



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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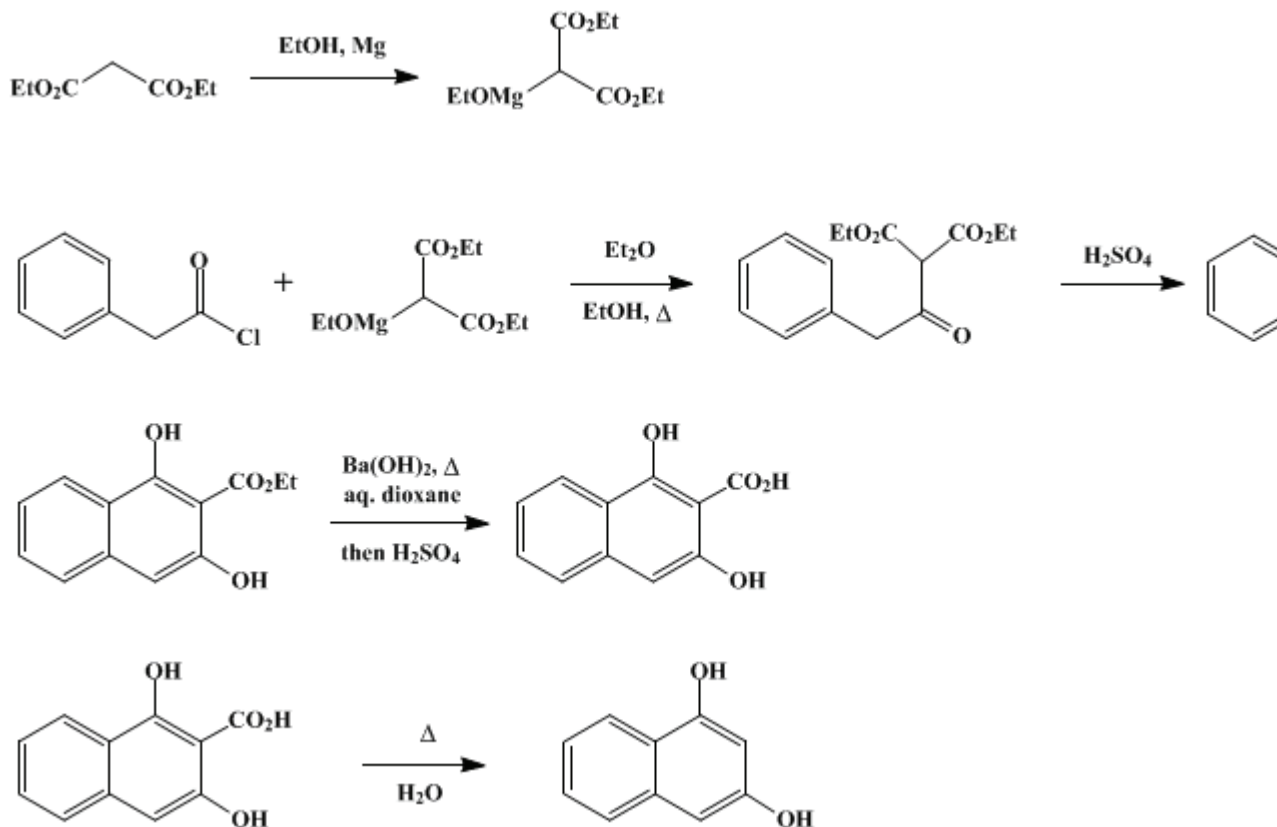
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.637 (1955); Vol. 25, p.73 (1945).

NAPHTHORESORCINOL

[1,3-Naphthalenediol]



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1. Procedure

A. *Ethyl phenylacetylmalonate*. A 1-l. three-necked round-bottomed flask is equipped with a dropping funnel (Note 1) and a reflux condenser provided with a calcium chloride tube. Before the apparatus is assembled, it is washed in the following manner with absolute ethanol which has been prepared in a distilling flask (Note 2). Ninety milliliters of the anhydrous ethanol is distilled through the dropping funnel into the apparatus, used for rinsing, and discarded. In the reaction flask are placed 12.5 g. (0.52 atom) of magnesium turnings, 1 ml. of carbon tetrachloride (Note 3), and 40 g. (0.25 mole) of malonic ester (Note 3); then 90 ml. of absolute ethanol is distilled into the dropping funnel and transferred to the flask. The reaction is started by heating and is controlled by applying an ice bath when the condenser begins to flood. When the reaction has subsided, 40 g. (0.25 mole) more of malonic ester is added at one time. After this reaction has subsided, the flask is cooled slightly, 180 ml. of dry ether is added, and the reaction mixture is heated on a steam bath for 1 hour. Then 88 g. (74 ml., 0.57 mole) of phenylacetyl chloride, diluted with 90 ml. of dry ether, is added slowly (in about 30 minutes) from the dropping funnel in portions at such a rate that the vigorous reaction subsides between additions. When the addition has been completed, the flask is warmed for 10 minutes on a steam bath. After the mixture has been cooled, 100 ml. of water is added dropwise in about 30 minutes. The oily layer is washed with two 100-ml. portions of water and dried over sodium sulfate, and the ether is removed by distillation under reduced pressure (water pump). The crude phenylacetylmalonate (87 ml.) which remains is a reddish, somewhat viscous oil.

