

TABLE II
 BIS-PHENOLS FROM FORMALDEHYDE

No.	Phenol	Pro- ced- ure	Pre- cipi- tant ^a	Time, hr.	M.p., °C.	Yield, %	Recrys- tallizing solvent	Empirical formula	Carbon		Analyses, %		Chlorine	
									Calcd.	Found	Calcd.	Found	Calcd.	Found
20	4,6-Di- <i>t</i> -butyl- <i>m</i> -cresol	A	3	1/4	215.3–216.3	92.0	Acetic acid	C ₂₁ H ₃₀ O ₂	82.26	82.38	10.69	10.65		
21	α ⁴ -Phenyl-2,4-xyleneol	A	1	1	121.5–121.9	22.0	Heptane	C ₂₉ H ₃₈ O ₂	85.26	84.96	6.91	7.02		
22	4-Chloro- <i>o</i> -cresol ^b	B	4	1/4	195.2–196.4	83.7	Benzene	C ₁₅ H ₁₄ Cl ₂ O ₂	60.61	60.91	4.75	4.49	23.86	23.80
23	6-Chloro- <i>o</i> -cresol	B	4	2	157.0–157.3	78.7	Benzene	C ₁₅ H ₁₄ Cl ₂ O ₂	60.61	60.67	4.75	5.02	23.86	23.86
24	4- <i>t</i> -Butyl- <i>o</i> -chloro-phenol	B	4	3	123.2–123.7	51.5	Acetic acid	C ₂₁ H ₂₆ Cl ₂ O ₂	66.12	66.17	6.87	6.85	18.62	18.85
25	6- <i>t</i> -Butyl-4-chloro- <i>m</i> -cresol	A	4	18	181.6–182.5	72.2	Heptane	C ₂₃ H ₃₀ Cl ₂ O ₂	67.47	67.54	7.39	7.45	17.32	17.25
26	4-Chloro-α ² -phenyl-isopseudocumenol	B	4	1/4	191.7–192.1	72.0	Heptane	C ₃₁ H ₃₀ Cl ₂ O ₂	73.64	73.57	5.98	6.17	14.03	13.96

^a 1, Heptane; 2, benzene; 3, glacial acetic acid; 4, water. ^b Shown in (7) as having m.p. 188°.

 TABLE III
 BIS-PHENOLS FROM BUTYRALDEHYDE

27	Thymol	A	1	3	165.1–165.8	98.5	Heptane	C ₂₄ H ₃₄ O ₂	81.31	81.57	9.67	9.79		
28	4,6-Di- <i>t</i> -butyl- <i>m</i> -cresol	A	3	14	123.5–124.1	26.0	Butanol	C ₂₄ H ₃₄ O ₂	82.51	82.40	11.00	10.95		
29	4- <i>t</i> -Butyl- <i>o</i> -cresol	A	3	14	130.8–131.5	89.1	Acetic acid	C ₂₆ H ₃₈ O ₂	81.64	81.69	10.01	10.15		
30	2- <i>t</i> -Butyl- <i>p</i> -cresol	A	1	18	126.4–127.2	88.5	Heptane	C ₂₈ H ₃₈ O ₂	81.64	81.30	10.01	9.75		
31	α ⁴ -Phenyl-2,4-xyleneol	A	1	5	108.8–109.2	76.5	Heptane	C ₃₂ H ₃₄ O ₂	85.31	85.55	7.61	7.75		
32	6- <i>t</i> -Amyl- <i>m</i> -cresol	A	1	14	162.8–163.6	43.0	Heptane	C ₂₈ H ₄₂ O ₂	81.90	81.60	10.31	10.35		
33	6- <i>n</i> -Butyl- <i>m</i> -cresol	A	1	2	121.4–122.0	53.5	Heptane	C ₂₅ H ₃₈ O ₂	81.64	81.96	10.01	10.08		

^a 1, Heptane; 2, benzene; 3, glacial acetic acid; 4, water.

