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New Methods of Preparing Phosphonates

BY RICHARD L. MCCONNELL AND HARRY W. COOVER, JR.

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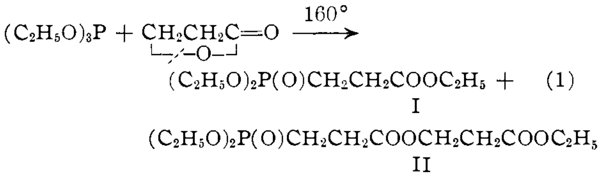
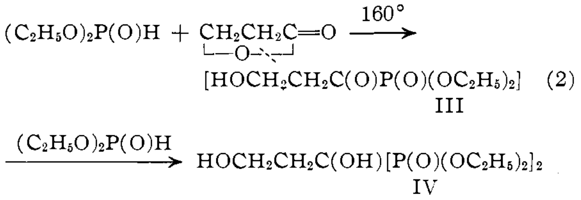
Trialkyl phosphites attack β-propiolactone at the β-carbon atom, causing an alkyl–oxygen cleavage of the lactone ring, to yield alkyl 3-(dialkylphosphono)-propionates. Dialkyl hydrogen phosphites cause an acyl–oxygen cleavage of β-propiolactone to yield dialkyl 3-hydroxypropionylphosphonates as intermediates which, in turn, react with more dialkyl hydrogen phosphite to produce tetraalkyl 1,3-dihydroxypropylidenediphosphonates. Thus dialkyl and trialkyl phosphites open the lactone ring in different ways. γ-Lactones, which are more stable, also react successfully but higher temperatures are required. These interactions of lactones and phosphites may be effected without catalysts; however, they are catalyzed by basic reagents such as tertiary amines, sodium alkoxides and sodium dialkyl phosphites. Dialkyl and trialkyl phosphites appear to open the lactam ring of caprolactam in the same manner. The products are 5-carbamoylpentylphosphonates.

During the investigation of the interaction of phosphites with β-propiolactone, we found that dialkyl hydrogen phosphites[1] and trialkyl phosphites[2] open the lactone ring in different ways.



$$(C_2H_5O)_3P + \underset{\llcorner\!-O-\!\lrcorner}{CH_2CH_2C{=}O} \xrightarrow{160^\circ} \underset{\text{I}}{(C_2H_5O)_2P(O)CH_2CH_2COOC_2H_5} + \underset{\text{II}}{(C_2H_5O)_2P(O)CH_2CH_2COOCH_2CH_2COOC_2H_5} \quad (1)$$



$$(C_2H_5O)_2P(O)H + \underset{\llcorner\!-O-\!\lrcorner}{CH_2CH_2C{=}O} \xrightarrow{160^\circ} \underset{\text{III}}{[HOCH_2CH_2C(O)P(O)(OC_2H_5)_2]} \quad (2)$$
$$\xrightarrow{(C_2H_5O)_2P(O)H} \underset{\text{IV}}{HOCH_2CH_2C(OH)[P(O)(OC_2H_5)_2]_2}$$

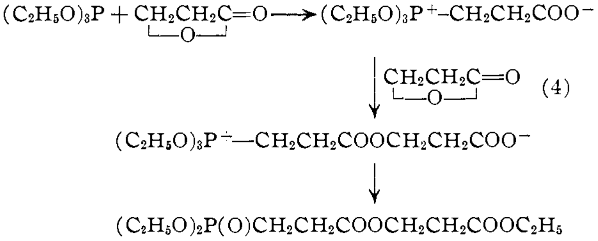
In reaction 1, the primary product is ethyl 3-diethylphosphonopropionate (I).[2] A small amount of II also is obtained. The triethyl phosphite is basic owing to the unshared pair of electrons on the phosphorus atom. This basic reagent attacks the lactone at the β-carbon atom, causing an alkyl–oxygen fission of the lactone ring. This is analogous to the action of ammonia, dimethylamine and ethylamine.[3] However, methylamine, diethylamine and propylamine give mostly acyl–oxygen cleavage.[3] There appears to be no correlation between the basic strength of the attacking reagent and the relative amounts of alkyl–oxygen and acyl–oxygen cleavage.

