Organic Syntheses

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). 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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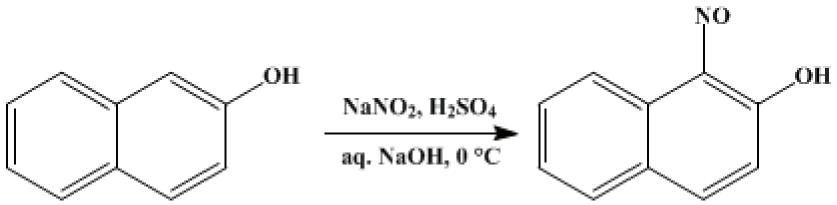
NITROSO-β-NAPHTHOL

[2-Naphthol, 1-nitroso-]



Submitted by C. S. Marvel and P. K. Porter.
Checked by H. T. Clarke and W. W. Hartman.

1. Procedure

In a 12-l. round-bottomed flask (Note 1) fitted with a mechanical stirrer is placed 500 g. (3.5 moles) of technical β-naphthol dissolved in a warm solution of 140 g. (3.5 moles) of sodium hydroxide in 6 l. of water. The solution is cooled to 0° in an ice and salt bath, and 250 g. (3.5 moles) of powdered technical sodium nitrite is added. Stirring is started, and 1100 g. (833 cc., 4.6 moles) of sulfuric acid (sp. gr. 1.32) is added from a dropping funnel at such a rate that the whole is added in one to one and one-half hours, the temperature being kept at 0°. During the reaction, crushed ice is added from time to time to maintain the temperature at 0°; about 1 kg. is generally used (Note 2). After all the sulfuric acid has been added, the solution should react acid to Congo red paper. The mixture is stirred one hour longer at the low temperature, and then the nitroso-β-naphthol, which has gradually separated during the reaction, is filtered with suction and washed thoroughly with water. The product is at first light yellow in color, but after three to four days it gradually changes to a dark brown. The moisture content seems to have some effect on the color.

After the product has been air-dried for about four days, the yield is about 665 g.; it melts at 97°. A sample of this partially dried product, on drying in a vacuum desiccator over sulfuric acid for twenty hours, loses about 10 per cent of its weight, and the melting point is 106°. By longer drying under ordinary conditions, the melting point of 106° is reached (Note 3). The total yield of dry product is about 595 g. (99 per cent of the theoretical amount).

This product is satisfactory for most purposes. It may be obtained in a crystalline condition, however, by recrystallizing from hot ligroin (b.p. 60–90°). About 2 g. of nitroso-β-naphthol will dissolve in 15 cc. of boiling ligroin. The product is not very soluble in cold ligroin, so that nearly all is recovered.

2. Notes

1. A large vessel is needed for the reaction, as the nitroso-β-naphthol separates in a finely divided condition and there is some tendency to foam.

It has been suggested that instead of a flask there be used a 13–14 l. bottle or crock with an opening of 20–22 cm. and equipped with a stirrer of heavy glass rod having four or five right-angle bends which extend to the top of the bottle and which are just small enough to fit the mouth. If the salt-ice mixture in the cooling bath is stirred well, a temperature of 0° may be maintained without internal cooling (L.F. Fieser, private communication).

2. It is very necessary to keep the temperature near 0° while adding the sulfuric acid, or a tarry product will be obtained. Vigorous stirring and the addition of the sulfuric acid at the proper rate are essential for a good product. Instead of the 1100 g. of sulfuric acid (sp. gr. 1.32) there can, of course, be added an equivalent amount of concentrated acid and sufficient ice to give a cold solution.

3. The final air-dried product is pure except for its moisture content, as is shown by the fact that on drying in a vacuum desiccator it has a very good melting point.

3. Discussion

Nitroso-β-naphthol can be prepared by the action of sulfuric acid upon a solution of potassium or sodium nitrite and the sodium salt of β-naphthol;[1] by the action of sodium nitrite upon an alcoholic solution of zinc chloride and β-naphthol;[2] by the action of sodium nitrite upon β-naphthol suspended in zinc sulfate solution;[3] and electrolytically from β-naphthol.[4]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 33
- Org. Syn. Coll. Vol. 2, 42

References and Notes

1. Fuchs, Ber. **8**, 1026 (1875); Groves, J. Chem. Soc. **45**, 295 (1884); Lagodzinski and Hardine, Ber. **27**, 3076 (1894).
2. Henriques and Ilinski, Ber. **18**, 705 (1885).
3. Koehler, Ger. pat. 25,469 [Frdl. **1**, 335 (1877–87)].
4. Emi, Repts. Imp. Ind. Research Inst., Osaka (Japan) **15**, No. I, 1 (1934) [C. A. **29**, 2457 (1935)].

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

ligroin

potassium or sodium nitrite

sulfuric acid (7664-93-9)

sodium hydroxide (1310-73-2)

sodium nitrite (7632-00-0)

β-naphthol (135-19-3)

zinc chloride (7646-85-7)

Nitroso-β-naphthol,
2-Naphthol, 1-nitroso- (131-91-9)

sodium salt of β-naphthol

zinc sulfate (7733-02-0)