Organic Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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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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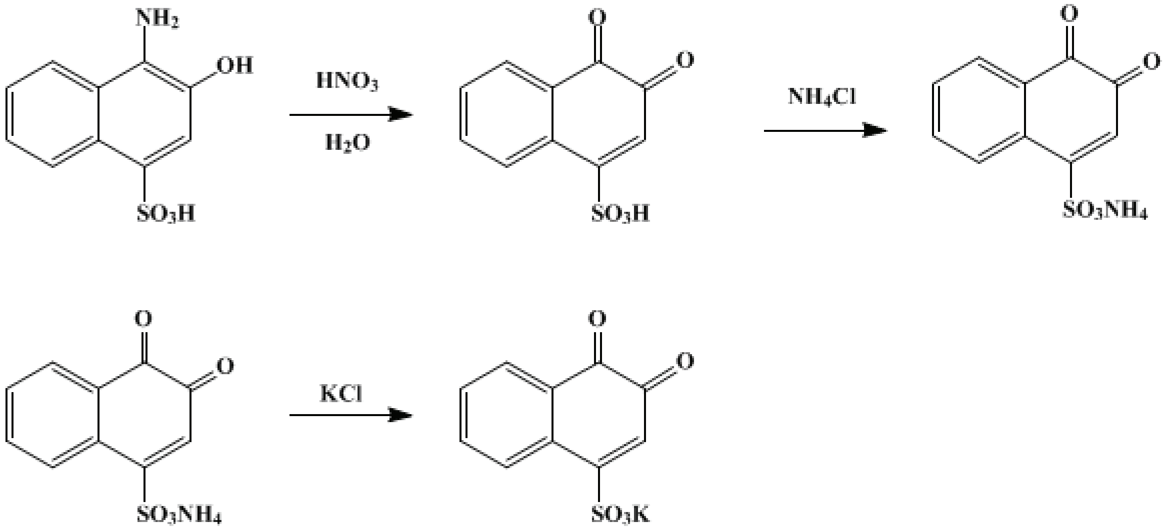
Organic Syntheses, Coll. Vol. 3, p.633 (1955); Vol. 21, p.91 (1941).

1,2-NAPHTHOQUINONE-4-SULFONATE, AMMONIUM AND POTASSIUM

[1-Naphthalenesulfonic acid, 3,4-dihydro-3,4-dioxo, ammonium and potassium salts]



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1. Procedure

A mixture of 145 ml. of nitric acid (sp. gr. 1.42) and 400 ml. of water in a 2-l. beaker is cooled to 30° in a slush of ice and water, and 350 g. (1.46 moles) of pure, anhydrous 1-amino-2-naphthol-4-sulfonic acid (Note 1) is weighed into a separate 2-l. beaker. The beaker is removed from the bath; a 10-g. portion of the 1-amino-2-naphthol-4-sulfonic acid is stirred into the solution, and the liquid is then allowed to become entirely motionless. Generally, oxidation starts during this addition; if not, 2 ml. of concentrated nitric acid is poured carefully down the side of the beaker without stirring. Oxidation commences in 1–2 minutes and the mixture turns yellow (Note 2).

The beaker is replaced in the ice bath, and 20–25 g. of 1-amino-2-naphthol-4-sulfonic acid is stirred into the mixture by hand. A second portion of 20–25 g. is added immediately and stirred. The mixture begins to froth and is covered with a layer of 100 ml. of ether which serves as an efficient subsident (Note 3). The remainder of the 1-amino-2-naphthol-4-sulfonic acid is added in 20–25 g. portions during the course of 3–4 minutes, the mixture being stirred well after each addition. Oxides of nitrogen are freely evolved, and a stiff yellow-orange paste is formed. The temperature is maintained between 25° and 30° by vigorous stirring and by controlling the rate of addition of the compound (Note 4). The oxidation is complete within 3–4 minutes after the last addition and gas is then no longer evolved. The thick mass is stirred until the temperature has dropped to 5–10° and then 175 ml. of saturated ammonium chloride solution (30°) is added.

