



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.

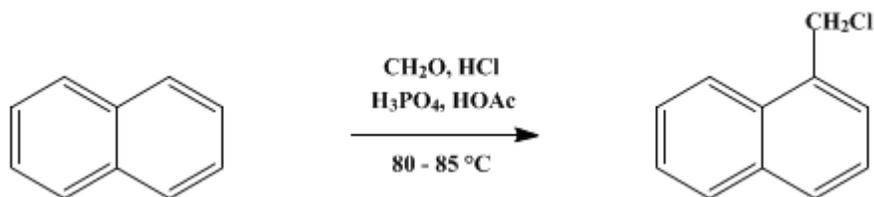
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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. 3, p.195 (1955); Vol. 24, p.30 (1944).*

## 1-CHLOROMETHYLNAPHTHALENE

### [Naphthalene, 1-chloromethyl-]



Submitted by Oliver Grummitt and Allen Buck.

Checked by C. F. H. Allen and J. VanAllan.

### 1. Procedure

*Caution! Both chloromethylnaphthalene and the by-products are lachrymators and vesicants. Although it is not necessary to work in a hood, precautions should be taken during the handling of the substance and apparatus.*

In a 3-l. three-necked flask, fitted with a reflux condenser and Hershberg stirrer, are placed 256 g. (2 moles) of naphthalene, 110 g. of paraformaldehyde (Note 1), 260 ml. of glacial acetic acid, 165 ml. of 85% phosphoric acid, and 428 g. (362 ml., 4.2 moles) of concentrated hydrochloric acid. This mixture is heated in a water bath at 80–85° and vigorously stirred for 6 hours (Note 2).

After the mixture has been cooled to 15–20° it is transferred to a 2-l. separatory funnel and the crude product is washed first with two 1-l. portions of water cooled to 5–15°, then with 500 ml. of cold 10% potassium carbonate solution, and finally with 500 ml. of cold water. The product is the lower layer in all the washings. After the addition of 200 ml. of ether, the solution is given a preliminary drying by being allowed to stand over 10 g. of anhydrous potassium carbonate, with frequent shaking, for 1 hour. The lower aqueous layer which forms is separated, and the ether solution is again dried over 20 g. of potassium carbonate for 8–10 hours (Note 3) and (Note 4).

The dried solution is distilled, first at atmospheric pressure to remove most of the solvent, and then under reduced pressure (Note 5). A fore-run of unused naphthalene amounting to 35–40 g. is collected at 90–110°/5 mm. (Note 6). This is followed by 195–204 g. of 1-chloromethylnaphthalene which boils at 128–133°/5 mm. or at 148–153°/14 mm. (74–77% based on naphthalene consumed) (Note 7) and (Note 8).

### 2. Notes

1. "Trioxymethylene" from the Eastman Kodak Company was used.
2. The level of the water bath should be maintained at the same height as that of the stirred reaction mixture.
3. Both the washing and drying operations must be done very carefully, because the presence of small amounts of water or acid is liable to cause the product to resinify during the final distillation.
4. The checkers added 50 ml. of dry benzene before distilling the solvent to remove traces of water by azeotropic distillation.
5. A clean, dry flask and a moderate rate of distillation help to overcome the tendency of the product to resinify.
6. Care should be taken to prevent clogging of the line by the naphthalene.
7. The oil pump should be protected from acid fumes by means of a trap containing alkali.
8. The residue left after distillation consists mainly of bis-(chloromethyl) naphthalene and di-1-naphthylmethane.

### 3. Discussion

1-Chloromethylnaphthalene has been made from naphthalene and a variety of reagents: methyl chloromethyl ether;<sup>1</sup> aqueous formaldehyde and hydrogen chloride with or without sulfuric acid as a condensing agent;<sup>2,3,4,5,6,7,8</sup> and paraformaldehyde with hydrogen chloride or hydrochloric acid.<sup>9,10,11</sup> Catalysts employed have been zinc chloride,<sup>2,12,13,14</sup> aluminum chloride,<sup>13</sup> phosphoric acid,<sup>15,16,17</sup> and *p*-toluenesulfonyl chloride.<sup>18</sup> Petroleum ether and glacial acetic acid have been used as solvents. The present method is a modification of that described by Cambron.<sup>15</sup>

The chloromethylation of aromatic hydrocarbons has been discussed by Fuson and McKeever.<sup>19</sup> It is reported that arsenic salts are helpful in the chloromethylation process.<sup>20</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 4, 690](#)

---

### References and Notes

1. Vavon, Bolle, and Calin, *Bull. soc. chim. France*, (5) **6**, 1032 (1939).
2. Blanc, *Bull. soc. chim. France*, (4) **33**, 319 (1923).
3. Jones, U. S. pat. 2,212,099 [*C. A.*, **35**, 462 (1941)].
4. Coles and Dodds, *J. Am. Chem. Soc.*, **60**, 853 (1938).
5. Reddelien and Lange, Ger. pat. 508,890 [*C. A.*, **25**, 716 (1931)].
6. Roblin and Hechenbleikner, U. S. pat. 2,166,554 [*C. A.*, **33**, 8628 (1939)].
7. Shmuk and Guseva, *J. Applied Chem. U.S.S.R.*, **14**, 1031 (1941) [*C. A.*, **39**, 4069 (1945)].
8. Badger, Cook, and Crosbie, *J. Chem. Soc.*, **1947**, 1432.
9. Darzens and Levy, *Compt. rend.*, **202**, 74 (1936).
10. Fieser and Novello, *J. Am. Chem. Soc.*, **62**, 1856 (1940).
11. Fieser and Gates, *J. Am. Chem. Soc.*, **62**, 2338 (1940).
12. Ruggli and Burckhardt, *Helv. Chim. Acta*, **23**, 443 (1940).
13. Ger. pat. 509,149 [*C. A.*, **25**, 711 (1931)].
14. Anderson and Short, *J. Chem. Soc.*, **1933**, 485.
15. Cambron, *Can. J. Research*, **17B**, 12 (1939).
16. Manske and Ledingham, *Can. J. Research*, **17B**, 15 (1939).
17. Lock and Walter, *Ber.*, **75**, 1158 (1942).
18. Palomo, *Afinidad*, **27**, 361 (1950) [*C. A.*, **44**, 9390 (1950)].
19. Fuson and McKeever, *Organic Reactions*, **1**, 63 (1942); John Wiley & Sons.
20. U. S. pat. 2,541,408 [*C. A.*, **45**, 6662 (1951)].

---

### Appendix

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

petroleum ether

trioxymethylene

[potassium carbonate](#) (584-08-7)

[sulfuric acid](#) (7664-93-9)

hydrogen chloride,  
hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

Benzene (71-43-2)

ether (60-29-7)

formaldehyde (50-00-0)

aluminum chloride (3495-54-3)

phosphoric acid (7664-38-2)

Naphthalene (91-20-3)

zinc chloride (7646-85-7)

methyl chloromethyl ether (107-30-2)

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

di-1-naphthylmethane

p-Toluenesulfonyl chloride (98-59-9)

bis-(chloromethyl) naphthalene

paraformaldehyde (30525-89-4)