Organic Syntheses

A Publication
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for the Preparation
of Organic Compounds

# Working with Hazardous Chemicals

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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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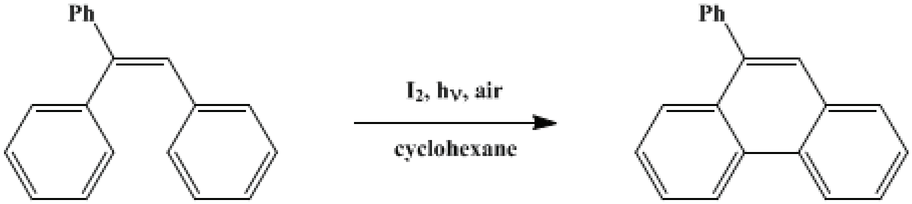
*Organic Syntheses, Coll. Vol. 5, p.952 (1973); Vol. 45, p.91 (1965).*

# 9-PHENYLPHENANTHRENE

## [Phenanthrene, 9-phenyl-]



Submitted by Frank B. Mallory and Clelia S. Wood[1].
Checked by William G. Dauben and Donald N. Brattesani.

## 1. Procedure

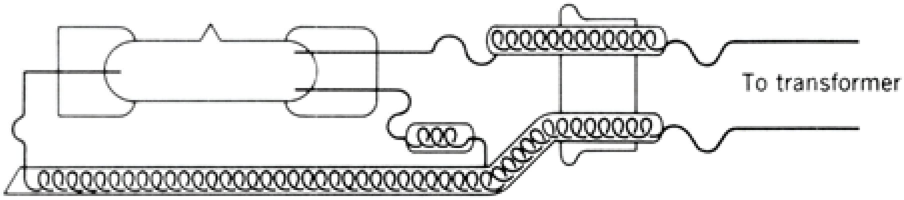
A solution of 2.56 g. (0.01 mole) of triphenylethylene[2] (Note 1) and 0.127 g. (0.5 mmole) of iodine in 1 l. of cyclohexane (Note 2) is placed in a 1.5-l. beaker and stirred magnetically (Note 3). A Hanovia water-cooled 19433 Vycor immersion well fitted with a 200-watt 654A-36 mercury lamp (Note 4) and (Note 5) is inserted into the beaker, and the lamp is started (Note 6). The irradiation is continued for about 3 hours (Note 7).

The reaction mixture is transferred to a 2-l. round-bottomed flask, and the solvent is evaporated under reduced pressure (Note 8). The residue is dissolved in 50 ml. of warm cyclohexane (Note 2), and the solution (Note 9) is poured onto a column of alumina (Note 10) 1.8 cm. in diameter and 6–7 cm. in length. The round-bottomed flask is rinsed with three 10-ml. portions of cyclohexane, and the rinsings are poured onto the column. The column is eluted with additional cyclohexane (about 100 ml.) until no appreciable amount of 9-phenylphenanthrene is obtained in the eluate. The elution of any yellow material from the column should be avoided. The total eluate is evaporated to dryness under reduced pressure (Note 8), and the residue is recrystallized from 40–45 ml. of 95% ethanol to give 1.65–1.90 g. (65–75%) of 9-phenylphenanthrene, m.p. 103.5–104.5° (Note 11), (Note 12), and (Note 13).

## 2. Notes

1. The triphenylethylene used by the submitters had been recrystallized from absolute ethanol, and the material melted at 68.0–68.6°.
2. Eastman Organic Chemicals practical grade cyclohexane is distilled before use.
3. A 4-cm. Teflon®-coated stirring bar gives sufficiently effective stirring.
4. This unit is sold as a Hanovia Laboratory Photochemical Reactor by the Hanovia Lamp Division, Engelhardt Industries, Inc., 100 Chestnut Street, Newark 5, New Jersey.
5. A relatively inexpensive light source and probe can be made as described below and used in place of the Hanovia unit. A 100-watt General Electric H100A4/T or H100A38-4 mercury lamp, available from the Lamp Department, General Electric Co., Nela Park, Cleveland, Ohio, is modified by cutting away the outer glass envelope and by detaching the inner quartz bulb from the screw base on which it is mounted. The two electrical leads from the lamp are then connected, as shown in Fig. 2, by means of insulated wire to a suitable power supply such as a General Electric 9T64Y-3518 or 9T64Y-1019 transformer. The modified mercury lamp is then inserted in a 17-mm. I.D. quartz tube which is about 30 cm. long and is sealed on one end. This tube is made from Clear Fused Quartz tubing available from the Lamp Glass Department, General Electric Co., Nela Park, Cleveland 12, Ohio.

