

benzene as the principal product. There was a marked absence of by-products.

Isobutene was condensed with benzene using aluminum chloride under the same conditions employed with ferric chloride. There was more polymerization of the isobutene and the yield of alkylated benzenes was 11% smaller.

To investigate the relative catalytic activities of ferric and aluminum chlorides on alkenes, two moles of isobutene was passed into separate 100-ml. portions of carbon disulfide containing 0.15 mole of the chlorides. With aluminum chloride, 27 ml. of a product was obtained which distilled between 145–260°, while with ferric chloride, only 10 ml. was obtained and this had a boiling range of 100–228°.

With propene and excess benzene and 0.3 mole of ferric chloride, 91% of the condensation products was isopropylbenzene, b. p. 152–153°, n_D^{20} 1.4930.⁹

With isobutene and benzene in equimolecular ratios and 0.3 mole of ferric chloride, 89% of the condensation products was *t*-butylbenzene, b. p. 167–168°, n_D^{20} 1.4960.⁹ It was converted to the acetamino derivative¹⁰ which melted at 168–170°.

(9) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1926, Vol. I, p. 277.

(10) Ipatieff and Schmerling, *THIS JOURNAL*, **59**, 1056 (1937); Simons and Archer, *ibid.*, **60**, 986, 2952 (1938).

Two moles of isobutene with one of benzene and 0.15 mole of ferric chloride gave 65% of a solid product which was identified as 1,4-di-*t*-butylbenzene since it melted at 75°; the product obtained by nitrating with fuming nitric and concd. sulfuric acids at 25° melted at 190.5°. The yellow product obtained by oxidation with chromic anhydride in glacial acetic acid sublimed at 100°. This agrees with the properties of 1,4-di-*t*-butylbenzene.¹¹ The solid derivative from the aluminum chloride catalyzed reaction was identical with the product obtained with ferric chloride as shown by a mixed melting point.

Conclusions

1. Ferric chloride will effect condensation of propene and isobutene with benzene at room temperature.

2. Condensation takes place at room temperature in greater yields than at higher temperatures.

3. Ferric chloride produces a larger yield of alkylated benzenes and less polymerization than aluminum chloride.

(11) Beilstein, 4th ed., Vol. V, p. 454.

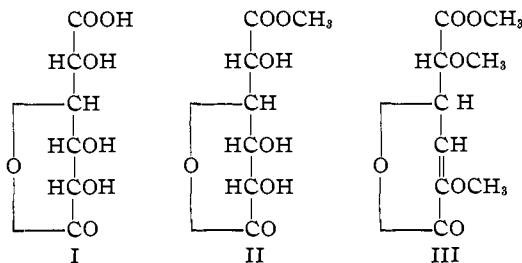
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Saccharolactone Methyl Ester

BY RICHARD E. REEVES

Crystalline saccharolactone (I) recently has been proved by Schmidt and Günthert¹ to be the 3,6-monolactone of saccharic acid. On mild treatment with diazomethane saccharolactone was found to yield a crystalline methyl ester (II), m. p. 113–114°. The structure of the ester was established by applying the procedure of Jackson and Hudson^{1a} as used by Schmidt and Günthert: namely, the isolation of oxalic and *d*-tartaric acids following periodic acid cleavage (between C₄–C₅) and subsequent oxidation with bromine in the presence of calcium carbonate.



(1) O. Th. Schmidt and P. Günthert, *Ber.*, **71**, 493 (1938).

(1a) E. L. Jackson and C. S. Hudson, *THIS JOURNAL*, **59**, 994 (1937).

Saccharolactone methyl ester (II) may be saponified to potassium acid saccharate, or converted to saccharic acid diamide. It gives a crystalline benzylidene compound whose structure has not been determined. The ester also reacts further with ethereal diazomethane to give the unsaturated lactone (III), m. p. 87°, which was previously described by Schmidt, Zeiser and Dippold.²

Experimental

All melting points reported in this paper were observed in a modified Fischer-Johns apparatus mounted on the stage of a polarizing microscope. Specific rotations were determined with the D-line of sodium light and at 26° unless otherwise specified.

Saccharolactone Methyl Ester.—Five grams of saccharolactone,^{3,4} m. p. 132–134°,⁵ was dissolved at room temperature in 350 cc. of dry methanol, and the solution immediately cooled in an ice-bath. To this was added a cold ethereal solution of diazomethane until a faint yellow coloration persisted for a few minutes after thorough mixing.

(2) O. Th. Schmidt, H. Zeiser and H. Dippold, *Ber.*, **70**, 2402 (1937).

(3) H. Kiliani, *ibid.*, **58**, 2344 (1925).

(4) K. Rehorst and H. Scholz, *ibid.*, **69**, 520 (1936).

(5) A lower melting sample of saccharolactone failed to yield the crystalline ester until purified by recrystallization from ether.

The diazomethane obtained from 25–30 g. of nitrosomethyl urea was required. The excess reagent was removed by addition of a trace of glacial acetic acid, and the solution rapidly concentrated to dryness under diminished pressure at 20°. The resulting sirup was dissolved in 10 cc. of absolute alcohol which upon standing in the ice-chest deposited 3.23 g. of crystalline saccharolactone methyl ester. After recrystallization from absolute alcohol, the product melted at 113–114°; sp. rot. +29.0° (*c*, 0.8, H₂O).

