nesium turnings in anhydrous ether. The tertiary alcohol formed was not isolated but dehydrated during the workup. 1,1,3-Trimethylindene (43.2 g., 98%) was recovered by distillation, b.p. 58°–62°/1.6 mm. (lit.,[7] b.p. 94°/15 mm.).

Anal. Calcd. for $C_{12}H_{14}$: C, 91.10; H, 8.90. Found: C, 90.97; H, 9.03.

1,3,3-Trimethyl-1-indanecarboxylic acid. 1,1,3-Trimethylindene (2.0 g., 0.013 mole) and 5 g. of 90% formic acid were added to 45 g. of concd. sulfuric acid at 0°–5°. After 1 hr. at 0°–5° the dark red solution was poured into water. 1,3,3-Trimethyl-1-indanecarboxylic acid (0.3 g., 12%) was isolated and recrystallized from petroleum ether to m.p. 129°–130°. This material had an infrared spectrum identical with, and did not depress the melting point of the acid, m.p. 131°–132°, obtained by the permanganate oxidation of the isomeric ketone.[1]

Peracid oxidation of the isomeric ketone. The isomeric ketone (40 g., 0.20 mole) was added to 23.2 g. (0.17 mole) of perbenzoic acid in 350 cc. of chloroform at 0°–5° and kept in the dark at this temperature for 1 week. The solution was allowed to stand for an additional month at 20° in the dark. The crude oxidation product showed a peak at 5.73 μ in its infrared spectrum consistent with the presence of ester carbonyl absorption. Saponification of 16.9 g. of the crude oxidation mixture and fractional distillation of the neutral products resulted in 2.9 g. (15%) of 1,3,3-trimethylindene, b.p. 110°–120°/18 mm., identified by comparison of its infrared spectrum with that of the synthetic sample prepared above.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, and Messrs. W. Mendelson and J. Zeger of the Johns Hopkins University for assistance in the early phases of this work.

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Isolation of the 1,4- and the 6,3-Lactones of D-Glucaric Acid[1]

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Received July 25, 1960

Oxidation of D-glucose or starch with nitric acid yields D-glucaric acid (saccharic acid)[2] which is readily isolated as the acid potassium salt.[2,3] Removal of the potassium ions followed by evaporation afforded the monolactone of D-glucaric acid.[2] This product which was originally thought to be the 6,3-lactone[4] and which played a major role in the conversion of D-glucose into L-gulose[5] was subsequently proved[6] to be a mixture by isolating and proving the structure of the two lactones, the 1,4-lactone having m.p. 98° and $[\alpha]_D + 34°$, and the 6,3-lactone having m.p. 149° and $[\alpha]_D + 45°$.[7] The separation was facilitated by making use of the fact that the 1,4-lactone crystallizes as a monohydrate which is readily soluble in acetone, whereas the 6,3-lactone which crystallizes in the anhydrous form is almost insoluble in acetone.

More recently the 1,4-lactone has been shown to have anti-β-D-glucuronidase activity[8] and, as it may be a useful chemotherapeutic agent in the cure of bladder cancer,[9] there have been many requests for samples of the D-glucaro-1,4-lactone. This publication is prompted by our reinvestigation of the preparation of the 1,4-monolactone which has brought to light some simplification in procedure and an improvement in the yield. The improvement in yield has resulted from making use of the observation that when an aqueous solution of potassium hydrogen D-glucarate is boiled for thirty minutes the salt of the 1,4-lactone is generated,[10] whereas the simplification follows from the use of a cation exchange resin to remove the potassium ions from the boiled solution containing the potassium salt of D-glucaro-1,4-lactone.[11]

EXPERIMENTAL

Preparation of D-glucaro-1,4- and 6,3-lactones. Corn starch or soluble starch was oxidized to D-glucaric acid by nitric acid. Nitric acid (1 l. of concentrated acid in 2 l. of water) was added to the starch (220 g.) in a 4-l. glass beaker. A few crystals of sodium nitrite were added to catalyze the oxidation and the solution was heated on the steam bath. The beaker was removed from the heat during the vigorous evolution of brown gases which usually occurred after about 2 to 4 hr. of heating. When the gas evolution had subsided, the brownish yellow solution was heated on the steam bath for 16 to 18 hr., the solution being allowed to evaporate to about a quarter of the original volume. The solution, which was light yellow, was diluted with water (0.5 volume) and concentrated under reduced pressure (bath temp. 50–55°), water being added repeatedly to remove residual nitric acid. After most of the nitric acid was removed, the yellow solution was neutralized with solid potassium carbonate and then acidified to *p*H 4 with acetic acid. The potassium hydrogen D-glucarate was allowed to crystallize for 3 days at 5°, recovered by filtration, and dried in the air (yield, 130 g.). The crude salt was recrystallized from boiling water,[12] charcoal being added to effect decolorization; yield 90 g., $[\alpha]^{25}_D$ +5.2° (*c* 1.3, water).

