736. *The Dissociation Constants of Some Cyclic Phosphinic Acids.*

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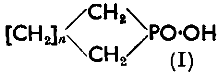
Synthesis of tetramethylene- and trimethylene-phosphinic acid was accomplished by organometallic routes. These acids and the previously reported pentamethylenephosphinic acid were shown to possess acidic dissociation constants indicative of stronger acidic properties than shown by analogous dialkylphosphinic acids.

In continuation of a study of acidic properties of acids of phosphorus,[1] we prepared and examined tetramethylene- and trimethylene-phosphinic acid (I; *n* = 2 and 1, respectively), as progressively more strained cyclic analogues of the previously reported pentamethylenephosphinic acid.[2]



(I)

The yield of tetramethylenephosphinic acid, prepared as described for the pentamethylene analogue,[2] was only 0·1% and, although models show no steric strain to account for this, they do account for the still smaller yield of the trimethylene analogue, which was prepared by ring closure of 3-bromopropylphosphonic dichloride, with magnesium, because of the impossibility of preparing the bifunctional Grignard reagent from 1 : 3-dibromopropane.

The apparent p*K* values for acidic dissociation of these acids, as well as for the analogous dialkylphosphinic acids, are shown in the Table.

Acid	pK_a'	Acid	pK_a'
$[CH_2]_3{>}PO_2H$	3·07	Me_2PO_2H [1]	3·08
$[CH_2]_4{>}PO_2H$	2·51	Et_2PO_2H [1]	3·29
$[CH_2]_5{>}PO_2H$	2·73	$Pr^n{}_2PO_2H$ [1]	3·46

It is evident that the cyclic acids are somewhat stronger acids than are their dialkyl, or open chain, analogues. There is not evident any definite trend of acidity amongst the three cyclic members reported here, *i.e.*, no relation of acidity to position in the homologous series. This is contrary to what was discovered by us amongst the dialkylphosphinic acids,[1] which showed excellent correlation of acidity with structure.

EXPERIMENTAL

Tetramethylenephosphinic Acid.—The acid was prepared by the method used previously for the synthesis of pentamethylenephosphinic acid,[2] but with the bifunctional Grignard reagent from tetramethylene bromide. The crude acid was converted by means of phosphorus pentachloride into its chloride which boiled at 1·3 mm. over the range of 64—107° and was effectively separated from polymeric materials. The crude chloride was hydrolysed to the free acid by means of warm water and the acid was isolated by evaporation, dissolution in a small volume of benzene, and precipitation with *n*-heptane. The acid was finally purified by extraction with hot *n*-heptane and cooling; the acid formed colourless flakes which, after being dried *in vacuo*, melted at 99—100° (Found: P, 25·6. $C_4H_9O_2P$ requires P, 25·8%). The yield of the pure *acid* was 100 mg. from 93 g. of tetramethylene bromide.

Trimethylenephosphinic Acid.—Trimethylene bromide (202 g.) and triethyl phosphite (33·2 g., 5 mols.) were refluxed until the evolution of ethyl bromide had ceased. The resulting diethyl 3-bromopropylphosphonate was hydrolysed *in situ* with 48% hydrobromic acid as described previously.[3] The acid, m. p. 106—107°, was obtained in average yield of 88%. This acid (30 g.) was treated with phosphorus pentachloride (65 g.), suspended in carbon tetrachloride (250 ml.), and yielded, after 2 hours' refluxing, 3-bromopropylphosphonic dichloride (14·7 g., 40%), b. p. 153—156°/23 mm. The relatively low yield of the dichloride was caused by the formation of undistillable tar during the distillation. The dichloride decomposes rather vigorously, with evolution of hydrogen bromide, when heated to ~180°. The dichloride was also prepared through the corresponding di*iso*propyl ester, b. p. 100°/1 mm., obtained in 56·5% yield from trimethylene bromide (300 g.) and tri*iso*propyl phosphite (100 g.); the yield of

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[1] Crofts and Kosolapoff, *J. Amer. Chem. Soc.*, 1953, **75**, 3379.
[2] Kosolapoff, *ibid.*, 1955, **77**, 6658.
[3] Kosolapoff, *ibid.*, 1944, **66**, 1511.

the ester was relatively poor because of incipient decomposition and evolution of hydrogen bromide which began after a major part of the ester had distilled.

3-Bromopropylphosphonic dichloride (93·1 g.), in dry ether (50 ml.), was added during 34 hr. to a stirred mixture of ether (600 ml.), magnesium turnings (9·4 g.) and iodine (1 crystal), under gentle reflux. Refluxing for 12 hr. gave no evidence of further reaction, the mixture at this juncture containing an orange-red precipitate (some 30 g.) and some 2 g. of magnesium. These components were separated mechanically. The ethereal solution was worked up as described for the tetramethylene and the pentamethylene analogues,[2] yielding a very small amount of a wax which was combined with the major part of the product described below. The orange-red solid was treated with ice and hydrochloric acid: a strong " phosphine " odour then became evident, indicating the presence of either tervalent phosphorus compounds or those with a phosphorus–phosphorus link. Accordingly, the crude aqueous solution was treated with 30% hydrogen peroxide (20 ml.) to oxidize any such substances to the quinquevalent state. The resulting solution was concentrated to remove the bulk of excess of hydrochloric acid, and the residual solution was freed from magnesium ions by means of an ion-exchange resin, and from the bulk of polymeric products and phosphonic acids by treatment with barium hydroxide, as described previously.[2] The resulting crude product was distillable in a high vacuum at approximately 100—120°, but the distilled product failed to crystallise. It was taken up in water, along with the small amount of product derived from the ethereal solution, described above, and neutralised with lead oxide at 50—60°. The clear filtrate from the precipitated insoluble lead salts (and excess of lead oxide) was treated with hydrogen sulphide. The residual solution, after removal of lead sulphide, was evaporated to dryness, yielding a colourless solid, which was extracted for 5 days with boiling benzene. The extract on evaporation gave 12 mg. of *trimethylenephosphinic acid* which melted unsharply at 65°, passing into a glass from which it crystallised to small flat needles only with extreme slowness (Found: P, 29·0. $C_3H_7O_2P$ requires P, 29·2%).

One of the runs in which 3-bromopropylphosphonic acid was prepared gave a curious by-product. During the hydrolysis of the crude ester with hydrobromic acid a dense liquid was formed. This was separated and distilled, without decomposition. The substance, a colourless liquid, had b. p. 176—178°/15 mm., 124—125°/1·2 mm., d_4^{26} 2·0312, n_D^{26} 1·6237, and molecular weight (determined ebullioscopically in benzene) 583. The substance was free from phosphorus and contained 70·4% of bromine. These data are not inconsistent with a pentabromododecane which might result from tetramerization of trimethylene bromide, possibly through formation of allyl bromide, with subsequent addition of hydrogen bromide. This material was not observed in several other runs made apparently under identical conditions.

Dissociation Constants.—These were calculated from titration data as described earlier.[1]

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