



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.

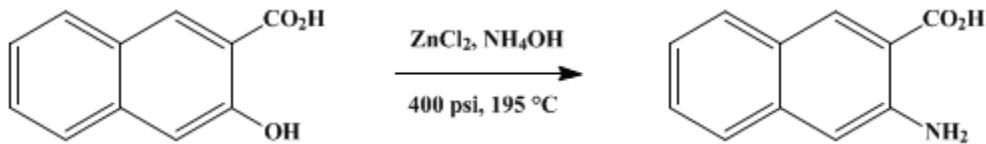
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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## 3-AMINO-2-NAPHTHOIC ACID

### [2-Naphthoic acid, 3-amino-]



Submitted by C. F. H. Allen and Alan Bell.

Checked by Nathan L. Drake, E. W. Reeve, and J. Van Hook.

### 1. Procedure

An autoclave (Note 1) is charged *successively* with 600 ml. (9.5 moles) of approximately 28% aqueous ammonia, 78 g. of zinc chloride (0.57 mole) (Note 2) and (Note 3), and 167 g. of 3-hydroxy-2-naphthoic acid (0.89 mole) (Note 4). The autoclave is closed, and then, with continuous stirring or shaking (Note 5), it is gradually heated, so that, at the end of 3 hours, the temperature is 195°. This temperature is maintained for 36 hours; the pressure is about 400 lb. (Note 6). The autoclave is allowed to cool to room temperature, with continuous stirring or shaking. The cover is removed, the solid is scraped off the walls, and the reaction mixture is transferred to a 5-l. flask. The autoclave is rinsed with two 700-ml. portions of water, which are added to the reaction mixture.

To the reaction mixture is added 660 g. of concentrated hydrochloric acid (sp. gr. 1.18), and the suspension is boiled for 30 minutes. It is then filtered, while hot, through a Büchner funnel. The residual cake is boiled again, for the same length of time, with a mixture of 500 ml. of water and 30 ml. of concentrated hydrochloric acid, and then filtered as before.

The combined filtrates, on cooling, deposit the hydrochloride of the aminonaphthoic acid; this is filtered with suction and is pressed as dry as possible. To obtain a second crop of the hydrochloride, the filtrate is heated to 85°, 500 g. of salt is added, and the solution is cooled.

The combined moist filter cakes are placed in a 5-l. flask with 1.3 l. of water, and, with stirring, sufficient 40% sodium hydroxide solution is added to make the solution just alkaline to Clayton yellow paper (Note 7); about 110 ml. is required. The mixture is heated to 85° and is filtered to remove a small amount of insoluble material. The filtrate is then made acid to Congo red by the addition of concentrated hydrochloric acid (about 100 ml. of acid is required). The mixture is stirred for 15 minutes, and then enough 10% sodium acetate solution is added so that Congo red paper is no longer turned blue; the amount needed depends on the acidity; usually about 15 ml. is sufficient.

The hot mixture is filtered; the aminonaphthoic acid is washed on the Büchner funnel with 400 ml. of hot water and is pressed as dry as possible. The product is dried at 50° to constant weight (24–36 hours). 3-Amino-2-naphthoic acid is a yellow, powdery substance, which melts at 214–215° (Note 8); the yield is 110–115 g. (66–70%) (Note 6). The quantities of starting materials are limited only by the size of the autoclave available; the yield (per cent) in large runs is the same as that obtained above.

### 2. Notes

1. An autoclave fitted for stirring or shaking is essential. An example of the former is the one furnished by the Will Corporation, catalog No. 1735. This is large enough so that three times the amounts specified may be handled. A hydrogenation autoclave of the type supplied by the American Instrument Company, catalog No. 406–21, having a capacity of about 1.4 l., may also be used. This type of autoclave is not fitted with a stirrer but is shaken by means of a "Bomb Shaker" in which the autoclave is placed. In using the hydrogenation autoclave, the long hydrogen inlet tube, which extends half way into the chamber of the autoclave, is unscrewed and removed. The inlet for hydrogen, on the outside of

the autoclave, is closed by means of a solid steel rod, the end of which is finished and held in place in the same manner as the ordinary steel pressure tubing.

