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 alcoholyzed	Catalyst, N	Time, hr.	Obsd. rot. $^1/_2$ dm.	Wt. loss calcd., % From obsd. rot.[b]	Wt. loss calcd., % 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 methylated 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.

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[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.

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(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).

Experimental

In a typical experiment, 2.10 g. (0.055 mole) of lithium aluminum hydride was suspended in 150 ml. of absolute ether in a 500 ml. 3-necked flask equipped with a dropping funnel and reflux condenser. The mixture was refluxed for several hours in order to dissolve the lithium aluminum hydride. Then 9.8 g. (0.050 mole) of benzenephosphonyl dichloride[5] in 40 ml. of absolute ether was added dropwise over a three-hour period. A white precipitate formed on the addition of each drop. The contents of the flask were stirred by means of a magnetic stirrer. The repulsive and penetrating odor of phenylphosphine could be noted from the beginning of the reaction. Stirring was continued for an hour after the addition was complete. The reaction mixture was then filtered with nitrogen pressure through a coarse line filter into a distilling flask. The ether was removed and the oily residue distilled in an atmosphere of nitrogen. The yield of phenylphosphine b.p.[6] 154–157°, was 3.0 g. (55%). In air this material ignites spontaneously at its b.p. and at room temperature gradually changes to white crystalline benzenephosphonous acid. *Anal.* Calcd. for $C_6H_5PO_2H_2$: neut. equiv., 142.1. Found: neut. equiv., 140.7.

Reduction with lithium borohydride was performed under similar conditions. Tetrahydrofuran[7] was used as the solvent, and the reaction mixture was refluxed for several hours after the addition of the phosphonyl dichloride. After the solvent was removed, a white solid was obtained together with the oily phosphine. The presence of this solid made the distillation of the phenylphosphine more difficult than when lithium aluminum hydride was used.

Because of the persistent and offensive odor of phenylphosphine, considerable difficulty was encountered in cleaning the apparatus at the conclusion of the experiment. The residual phenylphosphine was best destroyed by adding dilute hydrogen peroxide before disassembling the apparatus and then washing with a slow stream of water for 24 hours or longer.

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[5] Kindly furnished by the Victor Chemical Works.

[6] Previously reported b.p. 160–161°, *cf.* ref. 3 and 4.

[7] Kindly furnished by the E. I. du Pont de Nemours and Company.

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Arylcycloalkylamines. III. 2-(3,4-Dimethoxyphenyl)-cyclopropylamine[1]

BY ALFRED BURGER AND GILMER T. FITCHETT

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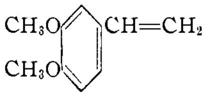
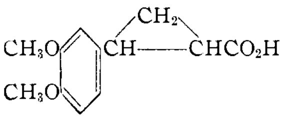
In view of the observation that substitution of the 3-position by a methyl group enhances the antispasmodic effect of 1-benzylisoquinoline derivatives,[2] we wished to prepare 1-(3,4-dimethoxybenzyl)-3,4-cyclopropano-3,4-dihydro-6,7-dimethoxyisoquinoline. Although we were unable to effect a Bischler–Napieralski ring closure of N-[2-(3,4-dimethoxyphenyl)-cyclopropyl]-homoveratramide, we are reporting the preparation of this compound from 2-(3,4-dimethoxyphenyl)-cyclopropylamine (III) and homoveratryl chloride.

For the synthesis of III, 3,4-dimethoxystyrene[3] (I) was condensed with ethyl diazoacetate, and the resulting mixture of ethyl 2-(3,4-dimethoxyphenyl)-cyclopropanecarboxylates was hydrolyzed to two stereoisomeric 2-(3,4-dimethoxyphenyl)-cyclopropanecarboxylic acids (II). One of them could be converted to the other one by distilling its chloride and hydrolyzing the latter. The more abundant of the two acids could be degraded to the amine III by the Curtius method, either from the acid chloride and sodium azide, or from the ester by way of the hydrazide, azide and urethan.

Considerable difficulties were encountered in the preparation of the starting material, 3,4-dimethoxystyrene (I), and we were unable to reproduce consistently the procedure described by Frank, *et al.*[3] In decomposing the Grignard complex from veratraldehyde and methylmagnesium iodide, extreme caution had to be exercised not to use strongly acidic conditions, or else a polymer of the styrene was formed exclusively.[4] Furthermore, distillation of 1-(3,4-dimethoxyphenyl)-ethanol under reduced pressure gave mainly the styrene (I) by spontaneous dehydration.



I



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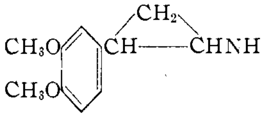

III

Experimental[5]

2-(3,4-Dimethoxyphenyl)-cyclopropanecarboxylic Acid.—A cold mixture of 51.2 g. (0.312 mole) of 3,4-dimethoxystyrene[3] and 62.5 g. (0.55 mole) of ethyl diazoacetate began to evolve nitrogen when it was warmed gradually to 50°. At 110° the exothermic reaction became self-sustaining and had to be retarded by cooling as the temperature rose to 150°. The mixture was then heated at 135–140° for another three hours, and the dark red material was fractionated. The main fractions distilled as thick yellow oils at 175° ($n^{25}\text{D}$ 1.5307) and 192–200° ($n^{25}\text{D}$ 1.5270) under 8.5 mm. but were combined (50 g., 63%) and hydrolyzed by refluxing with a solution of 47 g. of potassium hydroxide in 50 ml. of 85% ethanol for five hours. The alcohol was removed, the residue was acidified with 80 ml. of concentrated hydrochloric acid, and the precipitated mixture of carboxylic acids was allowed to crystallize in the refrigerator. The filtered crude material was dissolved in 3 l. of boiling water which, upon cooling, deposited 23.5 g. (29%) of colorless crystals; recrystallization rendered a sample melting at 105–105.5°.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.77; H, 6.06.

When the mother liquors of the acid of m.p. 105° were evaporated further, a brown solid separated out from which by repeated crystallizations from water, yellowish crystals of m.p. 107–109.5° were obtained.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 65.10; H, 6.12.

A mixture melting point of the two stereoisomers lay at 79–82°.

2-(3,4-Dimethoxyphenyl)-cyclopropanecarboxyhydrazide.—The acid of m.p. 105° was methylated with diazomethane in a 1:1 mixture of ether and methanol and the solvents were removed. The oily methyl ester (1.9 g.) was refluxed with a solution of 10 ml. of 100% hydrazine hydrate in 4 ml. of ethanol for five hours, and excess solvent and reagent

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[1] (a) **I**, A. Burger and W. L. Yost, THIS JOURNAL, **70**, 2198 (1948); (b) **II**, A. Burger, C. R. Walter, Jr., W. B. Bennet and L. B. Turnbull, *Science*, **112**, 2907 (1950).

[2] H. Kreitmair, *Arch. exptl. Pathol. Pharmakol.*, **164**, 509 (1932).

[3] R. L. Frank, C. E. Adams, R. E. Allen, R. Gander and P. V. Smith, THIS JOURNAL, **68**, 1365 (1946).

[4] This observation has been confirmed in a private communication from Dr. R. L. Frank, Edwal Laboratories, Inc., Ringwood, Illinois.

[5] All melting points are corrected. Microanalyses by Clark Microanalytical Laboratory, Urbana, Illinois.