In order to resolve the two unknown low frequencies of the *trans* molecule, whose sum we find to be 435 cm.$^{-1}$, it would be necessary to investigate the infrared absorption of the molecule in the region below 300 cm.$^{-1}$ to find δ_4. The torsional frequency, τ, could then be found by difference. Heat capacity measurements alone would not suffice since δ_6 would become important, giving rise to three parameters and making extraordinarily accurate measurements necessary.

The authors are indebted to Professor Roscoe G. Dickinson and to Dr. Verner Schomaker for helpful discussion and suggestions during the course of this research.

Summary

The gaseous equilibrium between *cis*- and *trans*-dichloroethylene has been studied between 185 and 275°, iodine being used to catalyze the isomerization. From the equilibrium data the value for ΔH^0 for the isomerization of *cis*-dichloroethylene has been calculated to be 723 cal./mole.

By combining these data with the available spectroscopic and electron diffraction data a value for the sum of two unknown frequencies in *trans*-$C_2H_2Cl_2$ has been calculated; and it has been shown that at 0° K. the *cis* form is more stable than the *trans* by about 530 cal./mole.

PASADENA, CALIFORNIA RECEIVED MARCH 1, 1941

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 818]

The Reduction of Tartaric Acid[1]

BY H. J. LUCAS AND W. BAUMGARTEN

Within recent years there has been a marked revival of interest in the tetroses and related compounds. Aside from the ozonolysis of diacetyl-*d*-xylal[2] the tetroses have been prepared mainly from the pentoses by the well-known degradation methods of Ruff,[3a] Wohl[3b,c,4] and Weermann.[5]

The desirability of using the tartaric acids as sources for tetroses and related compounds was recognized by Emil Fischer,[6] who was unsuccessful in attempts to reduce tartaric acid. Following the realization that the lactones, rather than the acids themselves, are the compounds which undergo reduction he planned to reduce esters of tartaric acid.[7] Since no subsequent statement has appeared, it is presumed that results were negative.[8] This report is made now, since the synthesis of *l*-threitol has been accomplished.

The extension of the Rosenmund[9] method to sugar chemistry by Cook and Major[10] and by Glattfeld and co-workers,[11] who have reduced the acid chlorides of acetylated hydroxy acids to acetylated hydroxy aldehydes with hydrogen in the presence of palladinized barium sulfate, suggested a similar method of attack here.

When tartaric acid, I, is heated with acetic anhydride[12] or with benzoyl chloride,[13] it is converted into diacetyltartaric anhydride, II, or dibenzoyltartaric anhydride. The dibenzoyl anhydride is converted by water into dibenzoyltartaric acid monohydrate. The anhydride was obtained when attempts were made to convert the acid to the acid chloride, as noted by others.[14] Diacetyltartaric acid was not obtained in satisfactory yields from the diacetyl anhydride.[15]

An acid chloride can be prepared from a half ester, obtained from one of the anhydrides through a reaction with an alcohol. Although dibenzoyltartaric anhydride reacts readily with primary alcohols, the resulting products are liquids. Moreover, they cannot be distilled without decomposition. However, diacetyltartaric anhy-

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[1] Dextrorotatory tartaric acid, *l*-(+)-*threo*-dihydroxysuccinic acid, is referred to simply as tartaric acid.

[2] W. Freudenberg, *Ber.*, **65**, 168 (1932).

[3] (a) Hockett, THIS JOURNAL, **57**, 2260, 2265 (1935); (b) Hockett, Deulofeu, Sedoff and Mendive, *ibid.*, **60**, 278 (1938); (c) Hockett and Maynard, *ibid.*, **61**, 2111 (1939).

[4] Iwadare, Fukunaga and Kubota, *Bull. Chem. Soc. Japan*, **12**, 116 (1937); *Chem. Abs.*, **31**, 5767 (1937).

[5] Weermann, *Rec. trav. chim.*, **37**, 16 (1917).

[6] E. Fischer, *Ber.*, **22**, 2204 (1889).

[7] E. Fischer, *ibid.*, **23**, 930 (1890).