 TABLE IV
 MISCELLANEOUS BIS-PHENOLS

No.	34	35	
Phenol	4,6-Di- <i>t</i> -butyl- <i>m</i> -cresol	2,4-Xyleneol	
Aldehyde	Isobutyraldehyde	2,4-Dichloro-benzaldehyde	
Procedure	A	A	
Precipitant ^a	3	1	
Time, hours	16	1	
M.p., °C.	118.1–118.6	193.7–194.1	
Yield, %	22.0	52.0	
Recrystallizing solvent	Butanol	Heptane	
Empirical formula	C ₂₄ H ₃₄ O ₂	C ₂₃ H ₂₂ Cl ₂ O ₂ ^b	
Analyses, %	Carbon		
	Calcd.	82.51	68.83
	Found	82.33	68.66
	Hydrogen		
Calcd.	11.00	5.53	
Found	11.31	5.79	

^a 1, Heptane; 2, benzene; 3, glacial acetic acid; 4, water.
^b Chlorine, %; calcd. 17.67; found 17.65.

Procedure A. 4,4'-Propylidenebis-(6-*t*-butyl-*m*-cresol).—Approximately 4 ml. of concentrated HCl was added to a well-stirred solution of 82.1 g. of 6-*t*-butyl-*m*-cresol (0.5 mole) and 14.5 g. of propionaldehyde (0.25 mole). The reaction was exothermic and the temperature rose from 30 to 75° within 5 minutes. The reaction mixture was further heated and held at 95° for 4 hours, 100 ml. of heptane was added and the mixture cooled and held 1 hour at 30°. The crystalline product was filtered, washed with two 20-ml. portions of cold heptane and recrystallized from the same solvent at boiling; yield 43.4% of fine white needles, m.p. 190.0–190.4°.

Procedure B. 2,2'-Methylenebis-(4-chloro-*o*-cresol).—Concentrated H₂SO₄ was added dropwise to a well-stirred solution of 71.3 g. of 4-chloro-*o*-cresol (0.5 mole) and 7.5 g. of trioxymethylene (0.25 mole) in 50 ml. of glacial acetic acid. The temperature rose rapidly to 95° and the mixture solidified after 8 ml. of acid had been added. After standing 15 minutes, 200 ml. of water was added and the mixture cooled to 30°. The solids were filtered and washed with cold water until free of acidity. The crude product was taken up in 200 ml. of benzene and following decolorization with 10 g. of Darco G-60 gave fine white plates; m.p. 195.2–196.4°, yield 83.7%.

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Alcoholysis of Cellulose with 2-Methoxyethanol^{2,3}

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Methanolysis of cellulose or its derivatives has been used a very few times as a tool in structural studies of cellulose.^{4,5} Partial methanolysis, or alcoholysis with other alcohols as well, has been suggested to replace hydrolysis or oxidation for the shortening of cellulose chains without the introduction of reducing end-groups in the production of industrial materials.⁶ Some data were given concerning the extent of reactions by the normal alcohols with from one to five carbon atoms. The present study is concerned with the extent of cleavage which can be obtained with a new alcohol—2-methoxyethanol—which does not appear to have been used previously for the alcoholysis of any polysaccharide. Its high reactivity makes this alcohol worth consideration as an alcoholic reagent for polysaccharides, particularly since the use of an autoclave is not required in order for the optimal reaction temperature to be reached.

That cellulose acetate is converted by acidic 2-

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture, New Orleans 19, La. Article not copyrighted.

(2) Known also as ethylene glycol monomethyl ether and as Methyl Cellosolve.

(3) Report of a study made under the Research and Marketing Act of 1946.

(4) J. C. Irvine and E. L. Hirst, *J. Chem. Soc.*, **121**, 1585 (1922); **123**, 518 (1923); E. Heuser and S. S. Aiyar, *Z. angew. Chem.*, **37**, 27 (1924).

(5) R. E. Reeves, L. W. Mazzeno, Jr. and C. L. Hoffpauir, *THIS JOURNAL*, **72**, 4773 (1950).

