which melted at 107.5–108.5° was prepared. When some of this material was mixed with crystals of the phenylhydrazide of 2,3-dihydroxybutyric acid (m. p. 109°), no depression in melting point was observed. It thus appears that 2,3-dihydroxybutyric acid had been formed in the reaction of the β-iodohydrin with sodium cyanide.

Summary

1. The addition of hydrogen cyanide to glycidol followed by hydrolysis of the addition product resulted in a 25–50% yield of 2,3-dihydroxybutyric acid lactone. Under certain conditions, 3-hydroxyisocrotonic acid lactone was formed.

2. Further attempts were made to prepare 2,2'-dihydroxyisobutyric acid from (a) β-glycerol chlorohydrin and heavy metal cyanides; (b) β-glycerol chlorohydrin diacetate, ethyl chloroformate and sodium amalgam; and (c) pentaerythritol by oxidation with barium or potassium permanganate. These attempts were unsuccessful.

3. α-Glycerol iodohydrin was prepared by a new procedure.

4. β-Glycerol iodohydrin was prepared and its melting point determined. The reaction of this compound with sodium cyanide in ethanol gave 2,3-dihydroxybutyric acid.

CHICAGO, ILLINOIS

RECEIVED AUGUST 26, 1932
PUBLISHED MARCH 7, 1933

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Dehydration of 2,2-Dimethylhexanol-1 and Related Tertiary Alcohols[1]

BY FRANK C. WHITMORE AND J. M. CHURCH[2]

An alcohol of the type, R_3CCH_2OH, can be dehydrated only with rearrangement. The purely aliphatic alcohols of this type which have been studied are tertiary-butylcarbinol,[3] tertiary-amylcarbinol[4] and 2-methyl-2-ethylbutanol-1.[4] In the present study a related alcohol with two methyl groups and a *n*-butyl group attached to the neo carbon has been dehydrated. This substance presented another opportunity to study the relative ease of migration of butyl and methyl groups. Meerwein[5] found that the butyl group migrated to a greater extent in the glycol containing two methyl and two butyl groups. A similar observation has been made by Krueger[6] in the case of two pinacolyl alcohols each containing two methyl and two butyl groups. In the present case in which there were two

---

(1) See Whitmore, THIS JOURNAL, **54**, 3274 (1932).

(2) Submitted in partial fulfilment of the requirements for the Ph.D. degree.

(3) *Cf.* Whitmore and Rothrock, THIS JOURNAL, **54**, 3431 (1932).

(4) Favorsky, *J. Russ. Phys.-Chem. Soc.*, **50**, 43–80 (1918); *Chem. Zentr.*, III, 666 (1923); Favorsky and Zalessky-Kibardine, *Bull. soc. chim.*, [4] **37**, 1227 (1925). The dehydration products of this alcohol are being studied exhaustively by C. W. Nash in this Laboratory.

(5) Meerwein, *Ann.*, **419**, 121 (1919).

(6) Whitmore and Krueger, unpublished results.

methyls and one butyl, the rearrangement of the butyl still predominated about 2:1. The dehydration of 2,2-dimethylhexanol-1 gave four of the five olefins which would be predicted.[1] Ozonolysis products of these olefins corresponding to 95% yields were isolated and identified.

The possible courses of the dehydration may be indicated as follows[7]

$(CH_3)_2(C_4H_9)CCH_2OH \longrightarrow (CH_3)_2(C_4H_9)CCH_2 +$ (1)
(1) By shift of butyl $\longrightarrow (CH_3)_2C^+CH_2C_4H_9$ (2)
(1) By shift of methyl $\longrightarrow (CH_3)(C_4H_9)C^+CH_2CH_3$ (3)
(2) By loss of proton from amyl $\longrightarrow (CH_3)_2C{=}CHC_4H_9$ (4)
(2) By loss of proton from methyl $\longrightarrow CH_2{=}C(CH_3)(C_5H_{11})$ (5)
(3) By loss of proton from butyl $\longrightarrow C_3H_7CH{=}C(CH_3)(C_2H_5)$ (6)
(3) By loss of proton from ethyl $\longrightarrow (CH_3)(C_4H_9)C{=}CHCH_3$ (7)
(3) By loss of proton from methyl $\longrightarrow CH_2{=}C(C_2H_5)(C_4H_9)$ (8)

