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 The only other cases in which a hydroxyl group has been replaced by hydrogen by the action of amalgamated zinc and hydrochloric acid are with β-hydroxy acids[2] and benzyl alcohol.[3]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), $n^{20}\mathrm{D}$ 1.4150, $n^{14}\mathrm{D}$ 1.4177. Hargreaves and Owen[5] report $n^{14}\mathrm{D}$ 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 $n^{20}\mathrm{D}$ 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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[3] W. Steinkopf and A. Wolfram, *Ann.*, **430**, 113 (1923).

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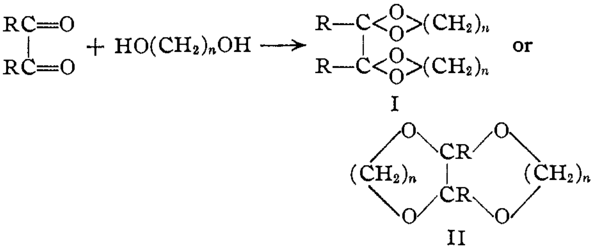
[5] G. H. Hargreaves and L. N. Owen, *J. Chem. Soc.*, 750 (1947).

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.



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).

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TABLE I

OBSERVED BOILING RANGES AND REFRACTIVE INDICES OF DIOLS

Diol	Type	Boiling range °C.	Boiling range Mm.	n^{20}_D
Ethylene glycol	1,2-Diprimary	191–195	760	1.4318
Trimethylene glycol	1,3-Diprimary	101–103	10	1.4395
Pentamethylene glycol	1,5-Diprimary	129–133	10–11	1.4513
1,3-Butylene glycol	1,3-Primary-secondary	101–102	10	1.4400
2,3-Butylene glycol	1,2-Disecondary	79	10	1.4383
2,4-Pentanediol	1,3-Disecondary	100–105	15	1.4356
2,5-Hexanediol	1,4-Disecondary	114–116	10	1.4492
11,12-Dihydroxytetracosane[a]	1,2-Disecondary	230–245	2	....
Pinacol	1,2-Ditertiary	M. p. 41.5		....
Diethylene glycol	1,5-Diprimary (1 chain oxygen atom)	120–128	10–11	1.4460

[a] Sample was 78% pure on basis of its hydroxyl equivalent.

TABLE II

ACETAL FORMATION FROM GLYOXAL AND DIOLS

	Diol	Reaction time, hours A[a]	Reaction time, hours B[b]	Water removed, %	Yield, %	Properties of product B.p. °C.	Properties of product B.p. Mm.	Properties of product M.p., °C.	Properties of product Crystallization and solvent
1	Ethylene glycol	8.0	5.5	96	88	120–121	40	86–89[d]	Cyclohexane
2	Trimethylene glycol	7.0	5.0	96	94	170–178	50	150–155	Twice-benzene + pet. ether twice-cyclohexane
3	Pentamethylene glycol		<1		..			Insoluble polymer only	
4	1,3-Butylene glycol	6.8	5.3	91	91	142–148	20	101–102	Twice-normal heptane
5	2,3-Butylene glycol	4.5	3.3	98	87–91	124–131	20	64–65	Twice-90% aq. methanol
6	2,4-Pentanediol	2.0	1.5	91	>86	115–118	5	117	3 times-cyclohexane
7	2,5-Hexanediol	0.9	0.2	86	57–66 monomer 32 polymer	132–135	10	98–99	Twice-normal pentane
8	11,12-Dihydroxytetracosane		<1	83	90	290–320	1[e,f]		
9	Pinacol	3.5	1.5	92	82–93	100–110	3	88–89	Twice-normal heptane
10	Diethylene glycol		<2		...			Insoluble polymer only	

TABLE II (*Continued*)