B. *Ethyl 1,3-dihydroxy-2-naphthoate*. In a 1-l. flask 1 volume (87 ml.) of the crude ester is added in one lot to 3 volumes (261 ml.) of concentrated **sulfuric acid** without cooling, and the solution is allowed to stand for about 1 week (Note 4). The whole mixture, including any precipitate which may have formed, is poured slowly with stirring into a mixture of 1 kg. of ice and 500 ml. of water (Note 5); the solid yellow ester is filtered with suction, washed with a small amount of cold water, pressed in the filter for 30 minutes with a rubber dam, and finally dried in a vacuum desiccator. The yield of ester melting at 80° is 58–68 g. (50–59% based on the malonic ester used).

Recrystallization of 50 g. of the ester from 300 ml. of 70% **ethanol** (Note 6) yields 45 g. of yellow, needle-like crystals melting at 82°.

C. *1,3-Dihydroxy-2-naphthoic acid*. In a 1-l. three-necked round-bottomed flask, fitted with a mechanical stirrer, a **nitrogen** inlet tube, and a condenser carrying a separatory funnel attached by means of a notched cork, is placed 20.9 g. (0.09 mole) of the recrystallized ester dissolved in 300 ml. of **dioxane**. The apparatus is flushed with **nitrogen**, the solution is stirred and heated on a steam bath, and a solution of 40 g. (0.13 mole) of **barium hydroxide octahydrate** in 500 ml. of water is added in the course of 1 hour. Heating and stirring are continued for 3 hours. The precipitated barium salt, which may vary in color from yellow to greenish gray, is filtered from the hot solution and transferred immediately to a cool (25°) solution of 11 ml. of concentrated **sulfuric acid** in 185 ml. of water in a 500-ml. three-necked round-bottomed flask fitted with a **nitrogen** inlet tube, a mechanical stirrer, and a condenser. The mixture is stirred in an atmosphere of **nitrogen** for 5 minutes without heating (Note 7). The precipitate is removed by filtration, washed with a small amount of distilled water, transferred to a beaker, and extracted with two 100-ml. portions of hot absolute **ethanol**. To the warm filtrate is added 200 ml. of water, and the solution is allowed to cool in an ice bath for 2 hours. The yield of the crude acid which is obtained by filtration as a fine, yellow powder melting at 135° (Note 8) is 16.5 g. (90%).

D. *Naphthoresorcinol*. In a 200-ml. three-necked round-bottomed flask, equipped with a **nitrogen** inlet tube, a stirrer, and a condenser, is placed 65 ml. of water; the water is then boiled to expel dissolved **oxygen**. To the boiling water is added 16.5 g. of the crude acid (Note 9), and the mixture is boiled with stirring for 2 hours in an atmosphere of **nitrogen**. The water is decanted from any pasty residue; the residue is boiled with 35 ml. of water for 2 hours, and the supernatant liquid is decanted through a filter and combined with the first solution. Just enough **sodium hydrosulfite** (about 0.3–0.5 g.) is added to decolorize the red solution, 15 g. of **sodium chloride** is dissolved in the solution, and the mixture is allowed to stand at 5° for 24 hours. The naphthoresorcinol precipitates first as an oil, which solidifies to a reddish solid on further cooling, and then as colorless or slightly yellow plates. The yield is 7.0–7.3 g. (54–56%). After standing over **calcium chloride** in a vacuum desiccator for 1 day, the white or slightly yellow plates melt at 119–122° and the reddish solid melts at 110–118°.

To 100 ml. of hot water are added 3.5 g. of the reddish solid, just enough **sodium hydrosulfite** to remove the red coloration, and 0.3 g. of Norit. The mixture is filtered, 7 g. of **sodium chloride** is dissolved in the filtrate, and the solution is allowed to stand in a closed container at 5° for 24 hours. The yield of naphthoresorcinol, which separates as large, nearly transparent plates melting at 122–124° (Note 10), is 2.6 g. (75% recovery).

