nitrogen and the remaining suspension centrifuged. The residue was washed twice with 30–60° petroleum ether and dried under a stream of nitrogen. Because of the very fine particle size, great difficulty was encountered in collecting the solid and no yield was determined. The product was a black powder that smoked on initial exposure to air and then was stable even when heated with a torch. *Anal.* Calcd. for Co_3P_2: P, 26.9. Found: P, 27.7.

Thermal Decomposition of Tris-trimethylsilylphosphine.—A mixture of 3.0464 g. of the phosphine and 1.4606 of triethylborine was heated in a 100-ml. sealed bulb for 19 hours at 108°. The bulb was opened to the vacuum system and no non-condensibles were found. Fractionation through a $-63°$ trap yielded a trace of PH_3 and C_2H_4. The material in the $-63°$ trap, 1.0534 g., was examined by infrared and was found to be a mixture of BEt_3 and a trimethylsilyl-containing group, of average molecular weight of 124.5, equivalent to 4.0 mmoles of Si_2Me_6. Comparison of the spectrum and an authentic spectrum of Si_2Me_6 showed bands at 3.35, 3.43, 7.95, 8.80 and 12.0 μ and the other bands in the mixture were attributed to the BEt_3. The non-volatile residue was heated with excess PCl_5 in a sealed tube at 200° for 10 hours to convert all of the BEt_3 to BCl_3 and EtCl and the Si–P residue to $SiMe_3Cl$ and PCl_3. Fractionation of the material through $-63°$, $-126°$ and into $-196°$ traps separated out the HCl and only $SiMe_3Cl$ was found in the $-126°$ trap. This indicated no BCl_3 and hence no BEt_3 in the non-volatile residue. Therefore, BEt_3 did not take part in the reaction but only catalyzed the decomposition of the phosphine. Heating of the phosphine in a 200-ml. bulb at 100° for 18 hours yielded only a very small amount of volatile $SiMe_3$ containing material showing the catalytic effect of the BEt_3.

Reaction of Tris-methylsilylphosphine with Diphenyldichlorosilane.—A mixture of 12.6 ml. of diphenyldichlorosilane, 17.6 ml. of tris-trimethylsilylphosphine and 50 ml. of Amsco Odorless Mineral Spirits was refluxed under nitrogen overnight. Only 2.1 g. of chlorosilane collected in a Dry Ice trap connected to the system indicating that more vigorous conditions were necessary for reaction. Therefore, the solvent was distilled away and the flask heated to 400° for 3 hours; 5.8 g. more of the chlorosilane was produced. The residue was a semi-solid from which a solid was isolated by dissolving the liquid in a 30–60° petroleum ether–Et_2O mixture and filtering the solid. After two recrystallizations from benzene the solid melted 265–269° and analyzed 18.7% Si, 8.3% P, and less than 0.1% Cl. This is a Si/P ratio of 5/2 indicating that it cannot have a ring structure as might be expected from analogy to silicon oxygen compounds and shows good agreement with the formula: $(R)(Si(C_6H_5)_2)[P(SiMe_3)Si(C_6H_5)_2]_2$-R where R could be OH or CH_3. Calcd. Si, 17.8; P, 7.95 for R = OH.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

The Formation of Linear Polymers from Diene Monomers by a Cyclic Polymerization Mechanism. V. Phosphorus-containing Dienes[1]

BY K. DARRELL BERLIN[2] AND GEORGE B. BUTLER

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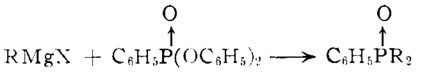
Diallylphenylphosphine oxide and dimethylallylphenylphosphine oxide have been synthesized. Both phosphine oxides polymerized in free radical systems to yield soluble polymers. A soluble polymer was isolated from the polymerization of allylphenyl allylphosphonate. Intrinsic viscosity measurements indicate the polymers are of low molecular weight. The polymerizations are examples of cyclic polymerization involving an intramolecular–intermolecular propagation step.