[8] The method of Bouveault and Blanc, *Compt. rend.*, **136**, 1676 (1903); **137**, 60 (1903), has been applied to the reduction of isobutyl tartrate, ethyl isopropylidenetartrate and isobutyl isopropylidenetartrate without success. Glattfeld and Mochel, THIS JOURNAL, **60**, 1011 (1938), have shown that esters of α,β-dihydroxyisobutyric acid cannot be reduced this way.

[9] Rosenmund, *Ber.*, **51**, 585 (1918).

[10] Cook and Major, THIS JOURNAL, **58**, 2410 (1936).

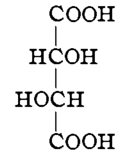
[11] Glattfeld and Mochel, *loc. cit.*; Glattfeld and Straitiff, THIS JOURNAL, **60**, 1384 (1938); Glattfeld and Kribben, *ibid.*, **61**, 1720 (1939).

[12] Chattaway and Parkes, *J. Chem. Soc.*, **123**, 663 (1923).

[13] Butler and Cretcher, THIS JOURNAL, **55**, 2605 (1933).

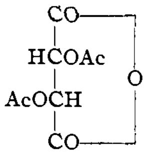
[14] Zetzsche and Hubacher, *Helv. chim. acta*, **9**, 291 (1926).

[15] Austin and Park, *J. Chem. Soc.*, **127**, 1926 (1925), state that diacetyltartaric acid results from the action of water in acetone. No yield is given.

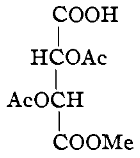


$$\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{HOCH}\\ |\\ \mathrm{COOH}\end{array}$$

I

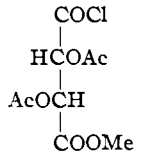


II



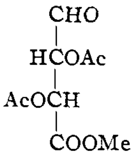
$$\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{HCOAc}\\ |\\ \mathrm{AcOCH}\\ |\\ \mathrm{COOMe}\end{array}$$

III



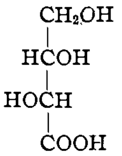
$$\begin{array}{c}\mathrm{COCl}\\ |\\ \mathrm{HCOAc}\\ |\\ \mathrm{AcOCH}\\ |\\ \mathrm{COOMe}\end{array}$$

IV



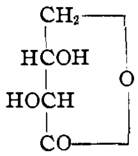
$$\begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{HCOAc}\\ |\\ \mathrm{AcOCH}\\ |\\ \mathrm{COOMe}\end{array}$$

V

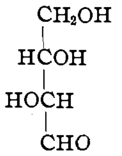


$$\begin{array}{c}\mathrm{CH_2OH}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{HOCH}\\ |\\ \mathrm{COOH}\end{array}$$

VI

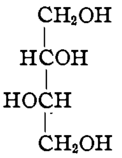


VII



$$\begin{array}{c}\mathrm{CH_2OH}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{HOCH}\\ |\\ \mathrm{CHO}\end{array}$$

VIII



$$\begin{array}{c}\mathrm{CH_2OH}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{HOCH}\\ |\\ \mathrm{CH_2OH}\end{array}$$

IX

dride, II, reacts vigorously with methanol to give the easily purifiable solid monomethyl diacetyltartrate, III.[16] This with thionyl chloride is converted into the crystalline acid chloride of monomethyl diacetyltartrate, IV.

The acid chloride can be reduced by the Rosenmund method in xylene at a temperature of 130 to 135°. When the reaction mixture stands at room temperature, methyl diacetyl-*l*-threuronate, V, separates in 55–60% yield.

The threuronate has a mild aldehyde odor, reduces warm Benedict solution and gives the characteristic uronic acid test with naphthoresorcinol.[17] The color of the resulting dye in ether is reddish violet and it has a strong absorption in the range 5200 to 6000 Å., similar to that of the dye from glucuronic acid, which absorbs in the region of the D line. The threuronate reacts with phenylhydrazine, *p*-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine, yielding solid derivatives with the last two.

In contact with water, hydrolysis of V takes place easily, for essentially three equivalents of sodium hydroxide must be added before the solution becomes alkaline. When an aqueous solution of V is concentrated, darkening gradually takes place. Finally, a dark gum is obtained, from which no crystalline product could be isolated.

