between propylene and maleic anhydride at 180°.[8] At the temperatures (200–250°) suggested by Alder, *et al.*,[8] the yields were extremely low.

1-Methylcyclohexene-2-one-5-carboxylic acid (VIa). a. *From β-methallylsuccinic anhydride and aluminum chloride in the presence of benzene.* This experiment has been described in our previous paper[1] but we wish to record the pertinent data that have been accumulated for this compound and its derivatives.

The *methyl ester* had b.p. 110–111° (1.0 mm.); n_D^{20} 1.4980; d_4^{20} 1.089. The ultraviolet absorption spectrum had maxima at 237 mμ (log ε 4.15) and 282 mμ (log ε 2.19) while the principal peaks in the infrared absorption spectrum were at 5.77, 5.98, and 6.13 μ. The ester decolorized aqueous permanganate solutions and bromine in carbon tetrachloride but was recovered unchanged when reductive ozonolysis was attempted.

The *2,4-dinitrophenylhydrazone* of the methyl ester formed as red microneedles from alcohol-ethyl acetate, m.p. 149.5–150.5°; λ_{max} 383 mμ (log ε 4.56).

Anal. Calc'd for $C_{15}H_{16}N_4O_6$: C, 51.74; H, 4.63; N, 16.09. Found: C, 51.71, H, 4.68; N, 16.05.

The *free acid* (VIa) formed as a microcrystalline powder from acetone-hexane, m.p. 92–94°.

Anal. Calc'd for $C_8H_{10}O_3$: Neut. Eq., 154.1. Found: Neut. Eq., 157.0.

(*b*) *From β-methallylsuccine anhydride and aluminum chloride in the presence of ethylene chloride.* To a cooled (0°) solution of 5.0 g. (0.03 mole) of anhydride (Ia) in 50 ml. of ethylene chloride was added over one-half hour 4.4 g. (0.33 mole) of aluminum chloride. The resultant green complex was stirred at room temperature for 24 hours, poured onto a mixture of ice and water, and the organic material was taken up in ether. The ethereal layer was extracted with carbonate solution and on acidification there was deposited 0.93 g. of VIa as a semisolid mass. On the basis of anhydride consumed (1.0 g. was recovered from the neutral fraction) the yield was 23%.

Quantitative hydrogenation. A solution of 0.115 g. of the methyl ester corresponding to VIa was dissolved in 10 ml. of glacial acetic acid containing 25 mg. of prereduced platinum oxide catalyst. At a pressure of 740 mm., one mole (19.1 ml.) of hydrogen was taken up in 72 minutes but the second mole (19.0 ml.) required 93 hours. The product was not characterized.

Aromatization of methyl 1-methylcyclohexene-3-one-5-carboxylate. The methyl ester (1 g.) was intimately mixed with 0.2 g. of a 10% palladium on charcoal catalyst and heated to 250° for 1.5 hours. The melt was taken up in ether, filtered, and the ether was evaporated. The oil then was triturated with hexane and the amorphous brown solid that precipitated was sublimed to give colorless microneedles of methyl 3,5-cresotate (VII), m.p. 90.5–91.5°; lit.,[9] m.p. 92–93°.

Anal. Calc'd for $C_9H_{10}O_3$: C, 65.04; H, 6.06. Found: C, 65.10; H, 6.04.

On saponification, this ester yielded 3,5-cresotic acid, m.p. 205–206°; lit.,[10] m.p. 208°.

Reduction and aromatization of VIa *to m-toluic acid.* To a solution of 0.80 g. (4.8 millimoles) of VIa (methyl ester) in 15 ml. of methanol was added 0.10 g. of sodium borohydride. After the exothermic reaction had subsided the solution was heated on the steam-bath for five minutes and then was quenched with dilute acid. The alcohol then was extracted with ether and evaporated to an oil.

To the oil was added 80 mg. of a 10% palladium on charcoal catalyst and the mixture was heated to 245° for 2 hours. The melt was taken up in ether, the solvent was removed, and the residual oil was saponified in the usual manner. After one recrystallization the acid melted at 107–108.5°, undepressed on admixture with authentic *m*-toluic acid, m.p. 107.5–108.5°.