The olefins (4), (5), (6) and (7) were formed as indicated by their ozonolysis products as follows

(4) Acetone and *n*-valeraldehyde
(5) Methyl *n*-amyl ketone and formaldehyde
(6) Methyl ethyl ketone and *n*-butyraldehyde
(7) Methyl *n*-butyl ketone and acetaldehyde

No evidence of ethyl *n*-butyl ketone could be found. This indicated the absence of (8) among the dehydration products. Olefins (4) and (5) appeared in the ratio 12:1, indicating a predominant loss of hydrogen from the newly formed amyl group as compared with the two methyl groups. In the case of (7) and (6) the ratio was 2:1 in favor of the loss of hydrogen from the newly formed ethyl group as compared with the butyl group. Since the first of these ratios was much higher than similar ratios obtained in dehydrating various alcohols containing methyl and amyl groups,[8] it was decided to dehydrate the tertiary alcohols corresponding to fragments (2) and (3), namely, dimethyl-*n*-amylcarbinol and methylethyl-*n*-butylcarbinol. The first of these gave olefins (4) and (5) in the ratio 1.4:1 and the second gave olefins (7) and (6) in the ratio 1.6:1 and also a 6% yield of olefin (8) as indicated by the amount of formaldehyde and ethyl *n*-butyl ketone obtained from the ozonolysis products. The difference between the values of 12:1 and 1.4:1 for the ratios of olefins (4) and (5) formed by dehydration *with rearrangement* of the primary alcohol by means of a small amount of concd. sulfuric acid and by dehydration of the tertiary alcohols by means of a small amount of 50% sulfuric acid is being studied further.

Experimental

Preparation of Dimethyl-*n*-butylcarbinol, its Chloride, and the Corresponding Grignard Reagent.—The carbinol, b. p. 139–142° (740 mm.), 59–61° (25 mm.), n^{20}_{D}

---

[7] The hydroxyl is assumed to be removed with its octet leaving the carbon indicated by a + with only a sextet of electrons. By shifts of electron pairs from the adjacent carbon atoms fragments (2) and (3) are obtained.[1]

[8] Whitmore and Williams, THIS JOURNAL, **55**, 406 (1933).

1.4176, was prepared in 8-mole lots from *n*-butyl Grignard reagent and acetone in 60% yields based on the *n*-butyl bromide used.[9] The tertiary chloride was prepared by hydrochloric acid in the usual way,[9] b. p. 70–72° (90 mm.), 34–36° (15 mm.), n^{20}_D 1.4205.

Dimethyl-*n*-butylcarbinylmagnesium chloride was prepared in 6-mole lots in 50–60% yields.[10] The details of a typical run follow. A 3-liter flask containing 146 g. of fresh magnesium turnings and a crystal of iodine was heated over a free flame to vaporize the iodine. The flask was stoppered and cooled and then fitted with a reflux condenser, an efficient stirrer and a dropping funnel. Addition of 5 cc. of the pure tertiary chloride and 1 cc. of *n*-butyl bromide started a vigorous reaction. This was maintained by suitable additions of portions of a mixture of 403 g. (3 moles) of the chloride with 500 cc. of dry ether and of a 300-cc. quantity of the same ether. The addition of the chloride solution was mainly at the rate of one drop per second. Vigorous stirring was used throughout the reaction. Then 300 cc. of dry ether was added and finally a more dilute solution of the chloride (403 g. and 1000 cc. of dry ether) was slowly added. The total time of addition of the chloride was sixty-eight hours. The mixture was then stirred for eight hours more, allowed to settle and an aliquot part was titrated with standard acid. Even with the care indicated, nearly half of the tertiary chloride was converted to heptylenes.