This is the first tetruronic acid of which the structure is definitely established. A few previously described compounds may be tetruronic acids, but some doubt exists as to the structures. Thus from the oxidation of *meso*-erythritol[18] Neuberg isolated an acid, $C_4H_6O_5$, in the form of the barium salt. Schmidt, *et al.*, isolated the calcium salt of 3-methylthreuronic acid by hydrolyzing the ozonolysis product of the unsaturated methylation product resulting from the action of diazomethane on saccharic acid, and on saccharolactonic acid.[19]

Reduction of the uronic ester, V, was attempted with aluminum isopropoxide and with hydrogen in the presence of a Raney nickel catalyst.[20] In neither case was any reduction product isolated. However, V can be reduced in aqueous solution by sodium amalgam, keeping the solution slightly basic. The reduction is stopped when the reducing power is lost. The reduction product was a sirup which could not be obtained crystalline. The procedure of Gätzi and Reichstein,[21] who obtained *l*-threonolactone, VII, in a crystalline form by means of high vacuum distillation at 0.3 mm., gave a sirup which would not crystallize. However the acid, VI, was characterized as the brucine salt. This salt has been described previously.[21,22]

Reduction of *l*-threonic acid with sodium amalgam was carried out under acidic conditions. Under these conditions the compound undergoing reduction presumably is the lactone, VII, which is in equilibrium with the acid. No attempt was made to isolate the first reduction product *l*-threose, VIII, the presence of which was indicated by reducing action of the solution toward Benedict solution. The reaction was continued until the solution had no reducing action. The final reduction product, *l*-threitol, IX, was isolated as dibenzylidene-*l*-threitol, and from this *l*-threitol was obtained.

The synthesis of *l*-threitol from tartaric acid is a confirmation of the configuration of the threitols, as determined by others. Thus Maquenne[23]

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[16] Wrobel, *Roczniki Chem.*, **13**, 588 (1933); *Chem. Abs.*, **28**, 5410 (1934).

[17] B. Tollens, *Ber.*, **41**, 1788 (1908); C. Neuberg, *Biochem. Z.*, **36**, 56 (1911).

[18] Neuberg, *ibid.*, **24**, 167 (1910); Neuberg and Hirschberg, *ibid.*, **27**, 327 (1910).

[19] Schmidt, Zeiser and Dippold, *Ber.*, **70**, 2402 (1937); Schmidt and Guenthert, *ibid.*, **71**, 493 (1938).

[20] E. Baer and H. O. L. Fischer, *J. Biol. Chem.*, **128**, 463 (1939), have reduced isopropylidene glyceric aldehyde to isopropylidene glycerol at room temperature and at high pressure.

[21] Gätzi and Reichstein, *Helv. chim. acta*, **20**, 1298 (1937); **21**, 186 (1938).

[22] Nef, Hedenburg and Glattfeld, This Journal, **39**, 1638 (1917).

[23] Maquenne, *Bull. soc. chim.*, [3] **23**, 587 (1900); Maquenne and Bertrand, *ibid.*, [3] **25**, 740 (1901).

obtained *d*-threitol from *d*-xylose through *d*-threose, and Hockett[3] obtained dibenzylidene-*d*-threitol from *d*-xylonic acid and *d*-xylose, through *d*-threose. The formation of *l*-threitol by the reduction of erythrulose does not establish its configuration.[24]

Experimental

Isobutyl Tartrate.—A mixture of 250 g. ($1^2/_3$ moles) of tartaric acid and 450 g. (5.3 moles) of isobutyl alcohol containing 3% hydrogen chloride was heated so as to obtain a slow distillation of the azeotropic mixture of the alcohol and water through a fractionating column until anhydrous alcohol came over. After excess alcohol had been distilled out, the product, which solidifies on cooling, distilled at 155–160° (5 mm.); yield 350 g. (80%).

Reduction of Tartaric Esters.—The isobutyl ester in absolute alcohol was added slowly to a mixture of sodium and absolute alcohol. After the sodium had disappeared, the alcohol was distilled off and the residue was taken up in water. The solution was neutralized with sulfuric acid, boiled with charcoal and the colorless solution was evaporated to dryness. From this residue no organic compound could be extracted with alcohol.