The structure of I was proved by preparing a sample of this compound by an Arbuzov reaction.

$$(C_2H_5O)_3P + BrCH_2CH_2COOC_2H_5 \longrightarrow \underset{\text{I}}{(C_2H_5O)_2P(O)CH_2CH_2COOC_2H_5} + C_2H_5Br \quad (3)$$

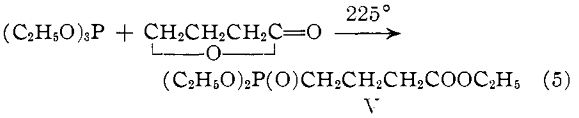
The physical properties and the infrared spectra of the materials obtained from the reactions illustrated by equations 1 and 3 were identical.

Probably the presence of compound II can be explained by the interaction of triethyl phosphite with a β-propiolactone molecule to produce a carboxylate ion, $(C_2H_5O)_3P^+{-}CH_2CH_2COO^-$; this ion then reacts with a second β-propiolactone molecule to produce a new carboxylate ion which is converted to the ethyl ester. The postulated reactions are shown in the equation



$$\begin{aligned} &(C_2H_5O)_3P + \underset{\llcorner\!-O-\!\lrcorner}{CH_2CH_2C{=}O} \longrightarrow (C_2H_5O)_3P^+{-}CH_2CH_2COO^- \\ &\qquad\Big\downarrow \underset{\llcorner\!-O-\!\lrcorner}{CH_2CH_2C{=}O} \quad (4) \\ &(C_2H_5O)_3P^+{-}CH_2CH_2COOCH_2CH_2COO^- \\ &\qquad\Big\downarrow \\ &(C_2H_5O)_2P(O)CH_2CH_2COOCH_2CH_2COOC_2H_5 \end{aligned}$$

γ-Butyrolactone reacted in a manner similar to β-propiolactone except that a higher temperature (225°) was required to open the γ-lactone ring, which is more stable. In this case, ethyl 4-(diethylphosphono)-butyrate (V) was the product.



$$(C_2H_5O)_3P + \underset{\llcorner\!--O--\!\lrcorner}{CH_2CH_2CH_2C{=}O} \xrightarrow{225^\circ} \underset{\text{V}}{(C_2H_5O)_2P(O)CH_2CH_2CH_2COOC_2H_5} \quad (5)$$

In reaction 2, diethyl hydrogen phosphite reacts with β-propiolactone to form tetraethyl 1,3-dihydroxypropylidenediphosphonate (IV).[1] This reaction, therefore, involves acyl–oxygen cleavage of the lactone ring to form III as an intermediate which, in turn, adds a second molecule of diethyl hydrogen phosphite at the carbonyl position to form IV.

It is not surprising that dialkyl hydrogen phosphites and trialkyl phosphites cause cleavages of the lactone ring in different positions since the former contain a replaceable hydrogen whereas the latter are basic in nature. It is interesting to note, however, that carboxylic acids attack at the β-carbon atom of β-propiolactone and produce an alkyl–oxygen cleavage.[4]

We also found that bases such as tertiary amines and sodium alkoxides catalyze the reaction of lactones with phosphites. In the presence of triethylamine or sodium methoxide, reactions illustrated by equations 1 and 2 take place at 25° rather than at reflux temperature (155–160°). Also, the reactions are completed in a much shorter time when a catalyst is used.

The presence of a catalyst tends to increase the

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[1] R. L. McConnell and H. W. Coover, Jr., THIS JOURNAL, **78**, 4450 (1956).

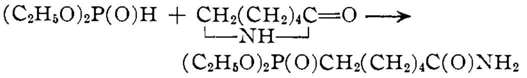
[2] H. W. Coover, Jr., and J. B. Dickey (to Eastman Kodak Company), U. S. Patent 2,652,416 (1953).

