



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.

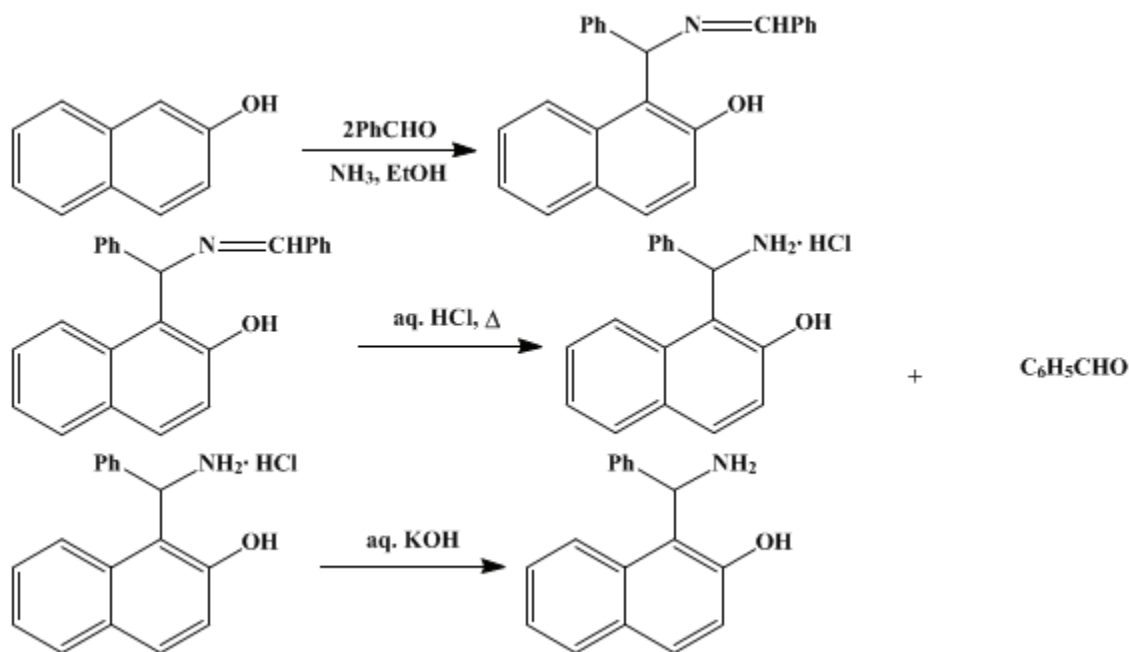
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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. 1, p.381 (1941); Vol. 9, p.60 (1929).*

## $\beta$ -NAPHTHOL PHENYLAMINOMETHANE

### [2-Naphthol, 1-( $\alpha$ -aminobenzyl)-]



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### 1. Procedure

In a 1-l. round-bottomed flask is placed a cold solution of 144 g. (1 mole) of  $\beta$ -naphthol in 200 cc. of 95 per cent alcohol (Note 1). To this solution is added first 212 g. (2 moles) of freshly distilled benzaldehyde (which has been previously freed from acid by shaking with 5 per cent sodium carbonate solution) and then about 200 cc. of 95 per cent alcohol which has been saturated with ammonia at room temperature. The solution becomes red and warms up spontaneously. The flask is stoppered and allowed to stand for two hours. Then the stopper is removed, and the excess ammonia is allowed to escape. After about twelve hours, the condensation product, which has separated as white needles, is filtered with suction and washed with 50 cc. of alcohol. The mother liquors on standing for three days deposit an additional quantity of the condensation product (Note 2). The yield is 284–306 g. (84–91 per cent of the theoretical amount) of a product which melts at 148–150°.

The condensation product thus obtained is introduced into a 5-l. round-bottomed flask arranged for steam distillation, and treated with three to four times its volume of 20 per cent hydrochloric acid. The mixture is steam distilled to remove all benzaldehyde formed by the hydrolysis (about two hours) (Note 3). Meanwhile, an abundant flocculent precipitate of light pink or white needles separates. The mixture in the flask is cooled thoroughly and filtered with suction. The yield is 240–260 g. (84–91 per cent of the theoretical amount) of a product which melts at 190–220° with decomposition (Note 4).

