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

RECEIVED FEBRUARY 25, 1952

In continuation of the study of sodium perborate as a reagent for the oxidation of organic compounds,[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

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(1) Mehta and Vakilwala, THIS JOURNAL, **74**, 553 (1952).

(2) Fenton and Jackson, *J. Chem. Soc., Trans.*, **75**, 1 (1899).

TABLE I

OXIDATION OF POLYHYDRIC ALCOHOLS WITH SODIUM PERBORATE

Alcohol	Wt. of alcohol in g.	Wt. of ferrous sulfate in g.	Acetic acid Volume in cc.	Acetic acid Strength in *N*	Wt. of sodium perborate in g.	Time of reaction in min.	Yield of oszaone, g.	Yield of oszaone, %	Melting point of osazone in °C. Found (uncorrected)	Melting point of osazone in °C. Fenton and Jackson[2]
Ethylene glycol	1.55	1.3	30	4	4.293	60	0.588	9.88	168	169.5
Glycerol	2.5	0.25	35	8	4.668	15	0.96	13.25	131	130–131
Erythritol	2.5	1.25	25	8	3.508	30	1.53	25.0	166	167
Mannitol	5.0	1.25	35	3	4.720	360	1.55	20.9	198	197–198
Dulcitol	2.0	1.0	15	3	1.89	480	...	...	205	206
Sorbitol	2.0	0.9	15	3	1.89	480	...	...	204	203

TABLE II

YIELDS OF OSAZONES

Alcohol	Hydrogen peroxide, Fenton and Jackson g.	Hydrogen peroxide, Present investigation g.	Hydrogen peroxide and boric acid (1 mol), g.	Sodium perborate alone, g.	Boric acid 1 mol. g.	Boric acid 2 mols. g.	Boric acid 3 mols. g.
Ethylene glycol	0.70	0.55	0.50	0.588	0.55	0.54	0.54
Glycerol	1.55	1.00	0.85	0.960	0.81	0.78	0.76
Erythritol	1.75	1.55	1.30	1.530	..	..	..
Mannitol	3.12	2.15	1.84	1.550	1.27	1.08	0.20

oxidation product with sodium perborate is a little less than with hydrogen peroxide except with ethylene glycol but there is a distinct advantage in the use of sodium perborate which can be added conveniently in any controlled quantities to a reaction mixture. This investigation has also shown that the presence of boric acid has a retarding effect on the oxidation of a polyhydric alcohol both with sodium perborate as well as with hydrogen peroxide.

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A Correction: Absorption Spectra of Azlactones[1]

BY F. W. SCHUELER AND CALVIN HANNA

RECEIVED JULY 7, 1952

Recently we have had our attention called to errors in some of the absorption maxima values we reported for certain azlactones.[2]

The corrected values for the azlactones reported in the above reference are listed in Table I. As will be seen upon comparison of these values with the values reported in the above-mentioned reference, the average errors for the first maxima and second maxima were 35 and 74 mμ, respectively. Such errors are clearly of such a constancy that they suggested a systematic error in the standardization of the instrument during the period through which these materials were studied.

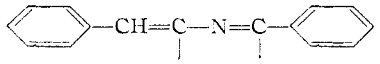
It has been the practice in many laboratories to check the standardization of the Beckman spectrophotometer only twice or three times a year. Following our experience with this instrument, however, we feel that the instrument should be checked before each use with a compound of known spectra before the determination of the spectra of compounds never before evaluated in these regards.

TABLE I

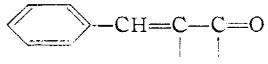
ABSORPTION SPECTRA OF AZLACTONES

No.	Max. 1 mμ	Max. 2 mμ	No.	Max. 1 mμ	Max. 2 mμ
1	259	377	15	265	386
2	268	387	16	244	365
3	271	376	17	257	370
4	261	365	18	232	328
5	259	360	19	264	369
6	259	376	20	265	401
7	264	393	21	264	396
8	257	373	22	264	394
9	260	362	23	259	383
10	...	359	24	260	361
11	...	360	25	225	286
12	...	290	26	245	482
13	259	372	27	240	475
14	247	366	28	240	425

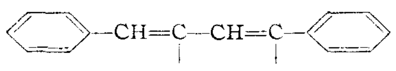
As a result of this correction it will be seen that the conjugated system

2 

better accounts for the spectra of the azlactones than the system

1 

originally indicated.[2] Moreover, a comparison of these corrected results on the azlactones, together with results obtained using the analogous crotonolactones,[3] indicates that chromophoric system operates in both. Thus, in the case of the crotonolactones, the conjugated system



is analogous to the system (2) indicated above for the azlactones.

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Indophenols of 8-Quinolinols

BY J. P. PHILLIPS, J. F. EMERY AND QUINTUS FERNANDO

RECEIVED JUNE 30, 1952

The indophenol formed by 8-quinolinol when treated with hydroxylamine in an alkaline oxidizing

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[1] This work was aided by a grant from the U. S. Public Health Service.

[2] F. W. Schueler and S. C. Wang, THIS JOURNAL, **72**, 2220 (1950).

[3] F. W. Schueler and Calvin Hanna, *ibid.*, **73**, 3528 (1951).