After the mixture has been cooled to 0°, the ammonium 1,2-naphthoquinone-4-sulfonate is collected on a 20-cm. Büchner funnel and as much of the mother liquor is removed as possible by pressing the cake with a porcelain spatula or glass stopper. The product is washed with three equal portions of a cold mixture of 150 ml. of saturated ammonium chloride solution and 100 ml. of water. The wash solution is removed as completely as possible, and the product is washed twice with 50-ml. portions of ethanol, followed by 300 ml. of ether in small portions (Note 5). The ammonium 1,2-naphthoquinone-4-sulfonate is spread out in a thin layer and dried to constant weight at 35–40°. An orange, microcrystalline product of bright appearance is thus obtained. The yield is 350–365 g. (94–98%). The ammonium salt is of good quality and is sufficiently pure for many purposes. No satisfactory method has been devised for its further purification, but it can be converted into a pure potassium salt as follows.

Seventeen hundred milliliters of water containing 0.3 ml. of liquid bromine is heated in a 2-l. Erlenmeyer flask to 50° on a steam bath (Note 6). The flask is removed, 50 g. of ammonium 1,2-naphthoquinone-4-sulfonate is added, and the mixture is shaken for a few minutes until solution is complete. Three grams of Norit is added, and the solution is stirred for 2–3 minutes. It is then filtered by suction and the clear orange filtrate is transferred to a 4-l. Erlenmeyer flask. Four hundred milliliters of saturated potassium chloride solution (30°) is added rapidly in one portion, and the flask is allowed to stand undisturbed. Orange crystals of potassium salt begin to separate immediately, and after standing for 30 minutes the contents of the flask are cooled to 0° in an ice-salt bath and the potassium 1,2-naphthoquinone-4-sulfonate is collected on a 15-cm. Büchner funnel. The solid is washed with 150 ml. of cold, dilute potassium chloride solution (30 ml. of saturated potassium chloride solution added to 120 ml. of water), and then with 150 ml. of ethanol in small portions followed by 300 ml. of ether. The potassium salt is dried to constant weight at 40–50°. The yield is 48–50 g. (90–92% based on the ammonium salt used). The product consists of orange needles free of colored decomposition products but still containing traces of ammonium salts. An ammonium-free compound is obtained by a second crystallization. Seventeen hundred milliliters of water containing 0.2 ml. of liquid bromine is heated to 60° in a 2-l. Erlenmeyer flask on a steam bath; the flask is removed, and 50 g. of the potassium salt is added. The salt dissolves rapidly; the solution is filtered with suction; and the clear orange filtrate is transferred to a 4-l. Erlenmeyer flask. Three hundred milliliters of saturated potassium chloride solution is added rapidly in one portion, and the flask is allowed to stand undisturbed. Orange needles of potassium salt appear in a moment or two, and after standing for 30 minutes the mixture is cooled to 0° in an ice-salt bath. The crystals are collected, washed, and dried as outlined above. The salt thus obtained weighs 45–49 g. (90–98% based on the potassium 1,2-naphthoquinone-4-sulfonate used). This product compared favorably with the sodium salt prepared by the more elaborate borax process[1] with respect to color, colored decomposition products and ammonia content (Note 7) and (Note 8).

