



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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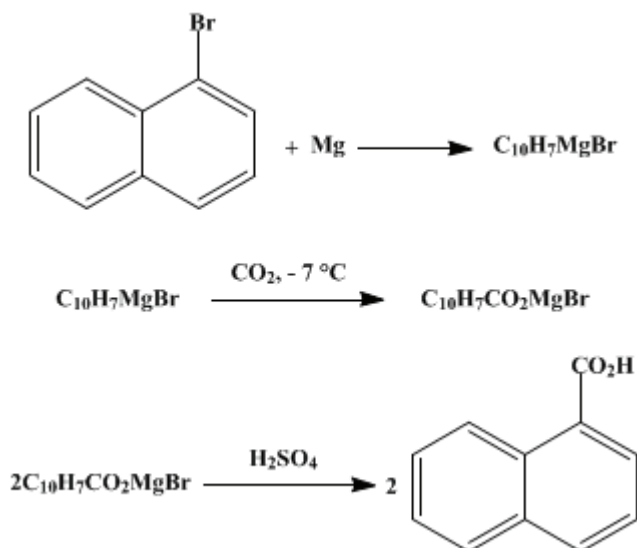
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.425 (1943); Vol. 11, p.80 (1931).

α -NAPHTHOIC ACID

[1-Naphthoic acid]



Submitted by Henry Gilman, Nina B. St. John, and F. Schulze.

Checked by C. R. Noller

1. Procedure

In a 2-l. three-necked flask, fitted with a mechanical stirrer, a reflux condenser, and a separatory funnel, is placed 24.3 g. (1 gram atom) of **magnesium turnings** (Note 1). The **magnesium** is covered with 100 cc. of anhydrous **ether**, and 10 cc. (15 g., 0.07 mole) of **α -bromonaphthalene** (Note 2) (with a crystal or two of **iodine**) (Note 3) is added to start the reaction. A warm water bath (45° or higher) is placed under the flask until the reaction starts. The stirrer is started, and a solution of 192 g. (0.93 mole) of **α -bromonaphthalene** in 500 cc. of anhydrous **ether** is added to the **magnesium** at such a rate that the reaction is vigorous but not violent. The addition requires from one and one-half to three hours. The water bath is again placed under the flask, and stirring and refluxing are continued for one-half hour after the addition of the halide is complete. The Grignard reagent which collects as a heavy oil in the bottom of the flask is dissolved by the addition of 533 cc. of dry **benzene** (Note 4).

The reaction mixture is then cooled by an ice-salt mixture. The separatory funnel is replaced by a two-holed rubber stopper containing a thermometer (bulb immersed in the reaction mixture) and a glass tube drawn out to make a fine capillary (Note 5). When the temperature of the reaction mixture has reached -7° , the condenser is replaced by an entry tube, 10 mm. in diameter and adjusted so that the end is about 50 mm. above the surface of the reaction mixture (Note 6). The reaction mixture is stirred, and dry **carbon dioxide** is added through this tube (Note 7). The rate of flow of the **carbon dioxide** is regulated so that the temperature of the reaction mixture does not rise above -2° . The time required for the completion of the reaction varies from one and one-fourth to one and one-half hours. When the reaction is complete, the temperature falls below -7° and does not rise on increasing the rate of flow of **carbon dioxide**.

The flask is placed in an ice bath, and 25 per cent **sulfuric acid** is added slowly, with stirring, until no further reaction takes place and all the excess **magnesium** has dissolved (Note 8). The oily layer is separated, and the water layer is extracted with two 100-cc. portions of **ether**. The combined **ether-benzene** extracts (Note 9) are shaken with three 100-cc. portions of 25 per cent **sodium hydroxide**. Each alkaline layer is extracted successively with a 100-cc. portion of **ether**, and the combined alkaline extracts are then heated to 100° to drive off volatile impurities.

The solution is cooled and acidified strongly with 50 per cent [sulfuric acid](#). The crude [α-naphthoic acid](#) is collected on a Büchner funnel, washed until free from sulfate, and dried. The yield of crude material melting at 142–155° is 130–135 g. This is dissolved in 400 cc. of hot [toluene](#), a small amount of Filter-Cel is added, and the solution is filtered through a hot Büchner funnel. The filtrate is cooled in an ice bath, filtered with suction, and the filter cake washed with cold [toluene](#) until the filtrate is practically colorless. A light-colored product melting at 159–161° is obtained. The yield is 118–121 g. (68–70 per cent of the theoretical amount) ([Note 10](#)).