Methyl cyclohexene-3-one-5-carboxylate (*VIb, methyl ester*). When 5.0 g. of anhydride Ib[11] was treated with aluminum chloride in ethylene chloride as described above for Ia, there was recovered 1.0 g. of unreacted anhydride and 1.35 g. (34%) of crude acid, VIb. This was esterified with absolute methanol and the methyl ester was fractionally distilled; b.p. 125–128° (1.1 mm.); n_D^{20} 1.4712. The infrared absorption spectrum had maxima at 5.75, 5.95, 6.15, and 6.24 μ while the ultraviolet absorption maxima were at 243 mμ (log ε 3.85) and 280 mμ (log ε 3.12).

The *2,4-dinitrophenylhydrazone* crystallized from 90% alcohol as dull orange microneedles, m.p. 144–146°; λ_{max} 384 mμ (log ε 4.40).

Anal. Calc'd for $C_{14}H_{14}N_4O_6$: C, 50.30; H, 4.22; N, 16.77. Found: C, 50.26; H, 3.93; N, 17.03.

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(8) Alder, Pascher, and Schmitz, *Ber.*, **76**, 47 (1943).

(9) Jacobsen, *Ber.*, **14**, 2357 (1881).

(10) Meldrum and Perkin, *J. Chem. Soc.*, **95**, 1889 (1909).

(11) We are grateful to Trevor B. Hill of this laboratory for preparing this anhydride in connection with another problem.

The Preparation of 2,3,6-Trihydroxybenzoic Acid and Its Methyl Ester[1]

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Received February 9, 1956

A method has been developed for the preparation of 2,3,6-trihydroxybenzoic acid (I) by demethylating 2,3,6-trimethoxybenzoic acid (II) using anhydrous aluminum chloride in a mixture of benzene and chlorobenzene.

Hotii, *et al.*,[4] attempted to prepare I by the potassium persulfate oxidation of *gamma*-resorcylic acid; however, a syrup was obtained and the pure acid was not isolated. The presence of I could only be shown by the methylation of the syrup with the subsequent isolation of the corresponding trimethoxy derivative, II.

The preparation of II by the carbonation of 2,3,6-trimethoxyphenyllithium has been described by Gilman and Thirtle.[5]

Since I is easily decarboxylated, especially at temperatures in excess of 100°, any method for its preparation had to take this into account. Our experience with the aluminum chloride demethylation of 2,3-dimethoxybenzoic acid indicated that the reaction would be incomplete in refluxing benzene.

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(1) This work was supported in part by the Michigan Heart Association.

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(4) Hotii, Komiyama, Otsuki, and Yamamura, *J. Pharm. Soc. Japan*, **72**, 1520 (1952).

(5) Gilman and Thirtle, *J. Am. Chem. Soc.*, **66**, 858 (1944).

For this reason, a mixture of benzene and chlorobenzene was finally chosen which gave a pot temperature of 100° at the boiling point. This compromise mixture minimized decarboxylation while ensuring complete demethylation.

An interesting phenomenon concerning the apparent isomerism of I in the solid state has been observed. The freshly crystallized material exhibits a distinct yellow color. After standing several months, the crystals become colorless. Both materials have the same neutralization equivalent. In aqueous solution, both forms give identical ultraviolet spectra. The yellow form converts to the colorless form on being heated in a melting point tube, the final melting point being the same as the colorless form.

Further work is now in progress on I as well as with 2,3,5-trihydroxybenzoic acid[6] and 2,4,5-trihydroxybenzoic acid.[7] The latter two acids have been reported as being yellow. Since both have the same hydroxyhydroquinone structure as I, it seems likely they will show the same type of isomerism.

EXPERIMENTAL[8]

2,3,6-Trimethoxybenzoic acid (II). This material was prepared by the method of Gilman and Thirtle[5] using ethyllithium and after recrystallization from ethylene dichloride was obtained in 77.8% yield, m.p. 148–149.5°; ref. 5 gives m.p. 149–150°.

2,3,6-Trihydroxybenzoic acid (I). To a mixture of 42.3 g. (0.20 mole) of II, 200 g. of benzene, and 315 g. of chlorobenzene was added with vigorous stirring 112 g. (0.84 mole) of anhydrous, sublimed aluminum chloride. The mixture was heated slowly taking approximately 15 minutes to reach refluxing temperature.[9,10] Heating was continued for a total of 45 minutes.

