



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.

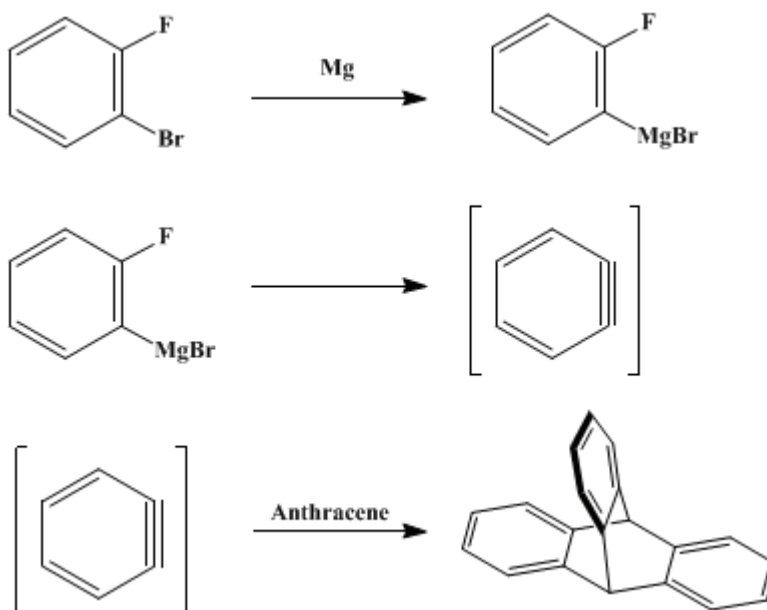
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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. 4, p.964 (1963); Vol. 39, p.75 (1959).

TRIPTYCENE

[9,10-*o*-Benzenoanthracene, 9,10-dihydro-]



Submitted by George Wittig¹

Checked by John D. Roberts, M. C. Caserio, E. S. Johnson, and L. Skattebøl.

1. Procedure

A 200-ml. three-necked flask, equipped with a ball-and-socket sealed mechanical stirrer, a pressure-compensated dropping funnel, and a reflux condenser connected to a mercury bubbler (Note 1), is charged with 0.8 g. (0.033 g. atom) of magnesium turnings, 7.5 g. (0.042 mole) of anthracene, and 35 ml. of anhydrous tetrahydrofuran (Note 2). In the dropping funnel there is placed a solution of 5.26 g. (0.03 mole) of *o*-fluorobromobenzene (Note 3) in 15 ml. of tetrahydrofuran. The system is flushed with dry nitrogen for 30 minutes to remove air. The gas flow is then stopped in order to prevent extensive loss of tetrahydrofuran. The mixture is heated to and maintained at 60° (bath temperature), and one-quarter of the *o*-fluorobromobenzene solution is added with stirring. The appearance of a yellow color which evidences the start of reaction may not be observed immediately, and another quarter of the solution is then added dropwise over a period of about 45 minutes. When the reaction commences, the remaining solution is added dropwise over a period of 1 hour, after which the mixture is refluxed gently for 90 minutes. The almost homogeneous dark-brown mixture is poured into 100 ml. of methanol, which precipitates much of the unreacted anthracene. Without filtering, the solvents are removed under reduced pressure and the yellow residue is treated with two 50-ml. portions of 5% hydrochloric acid, filtered, and vacuum-dried. The dry, yellow residue (10 g.) is dissolved in 45 ml. of hot xylene, then 5.0 g. (0.051 mole) of maleic anhydride is added. The mixture is refluxed for 20 minutes and set aside at room temperature for 2 hours. The maleic anhydride-anthracene adduct (about 9 g.) is removed by filtration, and the brown filtrate is refluxed for 2 hours with 80 ml. of 2*N* sodium hydroxide solution. When cool, the organic layer is separated, washed three times with 50-ml. portions of water (Note 4), and dried over calcium chloride. The solvent is removed at reduced pressure. The brown residue is dissolved in 70 ml. of carbon tetrachloride and chromatographed on 280 g. of acid-washed alumina, using 1 l. of the same solvent to elute. After evaporation of the solvent, there remains 2.4–2.9 g. of a yellow residue which is digested with two 10-ml. portions of pentane (Note 5). The residual crude triptycene is an almost white crystalline solid of melting point 240–248°. The yield is 2.14 g. (28%) (Note 6). Recrystallization of this material from cyclohexane gives pure white crystals of melting point 255–256°.

2. Notes

1. The mercury bubbler seals the system from the air. It is connected to the top of the reflux condenser by means of 8-mm. glass tubing more than 76 cm. high. The pressure in the system may be varied by adjusting the depth of the lower end of the tube. A constant stream of dry [nitrogen](#) may be substituted for the [mercury](#) bubbler, but this inevitably results in some loss of [tetrahydrofuran](#).
2. [Tetrahydrofuran](#) may be purified by distillation from [lithium aluminum hydride](#).
3. [o-Fluorobromobenzene](#) as supplied by the Aldrich Chemical Company, Milwaukee, Wisconsin, may be used without further purification.
4. Small amounts of [sodium chloride](#) may be added to facilitate separation of the phases.
5. The main impurity is a yellow oil which is readily soluble in [pentane](#).
6. The checkers report a yield of 1.35–1.68 g. (18–22%) of triptycene of melting point 245–255°.

3. Discussion

Triptycene has been prepared by Bartlett and co-workers² in a seven-step synthesis. It also has been obtained by the reaction of [fluorobenzene](#) with [anthracene](#) in the presence of [butyllithium](#)³ and by the reduction of the anthracene-benzoquinone adduct with [lithium aluminum hydride](#) or [sodium borohydride](#).⁴ The present method has been published.⁵

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 60](#)

References and Notes

1. University of Tübingen, Tübingen, Germany.
2. Bartlett, Ryan, and Cohen, *J. Am. Chem. Soc.*, **64**, 2649 (1942).
3. Wittig and Benz, *Angew. Chem.*, **70**, 166 (1958).
4. Craig and Wilcox, *J. Org. Chem.*, **24**, 1619 (1959).
5. Wittig and Benz, *Chem. Ber.*, **91**, 873 (1958).

Appendix

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

Triptycene

maleic anhydride-anthracene adduct

anthracene-benzoquinone

[calcium chloride](#) (10043-52-4)

[hydrochloric acid](#) (7647-01-0)

[methanol](#) (67-56-1)

[sodium hydroxide](#) (1310-73-2)

magnesium turnings (7439-95-4)
sodium chloride (7647-14-5)
carbon tetrachloride (56-23-5)
nitrogen (7727-37-9)
mercury (7439-97-6)
cyclohexane (110-82-7)
anthracene (120-12-7)
xylene (106-42-3)
Pentane (109-66-0)
Fluorobenzene (462-06-6)
butyllithium (109-72-8)
Tetrahydrofuran (109-99-9)
maleic anhydride (108-31-6)
lithium aluminum hydride (16853-85-3)
sodium borohydride (16940-66-2)
o-fluorobromobenzene (1072-85-1)
9,10-o-Benzoanthracene, 9,10-dihydro- (477-75-8)