The reduction was repeated, except that the alkali was neutralized by potassium bisulfite in one case, and by carbon dioxide in another. The results were negative.

Alkyl Isopropylidenetartrates.—When ethyl tartrate was heated with acetone and anhydrous copper sulfate for thirty-six hours, as in the method of Tsuzuki,[25] no reaction product was obtained. However, reaction took place when a small amount (a few drops per liter) of sulfuric acid was added. The yield was 50%. It was found preferable to carry out the reaction at room temperature on the shaking machine. Thus the isobutyl derivative was obtained in 60% yield by shaking for about twelve hours, 131 g. (0.5 mole) of isobutyl tartrate, 800 ml. (10 moles) of acetone and 195 g. (1.2 moles) of anhydrous copper sulfate. The product distilled at 125° (2 mm.). The yield from ethyl tartrate was similar.

It was thought that blocking of the hydroxyl groups in the isopropylidene compounds would facilitate reduction of the ester groups. However, no reduction product could be isolated when the ethyl or isobutyl isopropylidenetartrate was reduced as above.

Dibenzoyltartaric Anhydride.—This was prepared in practically quantitative yield by the procedure of Butler and Cretcher.[13] The melting point, 193°, was higher than values reported previously (173°). The monohydrate of the free acid, resulting when water is added to the anhydride, was reconverted into the anhydride by thionyl chloride or phosphorus pentachloride, thus confirming the observations of Zetsche and Hubacher.[14] Thionyl chloride in the presence of a small amount of zinc chloride acts similarly, although it converts phthalic, succinic and fumaric acids into the respective acid chlorides.[26]

A crystalline half ester could not be prepared by dissolving the anhydride in methyl alcohol, followed by removal of excess methanol at reduced pressure. The residual oil would not crystallize. This substantiates the results of Zetsche and Hubacher, who, however, heated the reactants. The sirupy product from the action of the anhydride on benzyl alcohol was converted into the anhydride with thionyl chloride.

Diacetyltartaric Anhydride, II.—This was obtained in 95% yield when 220 g. (1.5 moles) of tartaric acid was heated at 60° for twenty hours with 530 g. (5 moles) of acetic anhydride containing 3% of hydrogen chloride. The solid, after removal of acetic acid and excess acetic anhydride, was crystallized from benzene, m. p. 134°.

The neutralization equivalent was determined by titration in aqueous solution at room temperature, the saponification equivalent by the method of Redemann and Lucas.[27]

Anal. Calcd. for $C_8H_8O_7$: neutralization equiv., 108; sapon. equiv., 54. Found: neutral. equiv., 110; sapon. equiv., 53.5.

Monomethyl Diacetyltartrate, III.—When 40 ml. (1 mole) of methanol is added to 108 g. (0.5 mole) of diacetyltartaric anhydride, the solid dissolves with heating. After removal of excess methanol at reduced pressure, 93 g. (75% yield) of monomethyl diacetyltartrate is obtained after crystallization from isopropyl ether; m. p. 124.7° (cor.)[28]; $[\alpha]^{25}\text{D}$ $-18.4°$ (α $-0.75°$; *l*, 2; *c*, 2.32; MeOH).

Anal. Calcd. for $C_9H_{12}O_8$: C, 43.6; H, 4.84; neut. equiv., 248; sapon. equiv., 62. Found: C, 43.4; H, 4.88; neut. equiv., 244; sapon. equiv., 63.

The Acid Chloride of Monomethyl Diacetyltartrate, IV (*l-threo*-λ-Carbomethoxy-*α*,*β*-diacetoxybutyryl Chloride).—Under a reflux condenser a mixture of 45 g. of III and 45 ml. of redistilled (but yellow) thionyl chloride (b. p. 75–78°) was heated at 60° for about two hours, by which time all of the solid had dissolved. The excess thionyl chloride was removed at reduced pressure, and the residue was recrystallized twice from isopropyl ether, which had been carefully purified from water and peroxide, and stored over sodium. It separated as fine needles, yield 75%; m. p. 108.5° (cor.). The solid is not very stable, for it slowly liquefies even in a sealed tube, or in a desiccator. The compound was analyzed for chlorine by first hydrolyzing, and then determining chloride ion by the Volhard method.

