas presence of triethyl phosphate had little effect since polymers were obtained almost as hard and glassy as those formed without additives. It is evident therefore that phosphorus-amido groups inhibit the polymerization of diallyl esters. Such inhibitory action was not observed when similar polymerization tests with the diallyl esters were carried out in the presence of 5% of amides of aliphatic acids such as acetanilide, octadecanamide, urea or methacrylamide. It is of interest to note that the polymerization of methyl methacrylate, carried out in parallel experiments was not noticeably affected by the presence of 5% of phosphorus-amido compounds.

The reason for the failure of diallyl and dimethylallyl isoöctenylphosphonate (Table III) to polymerize was at first not apparent. Examination of

(22) Dissociation constants of some of the carboxylic acids with the organic radicals similar to the organic phosphonates listed in Tables I and II would lead to the conclusion that the parent acids in Table I are stronger than those in Table II. The cinnamic acid which corresponds to the styrylphosphonate is an exception.

the structure of the isoöctenyl radical indicated the presence of an allylic methylene group. This allylic methylene group may have a chain arresting effect on the polymerization reaction. The inhibitory action of allylic methylene group in the free radical type of polymerization has been reported by Frank and his co-workers²³ in their study of the copolymerization of isoprene with styrene.

In order to prove the validity of the theory of the inhibitory action of the allylic methylene group on the polymerization of diallyl isoöctenylphosphonate, the polymerization of diallyl isoöctylphosphonate was studied (Table II). The isoöctyl radical is identical in structure with the isoöctenyl radical except that the double bond is removed. Since the double bond is removed, the methylene group is no longer allylic in nature and therefore should not interfere with the polymerization reaction beyond the facts that the large alkyl group may exercise some steric effect and as a more positive radical than the methyl group. Tests showed that it actually polymerizes into a soft rubbery gel, almost identical in nature with that of the dimethallyl 2-octylphosphonate polymer. This finding would indicate that the allylic methylene group in the isoöctenyl radical is probably responsible for the failure of diallyl isoöctenylphosphonate to polymerize.

The monoallyl derivatives (Table III) are not expected to polymerize to any degree, for it is well-known that monoallyl compounds such as allyl acetate polymerize to a small extent. The low degree of polymerization of allyl acetate in the presence of benzoyl peroxide catalyst due to degradative chain transfer has been studied by Bartlett and Altschul.²⁴

Since such a marked difference was observed in the polymerization characteristics of the allyl esters of different phosphorus-containing acids, it was decided to study the differences in the behavior of the allyl and methallyl esters. The diallyl and dimethallyl isoöctenylphosphonates were chosen for this study since they were found to polymerize only to viscous liquids. Comparative rates of polymerization were followed by measuring the changes in viscosities. The results are presented in Table IV. It is apparent from these data that the dimethallyl ester polymerizes more rapidly than the corresponding diallyl esters.

Many polymers of diallyl organic phosphonates are

(23) R. L. Frank, C. E. Adams, J. R. Blegen, R. Deanin and P. V. Smith, *Ind. Eng. Chem.*, **39**, 887 (1947).

(24) P. D. Bartlett and R. Altschul, *THIS JOURNAL*, **67**, 816 (1945).

TABLE IV
POLYMERIZATION OF DIALLYL AND DIMETHALLYL ISO-
OCTENYLPHOSPHONATE AT 87-88°

Bz ₂ O ₂ , %	Viscosity in centipoises			
	Diallyl ester		Dimethallyl ester	
	24 hr.	48 hr.	24 hr.	48 hr.
0	5	5	6	7
2	10	10	52	54
4	18	18	340	390
6	30	31	2,260	2,770
8	50	51	14,650	25,300
10	79	88	145,000	215,000

of the self-extinguishing type. It had been assumed that this flame resistance is due to the presence of the phosphorus atom. The flame resistance values of a series of allyl phosphorus ester polymers are listed in Chart B along with the calculated values for the phosphorus contents of the monomers.

CHART B		
Compounds	Flame resistance	P, %
$\text{C}_6\text{H}_5\text{P}(\text{OCH}_2\text{CH}=\text{CH}_2)_2$	Good	13
$\text{CH}_3\text{P}(\text{OCH}_2\text{CH}=\text{CH}_2)_2$	Good	17.6
iso-C ₄ H ₇ P(OCH ₂ CH=CH ₂) ₂	Fair	14.4
OP(OCH ₂ CH=CH ₂) ₃	Poor	14.2
HP(OCH ₂ CH=CH ₂) ₂	Very poor	19.2

It is obvious from these data that there is no direct co-relationship between phosphorus content and flame resistance. However, during the preparation of these compounds, it was observed that the stability toward distillation decreases in the same order as the decrease in the flame resistance. Therefore, a definite correlation does exist between the thermal stability of the monomer and the flame resistance of the polymer. These results are in line with the fact that the thermally more stable plasticizers of the aryl phosphorus esters impart a greater degree of flame resistance to the resin with which it is used than the thermally less stable aliphatic phosphorus esters.

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CHICAGO HEIGHTS, ILLINOIS