Vacuum distillation using a 20-cm. Vigreux column gave 15 g. of thiophenol, 3 g. of product, b.p. 120–125° (3 mm.) and 5 g. of high boiling residue. The 3,5-dinitrobenzoate of the product had a m.p. 92–100°, indicating a mixture of the phenylthiopropanols. The reaction was repeated a third time using 85% phosphoric acid. Distillation gave 15 g. of thiophenol, 4 g. of product, b.p. 110–125° (1–2 mm.) and 5 g. of residue. The 3,5-dinitrobenzoate of the product had a m.p. 90–98°, again indicating a mixture of the phenylthiopropanols.

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Carbon-alkylation Reactions of Nitroalkanes. The Reaction of *p*-Nitrobenzyltrimethylammonium Iodide and Sodium 2-Propanenitronate

BY HAROLD SHECHTER AND RALPH B. KAPLAN

p-Nitrobenzyl halides react with sodium salts of nitro compounds to yield carbon-alkylated derivatives, whereas benzyl halides substituted in the para position with other groups, either electronegative or electropositive, give oxygen-alkylated products.[1] Recently Hamlin[2] reported that reaction of aqueous benzyldimethylphenylammonium chloride with the sodium salt of 1- or 2-nitropropane yields benzaldehyde and dimethylaniline. It has now been found that *p*-nitrobenzyltrimethylammonium iodide reacts rapidly with sodium 2-propanenitronate, in refluxing ethanol, to yield 2-methyl-2-nitro-*p*-nitrophenylpropane, trimethylamine and sodium iodide (Equation 1), whereas reaction of benzyltrimethylammonium iodide and sodium 2-propanenitronate occurs slowly in diethylene glycol at 150° to give benzaldehyde in low yields. It appears, therefore, that alkylation reactions of salts of nitroalkanes with benzyl halides or quaternary benzylammonium compounds follow similar courses and that alkylation of nitroparaffins by amines does not always proceed through an elimination–addition mechanism.[3]

$$p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{N(CH}_3)_3\text{I} + (\text{CH}_3)_2\text{CNO}_2\text{Na} \longrightarrow$$
$$p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{C(CH}_3)_2\text{NO}_2 + (\text{CH}_3)_3\text{N} + \text{NaI} \quad (1)$$

Experimental

2-Methyl-2-nitro-*p*-nitrophenylpropane.—*p*-Nitrobenzyltrimethylammonium iodide (30 g., 0.093 mole), m.p. 195°, lit. 198°,[4] was added to a mixture of sodium (2.2 g., 0.096 mole) and 2-nitropropane (65 g., 0.75 mole) in absolute ethanol (400 ml.) and the solution was then refluxed for 30 hours. As the solution was heated, the odor of trimethylamine became apparent, and trimethylamine was evolved continuously throughout the reaction. The brown mixture was then distilled until much of the alcohol had been removed. The residue, upon being cooled slowly, crystallized first to yield *p*-nitrobenzyltrimethylammonium iodide (5.3 g., 0.0165 mole, 17.7%), m.p. 194–195°, and then a crude mixture of the quaternary ammonium salt and 2-methyl-2-nitro-*p*-nitrophenylpropane. Decolorization and fractional recrystallization of the crude product from mixtures of ethanol and water yielded pure 2-methyl-2-nitro-*p*-nitrophenylpropane (12.4 g., 0.585 mole) in 63% yield; m.p. 64–65°, lit.[1c] 65°. The melting point of the product was not depressed by an authentic sample which was prepared from *p*-nitrobenzyl chloride and sodium 2-propanenitronate.[1c]

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[1] (a) T. Posner, *Ber.*, **31**, 657 (1898); (b) L. Weisler and R. W. Helmkamp, THIS JOURNAL, **67**, 1167 (1945); (c) H. B. Hass and M. L. Bender, *ibid.*, **71**, 1767 (1949); (d) H. B. Hass, E. J. Berry and M. L. Bender, *ibid.*, **71**, 2290 (1949); (e) H. B. Hass and M. L. Bender, *ibid.*, **71**, 3482 (1949).

[2] W. E. Hamlin, Abstract, Ph.D. Thesis, University of Illinois, 1949.

[3] H. R. Snyder and W. E. Hamlin, THIS JOURNAL, **72**, 5082 (1950).

[4] E. Stedman, *J. Chem. Soc.*, 1902 (1927).

The Clemmensen Reduction of Butyroin

BY WALTER T. SMITH, JR.

It was surprising to find that reduction of butyroin with amalgamated zinc and hydrochloric acid gave not octanol-4, as might be expected, but instead gave a ketone, octanone-4. This is unusual in two respects; first, in that a ketone is formed under conditions which usually result in the reduction of ketones to hydrocarbons and, second, in that it appears to involve the reduction of a hydroxyl group while leaving a carbonyl group untouched.