Cyclic polymerization was originally suggested by Butler and Angelo to explain the formation of soluble polymers when quaternary ammonium salts containing two allyl groups polymerized.[3] The mechanism involves an intramolecular–intermolecular propagation step which, in the case of a 1,6-diene system, would lead to linear chains composed of alternating six-membered rings (saturated) and methylene groups. Symmetrical and unsymmetrical 1,6-dienes, as well as dienes capable of forming rings containing more than six atoms, have been reported to undergo polymerization *via* cyclization.[4]

In this study the reaction was extended to include dienes which contained a phosphorus atom. The use of tertiary phosphine oxides of the type shown in the formula seemed particularly inviting since, in general, such compounds are thermally stable,[5] a characteristic which might be inherited by the polymers.

$$(CH_2{=}CHCH_2)_2(R)P{\rightarrow}O$$

An examination of the literature revealed, however, that tertiary phosphine oxides substituted with two allyl groups were unknown. Diallylphenylphosphine oxide (IIa) was first synthesized by condensation of diphenyl phenylphosphonate (I) with the allyl Grignard reagent as shown in the equation. In like manner dimethallylphenylphosphine oxide (IIb) was realized. The reaction is similar to that used to prepare di-*p*-tolylmethylphosphine oxide.[6]



$$RMgX + C_6H_5\overset{\overset{O}{\uparrow}}{P}(OC_6H_5)_2 \longrightarrow C_6H_5\overset{\overset{O}{\uparrow}}{P}R_2$$

I II

IIa, allyl = R
IIb, methallyl = R

Although these dienes take up bromine, a quantitative determination of unsaturation failed to give consistent results.[7] Several attempts were made to hydrogenate diallylphenylphosphine oxide quantitatively over platinum at atmospheric pressure, but in all trials the residual oil contained considerable unsaturation as indicated by infrared analysis. Hydrogenation of diallylphenylphosphine oxide could, however, be accomplished under pressure. Di-*n*-propylphenylphosphine oxide, the reduction product, was made by an alternative

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(2) Post-doctoral Fellow, 1958–1960.

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(4) Many pertinent references can be found in: M. D. Barnett, A. Crawshaw and G. B. Butler, *ibid.*, **81**, 5946 (1959).

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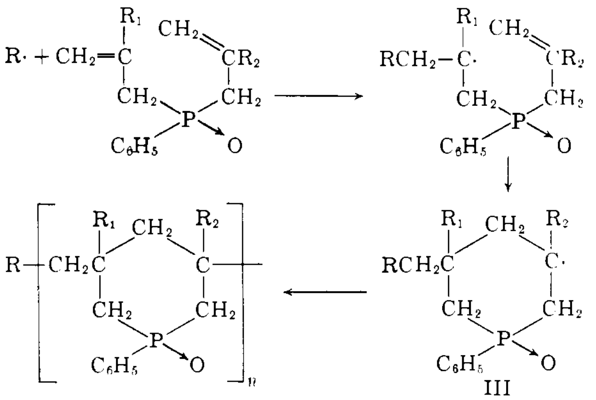
route since it was apparently unknown. Tertiary phosphine oxides have been reduced to phosphines by sodium and alcohol[8] or metal hydrides.[9]

The infrared spectrum of diallylphenylphosphine oxide possesses peaks which could be assigned to aromatic hydrogen (3025 cm.$^{-1}$), aliphatic hydrogen (2950 cm.$^{-1}$), a carbon–carbon double bond (1641 cm.$^{-1}$), a phenyl–phosphorus bond (1444 cm.$^{-1}$), a phosphoryl group ($P \rightarrow O$) (1172 cm.$^{-1}$) and a terminal methylene group (910 cm.$^{-1}$). Conspicuously absent was a band assigned to the P–O–aryl linkage at 1200 cm.$^{-1}$.[10] Dimethallylphenylphosphine oxide has absorption in the infrared which indicates the presence of aromatic hydrogen (3020 cm.$^{-1}$), aliphatic hydrogen (2900 cm.$^{-1}$), a carbon–carbon double bond (1635 cm.$^{-1}$), a phenyl–phosphorus link (1440 cm.$^{-1}$), a phosphoryl group (1190 cm.$^{-1}$) and a terminal methylene function (892 cm.$^{-1}$). Again the intense absorption at 1200 cm.$^{-1}$ (P–O–aryl) found in the spectrum of diphenyl phenylphosphonate was missing.

