TABLE II

α,β-DIAMINES ($RR'CNH_2$—$CH_2NR''R'''$) AND THEIR DERIVATIVES

R''	R'''	Temp., °C.	Time, hrs.	Yield, %	B. p., °C.	$n^{20}D$	Formula	Nitrogen, % Calcd.	Nitrogen, % Found	Phenylthiourea M. p., °C.	Phenylthiourea Nitrogen, % Calcd.	Phenylthiourea Nitrogen, % Found	Benzamide M. p., °C.	Benzamide Nitrogen, % Calcd.	Benzamide Nitrogen, % Found
							$R = CH_3$ $R' = CH_3$								
H	C_2H_5	80	41	42	140–141	1.4300	$C_6N_{16}N_2$	24.12	23.85				106–108^c	8.35	8.15
H	n-C_4H_9	100	49	84	183–185	1.4345	$C_8H_{20}N_2$	19.43	19.19	104–105	15.04	15.01	105–106^b	7.95	8.03
H	C_4H_{11}	100	50	82	230–230.5	1.4672	$C_{10}H_{22}N_2$	16.46	16.32	116–117	13.76	13.74	176–177^b	7.40	7.42
C_4H_8O	(morpholine)	80	25	85	208–210	1.4677	$C_8H_{18}N_2O$	17.71	17.60	153–153.5	14.32	14.24	119–121	10.68	10.53
H	$C(CH_3)_2CH_2OH$	80	25	20	233.5^d		$C_8H_{20}N_2O$	17.49	17.34	133–134^e	14.23	14.21			
H^f	C_4H_5	100	50	40	110–111^g	1.5450	$C_{10}H_{16}N_2$	17.06	16.85	132.5–133	14.03	13.81	145.5–147^b	7.52	7.30
^{h}	^{i}			*23*	*145–146*^{g}	*1.5270*	$C_{10}H_{16}N_2$	*17.06*	*17.16*				*193–194*	*10.44*	*10.35*
							$R = H$ $R' = C_2H_5$								
H	H	100	51	55	140	1.4490	$C_4H_{12}N_2$	31.80	31.72	174^a	15.63	15.50	186–187^b	9.45	9.38
H	C_2H_5	80	25	20	156–157	1.4431	$C_6H_{16}N_2$	24.12	23.92	110–111	16.72	16.65	115–116^b	8.64	8.71
H	n-C_4H_9	100	48	68	199–200	1.4422	$C_8H_{20}N_2$	19.43	19.17	105-106.5	15.04	14.80			
n-C_4H_9	n-C_4H_9	100	48	20	238–239	1.4463	$C_{12}H_{28}N_2$	13.99	13.82	54–55	12.53	12.42			
C_2H_5	C_2H_5	100	100	54	173	1.4347	$C_8H_{20}N_2$	19.43	19.20	73–74	15.04	15.02			
H	C_4H_{11}	100	50	55	242–244	1.4711	$C_{10}H_{22}N_2$	16.46	16.45	108–109.5	13.76	13.74	82–83^c	7.20	7.41
	^{j}			12	265–270	1.4832	$C_{10}H_{22}N_2$	16.46	16.45	148–148.5^a	12.72	12.80			
C_4H_8O	(morpholine)	80	25	85	222	1.4660	$C_8H_{18}N_2O$	17.71	17.48	140–141	14.32	14.24			
H	$CH(C_2H_5)CH_2OH$	100	50	51	258–260	1.4706	$C_8H_{20}N_2O$	17.49	17.42	159.5–160^k	11.19	11.01	185–186	7.60	7.50
H	$C_{12}H_{25}$	100	48	60	162–163^g	1.4550	$C_{16}H_{36}N_2$	10.93	10.93				102–102.5	6.03	5.95
H	C_6H_5	100	100	19	125–126^g	1.5491	$C_{10}H_{16}N_2$	17.06	16.92	118–119^a	12.88	12.73	117–118^b	7.52	7.47
	^{i}			9	164–165^g	1.5275	$C_{10}H_{16}N_2$	17.06	17.13	156–157	14.03	13.78			
CH_3	C_6H_5	120	100	14	124–125^l	1.5354	$C_{11}H_{18}N_2$	15.72	15.97	112–113	13.41	13.23	115–115.5	9.92	9.93