2. Notes

1. In order to measure the volume of **ethanol** to be used, an equal volume of water (90 ml.) is placed in the dropping funnel and a label is pasted at the level of the water. The funnel is then emptied and carefully dried.
2. A liter of commercial absolute **ethanol** is dried by means of sodium and ethyl phthalate¹ in a 2-l. distilling flask equipped with a reflux condenser. A short section of rubber tubing closed by a screw clamp is attached to the side arm of the flask. In the next step the condenser is set for downward distillation.
3. The **carbon tetrachloride**, **ether**, and malonic ester are dried over anhydrous **magnesium sulfate**. The malonic ester is distilled before use.
4. The yield of **ethyl 1,3-dihydroxy-2-naphthoate** is decreased to 45% if the **sulfuric acid** solution is allowed to stand for only 2 days.
5. After about 25 ml. of the **sulfuric acid** solution has been added, the mixture is stirred until a yellow

solid separates. Precipitation of the main portion of the product then occurs very smoothly as the remainder of the [sulfuric acid](#) solution is added.

6. The ester may be recrystallized also by solution in [dioxane](#) and precipitation by water.

7. An alternative procedure consists in decomposing the barium salt with [hydrochloric acid](#). However, in the checkers' hands this procedure did not yield a barium-free product.

8. The submitters obtained the pure acid as follows: To 0.5 g. of the crude acid was added 200 ml. of boiling water, and the mixture was heated for an instant to effect solution and filtered immediately. The filtrate was cooled by vigorous shaking in an ice bath. Addition of 1 ml. of concentrated [hydrochloric acid](#) to the solution caused the separation of crystals, which were collected after 30 minutes' additional cooling in ice, washed with ice water, and dried in vacuum over [phosphorus pentoxide](#). The recovery of material melting in the range of 138.5–140.5° to 146.5° was 62%.

9. The solid has a tendency to assume a semi-plastic consistency, but the size of the mass decreases as decarboxylation occurs.

10. If part of the material separates as an oil and solidifies, the appearance of the product may be poor, although the melting point is 122–124°. Separation as an oil may be prevented by slow cooling with shaking and seeding. An alternative procedure for final purification of naphthoresorcinol consists in sublimation at 120–130°/5 × 10⁻⁴ mm.

3. Discussion

Naphthoresorcinol has been prepared by heating [1-amino-3-hydroxy-4-naphthalenesulfonic acid](#) or its salt in water or slightly acidic solution,² by cyclization of [ethyl phenylacetylmalonate](#)³ or of [ethyl phenylacetoacetate](#),⁴ and by alkaline fusion of [1,3-naphtholsulfonic acid](#) or [1,3-naphthalenedisulfonic acid](#).⁵ Phenylacetyl malonic ester has been prepared by condensing [phenylacetyl chloride](#) and malonic ester with [sodium](#) in [ether](#),³ or with [magnesium](#).⁶

References and Notes

1. *Org. Syntheses Coll. Vol. 2*, 155 (1943).
 2. Friedlander and Rüdte, *Ber.*, **29**, 1609 (1896); Ger. pat. 84,990 [*Frld.*, **4**, 229 (1894–1897)]; Ger. pat. 87,429 [*Frld.*, **4**, 584 (1894–1897)]; Ger. pat. 90,096 [*Frld.*, **4**, 585 (1894–1897)].
 3. Metzner, *Ann.*, **298**, 374 (1897); Wagueich, Roberts, and Harrow, *Chemist-Analyst*, **31**, 59 (1942).
 4. Soliman and West, *J. Chem. Soc.*, **1944**, 53.
 5. Kozlov and Odintosov, *J. Appl. Chem. U.S.S.R.*, **17**, 719 (1944) [*C. A.*, **39**, 2744 (1945)].
 6. Ogata, Nosaki, and Takagi, *J. Pharm. Soc. Japan*, **59**, 105 (1939) [*C. A.*, **33**, 4230 (1939)].
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Malonic Ester

Naphthoresorcinol

phenylacetylmalonic ester

sodium and ethyl phthalate

Phenylacetyl malonic ester

ethanol (64-17-5)

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

ether (60-29-7)

magnesium,
magnesium turnings (7439-95-4)

sodium chloride (7647-14-5)

sodium sulfate (7757-82-6)

oxygen (7782-44-7)

carbon tetrachloride (56-23-5)

nitrogen (7727-37-9)

sodium hydrosulfite (7775-14-6)

sodium (13966-32-0)

barium hydroxide octahydrate (12230-71-6)

magnesium sulfate (7487-88-9)

dioxane (5703-46-8)

phenylacetyl chloride (103-80-0)

ethyl phenylacetoacetate

1,3-Naphthalenediol (132-86-5)

Ethyl 1,3-dihydroxy-2-naphthoate (6843-89-6)

1-amino-3-hydroxy-4-naphthalenesulfonic acid

Ethyl phenylacetylmalonate

1,3-naphtholsulfonic acid (3771-14-0)

1,3-naphthalenedisulfonic acid

phosphorus pentoxide (1314-56-3)

1,3-Dihydroxy-2-napthoic acid (3147-58-8)

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