with an amount of ether insufficient to dissolve the entire fraction and from the insoluble part the diol was recovered. The ether solution was concentrated and after discarding the first crop of crystalline material a second crop, decomposing at 139–140°, analyzed for a mono-tosyl ester.

Anal. Calcd. for $C_{35}H_{46}O_4S$: S, 5.7; Found: S, 5.35.

22-α-Naphthyl-3-hydroxy-bisnor-5-cholenol (X).—This compound was made in the same manner as the phenyl analog using α-naphthylmagnesium bromide. After several recrystallizations from chloroform and toluene it sublimed at 245°.

Anal. Calcd. for $C_{32}H_{42}O_2$: C, 83.66; H, 9.22. Found: C, 83.84; H, 9.29.

Diacetate (XI).—This compound was made by the usual method of treating the diol with acetic anhydride in pyridine. After recrystallization from alcohol, it melted at 198–200°.

Anal. Calcd. for $C_{36}H_{46}O_4$: C, 79.56; H, 8.54; CH_3CO, 15.8. Found: C, 79.80; H, 8.50; CH_3CO, 14.2.

Summary

1. A method is described for the preparation of 3-acetoxy-bisnor-5-cholenaldehyde semicarbazone (IV) in 50% yields, by the ozonolysis of dibromostigmasteryl acetate in the presence of pyridine.

2. The following compounds have been prepared: (a) 3-acetoxy-bisnor-5-cholenaldehyde semicarbazone (IV); (b) 3-hydroxy-bisnor-5-cholenaldehyde semicarbazone (V); (c) 3-acetoxy-bisnor-5-cholenaldehyde 2,4 dinitrophenylhydrazone (XIII); (d) the diethyl-acetal of 3-hydroxy-bisnor-5-cholenaldehyde (XII); (e) 22-phenyl-3-hydroxy-bisnor-5-cholenol (VI). From this diol (e) the following esters were prepared: (f) diacetate (VII); (g) dibenzoate (VIII); (h) dipalmitate (IX); (i) a mono-tosyl ester; (j) 22-α-naphthyl-3-hydroxy-bisnor-5-cholenol (X) and its diacetate (XI).

3. The ozonolysis of *i*-stigmasteryl methyl ether (XIV) yielded 30% of the 6-methoxy-bisnor-*i*-cholenaldehyde (XV), which was isolated as the semicarbazone (XVI), and this converted to 3-methoxy-bisnor-5-cholenaldehyde semicarbazone (XVII).

KALAMAZOO, MICHIGAN RECEIVED JANUARY 24, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Derivatives of γ-Valerolactone, 1,4-Pentanediol and 1,4-Di-(β-cyanoethoxy)-pentane[1]

BY ROBERT V. CHRISTIAN, JR.,[2] HORACE D. BROWN AND R. M. HIXON

Catalytic reduction of levulinic acid to γ-valerolactone and 1,4-pentanediol was studied in the early war period as a source for pentadiene.[3] Availability of the diol led to the condensation with acrylonitrile and the catalytic reduction of the resulting cyanoethoxy derivative to the corresponding diamine. From the diamine a series of salts was prepared for investigation as possible linear polymer intermediates or surface active agents.

Experimental[4]

Materials.—A technical grade of levulinic acid was used. It was found necessary to distil the acid *in vacuo* to free it from catalyst poisons (presumably mineral acids). Ethyl levulinate was prepared by the method of Ruzicka.[5] The acrylonitrile (Eastman Kodak Co. Practical grade) was used without further treatment. Raney nickel and copper–chromium oxide catalysts were prepared in the usual manner.[6] The acids used for the preparation of salts were either reagent grade or suitably purified practical or technical grades.

Reduction Procedure.—Hydrogenations were carried out in steel rocking bombs of standard design. Small runs (one mole or less of reactant) were made in a 500-ml. bomb. Production runs of γ-valerolactone were carried out in a copper-lined unit of 3.85 liters capacity.

