



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.

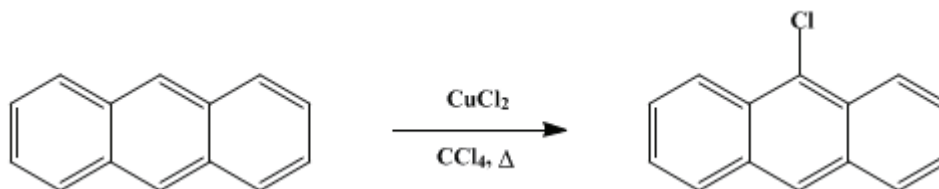
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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9-CHLOROANTHRACENE

[Anthracene, 9-chloro-]



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1. Procedure

In a dry, 1-l., two-necked flask, equipped with a mechanical stirrer and a reflux condenser fitted with a drying tube, are placed 17.8 g. (0.100 mole) of anthracene (Note 1), 27.2 g. (0.202 mole) of anhydrous cupric chloride (Note 2), and 500 ml. of carbon tetrachloride (Note 3). The reaction mixture is stirred and heated under reflux for 18–24 hours. The brown cupric chloride is gradually converted to white cuprous chloride, and hydrogen chloride is gradually evolved. At the end of the reaction the cuprous chloride is removed by filtration, and the carbon tetrachloride solution is passed through a 35-mm. chromatographic column filled with 200 g. of alumina (Note 4). The column is eluted with 400 ml. of carbon tetrachloride. The combined eluates are evaporated to dryness to give 19–21 g. (89–99%) of 9-chloroanthracene as a lemon-yellow solid, m.p. 102–104° (Note 5). Crystallization of the product from petroleum ether (b.p. 60–80°) gives 16–17 g. (75–80%) of 9-chloroanthracene as yellow needles, m.p. 104–106°.

2. Notes

1. Anthracene, B. D. H. (blue fluorescence), was used. Traces of ethylene glycol, glycerol, ethanol, or water considerably retard the reaction and lead to unsatisfactory results.
2. Anhydrous cupric chloride is dried in an oven at 110–120° for several hours and stored in a desiccator or over phosphorus pentoxide before use.
3. Chlorobenzene or *sym*-tetrachlorethane may be used instead of carbon tetrachloride as solvent, in which case the reaction is complete as soon as the mixture has reached reflux. The product is liable to be contaminated by a small amount of 9,10-dichloroanthracene.
4. Merck alumina or Spence Type H alumina was used.
5. The 9-chloroanthracene at this stage usually contains a small amount of unreacted anthracene.

3. Discussion

9-Chloroanthracene has been prepared by the action of chlorine,² *t*-butyl hypochlorite,³ 1,3-dichloro-5,5-dimethylhydantoin,⁴ or phosphorus pentachloride⁵ on anthracene. The present method is a one-step synthesis giving a high yield of 9-chloroanthracene from readily available starting materials.

The method outlined can be applied to the preparation in better than 90% yield of the 10-chloro derivatives of 9-alkyl,⁶ 9-aryl,⁶ and 9-halogenoanthracenes.⁷ For the less reactive substrates chlorobenzene should be used as solvent. This is the only satisfactory procedure for the preparation of 9-bromo-10-chloroanthracene.⁷ Other methods of chlorination lead to mixtures of the desired compound and 9,10-dichloroanthracene. Pyrene can likewise be converted to 1-chloropyrene (90% yield).⁸ Analogous procedures with cupric bromide lead to the brominated compounds in similar high yields.

References and Notes

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

petroleum ether

sym-tetrachlorethane

ethanol (64-17-5)

hydrogen chloride (7647-01-0)

phosphorus pentachloride (10026-13-8)

glycerol (56-81-5)

carbon tetrachloride (56-23-5)

chlorobenzene (108-90-7)

chlorine (7782-50-5)

ethylene glycol (107-21-1)

cuprous chloride (7758-89-6)

cupric chloride (7758-89-6)

anthracene (120-12-7)

cupric bromide (7789-45-9)

pyrene (129-00-0)

9-Chloroanthracene,
Anthracene, 9-chloro- (716-53-0)

9,10-dichloroanthracene (605-48-1)

1,3-dichloro-5,5-dimethylhydantoin (118-52-5)

9-bromo-10-chloroanthracene

1-chloropyrene (34244-14-9)

phosphorus pentoxide (1314-56-3)

t-BUTYL HYPOCHLORITE (507-40-4)