[3] T. L. Gresham, J. E. Jansen, F. W. Shaver, R. A. Bankert and F. T. Fiedorek, THIS JOURNAL, **73**, 3168 (1951).

[4] T. L. Gresham, J. E. Jansen and F. W. Shaver, *ibid.*, **72**, 72 (1950).

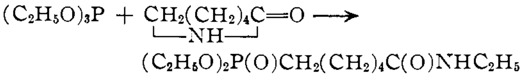
amount of polymer obtained from these reactions. The specific products obtained can be controlled by the ratio of reactants. For example, if equimolar quantities of β-propiolactone and triethyl phosphite are treated in the presence of triethylamine, the main products are $(C_2H_5O)_2P(O)CH_2CH_2COOCH_2CH_2COOC_2H_5$ (II) and $(C_2H_5O)_2P(O)CH_2CH_2CO(OCH_2CH_2CO)_2OC_2H_5$ (VI). If a 100% excess of triethyl phosphite is used, a small yield of I is obtained in addition to II, VI and $(C_2H_5O)_2P(O)CH_2CH_2CO(OCH_2CH_2CO)_nOC_2H_5$ (VII). When less than one mole of triethyl phosphite per mole of β-propiolactone is used, the reaction becomes a telomerization exclusively and polymeric materials, VII, which contain a diethylphosphono end group are obtained. These products range from viscous oils (mol. wt. about 500) to white solids (mol. wt. about 1150). Sodium methoxide tends to give higher molecular weight telomers than triethylamine. This is probably related to the stronger basicity of the sodium methoxide.

We also investigated the reaction of phosphites with lactams.



$$(C_2H_5O)_2P(O)H + \underbrace{CH_2(CH_2)_4C{=}O}_{NH} \longrightarrow (C_2H_5O)_2P(O)CH_2(CH_2)_4C(O)NH_2 \quad (6)$$

VIII



$$(C_2H_5O)_3P + \underbrace{CH_2(CH_2)_4C{=}O}_{NH} \longrightarrow (C_2H_5O)_2P(O)CH_2(CH_2)_4C(O)NHC_2H_5 \quad (7)$$

IX

The lactams were found to be much less reactive than the lactones. Diethyl hydrogen phosphite opened the lactam ring (reaction 6) to produce a phosphonosubstituted carboxamide VIII. It was assigned that structure rather than the isomeric structure, $NH_2CH_2(CH_2)_4C(O)P(O)(OC_2H_5)_2$, because of the following facts. The product readily liberated ammonia when treated with an aqueous sodium hydroxide solution and had none of the properties of an amine. Also, it seems likely that, if the acylphosphonate structure had formed, diethyl hydrogen phosphite would have added to the carbonyl group to yield a hydroxyalkylidenediphosphonate, as in reaction 2. Furthermore, infrared absorption analysis showed bands typical of a carboxamide. A considerable amount of a viscous, red, polymeric, phosphorus-containing material which was water-soluble was also obtained. Even though a large excess of diethyl phosphite was used, this polymeric material was always obtained. It is interesting to note that diethyl hydrogen phosphite opens the lactone and lactam rings in opposite ways.

A small yield of a distillable product was obtained by reaction 7; however, some unreacted caprolactam always distilled with it. Most of this caprolactam impurity would crystallize from the oily product on standing; however, the phosphorus derivative was never obtained analytically pure. Again a large amount of viscous, non-distillable, polymeric material was obtained, probably as the result of a telomerization reaction. The phosphorus derivative IX liberated a volatile base when treated with aqueous sodium hydroxide and had no amine properties, again indicating a carboxamide structure. Thus, both diethyl hydrogen phosphite and triethyl phosphite appear to open the lactam ring in the same way. Best results were obtained with the reactions illustrated by equations 6 and 7 when a 100% excess of the phosphite was used.

