aqueous potassium permanganate solution (2%) was added, in portions, over a period of 45 hours. The precipitated manganese dioxide was removed and the colorless filtrate acidified with dilute hydrochloric acid. The product separated as a gelatinous white precipitate, which was filtered off, washed and vacuum dried. The resultant white powder (2.65 g., 77% yield) was purified by dissolving in pyridine and reprecipitating with dilute hydrochloric acid; softening point (with some decomposition) 175–180°. *Anal.* Calcd. for $(C_{13}H_{13}NO_3)_n$: C, 66.89; H, 6.58; N, 6.00. Found: C, 66.88; H, 6.93; N, 6.10. The following results provided further support for the structure IV: (a) Infrared absorption bands at 3.7 (medium, broad shoulder), 5.81 (medium) and 7.70 μ (medium) for the COOH group, and a broad shoulder at 3.1 μ (medium) for the NH group, both the OH and NH bonds apparently being hydrogen bonded fairly strongly. The absorption bands due to the benzoyl group between 6.15 and 6.45 μ, quoted previously, were present also in this spectrum. (b) Potentiometric titration of this product in dimethylformamide with sodium methoxide in methanol–benzene solution, and using a glass–calomel electrode system afforded curves typical of carboxylic acids under these conditions.[9] (c) The product IV was heated in a dry tube at 230° (Woods metal-bath) for 15 minutes. A white sublimate of benzoic acid was formed, m.p. and mixed m.p. 117–118°. The residual polymer was insoluble and formed gels on standing with dimethylformamide and pyridine.

Degradation of Poly-(diallyldimethylammonium Bromide), V to VI.—The polymer V[3] was first ground, in a dry-box, to less than 100-mesh particle size and extracted with absolute ethanol for 48 hours. Quantitative hydrogenation work showed that the polymer was fully saturated after such treatment. A solution of V (20 g.) in water (50 ml.) was passed through a column of Amberlite resin (Rohm and Haas, Grade IRA 410; about 150 g. of moist resin) that had previously been converted to its hydroxide form by repeated elution with sodium hydroxide solution. The column was washed with water and the collected, bromide-free effluent (250 ml., *p*H greater than 13.0) evaporated down under reduced pressure at room temperature. The resultant semi-solid mass was vacuum dried and decomposed by heating at 55° *in vacuo* for 72 hours. The solid product (*p*H of 0.1% solution 11.07) was somewhat hygroscopic, readily soluble in methanol and slowly soluble in water. The following experiments were performed on this product: (1) Potentiometric titration with 0.1 *N* hydrochloric acid followed by back-titration with 0.1 *N* sodium hydroxide solution using a glass-calomel electrode system gave the following values: pK_B 8.60, units in the amine form 81%, units remaining in the hydroxide form 19%. (2) The product (0.225 g.) was titrated with 0.1 *N* hydrochloric acid to a *p*H of 3.05 and the solution hydrogenated quantitatively, using Adams catalyst and at atmospheric pressure in the usual way. The observed uptake of hydrogen was 8.2 ml. (S.T.P.).

VI to VII.—The polyamine VI (1.018 g.), dissolved in absolute methanol (200 ml.), was refluxed gently at 55° with methyl iodide (15 ml.) for four hours. The precipitated product was filtered, washed, and vacuum dried to afford a pale-yellow, water-soluble solid, m.p. 312° (closed capillary), yield 1.68 g. (78%). *Anal.* Calcd. for $(C_9H_{18}NI)_n$: I, 47.5. Found: I, 44.7.

VII to VIII.—The poly-(quaternary ammonium iodide) VII (0.91 g.) was converted to its hydroxide by passing an aqueous solution through a prepared column of Amberlite 410, as previously described. The iodide-free solution of hydroxide was evaporated under reduced pressure at room temperature to a small volume of pale-brown viscous solution. This was heated in a micro distillation apparatus leading into a saturated solution of picric acid in benzene. At a bath temperature of 170°, crystals formed momentarily in the picric acid solution. Water was removed from the benzene by azeotropic distillation and, on cooling, yellow crystals separated. Subsequent recrystallization from benzene afforded trimethylamine picrate, m.p. and mixed m.p. 214.5–215.5°, literature m.p. 215°.

