cose) in the methylated polysaccharide can be explained by the assumption that either the chain exists in the form of a continuous loop or that the number of glucose units is too great to allow the isolation of tetramethylglucose under the conditions employed.

The authors are indebted to Mr. W. H. Dore for making the diffraction patterns of the trimethylglucoses and for his interest and suggestions during the course of this investigation. The authors also express their appreciation to the Acme Brewery of San Francisco for supplying the yeast used in these investigations.

Summary

The structure of an insoluble polysaccharide isolated from yeast (*Saccharomyces cerevisiae*) was studied. The low specific rotations of the acetylated and methylated derivatives, and the upward mutarotation during hydrolysis suggest that the glucosidic linkages of the anhydroglucose units are predominantly of the β-type.

On methylation and subsequent hydrolysis of the polysaccharide 2,4,6-trimethylglucose was obtained as the sole product of hydrolysis. No end-group (tetramethylglucose) could be detected. This suggests that the molecule is probably of the closed chain type.

The molecular weight of the polysaccharide determined by the Staudinger viscosity method was approximately 6500.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BOSTON UNIVERSITY]

Catalytic Dehydration of 4-Morpholineëthanol[1a]

BY HARRY W. BLOCK[1b] WITH J. PHILIP MASON

The dehydration of 4-morpholineëthanol, if analogous to the dehydration of ethanol, should yield 2,2′-dimorpholinodiethyl ether and N-vinylmorpholine. The work done by Meyer and Hopff[2] indicates that N-vinylmorpholine would probably be quite unstable. These investigators prepared dimethylvinylamine by the distillation of neurine chloride and diethylvinylamine by the distillation of β-diethylaminoethyltrimethylammonium hydroxide. In the former case they obtained a 3% yield and in the latter a 2% yield. Both products polymerized readily.

Campbell and Campbell[3] pyrolyzed the Grignard complex of 2-methyl-2-hydroxy-1-dimethylaminopropane and obtained the solid hydrochloride of 1-dimethylamino-2-methyl-1-propene which was described as very unstable, decomposing quickly in moist air. On hydrolysis it yielded isobutyraldehyde and dimethylamine. Phou-Ti Sou[4] dehydrated alcohols of the type R_2NCH_2-$C(OH)R_2'$ with phosphorus pentachloride in ether solution and obtained some $R_2NCH{=}CR_2'$ which hydrolyzed readily in an alkaline solution to form $R_2'CHCHO$.

The products which were identified from the catalytic dehydration of 4-morpholineëthanol were acetylene, morpholine, 1,2-dimorpholinoethane, 2,2′-dimorpholinodiethyl ether, and unreacted morpholineëthanol.

Since no fraction having the properties expected of N-vinylmorpholine was obtained, an attempt was made to prepare this compound by treating morpholinoethyl chloride with alcoholic potassium hydroxide solution. However, the only product isolated from this reaction was morpholinoethyl ethyl ether.

There are two mechanisms possible for the formation of acetylene, morpholine and 1,2-dimorpholinoethane from morpholineëthanol. One possibility is that N-vinylmorpholine may be formed as an intermediate which loses acetylene to yield morpholine. The morpholine could react with morpholineëthanol to form 1,2-dimorpholinoethane. This reaction between morpholine and morpholineëthanol was suggested by Dr. A. L. Wilson.[5]

A second mechanism, suggested by Dr. Wilson,[5] is that morpholineëthanol may decompose to form morpholine and either ethylene oxide or acetalde-

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[1a] This name was suggested by Dr. E. J. Crane as preferable to β-4-morpholineëthanol used previously[12] by us.

[1b] Taken from the thesis submitted by Harry W. Block to the faculty of the Graduate School of Boston University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Meyer and Hopff, *Ber.*, **54B**, 2274 (1921).

(3) Campbell and Campbell, THIS JOURNAL, **60**, 1373 (1938).

(4) Phou-Ti Sou, *Bull. faculté sci. univ. franco-chinoise Peiping*, No. 5, 1-7 (1935); *C. A.*, **30**. 4463 (1936).

(5) Private communication.

hyde. This method of decomposition is supported by the dehydration of ethylene glycol,[6] of choline[7] (a quaternary ammonium hydroxide), and the fact that dehydration of ethylene oxide produces some acetylene.[8] The morpholine formed could react with morpholineëthanol to yield 1,2-dimorpholinoethane. Since it was expected that ethylene oxide, if formed, would be converted to acetaldehyde,[8] an attempt was made to check this mechanism by passing acetaldehyde through the catalyst tube under the same conditions used for the dehydration of morpholineëthanol. No evidence for the formation of acetylene was found in this experiment. The liquid product condensed by the water condenser was dried and distilled. One fraction was collected at 80–180° (760 mm.) and another fraction at 113–176° (56 mm.). Both fractions possessed similar distinctive aromas, markedly different from any odors that were encountered among the catalytic dehydration products of 4-morpholineëthanol. This experiment will be reported later when the products, both liquid and gaseous, have been identified.

