



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at [http://www.nap.edu/catalog.php?record\\_id=12654](http://www.nap.edu/catalog.php?record_id=12654)). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

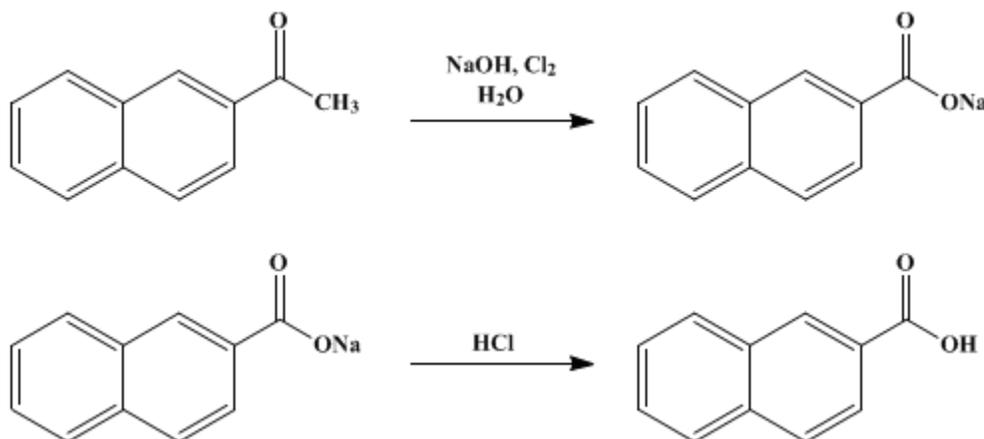
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

*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.428 (1943); Vol. 17, p.65 (1937).*

## $\beta$ -NAPHTHOIC ACID

### [2-Naphthoic acid]



Submitted by M. S. Newman and H. L. Holmes.

Checked by W. W. Hartman and F. W. Jones.

### 1. Procedure

In a 3-l. flask is placed a solution of 184 g. (4.6 moles) of sodium hydroxide in 300–400 cc. of water; sufficient ice is added to make the total volume about 1.5 l. Chlorine is passed into the solution, the temperature being kept below  $0^\circ$  by means of a salt-ice bath, until the solution is neutral to litmus, then a solution of 34 g. of sodium hydroxide in 50 cc. of water is added (Note 1) and (Note 2). The flask is now supported by a clamp and equipped with a thermometer and an efficient stirrer. The solution is warmed to  $55^\circ$ , and 85 g. (0.5 mole) of methyl  $\beta$ -naphthyl ketone (Note 3) is added. The mixture is vigorously stirred, and, after the exothermic reaction commences, the temperature is kept at  $60\text{--}70^\circ$  (Note 4) by frequent cooling in an ice bath until the temperature no longer tends to rise. This requires thirty to forty minutes. The solution is stirred for thirty minutes longer and then the excess hypochlorite is destroyed by adding a solution of 50 g. of sodium bisulfite in 200 cc. of water (Note 5). After cooling to room temperature, the reaction mixture is transferred to a 4-l. beaker and carefully acidified with 200 cc. of concentrated hydrochloric acid. The crude colorless acid is collected on a Büchner funnel, washed with water, and sucked as dry as possible with a rubber dam. After drying, the acid is crystallized (Note 6) from 600 cc. of 95 per cent alcohol, giving 75–76 g. (87–88 per cent of the theoretical amount) of  $\beta$ -naphthoic acid melting at  $184\text{--}185^\circ$  (corr.). By distilling 450 cc. of solvent from the mother liquor, an additional 9 g. (10 per cent of the theoretical amount) of acid, m.p.  $181\text{--}183^\circ$  (corr.), is obtained (Note 7).

### 2. Notes

1. It is reported that, in preparing a sodium hypochlorite solution by passing chlorine into sodium hydroxide, it is very difficult to determine the neutral point because of the instant bleaching of the indicator. If too much chlorine is added, even though the final solution may react alkaline because of the additional sodium hydroxide added later, oxidation of methyl  $\beta$ -naphthyl ketone to  $\beta$ -naphthoic acid does not take place. Consequently the following modified procedure for preparing the hypochlorite solution is recommended.

A solution of 218 g. (5.45 moles) of sodium hydroxide in 300 cc. of water in a 3-l. flask is cooled to room temperature with tap water. Next, 1250 g. of ice is added and chlorine is passed in rapidly until 161 g. (4.5 moles) has been taken up. External cooling is unnecessary. With the amount of ice specified, the solution will be at  $0^\circ$  when the addition of chlorine has been completed. From this point on the procedure is the same as that on p. 428. (Private communication from Edward C. Sterling.)

