



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.

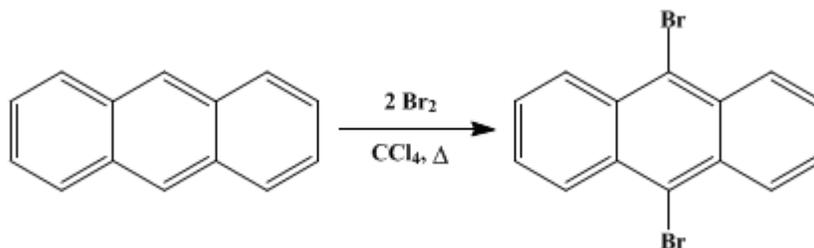
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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9,10-DIBROMOANTHRACENE

[Anthracene, 9,10-dibromo-]



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1. Procedure

To a suspension of 300 g. (1.35–1.43 moles) of **anthracene** of 80–85 per cent purity in 3 l. of **carbon tetrachloride** (Note 1), in a 5-l. flask fitted with dropping funnel, stirrer, and reflux condenser, is added slowly 567 g. (182 cc., 3.55 moles) of **bromine**. The bromination takes place in the cold with separation of the sparingly soluble **9,10-dibromoanthracene**; in order to prevent undissolved **anthracene** from becoming coated over, it is necessary to maintain vigorous stirring throughout the reaction. A tube from the top of the condenser conducts **hydrogen bromide** to cold water, in which it is absorbed (Note 2). The addition of the **bromine** occupies about one-half hour; the rate is so adjusted that a minimum of **bromine** is carried over with the **hydrogen bromide**.

When all the **bromine** has been added, the mixture is gently warmed on a steam bath with continual stirring, care being taken not to heat so rapidly as to cause undue loss of **bromine** by entrainment. Heating is continued until the mixture has boiled gently for one hour. The mixture is then allowed to cool for some hours, without stirring, and the crude **dibromoanthracene** is filtered off, washed with a little cold **carbon tetrachloride**, and dried. In this way 270–425 g. of a bright yellow product, which melts (Note 3) at 218–219° (corr.), is obtained. On concentrating the mother liquors, 15–150 g. more of crude material, m.p. about 216° (corr.), can be obtained.

To prepare a purer product, the crude **dibromoanthracene** is extracted with **carbon tetrachloride** (Note 4) in an apparatus similar to that described on p. 375, the extraction is carried to the point at which crystals just begin to separate from the boiling solvent, and a fresh quantity of **carbon tetrachloride** is then taken. About eight extractions are necessary, 1 l. being used each time. The **9,10-dibromoanthracene** so purified consists of brilliant yellow needles melting at 221–222° (corr.) (Note 5). A further quantity of pure product may be obtained by concentrating the mother liquor and recrystallizing the second crop so obtained. The recovered solvent may be employed for further extractions. The yield amounts to 400–420 g. (83–88 per cent of the theoretical quantity based on **anthracene** of 85 per cent purity).

2. Notes

1. The reaction may be carried out equally well with a larger proportion of solvent, but if less than the amount indicated is taken, difficulty may arise in stirring. **Carbon disulfide** may be employed instead of **carbon tetrachloride**, but this solvent presents no essential advantages and it is necessary to use a larger volume for the same amount of **anthracene**.
2. The watery solution of **hydrogen bromide**, on fractional distillation, readily yields 48 per cent **hydrobromic acid**, boiling at 125–126° /760 mm. (p. 26).
3. The observed melting points of the various products are 5–6° lower than the corrected values.
4. The crude product may be recrystallized from **toluene**, in which it is somewhat more soluble than in

carbon tetrachloride; the color of the product is, however, not quite so light, although the melting point is as high as if carbon tetrachloride were used. If desired, recrystallization may be effected from toluene without using the extraction apparatus, in which case about 10 l. of solvent in all will be required; for the filtration of the hot solution, a plug of glass wool, previously wetted with boiling toluene, may be employed, care being taken to warm the funnel adequately.

The bromination products of the impurities with which commercial anthracene is contaminated appear to be more soluble in carbon tetrachloride than is 9,10-dibromoanthracene; the yield can be slightly increased by fractional recrystallization of the products contained in the original mother liquor, but under laboratory conditions the gain does not compensate for the time involved.

5. When crystallized from xylene, samples have been obtained that melt as high as 226° (uncorr.) (E. de Barry Barnett, private communication).

3. Discussion

9,10-Dibromoanthracene can be prepared by the bromination of anthracene in dilute carbon disulfide solution.¹

References and Notes

1. Graebe and Liebermann, Ann. Suppl. 7, 275 (1870).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

HYDROBROMIC ACID,
hydrogen bromide (10035-10-6)

bromine (7726-95-6)

carbon tetrachloride (56-23-5)

toluene (108-88-3)

carbon disulfide (75-15-0)

9,10-Dibromoanthracene,
Anthracene, 9,10-dibromo- (523-27-3)

anthracene (120-12-7)

dibromoanthracene

xylene (106-42-3)