Diallylphenylphosphine oxide could be polymerized in bulk with benzoyl peroxide; yields 15–30%. Poly-(diallylphenylphosphine oxide) was soluble in alcohol, dimethylformamide and glacial acetic acid. An intrinsic viscosity determination of a sample melting at 85–115° gave a value of 0.026 (in alcohol). An infrared examination of the polymer showed only a small peak for a carbon–carbon double bond (1640 cm.$^{-1}$). Absorption assigned to the terminal methylene group (910 cm.$^{-1}$) in the monomer did not appear in the polymer. A sample of poly-(diallylphenylphosphine oxide) lost 21.9% of its original weight when heated at 210° for 4 hr. It began to darken in 10 min. and had the appearance of tar after 48 hr.

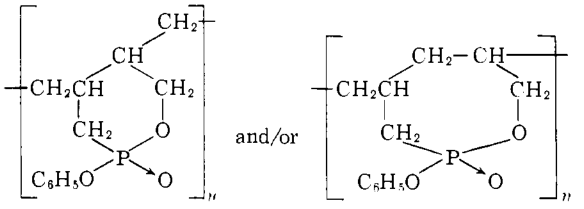
Polymerization of dimethallylphenylphosphine oxide was initiated by either α,α'-azodi-isobutyronitrile or benzoyl peroxide at 75°. The yields of polymer were low (less than 30%) with either initiator. Poly-(dimethallylphenylphosphine oxide) was soluble in alcohol, glacial acetic acid and dimethylformamide. A value of 0.04 was found for the intrinsic viscosity of an alcohol solution of the polymer; the sample melted at 130–165°. The infrared spectrum has only a small hump to indicate a carbon–carbon double bond (1635 cm.$^{-1}$) and does not have a peak for a terminal methylene group (892 cm.$^{-1}$) as is present in the spectrum of the monomer. When heated at 210° for 4 hr., the polymer decreased in weight by 32.5%.

In view of the low intrinsic viscosity measurements it appears likely that the polymers are not of high molecular weight. Polymerizations involving allyl groups have been reported to terminate through degradative chain transfer[11] which may be influential in retarding growth in our examples. Formation of the polymers is illustrated in the scheme below. It should be noted that the existence of a five-membered ring within the polymer structure is possible. If such a ring were to be created, however, it would necessitate formation of a primary radical rather than a secondary radical (or tertiary radical) at stage III. A five-membered ring has never been reported in cyclic polymerizations involving symmetrical 1,6-diene systems with terminal methylene groups.



$R_1 = R_2 = H, CH_3$

It has been shown that a seven-membered ring was formed during cyclic polymerization of a symmetrical 1,7-diene.[12] Potentially, allylphenyl allylphosphonate (IV) is capable of forming a six- or seven-membered ring during cyclization. That this ester does form a soluble polymer whose infrared spectrum shows negligible unsaturation appears to bear out the hypothesis. Although the polymer could possess either (or both) of the two structures shown, the seven-membered ring should be favored if stability of the radical formed in the propagation step is the governing factor in the cyclization process. The polymers obtained from bulk or solution polymerization (in benzene) have nearly identical infrared spectra. A sample of the bulk polymer melting at 92–115° gave a value of 0.09 for its intrinsic viscosity (in alcohol). A small quantity of the polymer heated at 210° lost 15.2% of its weight in 4 hr. The literature contains a reference to the polymerization of the monomer with benzoyl peroxide, but the authors indicate the isolation of colorless, sticky resins with a degree of polymerization of $n = 2$–3.[13] No mention was made of the possibility of cyclization.



Experimental[14]

Diphenyl Phenylphosphonate.—A generous supply of this compound was donated by the Victor Chemical Co.

Allylphenyl allylphosphonate was purchased from the Hooker Chemical Co.