γ-Valerolactone.[7]—The charge consisted of 580 g. (5 moles) of purified levulinic acid and 15 g. of Raney nickel. Hydrogen was introduced to an initial pressure of 700 p.s.i. The reduction started at about 100° and was complete after three hours. The maximum temperature reached was 220°. Separation of the catalyst and distillation of the reaction mixture gave 471 g. (94%) of γ-valerolactone; b. p. 87–90° (8–10 mm.).

1,4-Pentanediol. A. From γ-Valerolactone.—Using the method of Folkers and Adkins,[8] hydrogenations were made with 100 g. (1 mole) of γ-valerolactone, 6–8 g. of copper–chromium oxide catalyst and initial hydrogen pressures of 200 atmospheres. Yields of 1,4-pentanediol varied from 32 to 83%, the higher yields being obtained at a temperature of 240–260°. Reductions made at 270–290° gave low yields of diol and a low-boiling fraction (70–100°) from which a sample of α-methyltetrahydrofuran (b. p. 78–80°, $d^{20}{}_4$ 0.8548, $n^{20}{}_D$ 1.406[9]) was isolated.

B. From Ethyl Levulinate.—Hydrogenation of ethyl levulinate (0.7 mole, 8 g. copper–chromium oxide catalyst) without solvent at 250° and 200 atmospheres initial hydrogen pressure gave 72% of 1,4-pentanediol.

C. From Levulinic Acid.—The charge consisted of 92.8 g. (0.8 mole) of distilled levulinic acid and 8 g. of copper–chromium oxide catalyst with an initial hydrogen pressure of 200 atmospheres. Reduction, which began at 190° with a gage pressure of 267 atmospheres, took place

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[1] Taken in part from a thesis submitted by Robert V. Christian' Jr., to the Graduate Faculty of Iowa State College in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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[3] Unpublished studies by Horace D. Brown.

[4] All melting points and boiling points are uncorrected.

[5] Ruzicka, *Ber.*, **50**, 1367 (1917).

[6] Adkins, "Reactions of Hydrogen with Organic Compounds over Copper–Chromium Oxide and Nickel Catalysts," The University of Wisconsin Press, Madison, Wisconsin, 1937, pp. 20, 13.

[7] This method for the preparation of γ-valerolactone was developed during September, 1943. U. S. Patent 2,368,366 (*C. A.*, **39**, 4626 [1945]), which was granted January 30, 1945, describes essentially the same process.

[8] Folkers and Adkins, THIS JOURNAL, **54**, 1145 (1932).

[9] Compare Zelinskii and Shuikin, *Compt. rend. acad. sci. U. R. S. S.*, 60 (1933) [*C. A.*, **28**, 2002 (1934)].

in two steps. About 0.9 mole of hydrogen was taken up at 245° and an equal quantity at 300°. Total time required for completion of the reaction (as evidenced by cessation of hydrogen absorption) was one and one-third hours.

Fractionation of the filtered product gave 9 g. (11%) of γ-valerolactone (b. p. 89–92° at 16 mm.) and 36.5 g. (44%) of 1,4-pentanediol (b. p. 122–124° at 15 mm.). A forerun of 18 g. (b. p. 80–103° at atmospheric pressure) contained water and had a strong odor of α-methyltetrahydrofuran.

In another experiment using 0.5 mole of levulinic acid and 5 g. of copper–chromium oxide catalyst with an initial hydrogen pressure of 100 atmospheres and maximum reduction temperature of 273°, the yields of γ-valerolactone and 1,4-pentanediol were 62 and 21%, respectively.

1,4-Di-(β-cyanoethoxy)-pentane.—The reaction of 69 g. (1.3 moles) of acrylonitrile with 62 g. (0.6 mole) of 1,4-pentanediol in the presence of 3 ml. of 40% aqueous potassium hydroxide was carried out in the usual manner.[10] The product was taken up in ether, extracted twice with normal hydrochloric acid, and once with water. The ether solution was dried with anhydrous sodium sulfate and distilled under reduced pressure. 1,4-Di-(β-cyanoethoxy)-pentane was obtained as 104 g. (83%) of colorless liquid; b. p. 157° (1 mm.), $n^{28}\text{D}$ 1.4478, d^{28}_4 1.005.