Anal. Calcd. for C₇H₁₀O₇: C, 40.78; H, 4.85; OCH₃, 15.1; eq. wt., 103. Found: C, 40.91; H, 4.30; OCH₃, 15.5; eq. wt., 105.8.

The product reduces Fehling's solution, in contrast with the action of saccharolactone. Quantitatively,⁶ the reduction amounts to less than 1% of that of glucose. On standing for several months in a desiccator at room temperature the substance decomposes to form a yellow gum. It was noticed that a faint yellow coloration appeared whenever the crystals were dried in high vacuum.

Saponification of Saccharolactone Methyl Ester to Yield Potassium Acid Saccharate.—Saccharolactone methyl ester (200 mg.) was boiled for a few minutes with 2.2 cc. of *N* potassium hydroxide. Several drops of glacial acetic acid and a trace of Norite were added and the solution filtered. On cooling 162 mg. of potassium acid saccharate separated; sp. rot. +6.25° → +19.2° (twenty days in water containing 1 eq. HCl).

Anal. Calcd. for C₆H₉O₆K: K, 15.77. Found: K, 15.97.

Preparation of Saccharic Acid Diamide from Saccharolactone.—A solution of 260 mg. of saccharolactone in 2 cc. of methanol-ammonia (saturated at 0°) quickly deposited a gum which crystallized on standing at 0°. After recrystallization from 50% alcohol the saccharic acid diamide⁷ melted at 176–178°; yield 140 mg.

Benzylidene Derivative of Saccharolactone Methyl Ester.—Saccharolactone methyl ester, 1.2 g., was shaken with 1 g. of anhydrous zinc chloride and 6 cc. of benzaldehyde. The mixture soon solidified, at which time 10 cc. of benzene was introduced and the shaking continued for five hours. Petroleum ether was stirred into the mixture which was then filtered and washed with petroleum ether. The precipitate was then washed on the filter with water until free from chlorine ion. After recrystallization from methanol, m. p. 237–238°, yield 0.80 g.; sp. rot. +147° (*c*, 1.0 in pyridine).

Anal. Calcd. for C₁₄H₁₅O₇: C, 57.06; H, 5.09; OCH₃, 10.50; eq. wt., 147. Found: C, 57.00; H, 4.84; OCH₃, 11.13; eq. wt., 149.

(6) Hanes modification of the Hagedorn–Jensen method, C. S. Hanes, *Biochem. J.*, **23**, 99 (1929).

(7) M. Bergmann, *Ber.*, **54**, 2651 (1921)

The product is insoluble in water, ether, petroleum ether and benzene, difficultly soluble in hot acetone, absolute alcohol, ethyl acetate and methanol. It dissolves slowly in aqueous sodium hydroxide with liberation of benzaldehyde (odor).

Periodic Acid Cleavage of Saccharolactone Methyl Ester Followed by Oxidation to Yield Oxalic and *d*-Tartaric Acids.—To 618 mg. (3 mol.) of saccharolactone methyl ester in 3 cc. of water was added 10 cc. of 0.3 *M* periodic acid solution. After one hour at room temperature 7.5 cc. of 2 *N* hydriodic acid was introduced and the mixture shaken, filtered and extracted with chloroform to remove iodine. The aqueous solution was then neutralized with a slight excess of solid calcium carbonate and, under good stirring, 3 g. more of calcium carbonate was added with 1.5 cc. of bromine. The solution no longer reduced Fehling's solution. The precipitated calcium salts were removed by centrifugation and dissolved in 5 cc. of hot water by the dropwise addition of concd. hydrochloric acid. The solution was then neutralized to methyl orange by addition of sodium acetate and the precipitated calcium oxalate was collected and washed by centrifugation; yield 142 mg.

Anal. 66.7 mg. required 10.29 cc. 0.1 *N* permanganate. Calcd., 10.42 cc. 0.1 *N* permanganate.

The supernatant solution from the calcium oxalate precipitate was neutralized to phenolphthalein with 2 *N* sodium hydroxide. The precipitated calcium tartrate was collected and washed by centrifugation; yield 263 mg.

Anal. Calcd. for C₄H₄O₆Ca·4H₂O: Ca, 15.37. Found: Ca, 15.58.

A suspension of the calcium tartrate was shaken with the calculated amount of oxalic acid, filtered and on evaporation to dryness yielded crystalline *d*-tartaric acid, m. p. 160°; sp. rot. +14.8° (H₂O).

Unsaturated Lactone Ester (III) Obtained by the Action of Diazomethane.—Saccharolactone methyl ester, 315 mg., was treated with 20 cc. of 0.7 *M* diazomethane in ether, and allowed to stand in the ice-chest for one week. The supernatant solution was decanted from the crystals which separated; yield 142 mg.; m. p. 87–88°; sp. rot. (21°) + 79.5° (*c*, 1.25 in methanol). Schmidt, Zeiser and Dippold⁸ report for compound III, m. p. 87°, sp. rot. (20°) + 83.1° (methanol).

Summary

The methyl ester of saccharolactone <3,6> has been prepared and its structure proved by periodic acid cleavage followed by oxidation of the product to yield oxalic and *d*-tartaric acids.

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