Anal. Calcd. for $C_9H_{11}O_7Cl$: C, 40.5; H, 4.12, Cl, 13.3; sapon. equiv., 52.4. Found: C, 40.15; H, 4.18; Cl, 13.1; sapon. equiv., 57 to 59.

Other Half Esters and Acid Chlorides.—Diacetyltartaric anhydride with ethyl, isopropyl or isobutyl alcohol gives a liquid which could not be crystallized. The ethyl and isobutyl esters were converted to acid chlorides with thionyl chloride as above. Analysis for chlorine was made as above. The slightly low values are due to the tendency of the compounds to decompose slowly.

l-threo-*γ*-Carbethoxy-*α*,*β*-diacetoxybutyryl chloride, b. p. 137.5° at 6 mm. *Anal.* Calcd. for $C_{10}H_{13}O_7Cl$: Cl, 12.65. Found: Cl, 11.8.

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[24] Bertrand, *Compt. rend.*, **130**, 1472 (1900); Bertrand, *Bull. soc. chim.*, [3] **23**, 681 (1900).

[25] Tsuzuki, *Bull. Soc. Chim. Japan*, **10**, 255 (1935); **11**, 362, 587 (1936).

[26] Kyrides, THIS JOURNAL, **59**, 206 (1937).

[27] Redemann and Lucas, *Ind. Eng. Chem.*, *Anal. Ed.*, **9**, 521 (1937).

[28] Wrobel[16] reports m. p., 102°.

l-threo-γ-Carbisobutoxy-α,β-diacetoxybutyryl chloride, b. p. 147° at 6.5 mm. *Anal.* Calcd. for $C_{12}H_{17}O_7Cl$: Cl, 11.5. Found: Cl, 10.9.

Methyl Diacetyl-*l*-threuronate, V.—Hydrogen was passed vigorously into 60 ml. of xylene in which 32 g. of IV was dissolved and 5 g. of palladinized barium sulfate was suspended.[29] The temperature was 130 to 135° and the time, three to four hours. The reaction was stopped when the evolution of hydrogen chloride slackened, by which time the reduction was 75 to 80% complete. The rate of evolution was followed by passing the exit gas through aqueous sodium hydroxide. The catalyst was removed by centrifuging. On standing the threuronate crystallized in yields of 55 to 60%. An additional crop resulted when the xylene was removed at reduced pressure and the product was distilled at 3 mm. (b. p. 120 to 130°). The total crude yield was 65 to 70%.

The yield was lower when the acid chloride or the xylene was not pure, or when the reduction took longer, as was the case if the catalyst was not well suspended, if it became less active, or if the reduction was carried on toward completion. The purity of the product in some cases was so reduced that no solid separated. When the reduction was satisfactory, the solution was colorless, or nearly so. Whenever the solution was dark colored the yield was low. Distillation at low pressures was necessary whenever the product failed to crystallize, or was dark colored.

The ester crystallizes in nodules from toluene or from isopropyl ether, m. p. 84°. The former is preferable, for the loss is much less. Rotations were observed in water, in methanol and in methanol containing 1% of hydrogen chloride. The initial rotations (about five minutes was required for dissolving) were: $[\alpha]^{25}D$ −34.4 (α −2.23°; *l*, 2; *c*, 3.259; H_2O); $[\alpha]^{25}D$ −55.2 (α −3.68°; *l*, 2; *c*, 3.314; MeOH); $[\alpha]^{25}D$ −35.4 (α −1.12°; *l*, 1; *c*, 3.171; MeOH, HCl).

Anal. Calcd. for $C_9H_{12}O_7$: C, 46.5; H, 5.18. Found: C, 46.6; H, 4.96.

It gives a positive uronic acid test with naphthoresorcinol,[17] and the resulting reddish violet dye in ether absorbs strongly in the range 5200 to 6000 Å.

The threuronate has a mild aldehyde-like odor, reduces Benedict solution when warmed, and reacts with phenylhydrazine, *p*-nitrophenylhydrazine and with 2,4-dinitrophenylhydrazine. In the case of the last two, the derivatives were solids. These were prepared by carrying out the reactions in hot glacial acetic acid and adding water to throw out the products. These were recrystallized from hot alcohol. The respective melting points were: *p*-nitrophenylhydrazone, 143° (cor.); 2,4-dinitrophenylhydrazone, 148° (cor.).

