TABLE I

Temperature, °K.	1000	1200	1400	1600	1800
$\dfrac{F^0 - H_0^0}{T}$, cal./ deg. mole	-46.87	-48.15	-49.24	-50.20	-51.06
Temperature, °K.	2000	2200	2400	2600	2800	3000
$\dfrac{F^0 - H_0^0}{T}$, cal./ deg. mole	-51.83	-52.53	-53.18	-53.79	-54.35	-54.88

The values used in these calculations are: the moment of inertia, $I = 2.85 \times 10^{-40}$; and the characteristic frequency, $\omega = 3620$ calculated from the relationship

$$\rho = \frac{\omega_{OD}}{\omega_{OH}} \text{ and } \rho = \left[\frac{17.008}{18.014}\right]^{1/2}$$

A similar calculation for the OH molecule over the same temperature interval has an average deviation of 0.03 cal./deg. mole from the values given by the NBS.[1]

(1) Selected Values of Properties of Hydrocarbons, Circular C461 NBS Nov. 1947.

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Organic Phosphorus Compounds. I. Reactions of Methanephosphonyl Dichloride with Glycols[1]

BY A. F. MCKAY, R. O. BRAUN AND G. R. VAVASOUR

Methanephosphonyl dichloride combines with glycols to give phosphorus-containing heterocyclics. The general reaction is

$$RCHOH(CH_2)_nC(R)HOH + CH_3POCl_2 \longrightarrow$$

R = H or CH₃
n = 0-2

I
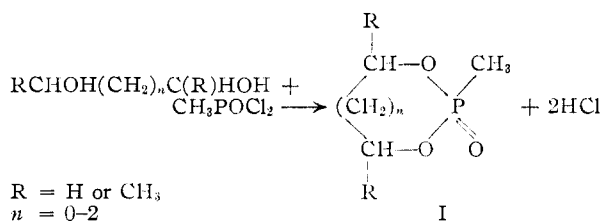
If no precautions are taken to remove the hydrogen chloride formed in this reaction, a mixture of methanephosphonic acid and methanephosphonic anhydride forms with a lowering of the yield of the cyclic product. When pyridine was used to remove the hydrogen chloride as formed, no methanephosphonic acid or its anhydride was present in the reaction mixture and the yield of cyclic product (I) was increased by 15%. This reaction does not appear to be general for all glycols because ethylene glycol and meso-2,3-butanediol have been observed to give linear products. These latter observations will be reported at a later date.

An attempt was made to hydrolyze the cyclic compound 2,4,5-trimethyl-2-oxo-1,3-dioxa-2-phosphacyclopentane into 2,3-butanediol and methanephosphonic acid in order to determine whether D-(−)-2,3-butanediol had retained its configuration in the cyclic product (I, R = CH₃, n = O). However, the conditions required for hydrolysis were too drastic to permit definite conclusions about the

(1) Issued as D.R.C.L. Report No. 90.

configuration of the cyclic product. The formal derivative of the resulting 2,3-butanediol possessed a specific rotation of −3.64° as compared with a value of −25.01°[2] given for the formal derivative of pure D-(−)-2,3-butanediol.

Experimental[3,4]

Methanephosphonyl Dichloride.—The methanephosphonyl dichloride used in this work had a melting point of 32.6°. Hofmann[5] reports a melting point of 32° for methanephosphonyl dichloride obtained by chlorination of methylphosphonic acid with two mole equivalents of phosphorus pentachloride.

D-(−)-2,3-Butanediol.—The D-(−)-2,3-butanediol[6] used in this work had a specific rotation of −13.0° at a temperature of 25°.

2,4,5-Trimethyl-2-oxo-1,3-dioxa-2-phosphacyclopentane. Method A.—D-(−)-2,3-Butanediol (90 g., 1.0 mole) was added dropwise to 121 g. (0.91 mole) of freshly distilled methanephosphonyl dichloride in absolute ether (200 cc.). The rate of addition of the butanediol was regulated to maintain the ether at a gentle reflux. After the addition of the glycol, which required 45 minutes, the stirred solution was refluxed for an additional hour. Then the ether was removed by distillation and the residue degassed at 100° and 17 mm. pressure. The residue on distillation in vacuo gave a water-white oil (b.p. 99–104° (1 mm.)) yield 85 g. (62.3%). This material was fractionated using a 6-inch Vigreux column equipped with a partial take-off head. The reflux ratio was held at 5:1. The main fraction (b.p. 86–88° (0.5 mm.)) solidified on standing, yield 82 g. (60.0%). The pure product had a setting point of 40.8° and it melted at 42–44° (capillary method). It was difficult to obtain a melting point by the capillary method because of the hygroscopic nature of the product.

Anal. Calcd. for $C_5H_{11}O_3P$: C, 40.00; H, 7.39; mol. wt., 150.12. Found: C, 40.04; H, 7.57; mol. wt., 152.4 and 159.0; $[\alpha]^{25}D$ −1.62 (11.226 g. in 25 cc. of CHCl₃).