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

TABLE I

Monomer (initiator[a])	Wt., g., monomer	Wt., g., initiator	Temp., °C.	Time	Intrinsic viscosity	Yield, %	M.p. of polymer, °C.
IIa (b′)	4.4150	0.1323	75	100 hr.	0.026	16.6	85–115
IIa (b′)	7.2987	.2189	75	18 days	[n]	31.5	108–115
IIb (b′)	9.9208	.2976	75	21 days	0.04	11	130–165
IIb (a′)	10.5609	.3168	75	46 days	[n]	28	160–185
IV (b′)	10.7757	.4809	70	40 hr.	0.09	28	92–115
IV (b′)	10.173[b]	.305	65	5 days	[n]	15	92–115

[a] a′ = α,α′-azo-di-isobutyronitrile, b′ = benzoyl peroxide. [b] In 3.037 g. of benzene. [n] = not determined.

Diallylphenylphosphine Oxide.—The allyl Grignard reagent was prepared in the manner described in reference 15. The entire system was swept with nitrogen, and a calcium chloride tube was placed on the condenser. To a solution of the allyl Grignard reagent (prepared from allyl bromide; filtered and titrated to be 1.79 molar) in anhydrous ether (800 ml.) was added, with stirring, a solution of 62.0 g. (0.2 mole) of diphenyl phenylphosphonate in 200 ml. of sodium-dried benzene. When the addition was complete (1 hr.), an additional 200 ml. of benzene was added. The mixture was heated at reflux (temperature of the mixture ranged from 60 to 70°) with stirring for 100 hr. after which it was allowed to stand overnight at room temperature. Decomposition was effected by the addition of 400 ml. of 10% aqueous ammonium chloride with cooling. The water layer was extracted twice with 200-ml. portions of benzene, and the residual semi-solid was extracted with hot benzene. The extracts were combined with the original organic phase, and the resulting solution was extracted twice with 200-ml. portions of 10% aqueous sodium hydroxide and once with 100-ml. of 5% aqueous sodium hydroxide. Sodium sulfate was used to dry the organic solution. Evaporation of the solvents left an oil which distilled at 169° (1.3 mm.). The distillate solidified to a white solid, melting at 48–50°, yield 23.1 g. (56%). Since the compound was hygroscopic, it was dried in a vacuum oven at 60° for 2 days and then stored in a desiccator over phosphorus pentoxide. By use of a 10-mole excess of Grignard reagent, yields of 50–56% were realized in several runs.

Anal.[16] Calcd. for $C_{12}H_{15}OP$: C, 69.90; H, 7.28; P, 15.05. Found: C, 69.87; H, 7.40; P, 14.89.

An effort was made to prepare the diallylphenylphosphine oxide from freshly distilled phenyldichlorophosphine oxide and the allyl Grignard reagent. The procedure was similar to that described above, but removal of the organic solvents left only a black oil which could not be distilled *in vacuo*,

The unsaturation present in the diene could not be determined quantitatively by bromination.[7] Several trials gave results which in most cases exceeded the theoretical amount of bromine. A quantitative reduction over platinum was attempted in a micro-hydrogenation apparatus. The reaction was stopped after the theoretical quantity of hydrogen had been absorbed. An infrared analysis of the residual oil indicated the existence of much residual unsaturation. The results were the same even when the mixture was allowed to stand in a nitrogen atmosphere for several hours after the theoretical uptake had been recorded. Hydrogenation under pressure, over platinum, has been reported to be successful for the reduction of certain unsaturated, tertiary phosphine oxides.[17] A solution of 6.372 g. (0.03 mole) of diallylphenylphosphine oxide in 40 ml. of absolute alcohol and 0.430 g. of platinum oxide were placed in a Paar hydrogenation apparatus. The mixture was shaken for 48 hr. under a hydrogen pressure of 15–25 lb. per sq. in. A practically quantitative yield of di-*n*-propylphenylphosphine oxide was obtained. The infrared spectrum of this new oxide was nearly superimposable on that of the synthetic di-*n*-propylphenylphosphine oxide.