Under the conditions used for the reduction, the octanone as well as the butyroin are essentially insoluble in the reaction mixture. It seemed likely that if the reaction mixture was homogeneous the octanone might be more easily reduced to octane. However, when runs were made in which the water was replaced by sufficient ethyl alcohol or acetic acid to make a completely homogeneous reaction mixture, the main product was still octanone-4.

Although the yield of octanone-4 is 36% when the reduction is carried out for only two hours, the amount of octanone formed is not decreased by its reduction to octane when the time of the reaction is extended. Thus, in runs of four, ten and twenty-seven hours the yield of ketone is 50–60%.

The amount of octane formed in any of the reactions, even those running for as long as twenty-seven hours, must be very small. The boiling point of the small foreruns rose steadily to that of octanone-4, with no leveling off near the boiling point of octane. In order to exclude the possibility that any octane which might be formed was escaping through the condenser, a twenty-hour run was made in which any vapors which escaped through the condenser were collected in a trap cooled in Dry Ice and isopropyl alcohol. Only a trace of liquid was collected in the trap and its refractive index was not that of octane. It appears that octanone-4 is resistant to reduction under the conditions employed here. When a sample of octanone-4 was refluxed with amalgamated zinc and hydrochloric acid for five days the forerun was not appreciably larger than in other runs on butyroin, although the recovered octanone-4 had a wider boiling range than originally.

The possibility that 4,5-octanediol might be an intermediate in the reaction was suggested by the fact that this glycol has been reported to yield octanone-4 when heated with dilute sulfuric acid in a sealed tube.[1] To test this possibility *meso*-4,5-octanediol was refluxed with hydrochloric acid of the same concentration used in the reductions. Although some ketone is formed in this way, the amount is so small that the glycol cannot be considered as an intermediate. The presence of amal-

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[1] L. Bouveault and R. Locquin, *Compt. rend.*, **140**, 1699 (1905).

gamated zinc along with the hydrochloric acid did not speed up the conversion of the glycol to ketone. In four hours, butyroin is converted to octanone-4 in 48% yield, while 4,5-octanediol gives only a 21% yield under the same conditions.

Although hydroxyl groups are usually not susceptible to reduction with amalgamated zinc and hydrochloric acid, the hydroxyl group of butyroin appears to be activated by the adjacent carbonyl group and is hence susceptible to reduction. The only other cases in which a hydroxyl group has been replaced by hydrogen by the action of amalgamated zinc and hydrochloric acid are with β-hydroxy acids[2] and benzyl alcohol.[3]

Work on the Clemmensen reduction of α-diketones and unsymmetrical acyloins is in progress and will be reported later.

Experimental

Clemmensen Reductions.—The following mixture was refluxed for 10 hours: 85 g. of amalgamated zinc,[4] 20 g. (0.134 mole) of butyroin, 60 ml. of water and 60 ml. of concd. hydrochloric acid. The organic layer was separated, washed 3 times with 50-ml. portions of water, dried over anhydrous sodium sulfate and distilled. The material distilling at 160–166° weighed 10.2 g. (60% yield), $n^{20}\text{D}$ 1.4150, $n^{14}\text{D}$ 1.4177. Hargreaves and Owen[5] report $n^{14}\text{D}$ is 1.4173 for octanone-4. The semicarbazone melted at 96–97° both alone and when mixed with an authentic sample.

In another run the 60 ml. of water was replaced by 90 ml. of 95% alcohol in order to give a homogeneous liquid. After 4 hours of refluxing the liquid was decanted from the zinc. A large amount of sodium sulfate and 100 ml. of ether was added but two layers did not separate. The sodium sulfate was removed by filtration and the filtrate was distilled through a Vigreux column until the temperature of the distillate reached 82°. At this point the residue in the distilling flask was washed with two 40-ml. portions of water. The organic layer was dried over calcium chloride and distilled to give 4.5 g. of octanone-4, b.p. 160–166°.

When 20 g. of butyroin, 85 g. of amalgamated zinc and 120 ml. of glacial acetic acid were refluxed for 4 hours no octanone or other reduction products were obtained and the butyroin was recovered.

The following mixture was refluxed for 20 hours: 20 g. of butyroin, 85 g. of amalgamated zinc, 60 ml. of concd. hydrochloric acid and 120 ml. of glacial acetic acid. (This much acetic acid was necessary to dissolve all of the butyroin.) The reaction mixture was poured with cooling onto 112 g. (2.8 moles) of sodium hydroxide. The resultant alkaline mixture was steam distilled. The organic layer from the distillate was separated, dried and distilled to give fractions with the following boiling points: 2.5 g., b.p. less than 160°, 7.6 g., b.p. 160–166°, 1.9 g., b.p. 166–179°, and a residue of 1.3 g.