Preparation of 2,2-Dimethylhexanol-1.—Several runs of dimethyl-*n*-butylcarbinylmagnesium chloride with formaldehyde, ranging from 0.8 to 3.2 moles, gave yields of the desired alcohol of 41–63%. A typical run follows. During five hours the formaldehyde obtained by heating 100 g. (3.3 moles CH_2O) of paraformaldehyde at 165–170° was carried by a slow stream of dry nitrogen over the surface of a rapidly stirred solution of 3.2 moles of the Grignard reagent in 2100 cc. of ether. The reaction mixture was then stirred and gently refluxed for eight hours. It was decomposed with ice and ammonium chloride in the usual way. The ether layer and extracts were dried with anhydrous sodium sulfate and potassium carbonate overnight, filtered and distilled. After removal of the ether the residue was twice fractionated with a high reflux ratio through a 90 × 2 cm. insulated packed partial condensation column.[11] The final fractions obtained were as follows.

	B. p., °C.	Mm.	G.	n^{20}_D	
1	36–88	731	17	1.3725	
2	88–90	731	119	1.3940	Heptylenes
3	90–140	731	15	1.4100	
4	54–60	14	45	1.4195	Unchanged chloride
5	60–80	14	12	1.4263	
6	80–82	14	260	1.4304	2,2-Dimethylhexanol-1
7	68–90	2	18	1.4428	
8	Residue		6	1.4609	Brown viscous oil

Dehydration of 2,2-Dimethylhexanol-1.—Heating the alcohol with 4% of its weight of concd. sulfuric acid for two hours gave only 5% dehydration. Several variations of this experiment and the use of *p*-toluene sulfonic acid also failed to give satisfactory results. Finally a mixture of the alcohol with 6% of its weight of concd. sulfuric acid and 4% of *p*-toluene sulfonic acid, heated for six hours with constant removal by distillation of the products, gave a 70% dehydration with a 63% yield of octylenes. A similar yield was obtained by using 8% by weight of concd. sulfuric acid but slightly more charring took place than when the sulfonic acid was also used. A typical experiment follows. A mixture of 52 g. (0.4 mole) of 2,2-dimethylhexanol-1 and 2.5 cc. of concd. sulfuric acid (sp. gr. 1.84) was added dropwise to a heated 50-cc. Claisen flask with an

---

(9) For details see Whitmore and Woodburn, THIS JOURNAL, **55**, 361 (1933).

(10) *Cf.* Whitmore and Badertscher, unpublished results.

(11) Whitmore and Lux, *ibid.*, **54**, 3451–3 (1932).

air-jacketed indented side-arm, 30 × 1 cm. The heat was regulated to allow olefins and water to distil over at about 120° as rapidly as they were formed. In one hundred minutes, 57 cc. of oil and 8 cc. of water had distilled. At the end of the process, sulfur dioxide became noticeable and some charred material remained in the flask. The oil layer was washed with water and with dilute sodium bicarbonate solution and dried with anhydrous sodium sulfate. Fractionation through a 70 × 1 cm. indented adiabatic total condensation column using a high reflux ratio[11] gave the following fractions (735 mm.).

	B. p., °C.	G.	n_D^{20}	
1	110–118	0.8	1.4153	Two layers
2	118–120	2.5	1.4167	
3	120–122	28.3	1.4188	Octylenes
4	122–165	2.8	1.4236	
5	165–170	5.8	1.4296	Unchanged alcohol
6	Residue	2.4		Brown viscous oil

Ozonolysis of Heptylenes from Dimethyl-*n*-butylcarbinyl Chloride.[12]—This olefin mixture, b. p. 88–90° (730 mm.), n_D^{20} 1.3946, was obtained as a by-product in the preparation of the chloride because of its partial decomposition during distillation. Since its ozonolysis products probably included both formaldehyde and acetone, it was studied before attacking the more complex mixture of olefins obtained by the dehydration of the alcohols.