[a] Diphenylthiourea. [b] Dibenzamide. [c] p-Bromobenzenesulfonamide. [d] M. p., 51–53°. [e] The phenylthiourea derivative of a sample of this compound obtained from Commercial Solvents Corporation through the courtesy of Dr. Murray Senkus gave a m. p. 133°. [f] Forms an oxalate, m. p. 190.5–191°. *Anal.* Calcd. for $C_{12}H_{18}N_2O_4$: N, 11.02. Found: N, 11.07 [g] Boiling point at 3 mm. [h] Forms an oxalate, m. p. 225–226°. *Anal.* Calcd. for $C_{12}H_{18}N_2O_4$: N, 11.02. Found: N, 10.89. [i] Assumed to have the structure $RR'C(NHC_6H_5)CH_2NH_2$. [j] Assumed to have the structure $CH_3CH_2CH(NHC_6H_{11})CH_2NH_2$. [k] Oxalate. [l] Boiling point at 5 mm.

micro Kjeldahl method; and all melting points were taken in a copper block with an ASTM thermometer calibrated for 40-mm. immersion.

Summary

1. An improved method of preparing anhydrous α,β-diamines (both amine groups primary) has been found.

2. A number of α,β-diamines (one amine group primary and the other secondary or tertiary) and their derivatives have been prepared.

3. It has been shown that cyclic ethylenimine rings rupture preferentially but not exclusively at the primary carbon atom in the presence of amines and ammonium chloride, an acid catalyst.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, VICTOR CHEMICAL WORKS]

Allyl Esters of Phosphonic Acids. I. Preparation and Polymerization of Allyl and Methallyl Esters of Some Arylphosphonic Acids

BY A. D. F. TOY

The use of organic esters of phosphoric acid as plasticizers for various resins is well known. These phosphorus containing esters have been of special importance because they not only are good plasticizers, but also impart a certain degree of flame resistance to the resins with which they are used. All these esters are incorporated with the resin as physical mixtures, but their usefulness is probably due to the fact that they serve as excellent hydrogen bonding agents.[1] It was thought to be of interest to study some phosphorus compounds which are not only plasticizers, but which (a) by themselves are capable of undergoing the process of polymerization into a resin or (b) upon mixing with other polymerizable monomers are capable of actually copolymerizing with and modifying the latter. Certain allyl esters of phosphoric acid, and substituted phosphoric acids, have been found to be modifiers for compounds such as styrene through copolymerization.[2] These compounds have been suggested for use in the preparation of polymeric materials.[3]

In our study of the chemistry of the esters of the organic phosphonic acids it has been noted that these substances are significantly different in many respects from the corresponding trisubstituted alkyl and aryl phosphates. For example, dioctyl benzenephosphonate possesses a somewhat higher thermostability than trioctyl phosphate. Likewise

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(1) Audrieth and Toy, THIS JOURNAL, 64, 1553 (1942).

(2) Britton and Marshall, U. S. Patent 2,186,360 (1940).

(3) Whitehill and Barker, U. S. Patent 2,394,829 (1946).

we have found that the allyl phosphonates also have somewhat different properties from those characterizing the related esters of phosphoric acid.

The present paper is the first of a series dealing with the allyl esters of phosphonic acids. The preparation and polymerization of allyl and methallyl esters of benzene-, *p*-toluene- and *p*-chlorobenzenephosphonic acids are described. These substances are capable of being polymerized into hard, transparent, infusible and insoluble resins when heated in the presence of a peroxide catalyst.

In the synthesis of these substances, a new convenient process was developed for the preparation of dichloroarylphosphine oxide based upon the action of chlorine on a slurry of phosphoric anhydride in a dichloroarylphosphine (equation 1).

$$3\mathrm{ArPCl_2} + \mathrm{P_2O_5} + 3\mathrm{Cl_2} \longrightarrow 3\mathrm{ArPOCl_2} + 2\mathrm{POCl_3} \quad (1)$$

The allyl esters were then obtained by reaction between the dichloroarylphosphine oxide and allyl alcohol in the presence of pyridine (equation 2).