2. Notes

1. The 1-amino-2-naphthol-4-sulfonic acid earlier described [*Org. Syntheses* Coll. Vol. **2**, 42 (1943)] is not quite pure and gives an oxidation product of somewhat inferior quality. The procedure in question yields a gray product containing water of hydration (the percentage yield reported is thus in error). On reinvestigating the matter it has been found that the darkening of the material can be minimized if not prevented entirely, and that the colored impurity can be removed completely by extraction with ethanol. The colorless, anhydrous sulfonic acid required for the present preparation is thus prepared by modifying the earlier procedure in the following respects. By stirring the mixture of nitroso-β-naphthol and sodium bisulfite solution vigorously by hand (wooden paddle), all the soluble product can be dissolved in 3–4 minutes. The solution is then filtered as rapidly as possible, using two 15-cm. Büchner funnels and changing filter papers frequently. The clear, golden-yellow filtrate is acidified immediately on completion of the filtration. The product is then light gray, whereas, if much time elapses before the bisulfite solution is acidified, the solution turns red and the aminonaphtholsulfonic acid may be deep purple-gray. After the product has been collected and washed with water, it is washed with warm ethanol until the filtrate is colorless; 1.5–2 l. of ethanol is required. The product is washed with two 100-ml. portions of ether and dried to constant weight at 60–80° in the absence of light. A pure white, dust-dry product which weighs 370–380 g. (75–78% based on the β-naphthol) is thus obtained. This product is used in the present procedure.
If technical 1-amino-2-naphthol-4-sulfonic acid is used, the yield of ammonium 1,2-naphthoquinone-4-sulfonate is 313 g. (84%) of a rust-colored product. If the technical material is washed with 2 l. of warm 95% ethanol the yield is 337 g. (90%) of an orange-colored ammonium salt.
2. It is important that the oxidation start at this point. Should oxidation not begin, a second 1–2 ml. portion of concentrated nitric acid is added; the acid is introduced along the side of the beaker with as little disturbance as possible.
3. It is necessary to add more ether from time to time to replace that which evaporates.
4. The temperature must be kept within this range. At lower temperatures the oxidation is slow and not

satisfactory; at higher temperatures the quinone is slightly decomposed.

5. The ethanol and ether remove the small amount of decomposition products and assist in the rapid drying of the product. It is advisable to dry the preparation as rapidly as possible.

6. Aqueous solutions of 1,2-naphthoquinone-4-sulfonate begin to decompose when heated to this temperature in the absence of bromine.

7. Tests for the purity of the product were devised by Folin and later improved by Danielson.[1] A direct comparison of the two preparations revealed no difference in the degree of purity of the product.

8. This purified salt is suitable for use in the procedures of Folin and of Sullivan for the determination of amino acids.

3. Discussion

Salts of 1,2-naphthoquinone-4-sulfonate have been prepared by the oxidation of 2-amino-1-naphthol-4-sulfonic acid with nitric acid,[2] or by the oxidation of the more readily available 1-amino-2-naphthol-4-sulfonic acid with the same reagent.[3,4,5]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 465

References and Notes

1. Danielson, *J. Biol. Chem.*, **101**, 507 (1933).
2. Witt and Kaufman, *Ber.*, **24**, 3162 (1891).
3. Folin, *J. Biol. Chem.*, **51**, 386 (1922).
4. Böniger, *Ber.*, **27**, 24 (1894).
5. Fieser, *J. Am. Chem. Soc.*, **48**, 2929 (1926).

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

1-Naphthalenesulfonic acid, 3,4-dihydro-3,4-dioxo, ammonium and potassium salts

ethanol (64-17-5)

ammonia (7664-41-7)

ether (60-29-7)

ammonium chloride (12125-02-9)

nitric acid (7697-37-2)

bromine (7726-95-6)

nitrogen (7727-37-9)

β-naphthol (135-19-3)

sodium bisulfite (7631-90-5)

Norit (7782-42-5)

potassium (7440-09-7)

Quinone (106-51-4)

Nitroso-β-naphthol (131-91-9)

potassium chloride (7447-40-7)

1-AMINO-2-NAPHTHOL-4-SULFONIC ACID (116-63-2)

aminonaphtholsulfonic acid

ammonium 1,2-naphthoquinone-4-sulfonate,
1,2-NAPHTHOQUINONE-4-SULFONATE, AMMONIUM (53684-60-9)

potassium 1,2-naphthoquinone-4-sulfonate (5908-27-0)

1,2-naphthoquinone-4-sulfonate

2-amino-1-naphthol-4-sulfonic acid