	Solubility in Water	Solubility in *n*-Heptane	Solubility in Cyclohexane	Analyses, % Mol. wt.[c] Calcd.	Analyses, % Mol. wt.[c] Found	Analyses, % Carbon Calcd.	Analyses, % Carbon Found	Analyses, % Hydrogen Calcd.	Analyses, % Hydrogen Found	Monomeric product (Glyoxal-bis-alkyleneacetal)
1	Slowly sol.	Insol.	Sl. sol.	146	162 154	49.3	49.5 49.1	6.8	6.9 6.9	Ethylene
2	Sol.	Insol.	Sl. sol.	174	173 180 168	55.2	54.5 55.0	8.1	8.2 8.3	Trimethylene
4	Sol.	V. sl. sol.	Slowly sol.	202	193 201	59.4	59.4 59.1 59.1	8.9	8.8 8.9 9.0	1-Methyltrimethylene
5	V. slowly sol.	Sol.	Sol.	202	210 212	59.4	59.6 59.2 59.5	8.9	9.1 9.2 9.1	1,2-Dimethylethylene
6	Sol.	Sol.	Sol.	230	245 247	62.6	62.6 63.2 62.6	9.6	9.6 9.6 9.8	1,3-Dimethyltrimethylene
7	V. sl. sol.	Sol.	Sol.	258	265 256 250 245	65.1	65.2 64.9	10.1	10.1 10.3	1,4-Dimethyltetramethylene
8	Insol.	Sol.	Sol.	763	677 684					1-*n*-Decyl-2-*n*-dodecylethylene
9	Insol.	Sol.	Sol.	258	236 261	65.1	64.9 65.4 65.0	10.1	10.0 10.2 10.2	Tetramethylethylene

[a] Total time, from first drop of water in moisture trap. [b] Corrected for time required to remove water present in the glyoxal solution. [c] If soluble, determined in cyclohexane by freezing point method, otherwise determined in benzene. [d] Melting point of eutectic mixture, 86°. Reference 2. [e] After repeated redistillation of middle fraction. [f] Analysis indicates virtually zero hydroxyl value.

by vacuum distillation, taking cuts of the boiling ranges given.

General Procedure for Preparation of Cyclic Acetals.—The apparatus consisted of a one-liter, three-necked flask, with standard taper ground glass joints, to which were attached a stirrer, a reflux condenser and Dean–Stark moisture trap. The flask was charged with a mixture consisting of one mole of glyoxal (193 g. of 30% aqueous solution), 2.4 moles of the diol, 1% of *p*-toluenesulfonic acid monohydrate (based on the total weight of diol and monomeric glyoxal) and 160 ml. of redistilled toluene. The heterogeneous mixture was agitated by means of an efficient stirrer and heated to its boiling point, using a Glas-Col heating mantle. For qualitative comparisons of reaction time, the reaction was assumed to start when the first drop of water appeared in the moisture trap and to be concluded when the rate of evolution of water was less than 1–2 ml. per hour. The course of the reaction was checked at intervals by determination of the refractive index of the toluene insoluble phase of the separated distillate, since toward the end of the reaction, this distillate consists essentially of unchanged diol. Further evidence of the progress of the reaction is the gradual increase in reaction temperature from around 87° (a little above the boiling point of the toluene-water azeotrope) to about 120–125° (varying somewhat with the diol used). Disappearance of the second liquid phase is further evidence of completion of the reaction.

The toluene solution was now cooled and washed with dilute sodium bicarbonate solution until free from acid, then with water. The combined washings were extracted with toluene or with chloroform to recover appreciable quantities of acetal which otherwise would be lost. After drying over anhydrous potassium carbonate or calcium chloride, the solvents were removed by distillation and the products, unless polymeric, were purified by vacuum distillation. Final purification involved several crystallizations, in case of solids, and redistillation of liquids.

Reaction times, yield data, properties and analytical data of the products obtained are given in Table II. Of the cyclic acetals prepared during this work, only glyoxal-bis-ethylene acetal has been described previously.

