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.

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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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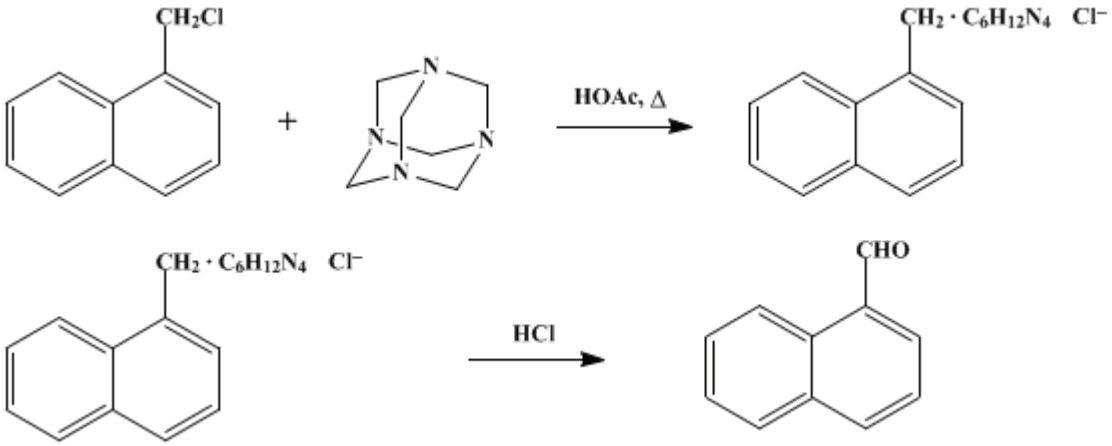
1-NAPHTHALDEHYDE



Submitted by S. J. Angyal, J. R. Tetaz, and J. G. Wilson[1].
Checked by R. S. Schreiber and Paul E. Marlatt.

1. Procedure

Precautions should be taken to avoid contact with 1-chloromethylnaphthalene, which is a lachrymator and a vesicant, and with the aldehyde, which seems to possess the same properties to a lesser degree.

In a 1-l. flask fitted with a reflux condenser are placed 106 g. (0.6 mole) of 1-chloromethylnaphthalene[2] (Note 1), 168 g. (1.2 moles) of hexamethylenetetramine, 250 ml. of glacial acetic acid, and 250 ml. of water. This mixture is heated under reflux for 2 hours. In about 15 minutes the solution becomes homogeneous, and then an oil starts to separate. After the reflux period, 200 ml. of concentrated hydrochloric acid is added and refluxing is continued for an additional 15 minutes (Note 2). After cooling, the mixture is extracted with 300 ml. of ether; the ether layer is washed three times with 100-ml. portions of water, then with 100 ml. of 10% sodium carbonate solution (Note 3), and again with 100 ml. of water. The ether extract is dried with about 15 g. of anhydrous sodium sulfate and filtered, and the ether is removed by distillation. The residual liquid is distilled under reduced pressure, the distillate being collected at 105–107°/0.2 mm. or 160–162°/18 mm. (Note 4). The yield of colorless 1-naphthaldehyde freezing between 0.0° and 2.5° (Note 5) is 70–77 g. (75–82%).

2. Notes

1. The chloromethylnaphthalene used melted at 24–26°. Material with a lower melting point can be used, but the yield is correspondingly smaller; e.g., a sample having a melting point of 15–18° gave a 73% yield of slightly impure 1-naphthaldehyde.

The checkers found that crude chloromethylnaphthalene obtained from the preparation in *Organic Syntheses*[2] could be used with good results. Naphthalene, paraformaldehyde, hydrochloric acid, and phosphoric acid are heated under reflux according to the procedure described. After the crude product is washed with water, 10% potassium carbonate, and water, it is dissolved directly in 500 ml. of glacial acetic acid, diluted with 500 ml. of water, and treated with hexamethylenetetramine by the procedure described above. The over-all yield of almost colorless 1-naphthaldehyde is 162 g., b.p. 162–164°/18 mm.; n_D^{25} 1.6503 (52% yield based on naphthalene).

In this variation of the preparation, it is best to use a wide-bore tube as a condenser to remove the unreacted naphthalene. After the naphthalene has been distilled, the wide-bore tube is replaced with an ordinary condenser and the naphthaldehyde is distilled in the usual manner.

2. The various amines and aldehydes present combine to form Schiff's bases. If these are not hydrolyzed by a strong acid, they will contaminate the final product.
3. Care should be exercised when washing the solution with sodium carbonate because some carbon dioxide is evolved.
4. The brown distillation residue contains some methylene-α-naphthylmethylamine.
5. The melting point of 1-naphthaldehyde given by Stephen[3] (33–34°) is apparently incorrect. A sample that was purified through the bisulfite addition compound and redistilled had a freezing point of 2.5°.
In no instance could the checkers obtain a completely colorless product even though it was redistilled several times with ordinary laboratory distilling apparatus.

