methanol caused elution of a yellow solid that was crystallized from aqueous methanol, m.p. 197.5–198.5°.

Anal. Calc'd for $C_{20}H_{24}N_2O_7$: N, 6.93. Found: N, 6.97.

Bromopicrin split. The procedures for the bromopicrin split and the isolation of tribromonitromethane have been described.[5] Method B was employed. From 48 mg. of 2,4-dinitroestradiol-17β there was obtained 30.5 mg. of tribromonitromethane. The infrared spectrum of this material was compared with the spectrum of a sample of tribromonitromethane from Eastman Kodak that was vacuum-distilled. The spectra were identical except for a few additional weak bands in the bromopicrin from the cleavage of the dinitrosteroid, indicating the presence of a minor component.[8] After evaporation of the bromopicrin on a watchglass at room temperature, a few micrograms of colorless crystals remained, subliming at 123–127°, ν_{Max}^{KBr} 1475, 1442, 1323, 1118, 1058, 881, and 642 cm.$^{-1}$. These bands accounted for the weak bands in the spectrum of the bromopicrin from the degradation of the dinitrosteroid. The small quantity precluded identification.

ARGONNE CANCER RESEARCH HOSPITAL AND
THE DEPARTMENT OF BIOCHEMISTRY.
THE UNIVERSITY OF CHICAGO
CHICAGO 37, ILLINOIS

(8) Scholl and Brenneisen, *Ber.*, **31**, 654 (1898), isolated dibromodinitromethane, m.p. 10°, as a minor component of tribromonitromethane resulting from the bromopicrin split of picric acid.

The Molecular Weights of Phosphonic and Phosphinic Acids

LEON D. FREEDMAN AND G. O. DOAK

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There is considerable evidence that phosphonic and phosphinic[1] acids are associated in the solid state and in certain organic solvents by hydrogen bond formation. This concept is supported by infrared absorption studies[2] and by molecular weight determinations.[3] On the other hand, freezing point depressions obtained with several phosphonic acids in aqueous solution are *larger* than the calculated values based on monomolecular formulas.[3c] Although these results are difficult to interpret unambiguously, since there must be considerable acidic dissociation in aqueous solutions of these acids, it has been suggested[3b,c,4] that hydrogen bonded aggregates of phosphonic acid molecules are present even in aqueous solution and are in fact responsible for the formation of relatively insoluble "acid" salts when solutions of phosphonic acids are partially neutralized.

Because of the low energy content of the hydrogen bond and the low activation energy involved in its formation and rupture, most types of molecules that are associated by hydrogen bonds dissociate rapidly when dissolved in polar solvents such as water, acetic, and formic acids.[5] For example, carboxylic acids, which are associated in the solid and vapor state and in non-polar solvents, exist in the monomeric form in acetic acid solution.[5] Unless the hydrogen bonds present in organophosphorus acids are extraordinarily strong, one would expect these compounds also to be present in polar solvents as single molecules.

After we found that many phosphonic and phosphinic acids are easily soluble in acetic acid, we used this solvent for cryoscopic molecular weight determinations of a number of aromatic, aliphatic, and alicyclic compounds. The results obtained are listed in Table I. It is seen that all the compounds

TABLE I

CRYOSCOPIC MOLECULAR WEIGHT DETERMINATIONS IN ACETIC ACID

Compound	Δt, °C.	Molecular Weight Calc'd	Found
	RPO_3H_2		
Ethylphosphonic acid[a]	0.393	110.0	110.6
n-Butylphosphonic acid[b]	.350	138.1	137.9
Cyclohexylphosphonic acid[c]	.251	164.1	165.9
Phenylphosphonic acid[d]	.266	158.1	164.1
p-Tolylphosphonic acid[d]	.375	172.1	171.4
	R_2PO_2H		
Dicyclohexylphosphinic acid[e]	.352	230.3	227.7
Diphenylphosphinic acid[d]	.287	218.2	216.9
Phosphafluorinic acid[e]	.102[f]	216.2	198.7
	Other compounds		
Phenylphosphinic acid[g]	.241	142.1	146.0
Triphenylphosphine oxide[h]	.290	272.2	289.7
Benzenearsonic acid[i]	.429	202.0	209.5
Benzoic acid[j]	.288	122.1	117.7

[a] Prepared by refluxing diethyl ethylphosphonate with concentrated hydrochloric acid for 24 hours and evaporating the resulting solution to dryness. [b] Prepared by refluxing dibutyl butylphosphonate with concentrated hydrochloric acid for 48 hours, evaporating the resulting solution to dryness, and recrystallizing the residue from benzene. [c] Prepared as described by Freedman, Doak and Petit, *J. Am. Chem. Soc.*, **77**, 4262 (1955). [d] Prepared as described by Doak and Freedman, *J. Am. Chem. Soc.*, **73**, 5658 (1951). [e] Prepared as described by Freedman and Doak, *J. Org. Chem.*, **21**, 238 (1956). [f] Because of the limited solubility of phosphafluorinic acid in cold acetic acid, a higher value of Δt could not easily be obtained. [g] Obtained from the Victor Chemical Works and recrystallized from benzene. [h] Prepared as described by Gilman and Brown, *J. Am. Chem. Soc.*, **67**, 824 (1945). [i] Prepared by the Bart reaction. [j] Reagent grade material from Merck and Co., Inc.

(1) The term "phosphinic acid" is used to include both monosubstituted compounds of the type RPO_2H_2 and disubstituted compounds of the type R_2PO_2H. This usage is in accord with the nomenclature proposed by the Organic Division's Advisory Committee on the Nomenclature of Organic Phosphorus Compounds; *cf. Chem. Eng. News*, **30**, 4515 (1952).

(2) (a) Daasch and Smith, *Anal. Chem.*, **23**, 853 (1951); (b) Bellamy and Beecher, *J. Chem. Soc.*, 1701 (1952).

(3) (a) Kosolapoff and Powell, *J. Am. Chem. Soc.*, **72**, 4291 (1950); (b) Kosolapoff and Powell, *J. Chem. Soc.*, 3535 (1950) (c) Ashby and Kosolapoff, *J. Am. Chem. Soc.*, **75**, 4903 (1953).

(4) Kosolapoff, *J. Am. Chem. Soc.*, **74**, 3427 (1952).

(5) Lassettre, *Chem. Revs.*, **20**, 259 (1937).

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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VENEREAL DISEASE EXPERIMENTAL LABORATORY
U. S. PUBLIC HEALTH SERVICE
SCHOOL OF PUBLIC HEALTH
UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, NORTH CAROLINA

(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

COSTAS H. ISSIDORIDES AND NAZAR S. APRAHAMIAN

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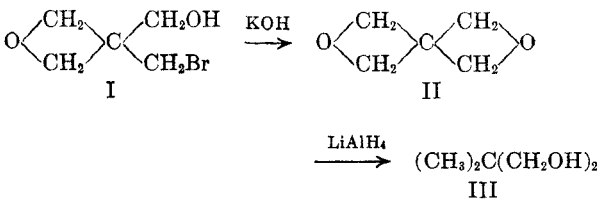
In a previous paper[1] we described the preparation of a new trimethylene oxide derivative of pentaerythritol to which we assigned the structure 3-bromomethyl-3-hydroxymethyloxetane (I). We would now like to present some further evidence for the proposed structure.



I II III

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 to 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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DEPARTMENT OF CHEMISTRY
AMERICAN UNIVERSITY OF BEIRUT
BEIRUT, LEBANON

(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.