Ozonized oxygen was passed for fifteen hours at the rate of 15 liters per hour through a solution of 49 g. (0.5 mole) of the olefin in 300 cc. of 0–35° saturated hydrocarbon[13] kept at −10°. Removal of the solvent at room temperature under reduced pressure left 64 g. of colorless liquid ozonide (87% yield). The ozonide was decomposed with zinc and water during about two hours.[12] During the decomposition, 35 cc. of oil was collected. An ether trap at 0° was used to remove organic material from the nitrogen stream used to sweep the products out of the decomposition mixture. This ether was used to extract the water layer of the distillate. The water layer gave qualitative tests for formaldehyde with the fuchsin and resorcinol tests and for acetone by the formation of iodoform and dibenzylidene acetone (m. p. and mixed m. p. 110°). Titration of the water layer with standard base and hydrogen peroxide showed 3.8 g. of formaldehyde and titration with standard iodine solution (for both formaldehyde and acetone) showed 9.0 g. of acetone. The oil layer was fractionated through the 70 × 1 cm. column at 733 mm. with a reflux ratio of about 20:1 to give seven fractions and a residue of 1.9 g. Fractions 1 and 2 had the odors of acetone and butyraldehyde, respectively. Fraction 3, 2.3 g., b. p. 72–75°, n_D^{20} 1.3861, gave the 2,4-dinitrophenylhydrazone of *n*-butyraldehyde, m. p. 120°, mixed m. p. 119°. Fraction 6, 16.5 g., b. p. 124–128°, n_D^{20} 1.3996, gave the semicarbazone of methyl *n*-butyl ketone, m. p. 116°, mixed m. p. 114°. The isolated ozonolysis products represented yields of 2-methylhexene-1 and -2 of 39 and 31%, respectively, thus indicating a slightly greater tendency for the loss of hydrogen from the two methyl groups than from the one butyl group during the decomposition of the dimethyl-*n*-butylcarbinyl chloride.

Ozonolysis of the Olefins from 2,2-Dimethylhexanol-1.—The treatment of 56 g. (0.5 mole) of the olefins, b. p. 120–122° (735 mm.), n_D^{20} 1.4188, with ozonized oxygen in the usual way gave 70.4 g. of a colorless liquid ozonide (88% yield). Decomposition of the ozonide gave 38 g. of oil. The reflux condenser at 25° allowed acetaldehyde to pass through into an ether solution from which acetaldehyde-ammonia, 1.6 g., m. p. 90°

---

[12] For details of technique see Whitmore and Church, THIS JOURNAL, **54**, 3712 (1932).

[13] Supplied by the Viking Corporation of Charleston, W. Va.