A further portion of the viscous solution of the hydroxide was vacuum dried and heated at 50° for 72 hours *in vacuo*. The polymeric residue was insoluble in all solvents.

Oxidation of VIII.—A sample of the insoluble polymer was stirred vigorously at room temperature for 16 hours with excess alkaline potassium permanganate solution. In a test for formate ion,[10] a portion of the filtered solution readily reduced mercuric chloride.

Acknowledgment.—The analyses reported in this paper were carried out by Galbraith Laboratories, Knoxville, Tenn., or by Weiler and Strauss, Microanalytical Laboratory, Oxford, England.

GAINESVILLE, FLORIDA

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[9] For examples see J. S. Fritz and N. M. Lisicki, *Anal. Chem.*, **23**, 589 (1951).

[10] F. Feigl, "Spot Tests," Vol. II, Elsevier Publishing Co., New York, N. Y., 1954, p. 246.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, TENNESSEE EASTMAN CO., DIVISION OF EASTMAN KODAK CO.]

The Acid-catalyzed Dehydration of 2,2,4-Trimethyl-1,3-pentanediol[1]

BY M. A. PERRY, F. C. CANTER, R. E. DEBUSK AND A. G. ROBINSON

RECEIVED DECEMBER 13, 1957

The acid-catalyzed, vapor-phase dehydration of 2,2,4-trimethyl-1,3-pentanediol led to products resulting from rearrangement rather than simple dehydration. The major product was 2,3,4-trimethylvaleraldehyde, which was formed in 45% conversion and 60% yield. Minor products identified were tetrahydro-2,2,4,4-tetramethylfuran, tetrahydro-2,3,4,4-tetramethylfuran and the cyclic acetal of 2,3,4-trimethylvaleraldehyde and 2,2,4-trimethyl-1,3-pentanediol. Triethyl phosphate was found to be an excellent catalyst for accomplishing this reaction. Mechanisms rationalizing the formation of these products are given.

Of the three reported[2-4] dehydrations of 2,2-dialkyl-1,3-diols, two[2,3] involved rearrangements, apparently through carbonium ion formation. Isovaleraldehyde and 3-methyl-2-butanone were reported to be formed when 2,2-dimethyl-1,3-propanediol was heated in a sealed tube at 200° with dilute sulfuric acid.[2,5] When 2,2,4-trimethyl-1,3-pentanediol was refluxed with dilute sulfuric acid, tetrahydro-2,2,4,4-tetramethylfuran was formed.[3] No rearrangement was reported in the dehydration of 3-ethyl-2,2-dimethyl-1,3-pentanediol, which gave 3-ethyl-2,2-dimethyl-3-penten-1-ol as the product.[4]

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[1] Presented at the Southeastern Regional Meeting of the American Chemical Society, Durham, N. C., November 14–16, 1957.

[2] A. Fischer and B. Winter, *Monatsh.*, **21**, 301 (1900).

[3] A. Franke, *ibid.*, **17**, 89 (1896).

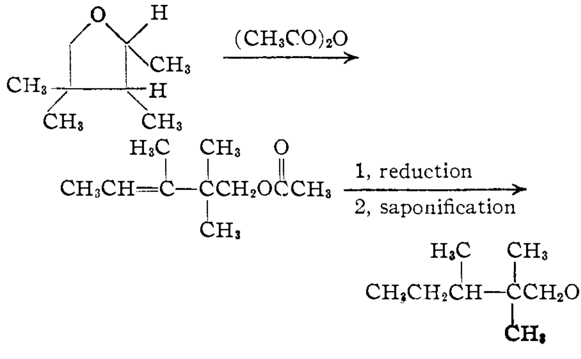
[4] M. Letellier, *Compt. rend.*, **146**, 344 (1908).