Anal. Calcd. for $C_{11}H_{18}O_2N_2$: N, 13.3. Found: N, 13.3, 13.4.

The dinitrile was an odorless liquid, soluble in organic solvents, but not appreciably soluble in water. Attempts to prepare a solid derivative of the dinitrile by treatment with alkaline hydrogen peroxide,[10,11] condensation with thioglycolic acid and dry hydrogen chloride,[12] or conversion to a phlorophenone[13] yielded only oils. A solid iminoester hydrochloride was obtained, however, by the usual methods.[14]

bis-(Ethyliminoester Hydrochloride) of 1,4-Di-(β-cyanoethoxy)-pentane.—A mixture of 42 g. (0.2 mole) of 1,4-di-(β-cyanoethoxy)-pentane and 23 g. (0.5 mole) of absolute ethanol was treated at −10° with excess, dry hydrogen chloride. The resulting thick sirup set to a mass of white crystals after standing for a week in the refrigerator. After removal of excess ethanol and hydrogen chloride *in vacuo*, the product weighed 75 g. (100%). A sample taken for analysis was pulverized, washed well with anhydrous ether and dried in a vacuum desiccator over sulfuric acid. A white powder melting at 103–104° with decomposition (gas evolution) resulted.

Anal. Calcd. for $C_{15}H_{32}O_4N_2Cl_2$: Cl, 18.89. Found: Cl, 18.84, 18.94.

1,4-Di-(γ-aminopropoxy)-pentane.—1,4-Di-(β-cyanoethoxy)-pentane (70 g., 0.33 mole) was reduced in the presence of 4 g. of Raney nickel catalyst and 30 ml. of liquid ammonia[15,16,17] with an initial hydrogen pressure of 200 atmospheres. Hydrogenation began at about 80°, proceeded rapidly at 115–120°, and was complete in fifty minutes. The maximum temperature reached was 122°. Distillation of the product, after removal of the catalyst, gave 1,4-di-(γ-aminopropoxy)-pentane as 55.5 g. (77%) of colorless liquid of b. p. 132–135° (2 mm.), d^{24}_4 0.9448, $n^{24}\text{D}$ 1.4596.

Anal. Calcd. for $C_{11}H_{26}O_2N_2$: N. E., 109.2; N, 12.8. Found: N. E., 110.4, 110.0; N, 12.6.

A forerun of approximately 5 g., boiling over a 20° range, was obtained. The residue decomposed extensively at 200–230° when an attempt was made to distil it at a pressure of 1 mm. Another experiment using hydrogen at an initial pressure of 130 atmospheres gave substantially the same yield of amine (82%).

1,4-Di-(γ-aminopropoxy)-pentane is soluble in organic solvents and miscible with water in all proportions. The aqueous solution of the compound is strongly basic to phenolphthalein (a 5% solution exhibits a *p*H in excess of 11) and can be titrated to a sharp end-point using methyl red indicator. On being exposed to the air, the amine rapidly absorbs carbon dioxide and eventually forms a sticky gum. An attempt to prepare the hydrochloride by precipitation from anhydrous ether solution with dry hydrogen chloride gave an oil which could not be induced to crystallize. The picrate was likewise obtained as an oil.

Salts of 1,4-Di-(γ-aminopropoxy)-pentane.—These compounds were prepared in 0.01 mole quantities by the following methods as indicated in the table.

Method A.—Solutions of the calculated quantities of the diamine and acid in appropriate amounts of absolute ethanol were well mixed and evaporated to dryness.

Method B.—The calculated quantity of the solid acid was added to the diamine dissolved in a little ethanol. The solution was evaporated to dryness.