was formed. The water layer when titrated with standard alkali and hydrogen peroxide and with standard iodine was found to contain 0.45 g. of formaldehyde and 14.6 g. of acetone. The water layer also gave a qualitative test for formaldehyde with resorcinol. The water layer after the titrations gave 2.6 g. of oil on extraction with ether. Thus a total of 56.8 g. of crude products was obtained from the ozonide (89.6% yield). The crude oil, after drying over anhydrous sodium sulfate, was fractionated three times through the 70 × 1 cm. column at 739 mm. to give twelve fractions and a residue of 6 g. Fraction 2, 1.2 g., b. p. 50–60°, n^{20}_{D} 1.3700 gave dibenzylidene acetone, m. p. and mixed m. p. 110°. Fractions 3 and 4, 5.3 g. b. p. 60–75°, n^{20}_{D} 1.379, gave the 2,4-dinitrophenylhydrazone of *n*-butyraldehyde, m. p. 118 and 119° and mixed m. p. 119 and 120°. Fraction 5, 1.8 g., b. p. 75–80°, n^{20}_{D} 1.380, was identified with difficulty as impure methyl ethyl ketone. Its 2,4-dinitrophenylhydrazone after many crystallizations from absolute alcohol melted at 98° instead of 113°. A mixture with the known 2,4-dinitrophenylhydrazone of methyl ethyl ketone melted at 103° while a mixture with the *n*-butyraldehyde derivative melted at 85°. It also gave the semicarbazone of methyl ethyl ketone which, after many recrystallizations from 50–70° petroleum ether, melted at 130° instead of 138°. A mixture with the known derivative melted at 133°. Fractions 6 and 7, 0.7 g. and 3.2 g., b. p. 80–98° and 98–103°, n^{20}_{D} 1.3841 and 1.3923, gave the 2,4-dinitrophenylhydrazone of *n*-valeraldehyde, m. p. and mixed m. p. 95°. Fraction 9, 9.7 g., b. p. 123–128°, n^{20}_{D} 1.3999, gave the 2,4-dinitrophenylhydrazone of methyl *n*-butyl ketone, m. p. 103°, mixed m. p. 105°, and the semicarbazone, m. p. 116°, mixed m. p. 114°. Fraction 11, 2.1 g., b. p. 145–150°, n^{20}_{D} 1.406, gave a semicarbazone which after many crystallizations melted at 101°. A mixture with the semicarbazone of methyl *n*-amyl ketone melted at 103°. One with the semicarbazone of ethyl *n*-butyl ketone (m. p. 103°) melted at 78°. The mother liquors from the semicarbazone of the methyl *n*-amyl ketone gave no indication of the semicarbazone of ethyl *n*-butyl ketone even after repeated crystallizations. The percentage yields of the carbonyl compounds obtained from the ozonide were as follows: formaldehyde, 3.4; acetaldehyde, 5.9; acetone, 56.9; butyraldehyde, 11 (estimated); methyl ethyl ketone, 11 (estimated); *n*-valeraldehyde, 10.0; methyl *n*-butyl ketone, 22.0; methyl *n*-amyl ketone 4.3. Thus the total isolated yield of ketone products was over 90% while that of the aldehydes was only 30%.

The Dehydration Products of Methylethyl-*n*-butylcarbinol.—This carbinol, which corresponds to the rearrangement of a methyl group in 2,2-dimethylhexanol-1, was prepared as follows. *n*-Butylmagnesium bromide (2.66 moles) was prepared from 415 g. (3 moles) of *n*-butyl bromide and 75 g. of magnesium in 1000 cc. of dry ether. To this was added during three hours 192 g. (2.66 moles) of redistilled methyl ethyl ketone,[14] b. p. 78–79° (735 mm.), n^{20}_{D} 1.3792. The mixture was decomposed with ice and dilute sulfuric acid and worked up in the usual way. The methylethyl-*n*-butylcarbinol boiling at 158–159° (731 mm.) and having n^{20}_{D} 1.4238 amounted to 290 g. (83% yield based on the Grignard reagent).

The carbinol was readily dehydrated by refluxing under a 80 × 2 cm. column with 5 cc. of 50% sulfuric acid and removing the water and olefin at the top of the column at a temperature of 115–125°. The product was dried with anhydrous copper sulfate and distilled through the same column.[11] The product, b. p. 119–120° (735 mm.) and n^{20}_{D} 1.4186, weighed 232 g. (93% yield). One mole (112 g.) of the olefin product was ozonized in the usual way to give 140 g. of colorless liquid ozonide (87% yield). Decomposition of the ozonide in the usual way gave 93 g. of oil, 3.75 g. of acetaldehyde-ammonia, m. p. 92°, and 1.56 g. of formaldehyde, determined iodimetrically. Ether extraction of the water layer after removal of the formaldehyde and acetaldehyde gave 6.5 g. of oil. Thus

---

(14) Supplied by the Shell Development Co. of Emeryville, Calif., through the courtesy of Dr. E. C. Williams.