In an attempt to polymerize caprolactam using catalytic amounts (5 mole %) of diethyl hydrogen phosphite or triethyl phosphite at the same reaction temperature (160°) used in reactions 6 and 7, unchanged caprolactam was recovered almost quantitatively.

Experimental

Ethyl 3-Diethylphosphonopropionate (I). (**Method A**).—Triethyl phosphite (33.2 g., 0.2 mole) and β-propiolactone (14.4 g., 0.2 mole) were mixed and heated to gentle reflux (155–160°) for 16 hours. Fractionation of the reaction mixture yielded 15.0 g. (32%) of the desired colorless phosphonate, b.p. 128–133° (2.6 mm.), n^{20}_D 1.4332, d^{20}_4 1.1009.

Anal. Calcd. for $C_9H_{19}O_5P$: C, 45.37; H, 8.04. Found: C, 45.10; H, 8.06.

After a small intermediate cut (1 g.) was collected, 6.0 g. (10%) of $(C_2H_5O)_2P(O)CH_2CH_2COOCH_2CH_2COOC_2H_5$ (II), was obtained, b.p. 175–177° (1.3 mm.), n^{20}_D 1.4440.

Anal. Calcd. for $C_{12}H_{23}O_7P$: P, 9.98. Found: P, 10.14, 10.20.

The distillation residue amounted to 10 g. and contained 8.92% phosphorus.

(**Method B**).—Triethyl phosphite (66.4 g., 0.4 mole) and ethyl 3-bromopropionate (36.2 g., 0.2 mole) were mixed and heated to reflux for 4 hours. By this time the evolution of ethyl bromide was complete. After distilling off the excess triethyl phosphite, 24.0 g. (50%) of product boiling at 127–129° (2.3 mm.), n^{20}_D 1.4334, d^{20}_4 1.0974, was obtained. The infrared absorption curve for this sample was identical with that obtained by method A.

(**Method C**).—Triethyl phosphite (135 g., 0.8 mole) and β-propiolactone (28.8 g., 0.4 mole) were mixed and stirred while triethylamine (5 ml.) was added. The temperature gradually rose to a maximum of 38°. The reaction mixture was stirred for 6 hours. After removing the excess triethyl phosphite, 9.5 g. (10%) of product boiling at 140–145° (5 mm.), n^{20}_D 1.4330, was obtained. The distillation residue was a light-yellow oil which contained 6.86% phosphorus.

(**Method D**).—The reaction described in method C was repeated using powdered sodium methoxide (0.5 g.) instead of triethylamine. The product consisted of 8.5 g. (9.0%) of I, b.p. 132–140° (4.0–4.3 mm.), n^{20}_D 1.4331. Some white solid (3.0 g.) precipitated from the light-yellow oil which remained as a distillation residue. The solid telomers had an average molecular weight of 1147 (ebulliometric determination in benzene). The oil had an average molecular weight of 460.

The following characteristic absorption bands were observed from the infrared spectra of samples of I

Absorption band, μ	Assignment	Absorption band, μ	Assignment
5.8	C═O (ester)	8.6	P—O—C_2H_5
8.0	P═O	9.7	C—OP
8.45	C—O (ester)	10.35	P—OC

Ethyl O-(3-Diethylphosphonopropionyl)-hydracrylate (II) **and Dihydracrylate** (VI) $(C_2H_5O)_2P(O)CH_2CH_2CO(OCH_2CH_2CO)_2OC_2H_5$.—Triethyl phosphite (66.4 g., 0.4 mole) and β-propiolactone (28.8 g., 0.4 mole) were mixed and triethylamine (5 ml.) was added with stirring. The temperature gradually rose to 130° over 30 minutes. The reaction mixture was stirred for 3 hours and then allowed to stand overnight. After removing the unreacted triethyl phosphite (34 ml.), the hydracrylate II (17 g.) was obtained, b.p. 130–140° (0.4 mm.).

