shaken. The bottom oil layer which separated amounted to 270 g. The oil was washed again with 250 ml. of water saturated with salt. The crude oil (232 g.) was directly vacuum distilled yielding 100 g. of low boiling material, b.p. 38 to 93° (63 to 2 mm.). The desired product then was obtained, b.p. 93–95° (2 mm.), as an almost colorless slightly viscous oil of mild odor amounting to 121.5 g. (51%), d^{20}_4 1.1579, n^{20}_D 1.4875. There was no residue.

Anal. Calcd. for $C_7H_{13}O_3N$: C, 52.8; H, 8.18; N, 8.82. Found: C, 52.9; H, 8.5; N, 8.9.

Another condensation was run in exactly the same fashion as described above except that a final wash with 100 g. of 5% sodium bicarbonate solution was given before distillation. On distillation the entire product distilled at 54–60° (27 mm.) (pot to 130° at end) leaving no residue in the still. There was evidence of decomposition as soon as the pot temperature reached 85°. The distillate was mainly cyclohexanone. Most of the nitromethane was volatilized into the vacuum line.

Another condensation was run in the regular manner. The crude product after a wash with 250 ml. of water saturated with salt amounted to 240 g. There was added 6 drops of glacial acetic acid with good stirring and the oil vacuum distilled yielding 107 g. of low boiling material, b.p. 35 to 87° (65 to 1.5 mm.). The 1-nitromethylcyclohexanol then was obtained, b.p. 86–87° (1.5 mm.), 120 g. (50% of theory).

1-Nitromethyl-*m*-methylcyclohexanol.—This compound was prepared in exactly the same manner as the first procedure above using 224 g. (2 moles) of *m*-methylcyclohexanone (Eastman Kodak Company). The 1-nitromethyl-*m*-methylcyclohexanol was obtained as a colorless liquid, b.p. 95° (1.5 mm.), d^{20}_4 1.1120, n^{20}_D 1.4810. The yield was 49.0% calculated on the nitromethane used (1.5 moles).

Anal. Calcd. for $C_8H_{15}O_3N$: N, 8.1. Found: N, 8.3.

1-Nitromethyl-*p*-methylcyclohexanol.—By the same procedure this compound was obtained with a yield of 53.6% calculated on the nitromethane used (1.5 moles). The product distilled at 98–99° (1.5 mm.) as a pale yellow liquid, slightly viscous, and of mild odor, d^{20}_4 1.1115, n^{20}_D 1.4818. On standing this compound solidified to a white solid, f.p. 31–32°.

Anal. Calcd. for $C_8H_{15}O_3N$: N, 8.1. Found: N, 8.4.

1-Nitroethylcyclohexanol.—This compound was prepared by the above general procedure by condensing 112.5 g. (1.5 moles) of nitroethane with 2 moles of cyclohexanone. The product was obtained as a pale yellow, slightly viscous liquid, b.p. 84–87° (1.5 mm.), d^{20}_4 1.1260, n^{20}_D 1.4840. The yield was 58.5 g. (22.6% of theory).

Anal. Calcd. for $C_8H_{15}O_3N$: N, 8.1. Found, N 8.4.

RESEARCH LABORATORIES
THE GIVAUDAN CORPORATION
DELAWANNA, N. J.

RECEIVED APRIL 30, 1951

NEW COMPOUNDS

Oxidation Products of 8-Chloro-1,3-Benzodioxan-6-hydroxymethyl-7-carboxylic Acid Lactone

5-Hydroxy-6-chloro-1,2,4-tricarboxylic Acid.—8-Chloro-1,3-benzodioxan-6-hydroxymethyl-7-carboxylic acid lactone,[1] 5 g., was dissolved in 250 ml. of water containing 10 g. of potassium hydroxide at 80° and a warm solution of 7.5 g. of potassium permanganate in 250 ml. of water was added with stirring over a period of 20 minutes. After filtration, the filtrate was cooled to room temperature, acidified and extracted with an equal volume of ether. The ethereal solution was evaporated to 100 ml. and 200 ml. of benzene was added, after which the volume was reduced to 100 ml. by heating. Cooling gave 3.2 g. of white solid. Several crystallizations from 50% formic acid produced white crystals, m.p. 243.0–243.5°. The compound gives a dark red color with aqueous ferric chloride.