The hydrochloride thus obtained varies from pure white to a light red in color, depending on the purity of the original reagents and on the length of time required for the hydrolysis. However, the color does not interfere with isolation of a pure white free base when the salt is treated with alkali. The salt is somewhat more stable than the free base, and, if the reagent is to be stored for some time, it should be kept in this form.

In order to obtain the amine, 200 g. of finely divided hydrochloride is placed in a 1500-cc. beaker

and stirred into a smooth paste with 300 cc. of water. To this is added 50 g. of crushed ice, and the mixture is cooled in an ice bath (Note 5). Then 750–800 cc. of 5 per cent aqueous [potassium hydroxide](#) is added slowly and with stirring until a nearly clear solution results. The cold solution is transferred to a separatory funnel and extracted eight to ten times with 300-cc. portions of [ether](#). The combined [ether](#) extract is dried overnight with 50 g. of anhydrous [sodium sulfate](#), filtered, and concentrated to about 300 cc. When the solution is cooled in an ice bath, the amine crystallizes and is filtered with suction. The first crop of crystals weighs 112–115 g. Further concentration of the mother liquors to about 100 cc. and cooling yield 14–18 g. more of the product (Note 6). The total yield is 127–131 g. (73–75 per cent of the theoretical amount) of a product which melts at 124–125° (Note 7). If desired, it may be purified by dissolving in an excess of dry [ether](#), evaporating the excess of solvent, and allowing the amine to crystallize. Thus, 24.5 g. of the amine, when dissolved in 800 cc. of dry [ether](#) and the solution filtered and evaporated in a current of air to 150 cc., yields 18–19 g. of product, melting at 124–125°

## 2. Notes

1. It is usually necessary to warm the alcohol in order to dissolve the [β-naphthol](#). This solution is then cooled before the addition of the [benzaldehyde](#).
2. Even after three days' standing, the reaction is not entirely complete, and an additional 8–10 g. of product may be obtained by allowing the mother liquors to stand for another three or four days.
3. Sometimes, when the distillation is carried on for too long a period, the hydrochloride coagulates to a hard red mass. If this happens, the product may be purified by crystallization from about 15 per cent [hydrochloric acid](#). Even the deeply colored hydrochloride yields a colorless amine.
4. The hydrochloride is almost insoluble in cold water. It is slightly hydrolyzed by boiling water.
5. The temperature should be kept below 20° during the addition of the alkali, or the product is decomposed and [ammonia](#) is evolved.
6. A small additional amount of impure product may be obtained by evaporating the mother liquors further and cooling the solution. This product amounts to only a few grams and needs to be purified by recrystallization from [ether](#).
7. This amine is of interest because it is readily resolved with [tartaric acid](#) to give the pure dextro and levo isomers.<sup>1</sup> These optically active bases are very useful in the resolution of various types of racemic substances.

## 3. Discussion

[β-Naphthol phenylaminomethane](#) has been prepared only by the method outlined in the procedure.<sup>2</sup>

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## References and Notes

1. Betti, Gazz. chim. ital. **36**, II, 392 (1906).
  2. Betti, Gazz. chim. ital. **31**, I, 385 (1901).
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## Appendix

### Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

[β-Naphthol phenylaminomethane](#)

[alcohol](#) (64-17-5)

[hydrochloric acid](#) (7647-01-0)

[ammonia](#) (7664-41-7)

ether (60-29-7)

sodium carbonate (497-19-8)

sodium sulfate (7757-82-6)

$\beta$ -naphthol (135-19-3)

benzaldehyde (100-52-7)

potassium hydroxide (1310-58-3)

tartaric acid (87-69-4)

2-Naphthol, 1-( $\alpha$ -aminobenzyl)- (481-82-3)