[5] Little evidence was presented by Fischer and Winter[2] to distinguish the reported product, isovaleraldehyde, from 2-methylbutyraldehyde. The latter aldehyde closely resembles isovaleraldehyde in all properties reported and its formation can be explained more readily than the formation of isovaleraldehyde.

We found that in the acid-catalyzed dehydration of 2,2,4-trimethyl-1,3-pentanediol, rearrangement with alkyl-group migration occurred, presumably through formation of a secondary carbonium ion. When the diol, with triethyl phosphate, was passed over Pyrex glass beads at 200°, four products were formed; of these, three were previously unknown. These products, an eight-carbon saturated aldehyde, two five-membered cyclic ethers and a cyclic acetal, were characterized and identified.

The eight-carbon aldehyde, the major product of the dehydration, was reduced easily to the corresponding alcohol and readily oxidized to the corresponding acid. Comparison of the physical properties of the aldehyde, alcohol, acid and their derivatives with the properties of known eight-carbon compounds showed that this aldehyde had never been described. Of the unreported eight-carbon aldehydes, 2,3,4-trimethylvaleraldehyde was a logical possibility. This tentative identification was shown to be correct by the synthesis of 2,3,4-trimethylvaleric acid and comparison of its properties with those of the acid obtained by oxidation of the unknown aldehyde. The synthesis of 2,3,4-trimethylvaleric acid was accomplished by dehydration, reduction and saponification of the Reformatsky reaction product of isobutyl 2-bromopropionate and 3-methyl-2-butanone. The acids were identical in physical properties and infrared spectra. The properties of the derivatives also were identical. Properties of 2,3,4-trimethylvaleraldehyde, 2,3,4-trimethyl-1-pentanol and 2,3,4-trimethylvaleric acid are given in the Experimental section.

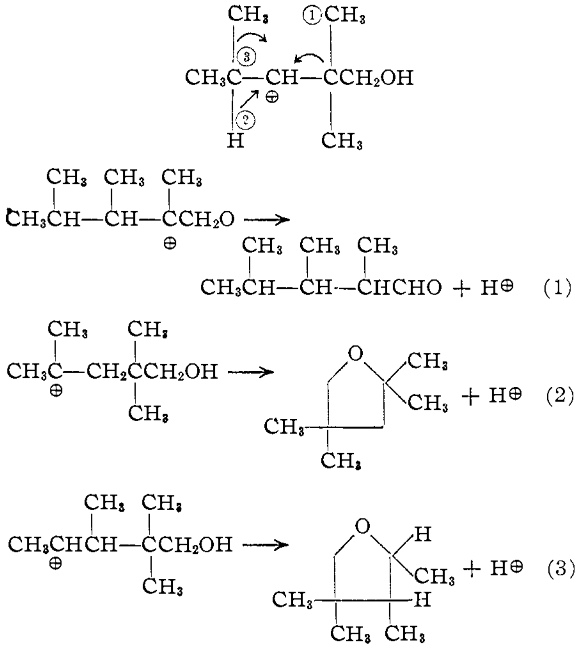
A second product of the dehydration was shown by infrared and elemental analyses to be an eight-carbon cyclic ether. When the ether was treated with acetic anhydride, the acetate of an unsaturated alcohol was obtained. This acetate was reduced and saponified, and an unknown alcohol was obtained. Infrared analysis revealed the presence of *gem*-dimethyl and primary hydroxyl groups in the alcohol. A logical possibility for this compound was 2,2,3-trimethyl-1-pentanol. The Reformatsky reaction was used to prepare 2,2,3-trimethylvaleric acid from ethyl 2-bromo-2-methylpropionate and 2-butanone. This acid was identical with the acid obtained by oxidation of the saturated alcohol derived from the cyclic ether. Since this alcohol was shown to be 2,2,3-trimethyl-1-pentanol, the cyclic ether must have been tetrahydro-2,3,4,4-tetramethylfuran. This possibility is illustrated by the equation



Another cyclic ether produced was shown by comparison of physical properties and infrared spectra to be the known tetrahydro-2,2,4,4-tetramethylfuran.