$$\mathrm{ArPOCl_2} + 2\mathrm{ROH} + 2\mathrm{C_5H_5N} \longrightarrow \mathrm{ArPO(OR)_2} + 2\mathrm{C_5H_5N.HCl} \quad (2)$$

Experimental

Dichloroarylphosphine Oxides

Dichlorophenylphosphine Oxide.—Dichlorophenylphosphine (1611 g., 9 moles) was placed in a 3-liter 3-necked flask equipped with a reflux condenser, stirrer, thermometer and a chlorine inlet; 511 g., 3.6 moles of finely divided phosphoric anhydride was added and slurried with the dichlorophenylphosphine. Chlorine gas was then passed into the slurry. The heat of reaction caused the temperature to rise to around 150°. However, as more phosphorus oxychloride was formed, it refluxed and lowered the liquid temperature to around 130°. The rate of the introduction of chlorine was such as to maintain steady reflux of the phosphorus oxychloride. The reaction was complete in about four hours as indicated by the fact that the temperature began to drop. The addition of chlorine was then discontinued and the mixture fractionated. After the removal of most of the phosphorus oxychloride at atmospheric pressure, the dichlorophenylphosphine oxide was obtained by distillation under reduced pressure, b. p. 137–138° at 15 mm. or 104° at 4 mm. The yield was 1550 g. (88.4%), n^{25}_{D} 1.5581, sp. gr. 1.197 at 25°. The identity of the product was verified (a) by hydrolysis to benzenephosphonic acid, melts at 161–162° (uncor.), and (b) by the fact that no depression was observed in a mixed melting point determination with the compound obtained by the oxidation of benzenephosphinic acid.

Dichloro-*p*-tolylphosphine Oxide.—In an initial experiment a slurry of 200 g. (1.035 mole) of dichloro-*p*-tolylphosphine and 54 g. (0.38 mole) of phosphoric anhydride was chlorinated at 35–40° to avoid possible ring or side chain chlorination. Upon completion of the reaction, the mixture was fractionated. The dichloro-*p*-tolylphosphine oxide obtained boiled at 140–142° at 11 mm. The yield was found to be 190 g. (87.5%), n^{25}_{D} 1.5542, sp. gr. 1.154 at 25°.

That chlorination of the tolyl radical does not occur is indicated by the fact that even better yields are obtained at higher temperatures. In another experiment the chlorination reaction was carried out rapidly at 145° using 150 g. of dichloro-*p*-tolylphosphine and 40 g. of phosphoric anhydride. A yield of 140 g. (91.7%) was obtained under these conditions.

Anal. Calcd. for $\mathrm{CH_3C_6H_4POCl_2}$: P, 14.8; Cl, 34.0. Found: P, 15.0; Cl, 34.1.

The compound is therefore identical with that previously described by Michaelis and Paneck.[4]

Dichloro-*p*-chlorophenylphosphine Oxide.—A slurry of 200 g. (0.936 mole) of dichloro-*p*-chlorophenylphosphine and 50 g. (0.352 mole) of phosphoric anhydride was chlorinated at 35–40°. Upon completion of the chlorination, the mixture was fractionated. The product so obtained boils at 121–123° at 3 mm. and is a water-white liquid. The yield was found to be 192 g. (88%), n^{25}_{D} 1.5743, sp. gr. 1.302 at 25°. This compound had previously been prepared by Michaelis[5] by the reaction of *p*-chlorophenylphosphorus tetrachloride with sulfur dioxide.

Anal. Calcd. for $\mathrm{ClC_6H_4POCl_2}$: P, 13.5; Cl, 46.5. Found: P, 13.4; Cl, 47.0.