Anal. Calcd. for $C_{15}H_{17}O_8N_3$: C, 49.05; H, 4.63; N, 11.43. Found: C, 49.11; H, 4.39; N, 11.06.

Anal. Calcd. for $C_{15}H_{16}O_{10}N_4$: C, 43.6; H, 3.88; N, 13.5. Found: C, 43.96; H, 4.5; N, 13.4.

The rotation in aqueous solution remained constant for about twelve hours, then decreased slowly thereafter. After twenty days $[\alpha]D$ was −4°. Color developed after two or three days. After twenty days the solution was dark brown.

In methanol the rotation decreased slowly from the start and after five days reached a constant value of −38°. By this time the solution was colored slightly, but not so much as the aqueous solution.

In methanol containing hydrogen chloride the rotation dropped rapidly, reaching zero in about one day. Then it became positive and in four days more was +22°. The solution was quite dark by this time.

Some attempts at reduction of the methyl diacetylthreuronate were unsuccessful. It was heated three to four hours with an excess of aluminum isopropoxide. The original material was recovered by distillation. The failure here to effect reduction agrees with the experience of others[30] with hydroxyaldehydes.

Hydrogenation was tried in methanol and dioxane as solvents. Neither low pressure hydrogenation with palladium oxide, nor high pressure hydrogenation with Raney nickel, was successful. The recovery of the threuronate in the first case by distillation was essentially quantitative. In the second case the reaction product was a dark colored solution, from which a small amount of the uronate could be recovered. The maximum pressure available was about 80 atmospheres. The temperature was 100 to 120°. Probably the hydrogenation would be possible at higher pressures and room temperature.[20] High temperatures should be avoided, because of polymerization.

***l*-Threonic acid, VI,** was obtained by reducing V with sodium amalgam in aqueous solution. When 23 g. (0.1 mole) of the crystalline methyl uronate was suspended in 150 ml. of water and cooled, the addition of approximately 0.3 mole of sodium hydroxide was required to make the solution alkaline. This shows that removal of the methyl and the two acetyl groups takes place easily, and that the compound being reduced was sodium *l*-threuronate. Reduction was accomplished by the addition of 3% sodium amalgam in 50-g. batches, keeping the liquid slightly alkaline to phenolphthalein by neutralizing the excess of base with sulfuric acid, and cooling to keep the temperature in the range 0 to 25°. After some twelve hours, when about twice the theoretical amount of sodium had been used, the solution no longer reduced Fehling solution. The solution was filtered, evaporated to dryness under reduced pressure, enough 6 *N* sulfuric acid was added to liberate the organic acid and the solution was poured into five times its volume of hot absolute alcohol. The mixture was allowed to stand some hours, the voluminous precipitate of sodium sulfate removed by filtration, and the filtrate concentrated by reduced pressure evaporation to a small volume. This was taken up in a second volume of alcohol and then, after filtering, concentration was effected as before. The residue was a pale colored sirup, presumably *l*-threonolactone, VIII.

This was converted to the brucine salt by dissolving in warm water, adding brucine until alkaline, cooling, removing excess brucine with chloroform, and evaporating to dryness. After crystallizing from alcohol, the solid recovered weighed 33 g., which is 62% of the theoretical,

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[29] Technical xylene, previously refluxed with metallic sodium for some time and distilled, was satisfactory. The catalyst was prepared as described in Gattermann, Wieland, "Laboratory Methods of Organic Chemistry," 22nd edition, The Macmillan Co., N. Y., 1932, p. 369.

[30] Meerwein and Schmidt, *Ann.*, **444**, 221 (1925).

calculated from V. The solid melted at 203–204°, dec. $[\alpha]^{25}\mathrm{D}$ −23° (α −0.95°; *l*, 1; *c*, 4.13; H_2O).[31]

Anal. Calcd. for $C_{27}H_{34}O_9N_2$: C, 61.25; H, 6.60; N, 5.52; CH_3O, 11.7. Found: C, 61.32; H, 6.6; N, 5.22; CH_3O, 11.8.