Analytical data showed that the fourth product of the dehydration of 2,2,4-trimethyl-1,3-pentanediol was a sixteen-carbon cyclic acetal. The product was assumed to be the cyclic acetal of 2,3,4-trimethylvaleraldehyde and 2,2,4-trimethyl-1,3-pentanediol since these were the only two compounds present in the reaction mixture capable of forming a cyclic acetal. The correctness of this assumption was shown by preparing an authentic sample of the acetal. This sample was found to be identical in physical properties and infrared spectrum with the acetal produced by the dehydration.

All of the products of the dehydration of 2,2,4-trimethyl-1,3-pentanediol may be explained by consideration of the possible migrations which may occur in the carbonium ion which would be formed by removal of the secondary hydroxyl group in the diol. The various possibilities are illustrated



The products—2,3,4-trimethylvaleraldehyde, tetrahydro-2,2,4,4-tetramethylfuran and tetrahydro-2,3,4,4-tetramethylfuran—were formed in relative amounts of 7, 4 and 1, respectively. The formation of relatively small amounts of tetrahydro-2,3,-4,4-tetramethylfuran might be expected since the formation of a secondary carbonium ion is required, according to the mechanism presented.

Experimental

Dehydration of 2,2,4-Trimethyl-1,3-pentanediol.—A solution of 600 g. (4.1 moles) of the diol in 1200 g. of benzene was passed through a bed (30 × 600 mm.) of 4-mm. Pyrex glass beads which had been previously coated with triethyl phosphate. The temperature of the bed was maintained at 250°, and the feed rate was maintained at 5 ml. of solution per minute. Effluent gases were condensed by water condensers and Dry Ice–acetone traps. Distillation of the condensate at 730 mm. gave, in addition to benzene

Product	Wt., g.	n^{20}_{D}	d^{20}_{4}	B.p., °C.
Tetrahydro-2,2,4,4-tetramethylfuran	138	1.4123	0.8161	121
Tetrahydro-2,3,4,4-tetramethylfuran	33	1.4250	.8766	132
2,3,4-Trimethylvaleraldehyde	234	1.4242	.8373	159
Residue	85			

Distillation of the residue at reduced pressure gave 81 g. of the cyclic acetal of 2,3,4-trimethylvaleraldehyde and 2,2,4-trimethyl-1,3-pentanediol, b.p. 85–90° (2 mm.).

The conversion of the diol to 2,3,4-trimethylvaleraldehyde was 44%; to tetrahydro-2,2,4,4-tetramethylfuran, 26%; to tetrahydro-2,3,4,4-tetramethylfuran, 6%; and to the cyclic acetal, 8%.

Anal. Calcd. for $C_8H_{16}O$ (tetrahydro-2,3,4,4-tetramethylfuran): C, 74.94; H, 12.58. Found: C, 74.97; H, 12.50. Calcd. for $C_8H_{16}O$ (2,3,4-trimethylvaleraldehyde): C, 74.94; H, 12.58. Found: C, 74.88; H, 12.52. Calcd. for $C_9H_{19}N_3O$ (semicarbazone, m.p. 120–121°, of 2,3,4-trimethylvaleraldehyde): N, 22.69. Found: N, 22.51. Calcd. for $C_{16}H_{32}O_2$ (cyclic acetal of 2,3,4-trimethylvaleraldehyde and 2,2,4-trimethyl-1,3-pentanediol): C, 74.94; H, 12.58. Found: C, 74.83; H, 12.55.