The mixture was cooled under argon, poured over 1 kg. of ice with stirring, and allowed to stand until the ice had melted. The aqueous portion was extracted with 2 × 100 ml. of ether, filtered, and acidified with 100 ml. of concentrated hydrochloric acid. The precipitation of the product was extremely slow. The mixture was allowed to stand overnight.

The product was removed by filtration,[11] washed with 100 ml. of water, air-dried for several hours, and then dried at 70° to constant weight, yielding 18.7 g. The main filtrate was extracted with 3 × 100 ml. of ether. The ether was removed by evaporation and the residue, weighing 12.8 g., was combined with main portion of product.

The product was recrystallized by repeated extractions (four) with the same 400 ml. portion of nitromethane. This technique was repeated with a fresh amount of nitromethane.[12] The total yield of pure material was 19.2 g., yellow, 56.4%, m.p. 188.5–190° with decomposition, blue-green color with alcoholic ferric chloride.

Anal.[13] Calc'd for $C_7H_6O_5$: C, 49.42; H, 3.56. Found: C, 49.35; H, 3.92.

Calc'd for $C_6H_5O_3COOH$: Neut. Equiv.,[14] 170.1. Found: 171.8 (colorless form); 171.9 (yellow form).

Methyl 2,3,6-trihydroxybenzoate. The method of Saraiya and Shah[15] was used. A mixture of 8.3 g. (0.049 mole) of I, 5.1 g. of sodium bicarbonate, 7.6 g. (0.06 mole) of dimethyl sulfate, and 120 ml. of acetone was refluxed for 5 hours. The cooled reaction mixture was filtered and the solid was washed with 100 ml. of acetone. The combined acetone portions were evaporated to dryness under reduced pressure. The cooled residue was treated with 80 ml. of 5% aqueous sodium bicarbonate. The solid which separated was collected, washed with 10 ml. of water, air-dried, and recrystallized from benzene, yielding 3.0 g. of pale yellow crystals, 33%, m.p. 137–139°, brown color with ferric chloride.

An analytical sample was prepared by successive recrystallizations from benzene and *n*-heptane, m.p. 139–140.5°.

Anal.[13] Calc'd for $C_8H_8O_5$: C, 52.18; H, 4.38. Found: C, 51.90; H, 4.44.

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[6] Corbett, Hassall, Johnson, and Todd, *J. Chem. Soc.*, 1 (1950).

[7] Thiele and Jaeger, *Ber.*, **34**, 2837 (1901).

[8] Melting points are uncorrected.

[9] If heating is too rapid, the mixture will set to a hard mass which will break up slowly with continued heating.

[10] A gas-scrubbing tower was used as described by Allen, *Org. Syntheses*, Coll. Vol. II, 1st ed., 4 (1943).

[11] It is advisable to use a porcelain spatula. Intense colors develop with iron equipment.

[12] Other solvents such as: acetic acid, acetonitrile, and ethylene dichloride, have been tried with less success.

[13] Analyses were done by: Spang Microanalytical Laboratory, P. O. Box 2, Plymouth, Michigan.

[14] Neutralization equivalents are ours. A *pH* meter is essential since a red color develops as base is added which obscures the end-point with indicators.

[15] Saraiya and Shah, *Proc. Indian Acad. Sci.*, **31A**, 187 (1950).

Derivatives of Sulfenic Acids. XXV. The Reaction of 1,2-Epoxides with 2,4-Dinitrobenzenesulfenyl Chloride[1,2]

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In continuing our studies of the reactions of sulfenyl halides, the reaction of 2,4-dinitrobenzenesulfenyl chloride (I) with selected 1,2-epoxides has been examined. To our knowledge, no previous account of this reaction has been recorded, although Stewart and Cordts[3] reported an analogous reaction with episulfides, in which the addition of 1-chloro-2-propanesulfenyl chloride to propylene sulfide led to *bis*(1-methyl-2-chloroethyl) disulfide, II, as shown in equation 1.

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[2] Part 3 in "Studies of Sulfenate Esters (Thioperoxides)." For Part 2, *Cf. J. Am. Chem. Soc.*, **77**, 6541 (1955).

[3] Stewart and Cordts, *J. Am. Chem. Soc.*, **74**, 5880 (1952). Note added in proof: *Cf.*, also, Brintzinger, Schmahl, and Witte, *Ber.*, **85**, 338 (1952), for a description of the reaction of two moles of 2-chloroethanesulfenyl chloride with ethylene oxide.