On the basis of the present evidence, the first of the above mechanisms is preferred.

Experimental

The apparatus was similar to that generally used for catalytic dehydrations. The catalytic dehydration tube consisted of a Corning glass no. 172 tube, 900 mm. long and 15 mm. in internal diameter. It was packed for a length of 850 mm. with 110–115 g. of 10–20 mesh activated aluminum oxide. This tube was coated with asbestos, wrapped with twenty-six feet of nichrome no. 24 wire, and insulated with another layer of asbestos. This heating unit, without a rheostat, gave a temperature of 270–300°, measured by a chromel X-copel thermocouple encased in a 5 mm. Pyrex tube which extended into the packed tube a distance of 400 mm. Preliminary experiments had shown that rather extensive decomposition occurred at temperatures above 300° with the formation of ammonia.

The vapors from the tube were first passed through a long water condenser. The receiving flask was connected to a 20-mm. test-tube immersed in a bath of dry-ice in methanol. The non-condensable vapors then were bubbled through a solution of ammoniacal silver nitrate.

To facilitate the passage of vapor through the system, slight suction was used. Generally, about four hours were required for one mole of 4-morpholineëthanol to pass through this system.

In a typical experiment, 130 g. of 4-morpholineëthanol was distilled through the catalyst tube at 270–280° in four and one-quarter hours. Most of the material was condensed in the water condenser. About 1 cc. of liquid condensed in the tube immersed in the bath of dry-ice in methanol. This was later proved to be water containing a trace of morpholine. Acetylene was liberated throughout the experiment and was identified by filtering the precipitate formed in the ammoniacal silver nitrate solution. When a small amount of this precipitate was dried over a flame on the end of a spatula, a sharp explosion resulted.

The total weight of the condensate in the first receiver was 109.7 g. The fractions listed in Table I were obtained by fractional distillation.

TABLE I

	Fraction	Grams	% of original condensate
I	to 135° (atm. press.)	44.6	41
II	35–110° (11 mm.)	6.5	6
III	to 145° (20 mm.)	29.4	27
IV	to 163° (9 mm.)	11.2	10
V	to 196° (12 mm.)	12.6	11
VI	Residue	3.1	3

Fraction I proved to be a solution of morpholine in water. To it was added 100 cc. of ether and 40 g. of anhydrous sodium carbonate. After shaking at frequent intervals for one hour the mixture was filtered and the sodium carbonate was washed three times with ether.

This wash ether was added to the ether extract and the ether was removed by distillation. Fifteen and four-tenths grams of the remaining liquid distilled at 110–140°, leaving a residue of 2 g. Redistillation yielded 14.4 g., b. p. 125–132°, which is the boiling point range of morpholine. A picrate was prepared which melted at 149°. A mixed melting point with a picrate prepared from commercial morpholine also was at 149°.

Fraction II was an intermediate fraction consisting of a mixture of morpholine and 4-morpholineëthanol and was not further separated.

Redistillation of fraction III yielded 29 g. which distilled at 121–130° (16 mm.). This boiling point range corresponds to that of 4-morpholineëthanol. The picrate melted at 125°, the picrate prepared from commercial 4-morpholineëthanol melted at 126° and the mixture melted at 126°.

Fraction IV was almost solid. It was dissolved in 10 cc. of ether and chilled in a bath of dry-ice in methanol. The solid was removed by filtration. Another crop was obtained by concentrating the filtrate and chilling as before. Further concentrating and chilling gave no additional precipitate. The total recovery was 7.2 g. of a white solid which melted at 74°. A mixture of this solid with some known 1,2-dimorpholinoethane[9] melted at 73°. The picrate melted at 233° with decomposition, and a mixture with some known 1,2-dimorpholinoethane picrate[9] melted at 235° with decomposition.

The ether filtrate from the treatment of fraction IV was believed to contain some 2,2′-dimorpholinodiethyl ether, so it was added to fraction V. After distillation of the ether a small amount of liquid distilled below 170° (7 mm.). This was considered to be a mixture of 4-morpholineëthanol and 2,2′-dimorpholinodiethyl ether and was not separated. At 173–183° (7 mm.), 9.9 g. of liquid distilled. Redistillation yielded 8.2 g., b. p. 180–183° (10 mm.). This is the

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(6) Hurd, "Pyrolysis of Carbon Compounds," Reinhold Publishing Co., New York, N. Y., 1929, p. 176.

(7) Ref. 6, p. 305.

(8) Ref. 6, p. 181.

