The reduction of **mandelonitrile acetate** was carried out after the manner of the benzoate. From 4.4 g. (0.025 mole) of the nitrile acetate there was obtained in seventy-five minutes 3.9 g. of phenylethylamine hydrochloride, a yield of 74.5%.

Conclusions

1. Benzonitrile was reduced catalytically in absolute alcoholic solution to pure benzylamine by means of palladinized charcoal when one equivalent, or more, of hydrogen chloride was present; without hydrogen chloride a mixture of benzylamine, dibenzylamine and ammonia was formed.
2. Benzaldoxime was similarly reduced to pure benzylamine when three equivalents, or more, of hydrogen chloride were present. With one equivalent, or more, of the acid a mixture of the primary and secondary bases resulted.
3. Mandelonitrile was reduced in absolute alcoholic solution containing hydrogen chloride to phenylethylamine, but the yields of primary amine were poorer because a non-basic by-product was formed.
4. The benzoate and acetate of mandelonitrile were also reduced; though the esters of phenylethanolamine were not formed, good yields of phenylethylamine were obtained.

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[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XVIII. PARA-NITROBENZYLIDENE GLYCOLS AND GLYCEROLS

BY HAROLD HIBBERT AND MURRAY G. STURROCK[1]

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In order to facilitate the isolation of the various isomeric forms obtained in condensing an aldehyde with glycerol,[2] it seemed advisable to try to find some aldehyde capable of yielding crystalline cyclic acetals.

Experiments carried out with *p*-nitrobenzaldehyde show that this material condenses readily with both ethylene and 1,3-trimethylene glycol, yielding crystalline five- and six-membered cyclic acetals, respectively. Preliminary experiments using glycerol in place of the glycols gave a mixture of a crystalline and liquid *p*-nitrobenzylidene glycerol, a detailed investigation of which is recorded in the following communication (Part XIX).

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[1] Presented to the Faculty of the Graduate School, McGill University, in June, 1927, in candidature for the degree of Master of Science. The authors' thanks are due to the National Research Council, Ottawa, for their kind support accorded one of them (M. G. S.) in the form of a Bursary.

[2] Hibbert and coworkers, THIS JOURNAL, 50, 2235, 2242, 3120 (1928).

Experimental Part

Preparation of *p*-Nitrobenzylidene Ethylene Glycol.—Twenty g. of *p*-nitrobenzaldehyde was mixed with 31 g. of ethylene glycol (2.5 times the theoretical) and 0.2 cc. of 40% sulfuric acid and the mixture heated, with agitation, on the steam-bath for six hours. On cooling, the product set to a solid mass of crystals. The latter were washed well with water, then a number of times with a saturated solution of sodium bisulfite and again with water. Recrystallization from alcohol gave 15 g. (60%) of pure *p*-nitrobenzylidene ethylene glycol; m. p. 90.5°.

Anal. Subs., 0.1689; CO_2, 0.3430; H_2O, 0.0700. Calcd. for $C_9H_9O_4N$: C, 55.38; H, 4.60. Found: C, 55.08; H, 4.57.

The product is soluble in *cold* acetone, chloroform and pyridine, in *hot* carbon tetrachloride, alcohol and carbon bisulfide, but is insoluble in ligroin.

Preparation of *p*-Nitrobenzylidene Trimethylene Glycol.—Using a procedure similar to the above, 25 g. of 1,3-trimethylene glycol yielded 10 g. (71%) of pure *p*-nitrobenzylidene trimethylene glycol, m. p. 111.5°, having approximately the same solubilities as its lower homolog.

Anal. Subs., 0.2306; CO_2, 0.4873; H_2O, 0.1100. Calcd. for $C_{10}H_{11}O_4N$: C, 57.4; H, 5.31. Found: C, 57.6; H, 5.31.

Preparation and Separation of the Isomeric *p*-Nitrobenzylidene Glycerols.—Twenty g. of *p*-nitrobenzaldehyde, 24 g. of glycerol and 0.2 cc. of 40% sulfuric acid were heated, with stirring, for about six to ten hours. The temperature used in different experiments varied from 100 to 160°. After cooling, water was added and the mixture extracted twice with ether. The latter solution was washed with a concentrated solution of sodium bisulfite and a small amount of water. The ether was evaporated under reduced pressure and the residue taken up with warm benzene. On cooling (and further evaporation, if necessary) crystals separated which were filtered off. Evaporation of the mother liquor yielded a second crop and the process was repeated until no further crystallization took place on long standing in the cold.