The brown crystalline residue (21.6 g., 27.6%) from the first distillation melted at 141–141.5°. It gave analytical values in good agreement with methanephosphonic anhydride.

Anal. Calcd. for $C_2H_6O_5P_2$: C, 13.79; H, 4.63; P, 35.62. Found: C, 14.00; H, 4.73; P, 35.37.

A sample (5 g., 0.028 mole) of methanephosphonic anhydride was hydrolyzed by warming with 0.6 cc. of water until the mixture was homogeneous. A quantitative yield of methanephosphonic acid (m.p. 105°, soft 102°) was obtained. After crystallization from methyl ethyl ketone, it melted at 108–109°. It did not depress the melting point of an authentic sample of methanephosphonic acid (m.p. 108–109°) prepared by the hydrolysis of methanephosphonyl dichloride. The previously reported[7] melting point of methanephosphonic acid is 105°.

Method B.—In this procedure 42.6 g. (0.47 mole) of D-(−)-2,3-butanediol was added dropwise to a refluxing solution of 60 g. (0.452 mole) of methanephosphonyl dichloride in 150 cc. of methylene chloride. The products were separated and identified as in Method A. The yield of 2,4,5-trimethyl-2-oxo-1,3-dioxa-2-phosphacyclopentane was 47.8 g. (70.5%) while the yield of methanephosphonic anhydride–methanephosphonic acid mixture (m.p. 138–141°) was 10.5 g. These products were identified by comparison and mixed melting point determinations with the products obtained above in method A.

Method C.—D-(−)-2,3-Butanediol (90.0 g., 1.0 mole) was added dropwise over a period of 70 minutes to 133 g. (1 mole) of methanephosphonyl dichloride and 158.2 g. (2 moles) of pyridine in methylene chloride (400 cc.). This rate of addition of butanediol kept the mechanically stirred reaction mixture at a gentle reflux. The stirring was continued for three hours after which the reaction mixture was

(2) H. K. Garner and H. J. Lucas, THIS JOURNAL, 72, 5497 (1950).

(3) All melting points and boiling points are uncorrected.

(4) Microanalysis by C. W. Beazley, Skokie, Illinois.

(5) A. W. Hofmann, Ber., 6, 303 (1873).

(6) D-(−)-2,3-Butanediol was obtained through the courtesy of Mr. J. Wheat, Department of Applied Biology, National Research Council, Ottawa, Canada.

(7) A. W. Hofmann, Ber., 5, 104 (1872).

allowed to stand overnight. The precipitate of pyridine hydrochloride was removed by filtration and washed with fresh methylene chloride (3 × 100 cc.), yield 228.1 g. (98.7%). After the filtrate and washings were combined, the solvent was flashed off at atmospheric pressure and a bath temperature of 70°. The residual yellow oil gave the following fractions on distillation; fraction I, 29.8 g. (b.p. < 150° (755 mm.)); fraction II, 113.3 g. (b.p. 93° (0.35 mm.)) and fraction III, residue including column hold-up 14.2 g. Fraction I contained traces of pyridine and a chlorine containing compound besides methyl ethyl ketone. Methyl ethyl ketone, which was formed from 2,3-butanediol during the reaction, was identified as its 2,4-dinitrophenylhydrazone (m.p. 109–110°). A mixed melting point determination with a known sample of methyl ethyl ketone 2,4-dinitrophenylhydrazone (m.p. 109–110°) gave no depression.

The white crystalline fraction II melted at 43–45° alone and on admixture with authentic 2,4,5-trimethyl-2-oxo-1,3-dioxa-2-phosphacyclopentane. The weight of fraction II represents a 75.5% yield. No methanephosphonic anhydride could be identified in the still residue from this reaction.

2-Methyl-2-oxo-1,3-dioxa-2-phosphacyclohexane.—Methanephosphonyl dichloride (90 g., 0.677 mole) in 200 cc. of absolute ether was treated with 58.0 g. (0.763 mole) of trimethylene glycol under the conditions described above for method A. Some difficulty was experienced during the distillation by the product crystallizing before reaching the receiver, so it was not possible to obtain a reliable boiling point for this fraction. After one crystallization from carbon tetrachloride it melted at 98–99.5°, yield 55.3 g. (60%).

Anal. Calcd. for $C_4H_9O_3P$: C, 35.30; H, 6.67; mol. wt., 136.09. Found: C, 35.45; H, 6.72; mol. wt., 143.6 and 141.9.

The stillpot residue (m.p. 139–141°) consisted of methanephosphonic anhydride containing a trace of methanephosphonic acid, yield 20 g. (34.0%).