(6) R. E. Reeves, U. S. Patent 2,520,963, Sept. 5, 1950.

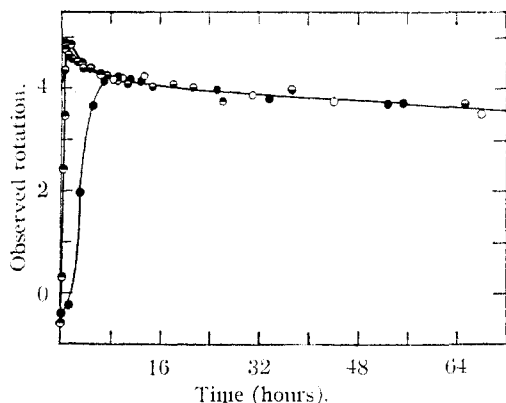


Fig. 1.—Glucose derivatives in acidic 2-methoxyethanol (5 g. of glucose or equivalent per 100 ml. of alcohol, 0.15 *N* *p*-toluenesulfonic acid, 100°): O, starch; □, α-D-glucose; ●, cellulose acetate; ■, 2-methoxyethyl β-D-glucoside.

methoxyethanol to glucosides in high yield is demonstrated by the data in Fig. 1, in which observed rotations are plotted against time of treatment of cellulose acetate, α-D-glucose, starch and 2-methoxyethyl β-D-glucopyranoside. The agreement of all rotations after the initial reaction period is indicative of comparable states for all—an indication which must mean conversion of each to a mixture of the anomeric glycopyranosides with very little destructive action. The α-isomer, the presence of which is indicated by the shift to the moderately high positive rotation, has not yet been obtained in crystalline form. No doubt, the extent of the mild destruction of optically active substances which does occur is measured by the slope of the straight line common to the four curves after they converge (at 9 hours). The line continues with this slope for at least five days. For the sake of convenience, the point for the five-day period has been omitted from the figure (also from Figs. 2–4). The more rapid rate of decrease in optical activity preceding the linear portion of the curve is evidently caused by some shift during the isomerization reaction. It is slightly reflected in the curves for the alcoholysis of cellulose acetate under the milder conditions.

p-Toluenesulfonic acid was chosen for the catalyzing acid in these reactions with 2-methoxyethanol. Hydrogen chloride, the alcoholysis catalyst used by Irvine and Hirst⁴ in their methanolysis of acetylated or methylated cotton, reacts rapidly with alcohols, and an effective concentration can be maintained only a short while at high temperatures. The concentration of hydrogen chloride in 2-methoxyethanol dropped from 0.15 to 0.03 *N* in two hours at 100°. The use of a sufficiently high concentration of this acid (0.25 *N* or higher) for complete alcoholysis of cellulose acetate in a one-step treatment resulted in severe discoloration. However, with *p*-toluenesulfonic acid the acidity is maintained, and there is little interference from colored products under a range of conditions suitable for complete alcoholysis of the acetate.

Initial changes in optical activity result from both deacetylation and chain cleavage making uncertain determinations of rate from the slopes

of the curves. However, the time of the occurrence of the maxima can be assumed to coincide with the time of near completion of alcoholysis under mild conditions, where the destruction of optically active substances is shown to be small. The validity of this assumption is confirmed by the correspondence between the rotation of alcoholized cellulose acetate and of 2-methoxyethyl β-glucopyranoside at this time. Hence, from the positions of the maxima in Figs. 2 and 3, the rate of alcoholysis can be shown to be proportional to the concentration of the acid in the range 0.15 to 0.50 *N*. Furthermore, the rate is increased about 1.7-fold per 10° increase in temperature in the range 90 to 110°. Yet, there is no clearly defined optimal value for either concentration of catalyst or temperature since conditions conducive to more rapid alcoholysis are accompanied by a more rapid rate of decrease of optical activity, presumably indicative of the destruction of glucosides.