Anal. Calcd. for $C_9H_5ClO_7$: Cl, 13.61. Found: Cl, 13.61, 13.72.

8-Chloro-1,3-benzodioxan-6,7-dicarboxylic Acid.—The lactone, 20 g., was dissolved in 1 l. of water containing 40 g. of potassium hydroxide at a temperature of 85° and a warm solution of 30 g. of potassium permanganate in 1 l. of water was added over a period of 20 minutes, the temperature being maintained at approximately 75°. After the permanganate had been reduced, the mixture was filtered and the filtrate was cooled to room temperature and acidified. Extraction with ether and evaporation of the ethereal layer gave a slightly colored solid which was dissolved in 100 ml. of water by boiling. The color was removed by activated charcoal and the filtrate was placed in the refrigerator overnight, after which period 6 g. of a white, voluminous precipitate, m.p. 167–170°, formed. One crystallization from water and two by solution in hot acetone followed by the addition of ligroin gave 3.3 g. of white crystals, m.p. 182.0–182.8°.

Anal. Calcd. for $C_{10}H_7ClO_6$: C, 46.44; H, 2.73; Cl, 13.71. Found: C, 46.18, 46.28; H, 2.54, 2.53; Cl, 13.67.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF TENNESSEE
KNOXVILLE, TENNESSEE
C. A. BUEHLER
ROY L. PRUETT

RECEIVED JULY 16, 1951

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(1) C. A. Buehler, James O. Harris, Comer Shacklett and Burton P. Block, THIS JOURNAL, **68**, 577 (1946).

3-Chloro-4-hydroxyphthalic Acid and its Derivatives

3-Chloro-4-methoxyphthalic Acid.—6-Methoxy-7-chlorophthalide,[1] 10 g., and 7 g. of potassium hydroxide were dissolved in 200 ml. of water at 80°. This solution at 50° was treated with a solution of 15 g. of potassium permanganate in 600 ml. of water, also at 50°, over a 30-minute period while the temperature was maintained at 50–55°. After standing for 2 hours, the mixture was filtered and the excess of permanganate was destroyed with sodium bisulfite. Filtration followed by acidification gave a solution which was extracted with an equal volume of ether. The ethereal solution was evaporated down to 100 ml. and then 100 ml. of benzene was added. Additional concentration to 75 ml. and cooling gave a white precipitate, 7.7 g., m.p. 181–183°, with loss of water. Two crystallizations from glacial acetic acid produced white needles, m.p. 184.5–185.0° although the value varies somewhat with the rate of heating.

Anal. Calcd. for $C_9H_7ClO_5$: C, 46.87; H, 3.06; Cl, 15.38; CH_3O, 13.46; neut. equiv., 116. Found: C, 46.80, 46.76; H, 2.78, 2.90; Cl, 15.41, 15.23; CH_3O, 13.33; neut. equiv., 116, 117.

3-Chloro-4-methoxyphthalic Anhydride.—3-Chloro-4-methoxyphthalic acid, 2 g., was heated at 190° in an oil-bath to give 1.7 g. of white solid. Crystallization from glacial acetic acid produced white crystals, m.p. 172.5–173.0°.

Anal. Calcd. for $C_9H_5ClO_4$: Cl, 16.68. Found: Cl, 16.62, 16.61.

3-Chloro-4-methoxyphthalimide.—The anhydride, 1.7 g., was mixed with an equal weight of urea and heated to 150°. Ammonia was evolved for about 10 minutes and then the liquid solidified. Crystallization from methanol gave 1.2 g. of a white, fluffy solid which after one more crystallization melted at 310.0–311.0°.

Anal. Calcd. for $C_9H_6ClNO_3$: Cl, 16.76; N, 6.62. Found: Cl, 16.69, 16.84; N, 6.56, 6.56.

3-Chloro-4-hydroxyphthalic Acid.—3-Chloro-4-methoxyphthalic acid, 2.3 g., was refluxed for 15 hours with 100 ml. of 48% hydrobromic acid to produce 1.7 g. of slightly brown needles, m.p. 206–207°. Crystallization from 85% formic acid gave white needles, m.p. 210.0–210.5°.

Anal. Calcd. for $C_8H_5ClO_5$: Cl, 16.37. Found: Cl, 16.32, 16.34.

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