give normal molecular weight values;[6] in other words, there is no evidence of polymerization. It may be concluded, therefore, that the hydrogen bonds which link the molecules together in the solid state are disrupted in acetic acid solution. It seems likely that in aqueous solution also phosphonic and phosphinic acids exist as single solvated molecules.

EXPERIMENTAL

With the exception of benzoic acid, all compounds studied were prepared or purified in this laboratory and were shown to be pure by analysis for at least one element. Further information on the compounds is given in the footnotes to Table I. The acetic acid used as the solvent was dried over Drierite and distilled before use. In order to avoid absorption of atmospheric moisture during the cryoscopic measurements, the modified Beckman apparatus previously described[7] was used. The concentration of solute was chosen to give a reasonable value of Δt and, with the exception of phosphafluorinic acid, does not represent the maximum concentration which can be obtained at the freezing point of acetic acid.

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[6] Normal molecular weights have been reported for tetralinephosphonic acid by Akashi, Hanabusa, and Oda, *J. Chem. Soc., Japan, Ind. Chem. Sect.*, **56**, 970 (1953) and for trimethylsilylmethylphosphonic acid by Keeber and Post, *J. Org. Chem.*, **21**, 509 (1956). In neither paper, however, is the solvent mentioned or any experimental details given.

[7] Doak, *J. Am. Chem. Soc.*, **68**, 1991 (1946).

Pentaerythritol Derivatives. III. 2,6-Dioxaspiro[3,3]heptane

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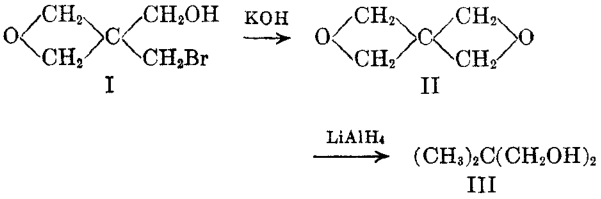
In a previous paper[1] we described the preparation of a new trimethylene oxide derivative of pentaerythritol to which we assigned the structure 3-bromomethyl-3-hydroxymethyloxetane (I). We would now like to present some further evidence for the proposed structure.



Treatment of I with potassium hydroxide gives 2,6-dioxaspiro[3,3]heptane (II) in a yield which, although poor (34%), compares favorably with that obtained by other methods (17–25%).[2,3]

Reduction of the spirocyclic compound with lithium aluminum hydride gives 2,2 dimethyl-1,3-propanediol (III). This reduction is very similar tc the reduction of 1,2-epoxides by lithium aluminum hydride and gives the expected product (III) in satisfactory yield.

EXPERIMENTAL[4]

2,6-Dioxaspiro[3,3]heptane (II). A mixture of 150 g. of potassium hydroxide and 20 ml. of water was placed in a flask fitted with an efficient stirrer, a dropping-funnel, and a condenser (set for downward distillation and connected through a receiver to a vacuum pump). The flask was surrounded by a heating bath kept at 120–130° and the pressure of the system was regulated at approximately 10 mm. While stirring vigorously, 40 g. of 3-bromomethyl-3-hydroxymethyloxetane (0.22 mole) was added dropwise to the mixture. After the addition was complete, the temperature of the bath was raised to 150° at 6 mm. and kept there until no more product distilled. The crude product (which usually solidifies in the condenser) was collected and recrystallized from 80–100° petroleum ether to give 7.5 g. (34%) of II melting at 89–90° (lit. m.p. 89–90°).[2]

2,2-Dimethyl-1,3-propanediol (III). To a well stirred mixture of 3.5 g. of lithium aluminum hydride (0.092 mole) in 40 ml. of dry tetrahydrofuran was added in the course of one hour a solution of 3.8 g. (0.038 mole) of 2,6-dioxaspiro[3,3]heptane in 60 ml. of tetrahydrofuran. The mixture was refluxed gently for 12 hours, concentrated by removal of about 50 ml. of solvent by distillation, treated successively with 12 ml. of ethyl acetate and 40 ml. of 6 N sulfuric acid, and finally steam-distilled. The residue from the steam-distillation was extracted repeatedly with ether. The combined ether extracts gave a crude product which was recrystallized from toluene to give 2.2 g. of III (56%) melting at 128–130°. A mixture with an authentic sample of neopentyl glycol melted at the same temperature.

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[1] Issidorides, Gulen, and Aprahamian, *J. Org. Chem.*, **21**, 997 (1956).

[2] Backer and Keuning, *Rec. trav. chim.*, **53**, 798 (1934); Govaert and Beyaert, *Proc. Acad. Sci. Amsterdam*, **7** (1939).

[3] Wawzonek and Issidorides, *J. Am. Chem. Soc.*, **75**, 2373 (1953).

[4] Melting points are not corrected.