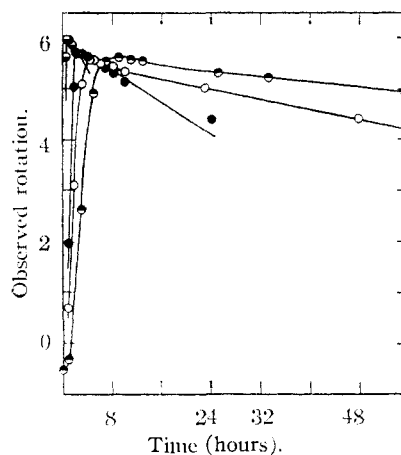


Fig. 2.—Influence of concentration of acid on the alcoholysis of cellulose acetate (2.5 g. of low viscosity acetate, 25 ml. of 2-methoxyethanol, variable amounts of *p*-toluenesulfonic acid, 100°): ●, 0.15 *N*; ○, 0.25 *N*; ●, 0.50 *N*; ●, 1.0 *N*.

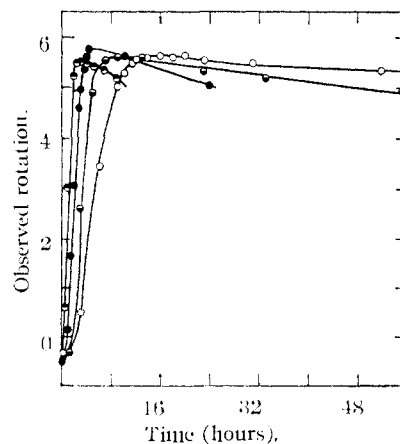


Fig. 3.—Influence of temperature on the alcoholysis of cellulose acetate (2.5 g. of low viscosity acetate, 25 ml. of 2-methoxyethanol, 0.15 *N* *p*-toluenesulfonic acid): ○, 90°; □, 100°; ●, 110°; ●, 120°.

The usable range of temperature and concentration is limited on the lower side by regeneration of

the cellulose, for enough chain cleavage should occur concurrently with deacetylation to avoid precipitation of the deacetylated or partly deacetylated cellulose acetate. That slight regeneration occurs at 90° with 0.15 *N* acid is shown by the development of a persistent turbidity. With 0.15 *N* acid at 100°, the solubility properties change from those of the acetate to those of the polysaccharide in one to two hours but without precipitation from solution. Hence, the best conditions for total alcoholysis approximate the 100° temperature and 2.5% concentration (near 0.15 *N*) of acid selected by Combs, McCloskey, Sundberg and Coleman as optimal for the alcoholysis of methylated disaccharides with *p*-toluenesulfonic acid in benzyl alcohol.⁷

2-Methoxyethanol is only slightly more reactive toward cellulose acetate than is its ethyl analog. These monoethers are compared in reactivity with ethylene glycol, propylene glycol and benzyl alcohol in Fig. 4. The reactivity of each alcohol for the cleavage of cellulose acetate is a function of its power as a solvent as well as of its ability to cleave the bonds between anhydroglucose residues. The experiments were performed with a low viscosity acetate in order to favor solubility, but only with benzyl alcohol and with 2-methoxyethanol were the reactions homogeneous throughout. Solution of the acetate in 2-ethoxyethanol required about one hour, and in each of the glycols about five hours, from the addition of the acid. The conclusion may be drawn that although the ethyl ether is slightly less reactive than the methyl ether, the latter retains a distinct advantage largely because it is a superior solvent. Ethylene and propylene glycol are less reactive than the monoethers toward glucose-glucose bonds and are much inferior in solvent power. Benzyl alcohol is indicated here to be more reactive than 2-methoxyethanol, but in the single example studied it was