2,4,7-Trimethyl-2-oxo-1,3-dioxa-2-phosphacycloheptane. —2,5-Hexanediol (11.8 g., 0.1 mole) was added to a solution of 13.3 g. (0.1 mole) of methanephosphonyl dichloride in 95 cc. of methylene chloride. The reaction conditions were similar to those described above in method A. The product (b.p. 73–76° (0.2 mm.)) was obtained in 64.6% yield (11.5 g.) as a water-white liquid, $n^{25}D$ 1.4525, $d^{24.5}_4$ 1.105.

Anal. Calcd. for $C_7H_{15}O_3P$: C, 47.20; H, 8.49; P, 17.39. Found: C, 47.61; H, 8.30; P, 17.35.

The non-distillable residue weighed 4.5 g.

Hydrolysis of 2,4,5-trimethyl-2-oxo-1,3-dioxa-2-phosphacyclopentane.—The cyclic product from the reaction of D-(−)-2,3-butanediol with methanephosphonyl dichloride was resistant to hydrolysis under the conditions for acid and alkaline hydrolysis of phosphite esters reported by Garner and Lucas.[2]

When more concentrated (30–50%) sulfuric acid solutions were employed decomposition occurred. The first successful hydrolysis was accomplished by refluxing 25 g. (0.167 mole) of 2,4,5-trimethyl-2-oxo-1,3-dioxa-2-phosphacyclopentane in 150 cc. of 50% aqueous potassium hydroxide solution for one hour. This solution was cooled and then strongly acidified with concentrated sulfuric acid. Paraformaldehyde (10 g.) was added and the formal derivative of 2,3-butanediol was removed as formed by use of an esterification apparatus. The formal derivative was separated from the aqueous phase, dried over anhydrous potassium carbonate and distilled. This proved to be the formal derivative of partly racemized D-(−)-2,3-butanediol (b.p. 94.5–95.8°(759 mm.)) yield 67%, $[\alpha]^{24}D$ −3.64°.

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Sodium Perborate as a Reagent in Organic Chemistry. II. Oxidation of Polyhydric Alcohols

By S. M. Mehta and R. S. Iyer

In continuation of the study of sodium perborate as a reagent for the oxidation of organic com-

pounds,[1] the graded oxidation of polyhydric alcohols with sodium perborate was studied and the present paper reports the results obtained.

Experiments with aqueous solutions or in the presence of dilute acetic acid gave no appreciable reaction either at the ordinary temperature or on heating. The addition of cobalt chloride, nickel chloride, manganese sulfate, chloroplatinic acid, potassium dichromate, cuprous chloride and iodine was also not effective. Vanadium pentoxide in an acid medium gave a fairly good reaction but it was found that the reaction proceeds satisfactorily in the presence of ferrous sulfate. However, in the latter case sufficient acetic acid must be added to prevent the precipitation of ferric borate which inhibits the reaction completely. The amount of ferrous iron used has no relation to the yield of the oxidation product.[2] In all the experiments the effect of (a) temperature, (b) strength of acetic acid used and (c) time of reaction were examined. In this paper the conditions which gave the best results have been given. In every experiment the crude osazone obtained was purified by recrystallization and the melting point of the purified product was determined.

In general, the yields of osazones and hence of the aldehydes formed, compare with those obtained with hydrogen peroxide as the oxidant, although slightly better yields are obtained with the latter. This is due to the part played by boric acid set free from the sodium perborate in the presence of acetic acid. This is further confirmed by the results obtained in experiments with increasing amounts of boric acid added to the reaction mixture.

General Procedure.—The polyhydric alcohol and sodium perborate were taken in molecular ratio. An aqueous solution of the alcohol containing the requisite amount of ferrous sulfate was treated with a solution of acetic acid of suitable strength. To this mixture the required quantity of sodium perborate (weight calculated on available oxygen = 9.3%) was added in small quantities. The solution was then refluxed on a boiling water-bath except that in the case of mannitol, dulcitol and sorbitol the reaction was carried out at 30, 40 and 40°, respectively. The reaction was allowed to proceed for a convenient length of time. The liquid was cooled to room temperature, diluted with water and then treated with freshly distilled phenylhydrazine dissolved in dilute acetic acid and the mixture left aside. The osazone formed was collected, washed with water, dried in air at room temperature and weighed. Table I summarizes the data obtained for a series of polyhydric alcohols.

Comparison of the Oxidation with Hydrogen Peroxide and Sodium Perborate.

—A set of experiments was conducted to compare the yields of the osazones formed after the oxidation of the alcohol (a) with hydrogen peroxide alone, (b) with hydrogen peroxide in the presence of boric acid, (c) with sodium perborate and (d) with sodium perborate in the presence of boric acid. Table II summarizes the results obtained. The yields of osazones were less than those given by Fenton and Jackson[2] although great care was taken to adhere as rigidly as possible (using $1/4$ the quantities) to the conditions described by them. The reactions with sodium perborate were carried out under the conditions already described.

From Table II it is observed that the yield of the

(1) Mehta and Vakilwala, This Journal, 74, 553 (1952).
(2) Fenton and Jackson, J. Chem. Soc., Trans., 75, 1 (1899).