the total yield of crude products from the ozonide was 82%. Fractionation of the oil through the 70 × 1 cm. column at 732 mm. gave twelve fractions and a residue of 2.1 g. Carbonyl compounds were identified in the various fractions in the usual way by m. p. and mixed m. p. determinations of their 2,4-dinitrophenylhydrazones and their semicarbazones. *n*-Butyraldehyde was found in fractions 1–3, 14.3 g., b. p. 63–74°, n^{20}_{D} 1.38. Methyl ethyl ketone was found in fractions 4 and 5, 14.2 g., b. p. 75–78°, n^{20}_{D} 1.379. Methyl *n*-butyl ketone was found in fractions 7 and 8, 25.2 g., b. p. 123–128°, n^{20}_{D} 1.400. Smaller amounts were also found in fractions 6 and 9. Ethyl *n*-butyl ketone was identified in fractions 10 and 11, 8.6 g., b. p. 143–148°, n^{20}_{D} 1.408. The percentage yields of carbonyl compounds were as follows: formaldehyde, 6.0; acetaldehyde, 7.0; methyl ethyl ketone, 23.0; butyraldehyde, 23.3; methyl *n*-butyl ketone, 38.6; ethyl *n*-butyl ketone, 4.3. Thus dehydration from the ethyl, butyl and methyl group occurred approximately in the ratio 6:3:1.

The Dehydration Products of Dimethyl-*n*-amylcarbinol.—This carbinol, which corresponds to the rearrangement of the butyl group in 2,2-dimethylhexanol-1, was prepared as follows. Methylmagnesium chloride (2.4 moles) in 500 cc. of dry ether was treated with 188 g. (1.3 moles) of ethyl caproate in 800 cc. of dry ether. The crude product was distilled through the 80 × 2 cm. column at 740 mm. A considerable amount of olefin collected at 116–118°. The carbinol boiled at 155–156°, n^{20}_{D} 1.4240. The carbinol was dehydrated with 5 cc. of 50% sulfuric acid in the same way as its isomer. The crude olefin was dried over sodium and distilled, b. p. 117–119° (740 mm.), n^{20}_{D} 1.4138, wt. 84 g. (55% yield based on the ethyl caproate). The olefin was ozonized in a 0.4 mole lot in the usual way to give 57.5 g. of ozonide (89% yield). The decomposition of the ozonide gave a 90% yield of crude carbonyl compounds including 1.1 g. of formaldehyde (determined by the hydrogen peroxide method), 10.1 g. of acetone and 44.7 g. of oil. The latter was fractionated at 734 mm. through the 70 × 1 cm. column to give seven fractions and a residue of 4.1 g. The carbonyl compounds were identified in the usual way. Acetone was found in fraction 1, 2.2 g., b. p. 55–60°, n^{20}_{D} 1.367; *n*-valeraldehyde in fraction 3, 3.1 g., b. p. 98–103°, n^{20}_{D} 1.392; methyl *n*-amyl ketone in fraction 5, 15.2 g., b. p. 145–150°, n^{20}_{D} 1.4085. The percentage yields of carbonyl compounds were as follows: formaldehyde, 10.1; acetone, 59.1; *n*-valeraldehyde, 10.1; methyl *n*-amyl ketone, 42.1. Thus the dehydration from the one *n*-amyl and the two methyl groups was about 3:2.

Summary

1. 2,2-Dimethylhexanol-1 has been dehydrated and the accompanying rearrangements have been determined by ozonolysis of the resulting olefins.

2. The related tertiary alcohols, methylethyl-*n*-butylcarbinol and dimethyl-*n*-amylcarbinol, have been dehydrated and their products similarly studied.

3. Certain peculiar relations have been noted in these dehydrations.

4. The heptenes from the decomposition of dimethyl-*n*-butylcarbinyl chloride have been ozonized.

STATE COLLEGE, PENNSYLVANIA

RECEIVED AUGUST 26, 1932
PUBLISHED MARCH 7, 1933