Discussion of Table II

In those cases which are uncomplicated by polymer formation, the relative ease of reaction with glyoxal of the diols studied is in the order: tertiary > secondary > primary. (Compare particularly pinacol, 2,3-butylene glycol and ethylene glycol.) The speed of the reaction increases also with the number of carbon atoms between the two hydroxyl groups (for example, in the cases of ethylene and trimethylene glycols). These relations are obscured when insoluble polymeric acetals are formed.

Boiling points of the cyclic bis-acetals, extrapolated to 760 mm. pressure by means of standard boiling point *vs.* pressure charts,[6] are in general 50–75° higher than that of the parent diol, except in the case of glyoxal-bis-ethylene acetal, where the difference is only about 20°. Solubilities of the bis-acetals are roughly determined by the number of alkyl substituents, and the length of the carbon chain between oxygen atoms. Thus, all those reported in this paper are appreciably soluble in water except those derived from pinacol, 2,5-hexanediol and 11,12-dihydroxytetracosane. On the contrary, they are all readily soluble in *n*-heptane except those derived from ethylene, trimethylene and 1,3-butylene glycols.

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Action of Sodium Cyanide on β-Hydroxypropionitrile and β-Hydroxypropionic Acid

BY LIU-SHENG TS'AI

In the study of exchange of β-hydroxypropionitrile with cyanide labeled with C^{14}, Ts'ai and Kamen[1] found that under alkaline conditions the cyanide, precipitated as silver cyanide after exchange, showed a drop in activity to such an extent that one could calculate a 9.2% randomization of cyanide and nitrile. The recovery of activity in the separated nitrile, however, was 10-fold too high for the amount of specific activity loss observed by the cyanide. This leads one to suspect that one possible explanation of the discrepancy would be by the reaction of cyanide with nitrile. Further investigation on this matter revealed that this is the case, and the results are reported in the present communication. The final product of the reaction was found to be succinic acid. This result is particularly interesting, since it probably involves a replacement of hydroxy group by a cyanide group which was subsequently hydrolyzed to acid.

It is also possible that β-hydroxypropionitrile under alkaline conditions first hydrolyzes to acid, and the resulting hydroxy acid then reacts with the cyanide. Experiment with β-hydroxypropionic acid and cyanide also gave succinic acid although the yield was not as good as that with β-hydroxypropionitrile. Under the present experimental conditions, it is difficult to decide whether it is the β-hydroxypropionitrile or the β-hydroxypropionic acid that actually reacts with the cyanide.

However the referee of this note has kindly suggested that in his opinion the reaction proceeds step-wise, first by elimination of water to yield acrylonitrile, which is then converted to succinonitrile, which in turn is hydrolyzed to the acid. He supports the first step by the work of Davis and Carpenter[2] who have demonstrated the dehydration of β-hydroxypropionitrile by Ca(OH)$_2$.

Still another possibility is that the sodium cyanide may be hydrolyzed to sodium formate. The formate may then react with the nitrile or the hydrolyzed acid. Separate experiments with sodium formate and β-hydroxypropionitrile and with sodium formate and β-hydroxypropionic acid, however, all gave negative results, thus proving that the formate is not responsible for the replacement reaction.

Experimental

Reaction of β-Hydroxypropionitrile with Sodium Cyanide.—A large test-tube containing 2.66 g. of β-hydroxypropionitrile, 8.82 g. of sodium cyanide and 15 ml. of water was held in a beaker of briskly boiling water for four hours. After cooling, 3 g. of sodium hydroxide was added and the nitrile hydrolyzed.[3] The combined ether extracts (seven extractions) gave a solid product of 0.98 g. (22.2%). This product after two recrystallizations had an acid equivalent of 59.07 g. and melted at 181–182° (m.p. of pure succinic acid simultaneously determined was 182–183°).

Anal. Calcd. for C$_4$H$_6$O$_4$: C, 40.68; H, 5.08. Found: C, 40.65; H, 5.14.

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