3. Discussion

1-Naphthaldehyde has been prepared from calcium α-naphthoate by distillation with calcium formate;[4] from α-naphthyl-carbinol by oxidation with chromic acid,[5,6] N-bromosuccinimide,[7] or N-chlorosuccinimide;[8] from α-naphthylglyoxylic acid by heating with aniline and hydrolyzing the anil;[9] and from α-naphthylmagnesium bromide and ethoxymethyleneaniline [10,11] or ethyl orthoformate.[12,13] This Grignard reagent also has been converted to the dithioacid with carbon disulfide and the acid taken to 1-naphthaldehyde (through the semicarbazone).[14]

1-Naphthaldehyde has been made from α-naphthonitrile by reduction with stannous chloride,[3,15,16] sodium triethoxyaluminohydride, [17] lithium triethoxyaluminohydride, [18] or diisobutylaluminum hydride; [19] from naphthalene by the action of aluminum chloride, hydrogen cyanide, and hydrochloric acid,[20] by treatment with dichloromethyl methyl ether in the presence of stannic chloride, [21] and by the reaction with carbon monoxide in the presence of boron trifluoride and hydrogen fluoride; [22] from α-naphthoyl chloride by reduction with lithium tri-*tert*-butoxyaluminohydride; [23] from α-naphthoic acid N,N-dimethylamide by reduction with lithium diethoxyaluminohydride; [24] from the 1,3-diphenyltetrahydroimidazole derivative of 1-naphthaldehyde by hydrolysis;[25] from the reaction of α-naphthylmethylpyridinium bromide with *p*-nitrosodimethylaniline and hydrolysis of the resulting nitrone; [26] by the decomposition of 1-(benzenesulfonhydrazidocarbonyl) naphthalene with sodium carbonate; [27] and by the oxidation of α-methylnaphthalene with selenium dioxide. [28]

1-Naphthaldehyde has been obtained by means of the Sommelet reaction [29] from α-chloro- or α-bromomethylnaphthalene and hexamethylenetetramine in aqueous alcohol [30,31,32,33,34] or glacial acetic acid. [35,36,37] This method has been improved in the present procedure by the use of 50% acetic acid as a solvent.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 811
- Org. Syn. Coll. Vol. 5, 121

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

1,3-diphenyltetrahydroimidazole derivative of 1-naphthaldehyde

1-(benzenesulfonhydrazidocarbonyl) naphthalene

α-chloro- or α-bromomethylnaphthalene

potassium carbonate (584-08-7)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

ether (60-29-7)

aniline (62-53-3)

carbon monoxide (630-08-0)

hydrogen cyanide (74-90-8)

sodium carbonate (497-19-8)

sodium sulfate (7757-82-6)

stannous chloride

carbon dioxide (124-38-9)

hydrogen fluoride (7664-39-3)

aluminum chloride (3495-54-3)

selenium dioxide (7446-08-4)

phosphoric acid (7664-38-2)

chromic acid (7738-94-5)

carbon disulfide (75-15-0)

Naphthalene (91-20-3)

Ethyl orthoformate

N-chlorosuccinimide (128-09-6)

hexamethylenetetramine (100-97-0)

stannic chloride (7646-78-8)

α-naphthylmagnesium bromide

α-naphthoyl chloride (879-18-5)

boron trifluoride (7637-07-2)

calcium formate (544-17-2)

α-Naphthonitrile (86-53-3)

ethoxymethyleneaniline (6780-49-0)

N-bromosuccinimide (128-08-5)

1-Chloromethylnaphthalene,
chloromethylnaphthalene (86-52-2)

α-methylnaphthalene (90-12-0)

1-Naphthaldehyde,
naphthaldehyde (66-77-3)

methylene-α-naphthylmethylamine

calcium α-naphthoate

α-naphthyl-carbinol (4780-79-4)

α-naphthylglyoxylic acid

sodium triethoxyaluminohydride

lithium triethoxyaluminohydride

diisobutylaluminum hydride (1191-15-7)

Dichloromethyl methyl ether (4885-02-3)

α-naphthoic acid N,N-dimethylamide

lithium diethoxyaluminohydride

α-naphthylmethylpyridinium bromide

p-nitrosodimethylaniline (138-89-6)

lithium tri-tert-butoxyaluminohydride

paraformaldehyde (30525-89-4)