Allyl Esters of Arylphosphonic Acids

Diallyl Benzenephosphonate. (a) By the Action of Dichlorophenylphosphine Oxide on Allyl Alcohol in the Presence of Pyridine.—In a 3-liter 3-necked flask, equipped with a stirrer, a thermometer and a dropping funnel were placed 464 g. (8 moles) of allyl alcohol and 632 g. (8 moles) of pyridine. To this mixture was added with stirring 780 g. (4 moles) of dichlorophenylphosphine oxide. The temperature of the addition was maintained at 2 to 5° by means of an ice-salt-bath. Six hours were required for the addition. Upon completion of the addition the mixture was allowed to come to room temperature. Four hundred cc. of water was then added, the oily layer separated was distilled immediately under reduced pressure. Prolonged standing of the crude wet ester causes some hydrolysis. In effecting the distillation, it was necessary to raise the temperature slowly and during this process, to maintain the pressure at about 20 mm. up to 50°, at less than 10 mm. from 50 to 100°, and at less than 5 mm. up to 120°. In heating the crude ester to the distillation point, gaseous products were evolved which made it difficult to maintain the necessary low pressure unless a high free air capacity pump was used or the heating carried out slowly. Heating of the material too rapidly at too high a pressure caused some decomposition and resulted in low yields of the product. In any event, it was essential to avoid heating the residue to a temperature much above 170°, to prevent rapid decomposition. The distillation of the product was best carried out at 1 to 2 mm. in the presence of a little copper resinate inhibitor. The yield of the distilled product was 777 g. (81.6%), b. p. 128° at 1 mm., n^{25}_{D} 1.5128, sp. gr. 1.1097 at 25°.

Anal. Calcd. for $\mathrm{C_6H_5PO(OCH_2CH{=}CH_2)_2}$: P, 13.0. Found: P, 12.96.

In another experiment, the original reaction was carried out at 25–30° instead of 2–5°. The yield of the distilled product was found to be 71%.

Substitution of dimethylaniline for pyridine was found to give lower yields and a product of lesser purity.

The reactions between dichlorophenylphosphine oxide and allyl alcohol in the presence of pyridine were also carried out using hexane and benzene as reaction media. While pyridine hydrochloride precipitates under these conditions, yields were consistently lower and more difficulty was experienced in working up the reaction mixture for isolation of the diallyl ester. Employment of a 20% excess of allyl alcohol using hexane as solvent did not appreciably increase the yield.

(b) By the Action of Dichlorophenylphosphine Oxide on Sodium Allylate in Toluene Solution.—To 46 g. (2 moles) of sodium dispersed in 2500 cc. of toluene there was added a 100% excess, 232 g. (4 moles) of allyl alcohol at 80–90°. The mixture was heated at 100° until all sodium had disappeared. To this slurry there was then added 195 g. (1 mole) of dichlorophenylphosphine oxide at 0 to 5°. The mixture was allowed to come to room temperature and then heated to 40°. Upon cooling, 900 cc. of water was added and the toluene layer separated and subjected to fractional distillation, yielding 100 g. (42%)

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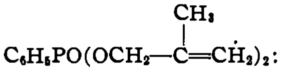
(4) Michaelis and Paneck, *Ann.*, **212**, 203–239 (1882).

(5) Michaelis, *ibid.*, **293**, 193–325 (1896).

of a product, b. p. 148–158° at 6 mm. This yellowish compound was not very pure since it polymerized to give a yellowish gel under conditions where pure diallyl benzenephosphonate would have polymerized into a very hard and strong solid.

The pure diallyl benzenephosphonate is soluble in water to the extent of 2 g. per liter. It is soluble in most of the common organic solvents. It absorbs carbon dioxide readily. It is stable at room temperature with very little change over a period of more than a year. However, when it was stored in the presence of 4.5% benzoyl peroxide, it became a gel after forty days at room temperature.

Dimethallyl Benzenephosphonate.—Three hundred and ninety grams (2 moles) dichlorophenylphosphine oxide was allowed to react with 316 g. (4 moles) of pyridine and 288 g. (4 moles) of methallyl alcohol at 2–5°. The reaction mixture was processed as described for diallyl benzenephosphonate. The water-white product boils at 140–143° at 2–3 mm. The yield was found to be 285 g. (53.5%), $n^{25}D$ 1.5057, sp. gr. 1.0728 at 25°.

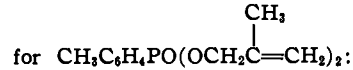


Anal. Calcd. for $C_6H_5PO(OCH_2-\overset{CH_3}{\overset{|}{C}}=CH_2)_2$: P, 11.66. Found: P, 11.84.

Diallyl *p*-Toluenephosphonate.—Seventy grams (0.335 mole) of dichloro-*p*-tolylphosphine oxide was allowed to react with 39 g. (0.67 mole) of allyl alcohol and 53 g. (0.67 mole) of pyridine at 2–5°. The crude diallyl *p*-toluenephosphonate was dried over anhydrous magnesium sulfate and then distilled. It boils at 134–136° at 1 mm. The yield was 47 g. (55.6%), $n^{25}D$ 1.5120, sp. gr. 1.089 at 25°.