When the reduction of V was attempted under acidic conditions, the reaction was much slower. Even when a larger amount of amalgam was used, the reduction was not complete. This shows the importance of keeping the medium slightly alkaline, rather than acidic.

Dibenzylidene-*l*-threitol.—The sirup from the reduction of V was dissolved in water, cooled to 0°, and with good agitation sodium amalgam was added at intervals. The mixture was kept acid to congo red by means of frequent additions of dilute sulfuric acid. After a short time a test portion reduced Benedict solution, indicating the presence of *l*-threose. No attempt was made to isolate this. Instead, the reduction was continued until the test was negative, requiring about 200% excess of sodium. After filtering, the filtrate was concentrated to a small volume (about 50 ml.) but not to dryness, and poured into a large volume (about 300 ml.) of absolute alcohol. After standing for some time, the solid was removed by filtration, the filtrate was evaporated under reduced pressure and the residue was taken up in alcohol. This was saturated with hydrogen chloride and a 10% excess of benzaldehyde added.[32] After a time, dibenzylidene-*l*-threitol crystallized in fine needles. It was allowed to stand in the cold overnight, collected by centrifuging and washed with alcohol, yield 15% from V. When crystallized from hot benzene, the melting point was 221–223° (cor.), $[\alpha]^{25}\mathrm{D}$ +79° (α +0.62°; *l*, 1; *c*, 0.78, $CHCl_3$).[33]

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.5; H, 6.05. Found: C, 72.5; H, 6.27.

***l*-Threitol, IX.**—When 0.45 g. (0.0015 mole) of dibenzylidene-*l*-threitol was heated with 20 ml. of 20% aqueous acetic acid, solution took place slowly and was complete after one hour. The solvent was removed at reduced pressure, the residue dissolved in a small amount of water, the solution filtered and the solvent removed as before. The residue was dissolved in a small amount of absolute alcohol, the insoluble matter centrifuged down and the solution cooled in a "dry-ice" bath. Crystallization was induced by scratching; colorless, thread-like needles separated. These were centrifuged down and recrystallized from a small volume of absolute alcohol, as above, to give 0.137 g. (0.0011 mole) of *l*-threitol, m. p. 88°. An additional amount of less pure material was recovered by evaporating the mother liquors. The yield of *l*-threitol is 73% for this step, 6.6% on the acid chloride, IV, and 4.6% on tartaric acid, I; $[\alpha]^{25}\mathrm{D}$ −4.2 (α −0.32; *l*, 1; *c*, 7.63; H_2O).[34]

Anal. Calcd. for $C_4H_{10}O_4$: C, 39.34; H, 8.19. Found: C, 39.28; H, 8.25.

Summary

l-threo-γ-Carbomethoxy-α,β-diacetoxybutyryl chloride can be obtained by the action of thionyl chloride on monomethyl diacetyltartrate. This acid chloride is easily reduced to methyl diacetyl-*l*-threuronate with hydrogen in the presence of palladinized barium sulfate.

Methyl diacetyl-*l*-threuronate can be reduced in basic solution to *l*-threonic acid by sodium amalgam. Reduction of *l*-threonic acid in acid solution by sodium amalgam yields *l*-threitol, the configuration of which is established by this synthesis.

Unsuccessful attempts were made to reduce ethyl tartrate, isobutyl tartrate, ethyl isopropylidenetartrate, and isobutyl isopropylidenetartrate. Also, the reduction of methyl diacetyl-*l*-threuronate was attempted by other means, but without success.

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[31] This salt is not as pure as the product of Gätzi and Reichstein,[21] who report the specific rotation as −19.3°.

[32] Since benzaldehyde is an excellent solvent for the product, only a slight excess was taken. Preliminary experiments on test portions were made to determine the proper amount.

[33] Previous values for dibenzylidene-*d*-threitol: Hockett,[3] m. p. 220–222°, $[\alpha]\mathrm{D}$ −77.9° (−78.2°); Maquenne,[23] m. p. 231°.

[34] Bertrand[24] found for *l*-threitol, $[\alpha]\mathrm{D}$ −4.4, m. p. 88°; Maquenne found for *d*-threitol, $[\alpha]\mathrm{D}$ +4.3, m. p. 88°.