2. The hypochlorite solution also may be prepared conveniently from the [calcium hypochlorite](#) sold by the Mathieson Alkali Works under the trade name "HTH" and specified to contain not less than 65 per cent of available [calcium hypochlorite](#).

In a 3-l. round-bottomed flask 250 g. of commercial [calcium hypochlorite](#) is dissolved in 1 l. of warm water, and a warm solution of 175 g. of [potassium carbonate](#) and 50 g. of [potassium hydroxide](#) in 500 cc. of water is added. The flask is stoppered and shaken vigorously until the semi-solid gel which first forms becomes quite fluid. The suspended solid is removed by filtration on a large Büchner funnel, washed with 200 cc. of water, and sucked as dry as possible with the aid of a rubber dam and an efficient suction pump. The filtrate of approximately 1.5 l. is placed in a 3-l. round-bottomed flask and is ready for the addition of [methyl  \$\beta\$ -naphthyl ketone](#).

Such a solution contains approximately 200 g. (2.3 moles) of [potassium hypochlorite](#). Sodium or potassium hypochlorite may be used, but the calcium salt is not satisfactory because the [calcium salt of  \$\beta\$ -naphthoic acid](#) is sparingly soluble.

3. The Eastman product, m.p. 53–55°, was used.

4. If the mixture is not cooled, the reaction will get out of control because of the rapid evolution of [chloroform](#), and some ketone may steam-distil.

5. It is advisable to test the solution after the addition of the [sodium bisulfite](#) with acidified [potassium iodide](#) solution to be sure that all the hypochlorite has been destroyed. If hypochlorite is present, the [chlorine](#) liberated when the solution is acidified forms a high-melting impurity.

6. The moist acid may be crystallized without drying, but more alcohol must be used to get the product into solution.

7. This method may be used for the preparation of larger quantities, a batch twenty times this size giving a yield of 87 per cent. It may be used also for the preparation of other aromatic acids where suitable ketones are available.

### 3. Discussion

[\$\beta\$ -Naphthoic acid](#) has been prepared principally by the hydrolysis of  [\$\beta\$ -naphthonitrile](#),<sup>1</sup> the over-all yields from  [\$\beta\$ -naphthylamine](#), from [sodium  \$\beta\$ -naphthalenesulfonate](#), and from [calcium  \$\beta\$ -naphthalenesulfonate](#) being given as (approximately) 20 per cent, 21 per cent, and 50 per cent, respectively.<sup>2</sup> The acid has been prepared also by the carbonation of the Grignard reagent from the less accessible  $\beta$ -bromo derivative;<sup>3</sup> by chlorination of  [\$\beta\$ -methylnaphthalene](#) followed by hydrolysis and oxidation;<sup>4</sup> and by the procedure described above.<sup>5</sup> The various methods for preparing  [\$\beta\$ -naphthoic acid](#) have been discussed by Wahl, Goedkoop, and Heberlein.<sup>4</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 3, 302](#)
- [Org. Syn. Coll. Vol. 4, 484](#)
- [Org. Syn. Coll. Vol. 6, 78](#)
- [Org. Syn. Coll. Vol. 8, 26](#)

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### References and Notes

1. Baeyer and Besemfelder, *Ann.* **266**, 187 (1891).
  2. Derick and Kamm, *J. Am. Chem. Soc.* **38**, 408 (1916).
  3. Gilman and St. John, *Rec. trav. chim.* **48**, 743 (1929).
  4. Wahl, Goedkoop, and Heberlein, *Bull. soc. chim.* (5) **6**, 533 (1939).
  5. Fieser, Newman, and Holmes, *J. Am. Chem. Soc.* **58**, 1055 (1936).
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## (Registry Number)

Sodium or potassium hypochlorite

alcohol (64-17-5)

potassium carbonate (584-08-7)

hydrochloric acid (7647-01-0)

sodium hydroxide (1310-73-2)

chloroform (67-66-3)

potassium iodide (7681-11-0)

sodium bisulfite (7631-90-5)

chlorine (7782-50-5)

potassium hydroxide (1310-58-3)

sodium hypochlorite (7681-52-9)

potassium hypochlorite

$\beta$ -Naphthoic acid,  
2-Naphthoic acid (93-09-4)

methyl  $\beta$ -naphthyl ketone

calcium hypochlorite (7778-54-3)

$\beta$ -naphthonitrile (613-46-7)

sodium  $\beta$ -naphthalenesulfonate (532-02-5)

calcium  $\beta$ -naphthalenesulfonate

$\beta$ -methylnaphthalene (91-57-6)

calcium salt of  $\beta$ -naphthoic acid

$\beta$ -naphthylamine (91-59-8)