2,3,4-Trimethyl-1-pentanol.—2,3,4-Trimethylvaleraldehyde (207 g., 1.62 moles) was reduced for 3 hr. at 125° with hydrogen at 2000 p.s.i. using 10% Raney nickel catalyst. The mixture was filtered and distilled to obtain 167 g. (80%) of 2,3,4-trimethyl-1-pentanol, b.p. 182° (730 mm.), n^{20}_{D} 1.4392, d^{20}_{4} 0.8498.

Anal. Calcd. for $C_8H_{18}O$: C, 73.78; H, 13.90. Found: C, 73.64; H, 13.77.

2,3,4-Trimethylvaleric Acid by Oxidation of 2,3,4-Trimethylvaleraldehyde.—Acidic permanganate oxidation[6] of 896 g. (7.0 moles) of 2,3,4-trimethylvaleraldehyde gave 711 g. (71%) of 2,3,4-trimethylvaleric acid, b.p. 223–225° (730 mm.), n^{20}_{D} 1.4345, d^{20}_{4} 0.9290. The amide melted at 162–163.5°.

Anal. Calcd. for $C_8H_{17}NO$: C, 67.11; H, 11.90. Found: C, 66.99; H, 11.89.

2,3,4-Trimethylvaleric acid by the Reformatsky Reaction.—Isobutyl 2-bromopropionate was condensed with 3-methyl-2-butanone using the procedure described by Newman and Evans.[7] When the reaction was carried out on a 3-mole scale, a 36% yield of isobutyl 3-hydroxy-2,3,4-trimethylvalerate was obtained, b.p. 146–148° (38 mm.). The hydroxy ester (185 g., 0.85 mole) was dropped slowly into 153 g. of refluxing acetic anhydride, and the mixture was refluxed for 30 min.[8] Distillation of the reaction mixture gave, in addition to acetic acid and acetic anhydride, 132 g. (83%) of isobutyl 2,3,4-trimethyl-2(or 3)-pentenoate, b.p. 126° (36 mm.). The unsaturated ester (118 g.) in 100 g. of ethyl alcohol with 30 g. of Raney nickel was reduced for 2 hr. at 125° with hydrogen at 1500 p.s.i. After removal of the catalyst by filtration, the filtrate was added to a solution of 1 mole of sodium methoxide in 500 ml. of methanol. This mixture was refluxed for 90 min., and then water was added. The alcohol was removed by distillation, and the aqueous residue was acidified with sulfuric acid. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic solution was dried over magnesium sulfate, filtered, and distilled to give 85 g. (85%) of 2,3,4-trimethylvaleric acid, b.p. 223–226° (730 mm.). The amide of this acid melted at 159–161.5°. A mixture of this amide with the amide of the acid obtained from 2,3,4-trimethylvaleraldehyde showed no depression in melting point.

Anal. Calcd. for $C_8H_{16}O_2$: neut. equiv., 144. Found: neut. equiv., 146.

Ring Opening of Tetrahydro-2,3,4,4-tetramethylfuran.—To a stirred mixture of 204 g. (2.0 moles) of acetic anhydride containing one drop of concentrated sulfuric acid was added dropwise 128 g. (1.0 mole) of fraction boiling at 132° from the dehydration of 2,2,4-trimethyl-1,3-pentanediol. The mixture was refluxed for 4 hr., then poured into twice its volume of water and neutralized with solid sodium carbonate. The organic layer was separated, dried over magnesium sulfate, and then distilled to give 126 g. (72%) of an unsaturated acetate, b.p. 185–198° (730 mm.), sapon. equiv., 174. The acetate was heated at 150° with hydrogen at 2000 p.s.i. for 2 hr. with 10% Raney nickel. After the catalyst was removed by filtration, 91 g. (73%) of a saturated acetate, b.p. 191–193° (730 mm.), was obtained. This product was refluxed for 4 hr. in a solution of 80 g. of sodium hydroxide in 640 g. of 50% aqueous ethyl alcohol. After the alcohol was removed by distillation, the aqueous residue was acidified with hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with ether. After being dried over magnesium sulfate, the combined organic solution was distilled to give 63 g. (94%) of 2,2,3-trimethyl-1-pentanol, b.p. 172–173° (730 mm.), n^{20}_{D} 1.4388. Both the 3,5-dinitrobenzoate and the 3-nitrophthalate were oils.