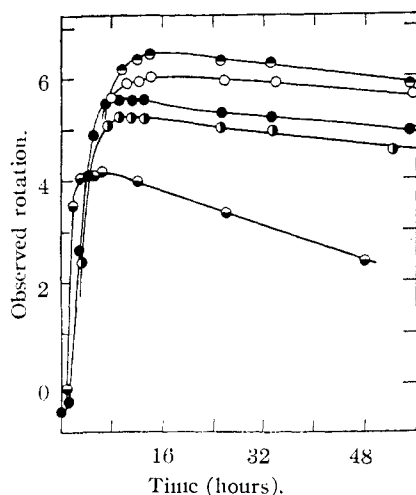


Fig. 4.—Alcoholysis of cellulose acetate (2.5 g. of low viscosity acetate, 25 ml. of alcohol, 0.15 *N* *p*-toluenesulfonic acid, 100°): O, ethylene glycol; ●, propylene glycol; ●, benzyl alcohol; ●, 2-ethoxyethanol; ●, 2-methoxyethanol.

(7) E. E. Combs, C. M. McCloskey, R. L. Sundberg and G. H. Coleman, *THIS JOURNAL*, **71**, 276 (1949).

less effective than the latter for the cleavage of fibrous materials.

In contrast to the members of the glycol family, the monofunctional alcohols with boiling points near 100° or above, as exemplified by *n*-propanol and *n*-butanol, are poor reagents for the alcoholysis of cellulose acetate. They tend to regenerate the cellulose, which then becomes insoluble. However, butanol can be used satisfactorily with low viscosity cellulose acetate if the temperature is kept for two hours at 120° (a temperature too destructive for long use) and is then lowered to 100°, other conditions being comparable to those of Fig. 4.

Although the major emphasis in the study of the reactivity of 2-methoxyethanol has been centered on the alcoholysis of a low viscosity acetate, the applicability of the reagent to other cellulosic materials has been explored. Two other acetates one of which was initially insoluble, were alcoholized without difficulty; hence, complete alcoholysis of all cellulose acetates may be possible under the conditions suggested.

Trimethylcellulose (Fig. 5) is characterized by great insolubility in 2-methoxyethanol in addition to its possession of the difficultly hydrolyzable β -link. Hence, it is alcoholized only slowly in contrast to cellulose acetate with its appreciable solubility and in contrast to starch, which although insoluble, has the more easily cleaved α -link. A commercial sample of degraded partially methylated cellulose eventually dissolved completely, but the procedure with 0.15 *N* acid required two days compared with less than half a day for the acetates.

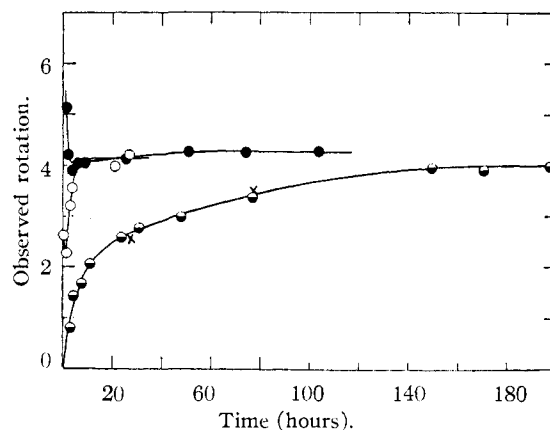


Fig. 5.—Alcoholysis of methylated polysaccharides (5 g. of trimethylglucose or equivalent per 100 ml. of 2-methoxyethanol, 0.15 *N* *p*-toluenesulfonic acid, 100°): ●, trimethylcellulose; O, trimethyl-D-glucose; ●, trimethylstarch; X, trimethylcellulose (separate experiment).

Results with several other cellulosic materials—cotton, hydrocellulose, mercerized cotton, decrystallized cotton and trimethylcellulose—are summarized in Table I. The measurement of optical activity and the measurement of weight loss are equally effective for the estimation of extent of degradation under mild alcoholic conditions.