(9) Knorr, *Ber.*, **35**, 4472 (1902).

boiling point of 2,2′-dimorpholinodiethyl ether as given by Sand.[10] The picrate melted at 177°. A picrate prepared from known 2,2′-dimorpholinodiethyl ether melted at 175°[11] and a mixture of the two picrates melted at 175°.

Table II gives a summary of the compounds obtained. The percentage yields are based upon the amount of 4-morpholineëthanol used.

TABLE II

	Grams	Yield, %
Water	..	..
Morpholine	15.4	12
β-4-Morpholineëthanol	29.0	22
1,2-Dimorpholinoethane	7.2	6
2,2′-Dimorpholinodiethyl ether	8.2	6
Acetylene	..	..

4-Morpholinoethyl Chloride with Alcoholic Potassium Hydroxide.—To 13.4 g. (0.09 mole) of 4-morpholinoethyl chloride was added 9.2 g. of potassium hydroxide in 9 cc. of water and 66 cc. of absolute alcohol. After heating on a steam-bath for two hours, the solution was cooled and diluted with 50 cc. of water. The alcohol was removed by distillation using a fractionating column. The aqueous solution was extracted with ether, the ether extract dried over solid sodium hydroxide and the ether removed by distillation. The residual liquid distilled at 93–97° (14 mm.) and was redistilled at 200–201° (uncor.) at atmospheric pressure. The yield was 11 g. (77%). Since this boiling point corresponds to that of 4-morpholinoethyl ethyl ether, a picrate was prepared. It melted at 102° and a mixture with some unknown 4-morpholinoethyl ethyl ether picrate[12] melted at 102°.

Summary

4-Morpholineëthanol was dehydrated by passing the vapors through a tube containing activated aluminum oxide at 270–280°. In addition to water, the products isolated were acetylene, morpholine, 1,2-dimorpholinoethane, 2,2′-dimorpholinodiethyl ether and unreacted 4-morpholineethanol. A further attempt to prepare N-vinyl morpholine by treating 4-morpholinoethyl chloride with alcoholic potassium hydroxide yielded only 4-morpholinoethyl ethyl ether.

BOSTON, MASS. RECEIVED AUGUST 19, 1940

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[10] Sand, *Ber.*, **34**, 2906 (1901).

[11] Mason and Malkiel, THIS JOURNAL, **62**, 1449 (1940).

[12] Mason and Block, *ibid.*, **62**, 1446 (1940).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF SWARTHMORE COLLEGE]

Arylsulfonyl Ureas

BY EDWARD H. COX AND SAMUEL M. RAYMOND, JR.

A search of the literature reveals that only two reactions for the preparation of arylsulfonyl ureas have been reported. Billeter[1] prepared benzenesulfonyl urea by the action of ammonia on benzenesulfonyl isocyanate, which was prepared from benzenesulfonyl chloride and silver cyanate. No yields are recorded for any of the reactions leading to the final product. The reaction of acid chlorides and silver cyanate gives only fair yields and is so highly exothermic as to require careful attention.[2]

Much earlier Cleve[3] reported the preparation of two sulfonyl urea derivatives of naphthalene, by the action of potassium cyanate on the aminonaphthalene sulfonamides. The compounds were apparently impure products, and neither experimental details nor analyses are given.

We attempted some methods of preparing arylsulfonyl ureas without success. The hydrolysis of benzenesulfonyl guanidine[4] by barium hydroxide solution produced benzenesulfonamide while the original guanidine was recovered after treatment with boiling hydrochloric acid. From analogy in the pyrimidine series[5] we subjected benzenesulfonyl methylisothiourea to boiling hydrochloric acid. Methyl mercaptan and benzenesulfonamide were produced.

McKee[6] has reported that when phenyl methylisourea was heated with hyrochloric acid, phenylurea and methyl chloride were produced. We have applied this reaction with success in the preparation of arylsulfonyl ureas. When the arylsulfonyl ethylisoureas are treated with hydrochloric acid, the arylsulfonyl ureas are produced in good yields.

Experimental Part

The procedure for the preparation of the following arylsulfonyl ureas, with but slight changes, is the same as that given for benzenesulfonyl urea. The melting points and analyses for both the isoureas and ureas are given in tabular review. It is recommended that the starting material,

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[1] Billeter, *Ber.*, **37**, 694 (1904).

[2] Communication from Professor A. J. Hill, Yale University.

[3] Cleve, *Ber.*, **21**, 3266, 3273 (1888).

[4] Ackermann, *Z. physiol. Chem.*, **47**, 366 (1906).

[5] Wheeler, Johnson and Johns, *Am. Chem. J.*, **37**, 394 (1907).

[6] McKee, *ibid.*, **26**, 230 (1901).