The combined yield of crystals was treated with animal charcoal and recrystallized from hot benzene, giving pure *p*-nitrobenzylidene glycerol, m. p. 85°, initially, increasing on standing to 99°.

Anal. Subs., 0.1224; CO_2, 0.2411; H_2O, 0.0535. Calcd. for $C_{10}H_{11}O_5N$: C, 53.5; H, 4.93. Found: C, 53.7; H, 4.84.

The oil from the mother liquor was dissolved in benzene, the solution heated with animal charcoal, filtered and the oily layer which separated on cooling further purified by precipitating several times from small volumes of benzene at −15°. The oil thus obtained proved to be the isomer of the above crystalline compound.

Anal. Subs., 0.2004; CO_2, 0.3028; H_2O, 0.0888. Calcd. for $C_{10}H_{11}O_5N$: C, 53.3; H, 4.93. Found: C, 53.5; H, 4.84.

Preparation of the Benzoates of the Isomeric *p*-Nitrobenzylidene Glycerols.—The benzoates of the two isomeric glycerol acetals were prepared in each case by dissolving 3 g. of the acetal in dry pyridine, adding an equal volume of benzoyl chloride and then warming slightly. After allowing ten minutes for completion of the reaction, the product was poured into 250 cc. of water, when the benzoates separated as a white or yellow paste.

The benzoate of the crystalline isomer was recrystallized from benzene; m. p. 198°.

Anal. Subs., 0.1388; CO_2, 0.2924; H_2O, 0.0524. Calcd. for $C_{17}H_{15}O_6N$: C, 62.07; H, 4.59. Found: C, 61.92; H, 4.52.

The benzoate of the liquid isomer was recrystallized from alcohol; m. p. 178°.

Anal. Subs., 0.1284; CO_2, 0.2909; H_2O, 0.0513. Calcd. for $C_{17}H_{15}O_6N$: C, 62.07; H, 4.59. Found: C, 61.78; H, 4.43.

Summary

1. *p*-Nitrobenzaldehyde condenses readily with ethylene glycol and 1,3-trimethylene glycol to give the corresponding cyclic acetals.

2. Preliminary experiments indicate that *p*-nitrobenzaldehyde readily condenses with glycerol to give an isomeric mixture of cyclic acetals.

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[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XIX. STRUCTURAL, GEOMETRICAL AND OPTICAL ISOMERISM OF THE PARA-NITROBENZYLIDENE GLYCEROLS AND THEIR DERIVATIVES

BY HAROLD HIBBERT AND NEAL M. CARTER[1]

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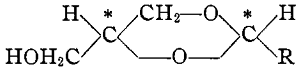
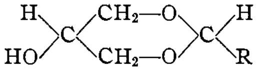
Introduction

In previous communications[2] it has been pointed out that when an aldehyde (RCHO) condenses with glycerol, there results a "partition" of the aldehyde between the 1,2- and the 1,1'-hydroxyl groups, so that in the subsequent condensation structural isomers are formed, namely, five- and six-membered cyclic acetals.

An examination of these general types A and B

(A)


(B)


shows that the five-membered ring (A) should exist in two geometrically isomeric, optically resolvable racemic forms, due to the presence of the two asymmetric carbon atoms (*). On the other hand, the six-membered acetal, (B), representing as it does a case of pseudo-asymmetry, should exist only in two geometrically isomeric, non-resolvable modifications.

Only a few references to geometrical isomerism in *heterogeneous* ring systems are to be found in the literature. Among the better-known examples is its application to explain the difference between paraldehyde

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[1] Research Fellow, McGill University. This work was carried out under the auspices of the coöperative research organization embracing the Canadian Pulp and Paper Association, the Pulp and Paper Division of the Forest Products Laboratory of Canada and the Department of Industrial and Cellulose Chemistry, McGill University. The authors wish to express their thanks for the support accorded them.

[2] Hibbert and coworkers, THIS JOURNAL, **50**, (a) 2235, (b) 2242, (c) 3120 (1928).