Experimental

Observed optical rotations were for the D-line of the sodium vapor lamp on solutions in 1-dm. tubes. Alcoholysis temperatures were controlled to $\pm 1^\circ$. *p*-Toluenesulfonic

TABLE I

ALCOHOLYSIS OF COTTON CELLULOSE AND DERIVATIVES^a

1-g. sample in 20 ml. of *p*-toluenesulfonic acid in 2-methoxyethanol; temperature, 100° unless otherwise indicated

Substance alcoholized	Catalyst, N	Time, hr.	Obsd. rot. 1/2 dm.	Wt. loss calcd., %	
				From obsd. rot. ^b	From residue ^c
Cotton	0.15	28	+0.22	5.3	5.3
Cotton	0.15	48	.36	8.9	8.9
Cotton	1.0	24	.82	20.0	21.0
Cotton at 120°	1.0	24	81.0 ^d
Hydrocellulose	0.15	24	.18	4.3	5.2
Hydrocellulose	.15	48	.34	8.0	6.4
Mercerized cotton	.15	24	.46	10.3	9.2
Decrystallized cotton	.15	24	.70	17.0	18.0
Decrystallized cotton	.15	48	.92	22.0	22.0
Trimethylcellulose	.15	27	2.72	62.0	62.0
Trimethylcellulose	.15	77	3.70	84.0	82.0
Trimethylcellulose ^e	.15	197	4.28	97.0	90.0
Trimethylcellulose	.50	77	4.07	92.0	93.0 ^d
Nitrogen dioxide oxycellulose ^e	.15	24	77.0

^a Empire cotton purified by extraction with ethanol and an alkali-boil; hydrocellulose with aldehyde end-group content of 0.042 millimole/gram; mercerized cotton rated at 72% crystallinity by the acid hydrolysis method of Nelson and Conrad; cotton decrystallized by treatment with the ethylamine procedure of Segal, Nelson and Conrad, rated at 19% crystallinity by acid hydrolysis; trimethylcellulose, 44.9% methoxyl (anhydrous basis); nitrogen dioxide oxycellulose, anhydroglucuronic acid content 70% and moisture 13%. ^b Calculated on anhydrous basis. The amount of unsubstituted glucoside in the filtrate was calculated from the optical rotation of 1 g. of glucose in 20 ml. of 0.15 N *p*-toluenesulfonic acid after 24 hr. at 100°. This value is 3.95°; see Fig. 1. The amount of methyl substituted glucoside was estimated from the rotation observed for 200 mg. of 2,3,6-trimethyl-D-glucoside after 24 hr. at 100° in 4 ml. of 0.15 N *p*-toluenesulfonic acid. This value is 4.05°; see Fig. 5. ^c Weights of original samples and residues have been corrected for moisture content. ^d On basis of air-dry weights. ^e 2 g. of trimethylcellulose in 40 ml.; 10 g. nitrogen dioxide oxycellulose in 200 ml.

acid was used as the monohydrate. Experimental details in addition to those shown in Table I and in Figs. 1-5 are described below.

Alcoholysis of Cellulose Acetate.—A mixture of 2.5 g. of acetate and 12.5 ml. of alcohol was heated in a flask attached to a reflux condenser until solution or saturation took place. To the solution or suspension was added after cooling 12.5 ml. of the alcohol containing acid of the required strength. See Figs. 1-4 for observed rotations.

Alcoholysis of Cotton, Mercerized Cotton, Decrystallized Cotton, Hydrocellulose, Trimethylcellulose and Nitrogen Dioxide Oxycellulose.—Residues (Table I) were washed with 2-methoxyethanol and with ether and were dried in air. Moistures were determined as weight lost over phosphorus pentoxide *in vacuo* at 100°. All residues were pure white except that from the cotton treated with 1 N acid at 120°. In the case of trimethylcellulose, Fig. 5, the mixture, containing 2 g. of cellulose derivative in 40 ml. of reagent, was shaken occasionally and rotations were made on the supernatant liquid after settling. In the case of the oxycellulose, the gelatinous nature of the residue was overcome by washing on the centrifuge with alcohol followed by ether.