2. Notes

1. The finer commercial grade of turnings was used. After the reaction had once started, it proceeded smoothly with any grade of commercial turnings.
2. The [α-bromonaphthalene](#) ([Org. Syn. Coll. Vol. I, 1941, 121](#)) was purified by distillation under reduced pressure. The fraction boiling at 144–147°/16 mm. was collected.
3. The checker was more successful in starting the reaction within a reasonable length of time when as much as 0.5 g. of [iodine](#) was added.
4. It is necessary to dissolve the Grignard reagent in [benzene](#) to prevent it from solidifying when the solution is cooled. The [benzene](#) should be added to the solution before it cools, as the hardened mass is difficult to redissolve.
5. This is to allow the [carbon dioxide](#) which does not react to escape slowly in order that the pressure in the flask does not become too great.
6. The inlet tube is placed at this distance above the surface of the reaction mixture in order to prevent clogging.
7. The [carbon dioxide](#) from an ordinary commercial cylinder was dried by passing it through two wash bottles containing sulfuric acid.
8. Cooling the solution externally with ice permits rapid hydrolysis without danger of loss of material through refluxing (cf. [Org. Syn. Coll. Vol. I, 1941, 361](#)).
9. If the [ether-benzene](#) solution is not entirely clear, it should be filtered before extraction with [sodium hydroxide](#).
10. A second recrystallization from [toluene](#) gives an almost white product melting at 160.5–162°.

3. Discussion

[α-Naphthoic acid](#) has been prepared from [α-naphthylmagnesium bromide](#) and [carbon dioxide](#), gaseous¹ or solid;² by hydrolysis of [ethyl α-naphthoate](#), prepared in turn from [α-naphthylmagnesium bromide](#);³ by hydrolysis of [α-naphthyl cyanide](#);⁴ and from [methyl α-naphthyl ketone](#) and [potassium hypochlorite](#).² The acid has been obtained by fusing [sodium formate](#) and [sodium α-naphthalenesulfonate](#),⁵ and by passing [carbamyl chloride](#) into [naphthalene](#) and [aluminum chloride](#) and hydrolyzing the [α-naphthamide](#) thus formed.⁶ The methods for preparing [α-naphthoic acid](#) have been discussed by Wahl, Goedkoop, and Heberlein.⁷

The procedure described above⁸ was developed from the methods of Acree,¹ of Blicke,¹ and of Whitmore and Fox.¹

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 282](#)

References and Notes

1. Acree, *Ber.* **37**, 625 (1904); Blicke, *J. Am. Chem. Soc.* **49**, 2846 (1927); Whitmore and Fox, *ibid.* **51**, 3363 (1929).
2. Fieser, Holmes, and Newman, *ibid.* **58**, 1055 (1936).
3. Loder and Whitmore, *ibid.* **57**, 2727 (1935), and p. 282, above.
4. Merz and Mühlhäuser, *Ber.* **3**, 712 (1870).

5. Meyer, *ibid.* **3**, 364 (1870).
 6. Gattermann and Schmidt, *ibid.* **20**, 860 (1887).
 7. Wahl, Goedkoop, and Heberlein, *Bull. soc. chim.* (5) **6**, 533 (1939).
 8. Gilman, St. John, and St. John, *Rec. trav. chim.* **48**, 594 (1929).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

sulfuric acid (7664-93-9)

Benzene (71-43-2)

ether (60-29-7)

sodium hydroxide (1310-73-2)

magnesium,
magnesium turnings (7439-95-4)

carbon dioxide (124-38-9)

iodine (7553-56-2)

aluminum chloride (3495-54-3)

toluene (108-88-3)

α -Bromonaphthalene (90-11-9)

Naphthalene (91-20-3)

sodium formate

potassium hypochlorite

Ethyl α -naphthoate (3007-97-4)

α -naphthylmagnesium bromide

α -Naphthoic acid,
1-Naphthoic acid (86-55-5)

α -naphthyl cyanide (86-53-3)

methyl α -naphthyl ketone (941-98-0)

sodium α -naphthalenesulfonate (130-14-3)

carbonyl chloride

α -naphthamide (2243-81-4)

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