Method C.—The calculated amount of the solid acid was added to a solution of the diamine in water. The resulting mixture was evaporated to dryness.

Method D.—Aqueous solutions of the theoretical quantities of the diamine and acid were well mixed and evaporated to dryness.

Those salts which did not solidify at once were placed in a vacuum desiccator over sulfuric acid. In some cases, trituration with a little absolute ethanol and ether hastened the crystallization. The solid salts were recrystallized from mixtures of absolute ethanol and ether with the exception of the oxalate which was recrystallized from ethanol and water.

Discussion

For the reduction of levulinic acid to γ-valerolactone satisfactory reduction rates were obtained with initial hydrogen pressures of 35 atmospheres or above and temperatures of 175–200°. However, reduction has been observed at 100–150° with an initial pressure of 250 p.s.i.

The occurrence of α-methyltetrahydrofuran as a by-product in the hydrogenation of γ-valerolactone to 1,4-pentanediol has not been observed heretofore. The ease with which 1,4-pentanediol can be dehydrated to form the cyclic ether[18] suggests that here the diol is the precursor of the latter compound. This would appear to be in contrast to the previously reported[19] hydrogenolysis, in the presence of Raney nickel, of the carbonyl oxygen in γ-valerolactone without cleavage of the lactone ring. In the present work the presence of amyl alcohols[8] was indicated but no attempt was made to isolate this fraction. Hill and Adkins[20] have reported a 60% yield of 1,4-pentanediol from ethyl levulinate in dioxane or ethanol solution at 250° and 250 atmospheres pressure.

There was some indication that potassium hydroxide was superior to trimethylbenzylammonium hydroxide[10,16] as a catalyst for the addition of acrylonitrile to 1,4-pentanediol.

In the hydrogenation of 1,4-di-(β-cyanoethoxy)-pentane, absorption of hydrogen began in the

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[10] Bruson and Riener, THIS JOURNAL, **65**, 23 (1943).

[11] Radziszewski, *Ber.*, **18**, 355 (1885); Deinert, *J. prakt. Chem.*, [II] **52**, 431 (1895).

[12] Condo, Hinkel, Fassero and Shriner, THIS JOURNAL, **59**, 230 (1937).

[13] Howells and Little, *ibid.*, **54**, 2451 (1932).

[14] Pinner, *Ber.*, **16**, 352, 1643 (1883).

[15] Schwoegler and Adkins, THIS JOURNAL, **61**, 3499 (1939); Huber, *ibid.*, **66**, 876 (1944); Whitmore, *et al.*, *ibid.*, **66**, 725 (1944).

[16] Utermohlen, *ibid.*, **67**, 1505 (1945).

[17] Wiedemann and Montgomery, *ibid.*, **67**, 1994 (1945).

[18] Freer and Perkin, *J. Chem. Soc.*, **51**, 837 (1887); Lipp, *Ber.*, **22**, 2569 (1889); Froebe and Hochstetter, *Monatsh.*, **23**, 1088 (1902).

[19] Reference 6, p. 78.

[20] Hill and Adkins, THIS JOURNAL, **60**, 1033 (1938).

temperature range 80–90° in agreement with the observation of Utermohlen.[16] The reaction temperature was allowed to rise to 120–125° with the formation of only small quantities of low-boiling materials which may have been hydrogenolysis products. Utermohlen[16] reported some cleavage at 125° in the hydrogenation of β-alkoxypropionitriles and Wiedemann and Montgomery[17] obtained substantial quantities of hydrogenolysis products from the reduction of di-(β-cyanoethyl)-ether at 100–110°.