A mixture of 20 g. of butyroin, 85 g. of amalgamated zinc, 60 ml. of water, and 60 ml. of concd. hydrochloric acid was refluxed for 20 hours. The top of the condenser was fitted with a cork holding a glass tube leading to a 25 by 2500 mm. test-tube in a Dry Ice–isopropyl alcohol-bath. The liquid collected in the trap weighed only 0.6 g. Its $n^{20}\text{D}$ was 1.4025. The corresponding value for octane is 1.3890 and for octanone-4 is 1.4150.

Attempted Reduction of Octanone-4.—The following mixture was refluxed for five days: 13 g. of octanone-4, 85 g. of amalgamated zinc, 60 ml. of water and 60 ml. of concd. hydrochloric acid. The mixture was cooled, the organic layer was separated, washed with 50- and 25-ml. portions of water, dried and distilled to give 1.1 g., b.p. less than 145°, 7.8 g., b.p. 145–166° and 1.1 g. of residue.

Conversion of 4,5-Octanediol to Octanone-4.—The following mixture was refluxed for 4 hours: 8 g. of *meso*-4,5-octanediol, 34 g. of amalgamated zinc, 24 ml. of water and 24 ml. of concd. hydrochloric acid. The layers were separated with the aid of 30 ml. of ether and the ether layer was dried and distilled to give 1.5 g. (21%) of octanone-4, b.p. 160–170°. Under similar conditions butyroin is converted to octanone-4 in 48% yield.

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(2) J. W. Cook and W. Lawson, *J. Chem. Soc.*, 827 (1933).

(3) W. Steinkopf and A. Wolfram, *Ann.*, **430**, 113 (1923).

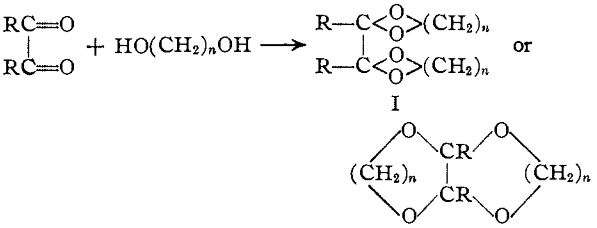
(4) E. L. Martin, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 163.

(5) G. H. Hargreaves and L. N. Owen, *J. Chem. Soc.*, 750 (1947).

Some Cyclic Acetals of Glyoxal

BY M. M. SPRUNG AND F. O. GUENTHER

This paper describes the preparation and properties of a number of cyclic acetals derived from glyoxal and dihydric alcohols. In this reaction, ring closure can occur in either of two directions.



I

II

Glyoxal-bis-ethylene acetal which was first obtained by Doncin,[1] was assigned a structure corresponding to II by Böeseken, Tellegen and Henriquez,[2] who isolated two isomeric modifications (presumably *cis* and *trans*). However, in the case of biacetyl and ethylene glycol, Böeseken and Tellegen[3] obtained two isomeric bis-acetals, which they considered to be structural isomers, representative of I and II, respectively. They prepared cyclic acetals also from ethylene glycol with benzil, 1-phenyl-1,2-propanedione, methylglyoxal and phenylglyoxal; and from 2,3-butylene glycol and trimethylene glycol with 2,3-butanedione. Ring sizes and stereoisomeric relationships were not elucidated.

In the present work one purpose was to ascertain the effect of the structure of the diol on its reactivity toward glyoxal in cyclic acetal formation. The effects of substitution on the carbon atoms bearing the hydroxyl groups and of the positions of the hydroxyl groups were therefore studied.

Table I lists the diols studied and gives the boiling ranges and refractive indices of the particular samples used.

Experimental

Materials.—The glyoxal was a 30% aqueous solution, obtained from the Carbide and Carbon Chemicals Corporation. 2,4-Pentanediol was prepared in 40–50% yield by reduction of acetylacetone with sodium in absolute ethanol according to the procedure of Bauer.[4] 2,5-Hexanediol was prepared in 60–65% yield by the reduction of acetonylacetone with lithium aluminum hydride, following the procedure of Nystrom and Brown.[5] The remaining diols listed in Table I were commercial products or were Eastman Kodak Co. organic chemicals. They were purified, in general,

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(1) L. Doncin, *Monatsh.*, **16**, 8 (1895).

(2) J. Böeseken, F. Tellegen and P. C. Henriquez, *Rec. trav. chim.*, **50**, 909 (1931); **54**, 737 (1935). See also W. Baker and F. B. Field, *J. Chem. Soc.*, 88 (1932); W. Baker and A. Shannon, *ibid.*, 1598 (1933).

(3) J. Böeseken and F. Tellegen, *Rec. trav. chim.*, **57**, 133 (1938).

(4) M. E. Bauer, *Compt. rend.*, **154**, 1092 (1912).

(5) R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 1197 (1947).