Di-*n*-propylphenylphosphine Oxide.—The *n*-propyl Grignard reagent, prepared from 36 g. (1.5 g. atoms) of magnesium turnings, 123 g. (1.0 mole) of *n*-propyl bromide and 400 ml. of anhydrous ether, reacted with 62.0 g. (0.2 mole) of diphenyl phenylphosphonate (dissolved in 150 ml. of anhydrous benzene) to give di-*n*-propylphenylphosphine oxide; yield 20.0 g. (47.6%). The procedure was similar to that used to prepare diallylphenylphosphine oxide. Di-*n*-propylphenylphosphine oxide distilled at 121–124° (0.5–1 mm.) and partially solidified upon standing. The infrared spectrum[18] contains bands assignable to aromatic hydrogen (3005 cm.^{-1}), aliphatic hydrogen (2950 cm.^{-1}), a phenyl–phosphorus linkage (1447 cm.^{-1}) and a phosphoryl group (1170 cm.^{-1}). Absorption of medium intensity was also present at 1115, 740 and 695 cm.^{-1}.

Anal. Calcd. for $C_{12}H_{19}OP$: C, 68.57; H, 9.04; P, 14.76. Found: C, 67.81; H, 9.19; P, 14.27, 14.44.

Dimethallylphenylphosphine Oxide.—To a solution of the methallyl Grignard reagent, prepared from 72.0 g. (3.0 g. atoms) of magnesium and 181.0 g. (2.0 moles) of methallyl chloride in 1200 ml. of dry ether, was added a solution of 31.0 g. (0.1 mole) of diphenyl phenylphosphonate in 150 ml. of dry benzene. From this point the procedure was similar to that described in the preparation of diallylphenylphosphine oxide. Dimethallylphenylphosphine oxide distilled at 156–161° (3 mm.), yield 11.0 g. (47%). The compound was a white, hygroscopic solid which could be recrystallized from a benzene–petroleum ether mixture; melting point 67–69° (melt is cloudy up to 71°).

Anal. Calcd. for $C_{14}H_{19}OP$: C, 71.79; H, 8.11; P, 13.24. Found: C, 71.89; H, 8.39; P, 13.01.

Polymerizations. Poly-(diallylphenylphosphine oxide).—Data for the polymerizations can be found in Table I. A general procedure was as follows. The monomer and catalyst were placed in a vial which was then swept with nitrogen, capped, and placed in an oven. The polymerization mixture was poured into anhydrous ether from which the polymer precipitated as a white solid. Partial purification was accomplished by dissolving the polymer in a minimum of alcohol and reprecipitating it by addition of dry ether. Poly-(diallylphenylphosphine oxide) could not be purified to give an accurate analysis.

Anal. Calcd. for $C_{12}H_{15}OP$: C, 69.90; H, 7.28; P, 15.05. Found: C, 68.98; H, 7.17; P, 14.05.

Poly-(dimethylallylphenylphosphine oxide).—The procedure for the preparation and purification of the polymer was similar to that described for poly-(diallylphenylphosphine oxide); see Table I for additional data.

Anal. Calcd. for $C_{14}H_{19}OP$: P, 13.24. Found: P, 12.83, 12.96.

Poly-(allylphenyl allylphosphonate).—The polymerization carried out in bulk was similar to that described in the preparation of the other polymers. Solution polymerization in benzene gave a polymer whose infrared spectrum was nearly identical to that of the bulk polymer. Only a small hump indicates the existence of residual unsaturation (1640 cm.^{-1}). The intense band found in the spectrum of the monomer for the terminal methylene group (920 cm.^{-1}) was also present as a small hump. The polymer did not absorb bromine and was not hygroscopic. Since the solution polymer was easier to purify, it was analyzed. The compound was soluble in alcohol and glacial acetic acid. Other data are given in Table I.

Anal. Calcd. for $C_{12}H_{15}OP$: C, 60.50; H, 6.30; P, 13.02. *Found*: C, 60.83; H, 6.38; P, 13.06.

GAINESVILLE, FLA.

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(18) The infrared spectra were recorded by Mr. George Price and Mr. Leo Pijanowski, Jr.