TABLE I

SALTS OF 1,4-(γ-AMINOPROPOXY)-PENTANE

Salts	Method of preparation	M. p., °C.	Nitrogen, %[a] Calcd.	Nitrogen, %[a] Found
Disulfamate	B	*ca.* 65[b]		
Diacetate	A	Oil		
Dipropionate	A	Oil		
Dibutyrate	A	Oil		
Dilevulinate	A	Gum		
Dibenzoate	A	Gum		
Oxalate	A	196–198	9.09	9.65
Malonate	A	Gum		
Succinate	A	121–122	8.33	8.42
Glutarate	B	Gum		
Adipate	A	136–138	7.69	7.92
Sebacate	A	*ca.* 50[c]		
Maleate	B	129–131	8.38	8.62
Itaconate	C	Gum		
Phthalate	B	125–126	7.29	7.38
Dioxalate	D	108–110	7.04	7.26
Dimalonate	C	Gum		
Disuccinate	C	92–94	6.17	6.33
Diglutarate	C	Gum		
Diadipate	C	102–103	5.49	5.53
Dimaleate	C	80–85[c]		
Diphthalate	B	Gum		

[a] By micro Dumas. [b] White, deliquescent solid which darkened and exhibited a lower melting point after recrystallization from an absolute ethanol–ether mixture. [c] Soft solid which separated as an oil when recrystallized and could not be obtained in a satisfactorily crystalline state.

The salts of 1,4-di-(γ-aminopropoxy)-pentane were obtained as solids only when the acid was dibasic and contained an even number of carbon atoms. Although the compounds were white powders which appeared amorphous, X-ray examination[21] of the oxalate and succinate showed well defined powder diagrams indicating microcrystallinity. These salts were hygroscopic substances, easily soluble in water or absolute ethanol with the exception of the oxalate which was insoluble in ethanol. They were insoluble in ether and other non-polar solvents.

Summary

1. γ-Valerolactone has been prepared in good yield by hydrogenation of levulinic acid in the presence of Raney nickel.

2. α-Methyltetrahydrofuran has been identified as a by-product from the reduction of γ-valerolactone over copper–chromium oxide.

3. Levulinic acid has been hydrogenated directly to 1,4-pentanediol using copper–chromium oxide catalyst.

4. 1,4-Di-(β-cyanoethoxy)-pentane and 1,4-di-(γ-aminopropoxy)-pentane have been prepared and characterized.

5. A series of salts of 1,4-di-(γ-aminopropoxy)-pentane has been prepared.

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[21] Kindly carried out by Mr. Harvey Dube.

AMES, IOWA RECEIVED APRIL 1, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BANTING INSTITUTE, UNIVERSITY OF TORONTO]

The Condensation of Nitromethane with D- and L-Arabinose: Preparation of L-Glucose and L-Mannose

BY JOHN C. SOWDEN AND HERMANN O. L. FISCHER

In a recent publication from this Laboratory[1] we described the condensation of nitromethane with several aldopentoses and with D-glucose, under the influence of alkali, to give sirupy mixtures containing the corresponding pairs of carbohydrate C-nitroalcohols. These crude sirups were converted, on acetylation and subsequent treatment of the sirupy acetates in benzene solution with sodium bicarbonate, to the corresponding crystalline, acetylated carbohydrate nitroölefins in yields of from 5 to 40%.

It now has been found possible to isolate and separate the crystalline nitroalcohols themselves which result from the condensation of nitromethane with D- and L-arabinose. The first products of the condensation of nitromethane with the arabinoses, as described previously,[1] were mixtures of the amorphous sodium salts of the nitroalcohols. Following removal of the sodium from these crude products by means of ion-exchange, the mixed nitroalcohols were obtained in crystalline condition and could be separated readily into the pure epimeric pairs of nitroalcohols by fractional crystallization from ethanol. The yield of mixed, crystalline carbohydrate C-nitroalcohols was about 60% while the combined yield of the pure, separated isomers was about 40%. Unlike the addition of hydrocyanic acid to the arabinoses, which gives mainly the mannonic acid lactones, the addition of nitromethane seems to give the nitroalcohols with the glucose and mannose configurations in nearly equal amounts.

The isomeric carbohydrate C-nitroalcohols re-

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[1] Sowden and Fischer, THIS JOURNAL, **69**, 1048 (1947).