A suspension of pure, recrystallized potassium hydrogen D-glucarate (129 g.) in water (525 ml.) was gently refluxed for 35 min[10]. The solution which had become yellow was

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[12] The heating in boiling water should be as brief as possible, otherwise the potassium hydrogen glucarate undergoes transformation.

cooled and kept at 5° for 12 hr. The liquid was separated by filtration, and the unchanged crystalline potassium hydrogen D-glucarate was suspended in water (300 ml.) and treated as before. The crystals from the second treatment were recovered and again treated with water (300 ml.) as above. The crystalline potassium hydrogen D-glucarate (18.0 g.) which separated after this third heating and cooling was not treated further.

The yellow solutions from the above three heat treatments of the potassium hydrogen salt were combined and deionized by passing through a column of Amberlite IR-120[13] cation exchange resin (H form). The acidic effluent from the cation exchange column was concentrated under reduced pressure (bath temp. 30–35°). The resulting thick, yellow sirup was stirred with a 1:1 mixture of water and acetone (50 ml.) and concentrated in an air stream. Crystallization commenced shortly after the heavy, viscous sirup was seeded with a mixture of D-glucaro-1,4- and 6,3-lactones. The crystallization was continued for 4 days under the air stream. The crystalline matrix was triturated with acetone (100 ml.) and the crystalline 6,3-lactone separated by filtration and washed with acetone (300 ml.). The yield of D-glucaro-6,3-lactone was 15.2 g. (17.6% of the potassium salt converted); m.p. 138–142°, $[\alpha]^{23}_D$ +58.5° (*c* 1.3, water) changing to $[\alpha]^{27}_D$ +23.7° (87 days).

The combined yellow acetone filtrate and washings were concentrated in an air stream and seeded with the 1,4-lactone. Crystallization was allowed to proceed to completion. After about 4 weeks the crystalline mass was triturated with ethyl acetate (125 ml.) and washed by decantation first with ethyl acetate and then with diethyl ether. The yield of D-glucaro-1,4-lactone was 56.0 g. (64% of the potassium salt converted); m.p. 90–100°, $[\alpha]^{27}_D$ +43.6° (*c* 1.2, water) changing to +27° in 8 days.

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(13) A product of the Rohm and Haas Co., Philadelphia, Pa.

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p-Vinylbenzoic Acid

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Received July 26, 1960

Several preparations of *p*-vinylbenzoic acid have been reported.[1-4] All are four- to six-step syntheses of low over-all yields (10–20%). A recently published[4] synthesis from ethylbenzene gave a yield of 24% of material of doubtful purity.

The preparation of *p*-vinylbenzoic acid reported here is a three-step synthesis from an ordinary molding-grade polystyrene. The yield, 18%, is only average compared to that of the other methods, but the simplicity of the procedure moderates this objection considerably. Polyvinylacetophenone was prepared by Friedel-Crafts acetylation of polystyrene. Thermal depolymerization yielded *p*-vinylacetophenone, and hypochlorite oxidation of the ketone gave *p*-vinylbenzoic acid.

The low-yield step in the various published syntheses of *p*-vinylbenzoic acid has been the formation of the vinylic double bond. The necessary high temperature or prolonged reaction time causes polymerization of the product. The negative group, carboxy, alkoxycarbonyl, or cyano, on the ring of the styrene molecule renders it more sensitive to polymerization. Previously this low-yield step has been the fourth or fifth reaction in the sequence, which makes it particularly objectionable. The double-bond formation in the present synthesis does not afford a better yield, but it occurs in the second step. Furthermore, the first step, acetylation of polystyrene, can be conducted on a large scale with little additional effort.

The preparation of polyvinylacetophenone and its depolymerization have been described,[5] but the yield reported for the pyrolysis could not be repeated. Heat transfer to the partially pyrolyzed polymer in the spherical flask was poor. A special pyrolysis tube overcame this problem somewhat. This apparatus probably could be used to advantage in many pyrolysis reactions which leave a nonvolatile residue. Redistillation of the pyrolysis product gave *p*-vinylacetophenone contaminated with *p*-methylacetophenone which boils a few degrees lower. Recrystallization from *n*-heptane constituted the best purification.

Excess hypochlorite causes increased polymer formation in the oxidation reaction. Consequently, the potassium hypochlorite was standardized by titration with thiosulfate in a conventional iodometry procedure, and only the calculated amount was used. The conventional recrystallization of *p*-vinylbenzoic acid from aqueous alcohol does not remove the contaminating polymeric acid. The monomer is highly soluble in ethyl ether; the polymer is quite insoluble in ether. Filtration affords the separation, and the low temperature of this process prevents further polymerization. Titration of the double bond of *p*-vinylbenzoic acid with bromine was found to be a better measure of purity than melting point.

EXPERIMENTAL

Polyvinylacetophenone. This polymer was prepared in 91% yield by a modification[6] of the published[5] procedure with carbon tetrachloride as solvent. An equivalent of aluminum chloride and a 10% excess of acetyl chloride were used. The dried polymer–aluminum chloride complex was decomposed in dilute hydrochloric acid and ice. The polymer was washed thoroughly with water but not reprecipitated.

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