Anal. Calcd. for $C_8H_{18}O$: C, 73.78; H, 13.90. Found: C, 73.84; H, 13.86.

2,2,3-Trimethyl-1-pentanol by the Reformatsky Reaction.—Three moles of ethyl 2-bromo-3-methylpropionate was condensed with 3 moles of 2-butanone. The product was dehydrated as described in the preparation of 2,3,4-trimethylvaleric acid. The yield of unsaturated ester boiling at 82–85° (21 mm.) was 195 g. (38%), n^{20}_{D} 1.4383. Reduction of this ester at 125° with hydrogen at 1500 p.s.i. for 7 hr. with 10% Raney nickel gave, after the catalyst had been removed by filtration, 196 g. (quantitative yield) of ethyl 2,2,3-trimethylvalerate, b.p. 82° (28 mm.). One mole of the saturated ester was added dropwise to a stirred, refluxing mixture of 600 ml. of ether and 20.9 g. of lithium aluminum hydride. Excess hydride was hydrolyzed by addition of a water–tetrahydrofuran solution, and then a 10% solution of hydrochloric acid was added until the inorganic salts clumped together in the bottom of the flask. The ether solution was filtered, dried over magnesium sulfate, and distilled to give 98 g. (76%) of 2,2,3-trimethyl-1-pentanol, b.p. 172–175° (730 mm.), n^{20}_{D} 1.4387. The infrared spectrum of this product was identical with the spectrum of the alcohol derived from tetrahydro-2,3,4,4-tetramethylfuran.

2,2,3-Trimethylvaleric Acid from 2,2,3-Trimethyl-1-pentanol.—The 2,2,3-trimethyl-1-pentanols from the two sources were oxidized in the same manner as 2,3,4-trimethylvaleraldehyde. The two acids obtained were used, without distillation, to prepare the *p*-phenylphenacyl esters. The ester of authentic 2,2,3-trimethylvaleric acid melted at 55–56°. The ester of 2,2,3-trimethylvaleric acid derived from tetrahydro-2,3,4,4-tetramethylfuran melted at 53–54.5°. A mixture of the two esters melted at 54–55.5°. The ester of authentic 2,2,3-trimethylvaleric acid was analyzed.

Anal. Calcd. for $C_{22}H_{26}O_3$: C, 78.07; H, 7.75. Found: C, 77.88; H, 7.73.

Cyclic Acetal of 2,3,4-Trimethylvaleraldehyde and 2,2,4-Trimethyl-1,3-pentanediol.—A mixture of 128 g. (1 mole) of 2,3,4-trimethylvaleraldehyde, 146 g. (1 mole) of 2,2,4-trimethyl-1,3-pentanediol and 1500 ml. of benzene was refluxed under a water separator. Five grams of *p*-toluenesulfonic acid was used as a catalyst; 16 ml. of water formed by the reaction was removed. The mixture was neutralized with sodium acetate, and then was distilled to give, after removal of benzene, 231 g. (90%) of the cyclic acetal, b.p. 87–92° (2 mm.). The infrared spectrum of this product was identical with that of the cyclic acetal obtained in the dehydration of 2,2,4-trimethyl-1,3-pentanediol.

KINGSPORT, TENN.

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(6) The procedure described by J. R. Ruhoff, "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Editor, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 315, was followed with the modification that the amount of water used was reduced by one-third.

(7) M. S. Newman and F. J. Evans, Jr., THIS JOURNAL, **77**, 946 (1955).

(8) Oxalic acid, iodine in benzene and thionyl chloride failed to effect this dehydration.