After making a run, the hydrogenation autoclave is poisoned for hydrogenations. It may be cleaned by filling it with 5% hydrochloric acid and rubbing the inside walls with a cloth or brush. It should then be washed with water and dried; any solid matter adhering to the walls is removed by rubbing with emery paper. Care must be taken not to scratch either the copper gasket or the groove into which the gasket fits. All parts of the hydrogenation autoclave, including the head, must be thoroughly cleaned. Traces of the reaction product will cause pitting in a few hours if they are allowed to remain in contact with the steel while the bomb is exposed to the air.

After the hydrogenation autoclave is cleaned it is best to carry out one or two ester hydrogenolyses with copper chromite in order to remove the last traces of "poison." The bomb may then be used for hydrogenations.

2. The zinc chloride should not contain appreciable amounts of the oxychloride.
3. Since zinc chloride and aqueous ammonia react with evolution of heat, the solid must be added gradually and with hand stirring. It is best to carry out this operation under a hood.
4. A technical grade of 3-hydroxy-2-naphthoic acid, m.p. 211–214°, was used.
5. Continued stirring or shaking is required throughout, i.e., from the time heating is begun until the reaction product has again attained room temperature. With a hydrogenation autoclave there will be no trouble due to leaks, but with the stirrer type of autoclave the packing around the stirrer shaft may leak. In this event the pressure will fall and a longer period of time will be required. If a large quantity of ammonia escapes, the yield will be diminished, but the run should be finished and the unused hydroxynaphthoic acid should be recovered and used in another run.
6. In a run in which the gaskets leaked, the pressure never exceeded 200 lb. In this run, the (stirrer-type) autoclave was operated for 5 days; the yield was 67%.
7. Clayton yellow paper (thiazole paper) is paper impregnated with the dye formed by coupling diazotized primuline sulfonic acid with primuline sulfonic acid. The color change occurs at pH 11–12. If this paper is not available, a little less than the estimated amount of alkali should be used. The mixture is warmed to 85°, and a small test portion is removed and warmed with more alkali. If any appreciable amount of the insoluble matter dissolves, more alkali is needed.
8. This product is pure enough for most purposes. It can be recrystallized from ethanol (10 g. dissolves in 100 ml. of hot ethanol); the recovery is 78% (7.8 g.), and the purified product melts at 216–217°.

### 3. Discussion

3-Amino-2-naphthoic acid has been prepared by heating 3-hydroxy-2-naphthoic acid with ammonia under pressure, in the presence of catalysts. These catalysts include zinc (or calcium) chloride,<sup>1,2,3,4</sup> alone or with the addition of aluminum chloride.<sup>5</sup> Zinc oxide or carbonate and ammonium chloride,<sup>6,7,8</sup> or ferrous ammonium salts,<sup>9,10</sup> have also been used. When sodium hydroxynaphthoate is heated with 35% ammonia at 260–280°, the product is contaminated with considerable amounts of β-naphthol and β-naphthylamine.<sup>11</sup> Modifications of Henle's procedure<sup>4</sup> have been described.<sup>12</sup>

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 573

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### References and Notes

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**Appendix**  
**Chemical Abstracts Nomenclature (Collective Index Number);**  
**(Registry Number)**

hydrochloride of the aminonaphthoic acid

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

ammonium chloride (12125-02-9)

sodium acetate (127-09-3)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

β-naphthol (135-19-3)

copper (7440-50-8)

aluminum chloride (3495-54-3)

zinc chloride (7646-85-7)

zinc oxide

**COPPER CHROMITE**

3-Amino-2-naphthoic acid,  
2-Naphthoic acid, 3-amino- (5959-52-4)

3-hydroxy-2-naphthoic acid (92-70-6)

aminonaphthoic acid

hydroxynaphthoic acid (2283-08-1)

ferrous ammonium

sodium hydroxynaphthoate

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

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