Anal. Calcd. for $CH_3C_6H_4PO(OCH_2CH=CH_2)_2$: P, 12.3. Found: P, 12.4.

Dimethallyl *p*-Toluenephosphonate.—Seventy grams (0.335 mole) of dichloro-*p*-tolylphosphine oxide and 48.5 g. (0.67 mole) of methallyl alcohol and 53 g. (0.67 mole) of pyridine were allowed to react under conditions outlined above. The product boils at 146–149° at 1 mm. The yield was found to be 63 g. (67.2%), $n^{25}D$ 1.5070, sp. gr. 1.057 at 25°.

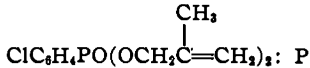


Anal. Calcd. for $CH_3C_6H_4PO(OCH_2\overset{CH_3}{\overset{|}{C}}=CH_2)_2$: P, 11.1. Found: P, 11.1.

Diallyl *p*-Chlorobenzenephosphonate.—Seventy-five grams (0.327 mole) of dichloro-*p*-chlorophenylphosphine oxide was allowed to react with 38 g. (0.655 mole) of allyl alcohol and 52 g. (0.658 mole) of pyridine. The diallyl *p*-chlorobenzenephosphonate was found to boil at 136–139° at 2 mm. The yield was 35 g. (40%), $n^{25}D$ 1.5208.

Anal. Calcd. for $ClC_6H_4PO(OCH_2CH=CH_2)_2$: P, 11.4; Cl, 13.0. Found: P, 11.6; Cl, 13.05.

Dimethallyl *p*-Chlorobenzenephosphonate.—Seventy grams (0.305 mole) of dichloro-*p*-chlorophenylphosphine oxide was allowed to react with 47.5 g. (0.66 mole) of methallyl alcohol and 52 g. (0.66 mole) of pyridine. The dimethallyl *p*-chlorobenzenephosphonate boiled at 137–140° at 1 mm. The yield was found to be 50 g. (53.8%). $n^{25}D$ 1.5162, sp. gr. 1.145 at 25°.



Anal. Calcd. for $ClC_6H_4PO(OCH_2\overset{CH_3}{\overset{|}{C}}=CH_2)_2$: P, 10.3; Cl, 11.8. Found: P, 10.5; Cl, 11.9.

Polymerization

In a preliminary study of the polymerization of the allyl esters of the arylphosphonic acids, it was found that all are capable of polymerizing into hard, clear, infusible and insoluble resins. The first experiments were carried out using 10-cc. samples of the monomer catalyzed with 2% benzoyl peroxide. The solution was put under nitrogen atmosphere and heated in an oil-bath at 85–90°, for eighteen to twenty hours. The monomer first became a viscous liquid, then a gel and finally a hard solid. The color of these resins varied from water-white to light yellow. The hardness of the resins when polymerized under identical conditions was found to depend on the chemical constitution of the monomer. The polymerization characteristics of these esters are very similar to those of the allyl esters of the organic dibasic acids.[6] The allyl arylphosphonate resins were found to possess the interesting property of flame resistance, being self-extinguishing when removed from the flame. The monomeric esters were also found to be capable of copolymerization with such unsaturated organic compounds as vinyl acetate, methyl methacrylate, diallyl esters of organic dibasic acids and unsaturated polyesters.

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Summary

1. The preparation of dichlorophenyl-, dichloro-*p*-tolyl- and dichloro-*p*-chlorophenylphosphine oxides may be affected readily by chlorination of a slurry of phosphoric anhydride and the corresponding dichloroarylphosphine.

2. The dichloroarylphosphine oxides have been converted into the diallyl and dimethallyl esters of the arylphosphonic acids by action of the respective alcohols in the presence of pyridine.

3. The diallyl and dimethallyl esters of benzene-, *p*-toluene- and *p*-chlorobenzenephosphonic acids undergo peroxide catalyzed polymerization to form clear, infusible, insoluble resins and also are capable of copolymerization with various unsaturated organic compounds.

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