Anal. Calcd. for $C_{12}H_{23}O_7P$: P, 9.98. Found: P, 10.02, 10.23.

The next fraction was VI (19 g.), b.p. 144–151° (0.4 mm.), n^{20}_D 1.4493.

Anal. Calcd. for $C_{15}H_{27}O_9P$: P, 8.10. Found: P, 8.07.

The distillation residue was negligible.

Ethyl O-(3-Diethylphosphonopropionyl)-polyhydracrylate (VII).—Triethyl phosphite (16.6 g., 0.1 mole) and β-propiolactone (28.8 g., 0.4 mole) were mixed and cooled in a water-bath while triethylamine (5 ml.) was added dropwise with vigorous stirring. The temperature rose to 40° and remained there for 30 minutes. The water-bath was removed and the reaction mixture was stirred for 4 hours, then allowed to stand overnight. The unreacted starting materials were removed by distilling to a temperature of 65° (3.0 mm.). The product, obtained as residue, was a viscous, light-yellow oil, $n^{20}D$ 1.4570, having an average molecular weight of 490 (ebulliometric determination in benzene).

Ethyl 4-(Diethylphosphono)-butyrate (V). (Method A).—Triethyl phosphite (66.4 g., 0.4 mole) and γ-butyrolactone (34.4 g., 0.4 mole) were mixed in a rocking autoclave and reacted at 225° for 36 hours. After unreacted starting materials had been removed, 12 g. (12%) of V, b.p. 129–133° (1.8 mm.), $n^{20}D$ 1.4382, $d^{20}{}_4$ 1.1069, was obtained.

Anal. Calcd. for $C_{10}H_{21}O_5P$: P, 12.28. Found: P, 12.18, 12.13.

(Method B).—Triethyl phosphite (166 g., 1.0 mole) was treated with ethyl 4-bromobutyrate (195 g., 1.0 mole) in a typical Arbuzov reaction. The product (111.6 g., 44%) was collected at 138–148° (3.2 mm.). Upon redistillation, it boiled at 117–119° (0.4 mm.), $n^{20}D$ 1.4391, $d^{20}{}_4$ 1.0860.

Anal. Calcd. for $C_{10}H_{21}O_5P$: C, 47.61; H, 8.39; P, 12.28. Found: C, 47.62; H, 8.18; P, 12.15.

The infrared spectra of samples of V obtained by methods A and B were identical. The following characteristic absorption bands were observed from their spectra

Absorption band, μ	Assignment	Absorption band, μ	Assignment
5.8	C=O (ester)	8.6	P–O–C_2H_5
8.0	P=O	9.7	C–OP
8.5	C–O (ester)	10.4	P–OC

Diethyl 5-(Carbamoylpentyl)-phosphonate (VIII).—Caprolactam (22.6 g., 0.2 mole) and diethyl hydrogen phosphite (55.2 g., 0.4 mole) were mixed and heated at 160° for 8 hours. Fractionation of the reaction mixture gave 31.0 g. of unreacted diethyl hydrogen phosphite, b.p. 51–52° (0.7 mm.), an intermediate cut of 3.5 g., b.p. 53–105° (0.7 mm.), and 12 g. (24%) of product, b.p. 105–108° (0.5–1.0 mm.), $n^{20}D$ 1.4418, $d^{20}{}_4$ 1.0608.

Anal. Calcd. for $C_{10}H_{22}NO_4P$: N, 5.57; P, 12.33. Found: N, 5.39; P, 12.83, 12.93.

