



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.

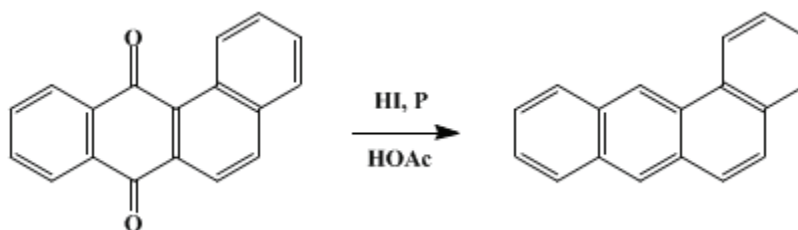
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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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REDUCTION OF QUINONES WITH HYDRIODIC ACID: BENZ[*a*] ANTHRACENE



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1. Procedure

*Caution! Benzene has been identified as a carcinogen; OSHA has issued emergency standards on its use. All procedures involving benzene should be carried out in a well-ventilated hood, and glove protection is required. Benz[*a*]anthracene is also a known carcinogen.*

A 500-mL, one-necked, round-bottomed flask is equipped with a magnetic stirring bar and an efficient condenser, and charged with 10.3 g (0.04 mol) of benz[*a*]anthracene-7,12-dione (Note 1), 5 g (0.16 mol) of red phosphorus (Note 2), and 100 mL of glacial acetic acid. The stirred suspension is heated to reflux, and 60 mL of 56% hydriodic acid (ca. 0.44 mol) (Note 3) is introduced through the condenser. The suspension is heated at reflux for 24 hr. The hot reaction mixture is poured into 500 mL of distilled water containing ~30 g of sodium bisulfite. The suspension is stirred for 16 hr and filtered. The dry filter cake is transferred to a beaker and treated with sufficient hot dichloromethane (~120 mL) to dissolve all of the benz[*a*]anthracene, and the mixture is filtered once again to remove the residual phosphorus. The volume of the filtrate is reduced to 40 mL. The solution is adsorbed on basic alumina, activity I (Note 4). A 2-cm × 40-cm chromatography column is slurry-packed with ca. 10 g of basic alumina and the benz[*a*]anthracene adsorbed on alumina is added to the top of the column. Elution with 5% benzene in hexane (occasional rinsing of the column tip with benzene to remove crystallized product may be necessary) and evaporation of the solvent in a rotary evaporator affords 7.7–7.9 g (84–87%) of pure, white benz[*a*]anthracene, mp 159.5–160°C (Note 5).

2. Notes

1. Benz[*a*]anthracene-7,12-dione, 12-dione, available from Eastman Organic Chemicals, was used without further purification.
2. Phosphorus, which serves to scavenge the I₂ produced, can be omitted. However, the product tends to retain traces of a yellow impurity that is difficult to remove.
3. The hydriodic acid employed was a 56% aqueous solution preserved with ~0.8% hypophosphorous acid obtained from Fisher Scientific Co. Once a bottle is opened, the contents tend to deteriorate, becoming dark-colored in less than 2 days. However, shelf life can be extended indefinitely if the container is purged with dry nitrogen before resealing.
4. Alumina sufficient to adsorb the complete solution is added, then the solvent is removed under vacuum. While benz[*a*]anthracene, mp 157–158°C, sufficiently pure for most purposes, can be obtained by crystallization of the crude product from ethanol-water, "filtration" through alumina removes residual, colored impurities, affording a pure, white product.
5. Pure benz[*a*]anthracene has been reported to melt at 158–159°C,² 160°C,³ and 167°C.⁴ The submitters report a melting point of 164–164.5°C. The submitters conducted this preparation on a scale five times larger and reported yields of up to 95%.

3. Discussion

The synthetic procedure described is based on that reported earlier for the synthesis on a smaller scale of anthracene, benz[a]anthracene, chrysene, dibenz[a, c]anthracene, and phenanthrene⁵ in excellent yields from the corresponding quinones.⁶ Although reduction of quinones with HI and phosphorus was described in the older literature, relatively drastic conditions were employed and mixtures of polyhydrogenated derivatives were the principal products.⁷ The relatively milder experimental procedure employed herein appears generally applicable to the reduction of both *ortho*- and *para*-quinones directly to the fully aromatic polycyclic arenes. The method is apparently inapplicable to quinones having an olefinic bond, such as *o*-naphthoquinone, since an analogous reaction of the latter provides a product of undetermined structure (unpublished result). As shown previously,⁶ phenols and hydroquinones, implicated as intermediates in the reduction of quinones by HI, can also be smoothly deoxygenated to fully aromatic polycyclic arenes under conditions similar to those described herein.

Although previous experience indicates that phosphorus is not essential for these reductions,^{6,8} purification of the product is more difficult with its omission. With hydrocarbons sensitive to further reduction, phosphorus can have a deleterious effect through promotion of hydrogenation of the desired product. Whether or not phosphorus should be employed in an individual case will be dictated by experience with the particular compound and by the degree of purity required.

While the reduction of polycyclic quinones to phenols, hydroquinones, dihydrodiols, dihydro arenes, and arenes by a variety of reagents has been described, no entirely satisfactory general method is currently available for reduction directly to the fully aromatic arenes. Reagents previously employed for this purpose include LiAlH₄,^{9,10} NaBH₄,^{11 12 13} NaBH₄-BF₃,^{11,14} diborane,¹⁴ aluminum and cyclohexanol,¹⁵ zinc dust distillation,¹⁶ and diphenylsilane.¹⁷ These methods commonly furnish lower yields and are less general than the present procedure.

References and Notes

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

red phosphorus

alumina

Benz[a]anthracene-7,12-dione, 12-dione

hypophosphorous acid

quinones

o-naphthoquinone

$\text{NaBH}_4\text{-BF}_3$

acetic acid (64-19-7)

Benzene (71-43-2)

Cyclohexanol (108-93-0)

PHOSPHORUS (7723-14-0)

nitrogen (7727-37-9)

aluminum (7429-90-5)

sodium bisulfite (7631-90-5)

zinc (7440-66-6)

hydriodic acid (10034-85-2)

anthracene (120-12-7)

dichloromethane (75-09-2)

phenanthrene (85-01-8)

LiAlH_4 (16853-85-3)

Benz[a]anthracene (56-55-3)

hexane (110-54-3)

NaBH_4 (16940-66-2)

chrysene (218-01-9)

diphenylsilane (775-12-2)

benz[a]anthracene-7,12-dione (2498-66-0)

dibenz[a, c]anthracene (215-58-7)