In contrast to the behavior of 2-methoxyethanol, benzyl alcohol reacted with oxycellulose to produce an easily filterable residue, less extensively degraded: weight 1.4 g. from 2 g. of oxycellulose as compared with 2.17 g. residue from 10 g. of oxycellulose similarly treated with 2-methoxyethanol. Use of the former alcohol with higher temperature and concentration of catalyst resulted in major destruction without reaching the extent of cleavage obtained with the latter.

Alcoholysis of Starch and Methyl Starch.—One gram of purified sweet potato starch (moisture 10.0%) or of methyl-

ated sweet potato starch (43.4% methoxyl, anhydrous basis; 2.2% moisture) was covered with 20 ml. of reagent and heated with occasional shaking until in solution, *i.e.*, for about 8 hr. in the case of starch and only a few minutes in the case of the methylated derivative. Subsequently observed rotations are shown in Figs. 1 and 5.

Reaction of D-Glucose and of 2,3,6-Trimethyl-D-glucose with 2-Methoxyethanol and the Isomerization of 2-Methoxyethyl β-D-Glucoside.⁸—Rotations plotted in Figs. 1 and 5 were made on solutions of compositions as follows: for glucose, 1 g. with 20 ml. of reagent; for trimethylglucose and the glucoside, 200 mg. each with 4 ml. of reagent. Samples withdrawn for reading were returned as quickly as possible (within 5 minutes). Because of errors in handling the small volume, the latter portion of the glucoside curve was rechecked in a second experiment and the curve shown is a composite of the two.

Acknowledgment.—The following supplied samples or analyses used in this investigation: L. Segal, L. W. Mazzeno, Jr., Mary L. Nelson, and S. M. Stark, Jr. The nitrogen dioxide oxycellulose was received through courtesy of Research Laboratories, Tennessee Eastman Corp., Kingsport, Tenn.

(8) The trimethylglucose, m.p. 118-122°, was prepared by the procedure of H. C. Carrington, W. N. Haworth, E. L. Hirst and M. Stacey, *J. Chem. Soc.*, 1901 (1939); the glucoside, m.p. 114-115°, by the method of B. Helferich and R. Hiltmann, *Ann.*, **531**, 160 (1937).

The Reduction of Benzenephosphonyl Dichloride

BY LEON D. FREEDMAN AND G. O. DOAK

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The difficulty in reducing phosphoric acid and its derivatives is well-known.¹ Since a wide variety of aromatic phosphonic acids can be synthesized by the diazo reaction,² the reduction of such compounds would provide a convenient method for the preparation of the corresponding phosphonous acids. Reduction of phosphonic acids was not accomplished by treatment with sulfur dioxide and hydriodic acid, phenylhydrazine, phosphorus trichloride, sodium hyposulfite, zinc dust and alkali, amalgamated zinc and hydrochloric acid, or red phosphorus and iodine. An attempt to reduce benzenephosphonyl dichloride with phosphorus trichloride was also unsuccessful. Lithium aluminum hydride, on the other hand, readily reduces benzenephosphonyl dichloride to phenylphosphine at the reflux temperature of ether.³ Since phosphonyl dichlorides can be prepared from the corresponding acids, and since phosphines are readily oxidized to phosphonous acids by air or oxygen,⁴ this reduction of a phosphonyl dichloride permits conversion of a phosphonic acid to a phosphonous acid.

We have found that the reduction of benzenephosphonyl dichloride to phenylphosphine can also be effected with lithium borohydride. This milder reducing agent has the advantage that it does not attack nitro groups; the preparation of nitro-substituted phenylphosphines by this method thus seems possible.

(1) Cf. W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1938, p. 100.

(2) G. O. Doak and L. D. Freedman, *THIS JOURNAL*, **73**, 5658 (1951).

(3) Very recently, R. J. Horvat and A. Furst, *ibid.*, **74**, 562 (1952), have described the reduction of phenyldichlorophosphine to phenylphosphine by means of lithium aluminum hydride.

(4) H. Köhler and A. Michaelis, *Ber.*, **10**, 807 (1877).