The distillation residue amounted to 26.6 g. of transparent, amber resinous material which contained 6.86% nitrogen and 11.84% phosphorus. Both VIII and the residue liberated a volatile base when treated with aqueous sodium hydroxide. The following characteristic absorption bands were observed from the infrared spectrum of VIII

Absorption band, μ	Assignment	Absorption band, μ	Assignment
3.05, 3.24	NH_2 (amide)	8.6	P–O–C_2H_5
6.05	C=O (amide)	9.6	C–OP
8.0	P=O	10.25	P–OC

Reaction Product of Caprolactam and Triethyl Phosphite.—Caprolactam (11.3 g., 0.1 mole) and triethyl phosphite (33.2 g., 0.2 mole) were mixed and refluxed for 32 hours at 165–170°. After removing the excess triethyl phosphite, 7.5 g. of distillate boiling at 106–109° (1.6 mm.) was obtained. After standing for a few minutes, 2.0 g. of caprolactam (m.p. 67–68°) crystallized from the distillate, leaving a light-yellow oil, $n^{20}D$ 1.4790.

Anal. Calcd. for $C_{12}H_{26}NO_4P$: N, 5.02; P, 11.09. Found: N, 7.10; P, 8.58, 8.71.

The product apparently still contained some dissolved caprolactam since the nitrogen and phosphorus analyses obtained were intermediate between the values required for IX and caprolactam. The distillation residue amounted to 9 g. and was a viscous, amber colored, water-soluble liquid which contained both phosphorus and nitrogen. Both the distillate and the residue liberated a volatile base when treated with aqueous sodium hydroxide.

Acknowledgment.—We would like to express our appreciation to Mr. J. H. Chaudet and Mr. Cham Canon for their help in interpreting the infrared data presented.

KINGSPORT, TENN.

[CONTRIBUTION FROM RESEARCH LABORATORIES OF VICTOR CHEMICAL WORKS]

Phenoxymethylphosphonic Acids and Phosphonic Acid Ion-exchange Resins[1]

BY EDWARD N. WALSH, THOMAS M. BECK AND A. D. F. TOY

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A series of substituted phenoxymethylphosphonic acids has been prepared from the reaction of sodium phenoxides with disodium chloromethylphosphonate. These acids condense with formaldehyde under alkaline conditions to form methylolated phenoxymethylphosphonic acids, analogous to saligenin, and when heated under acidic conditions with excess formaldehyde, form insoluble thermosetting resins which possess ion-exchange properties. Phenoxymethylphosphonic acid resins behave as dibasic acids having equivalence points at *p*H 5.0 and *p*H 10.2. The preference of the resin for ions was determined.

Introduction

A series of substituted phenoxymethylphosphonic acids[2] was prepared, originally for evaluation as herbicides. The method of preparation, analogous to that of aryloxyacetic acids[3] except for the higher temperatures required, is shown in equation 1.

$$C_6H_5ONa + ClCH_2PO_3Na_2 \xrightarrow{2\ HCl} C_6H_5OCH_2PO_3H_2 + 3NaCl + H_2O \quad (1)$$

These new compounds are listed in Table I.

In the course of this investigation phenoxymethylphosphonic acid was found to condense with formaldehyde in a reaction similar to the condensation of phenol with formaldehyde[4] to form resinous products. When disodium phenoxymethylphosphonate is refluxed with an excess of aqueous formaldehyde, a saligenin type compound is formed in accord with equation 2, which will not

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[1] Presented before the Division of Organic Chemistry, 127th National Meeting, American Chemical Society, Cincinnati, Ohio, March 29 to April 7, 1955.

[2] The preparation of sodium alkyl 2,4-dichlorophenoxymethylphosphonates by a method similar to ours was recently reported by Maguire, *et al.*: M. H. Maguire, G. Shaw and C. G. Greenham, *Chemistry and Industry*, **27**, 668 (1953); M. H. Maguire and G. Shaw, *J. Chem. Soc.*, 1756 (1955); G. Greenham, *Australian J. Sci.*, **16**, 66 (1953).

[3] W. Heintz, *Ann. Physik*, **109**, 489 (1860); *Jahresber. Fort. Chem.*, 361 (1859).

[4] L. Lederer, *J. prakt. Chem.*, **50**, 224 (1894); O. Manasse, *Ber.*, **27**, 2408 (1894).