**Fig. 2**



Irradiations with this type of light source are carried out using a 1-l. Erlenmeyer flask as the reaction vessel instead of a 1.5-l. beaker. The flask is placed in a cold-water bath that is supported on a magnetic stirrer. The bath can be made from a 10-qt. polyethylene bucket with a ¾-in. hole bored about 1 in. from the top of the bucket and a piece of rubber tubing with a 5/8-in. bore and 1/8-in. wall inserted as a drain. A stream of 24° tap water run into the bucket at a flow rate of 5 l. per min. maintains the temperature of the reaction mixture below 33°.

6. Unfiltered light from mercury lamps is damaging to the eyes; suitable precautions, such as wearing appropriate glasses and surrounding the reaction vessel with aluminum foil, should be taken.

7. The irradiation time required depends on the type of light source used and can be determined by following the progress of the reaction by infrared spectroscopy. A 10-ml. aliquot is withdrawn from the reaction mixture and evaporated to dryness under reduced pressure; the residue is dissolved in 0.5 ml. of carbon tetrachloride, and the spectrum is obtained using 0.1-mm. sodium chloride cells. A new peak appears at 899 cm.$^{-1}$, and the ratio of the absorbance of the peak at 703 cm.$^{-1}$ to that of the peak at 727 cm.$^{-1}$ continuously decreases during the course of the reaction. Using these spectral criteria, the submitters judged the reaction to be complete after 4 hours of irradiation with the lamp described in (Note 5); however, the recrystallized products from 4-hour reactions melted about 0.4° lower than those from 5-hour reactions. The submitters found that varying the irradiation time from 4 hours to 8 hours had no significant effect on the yield of 9-phenylphenanthrene. The extent of the reaction can also be monitored by gas-liquid chromatography.

8. It is convenient to use a rotary evaporator and a water aspirator for this operation.

9. This solution may be purple in color owing to incomplete removal of iodine during the reduced-pressure evaporation.

10. The submitters used Merck 71707 aluminum oxide. The checkers used Woelm neutral alumina, Activity I.

11. A sample of 9-phenylphenanthrene that had been exhaustively purified by zone refining and by recrystallization melted at 104.1–104.7°. The melting point has been reported as 104–105°[3,4,5] and as 105–106°.[6,7]

12. Reactions carried out at higher concentrations or on larger scales give slightly lower yields of less pure material. To obtain larger amounts of the product, the submitters recommend irradiating in batches on the scale specified in the procedure and combining the reaction mixtures prior to the chromatographic purification.

13. Using the apparatus described in (Note 5), the submitters obtained 2.08–2.17 g. (82–85%) of 9-phenylphenanthrene.

## 3. Discussion

This preparation is based on a procedure published by the submitters.[8,9] 9-Phenylphenanthrene has been prepared previously by the reaction of phenyllithium with 9-chlorophenanthrene,[10] by the high-temperature dehydrogenation with palladium on charcoal of the Diels-Alder dimer of 1-phenyl-1,3-butadiene,[11] and by the acid-catalyzed cyclization of the alcohol formed from the reaction of 2-biphenylylmagnesium iodide and 2-phenoxyacetophenone.[3]

## 4. Merits of the Preparation

This preparation illustrates a reasonably general method for obtaining 1-, 3-, or 9-substituted phenanthrenes in good yields from the photocyclization of the corresponding *o*-, *p*-, or α-substituted stilbenes.[8,9] The submitters have obtained satisfactory results with bromo, chloro, fluoro, methoxy, methyl, phenyl, trifluoromethyl, and carboxyl substituents. α-Styrylnaphthalene gives chrysene, β-styrylnaphthalene gives benzo[*c*]phenanthrene, and 1,2-di-α-naphthylethylene gives picene.

The photocyclization has been found not to occur with stilbenes substituted with acetyl, dimethylamino, or nitro groups. Iodo substituents are replaced by hydrogen by photolysis in cyclohexane solution.[9,12] *m*-Substituted stilbenes give mixtures of 2- and 4-substituted phenanthrenes which generally are difficult to separate.

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## References and Notes

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

alumina

ethanol (64-17-5)

hydrogen (1333-74-0)

carbon tetrachloride (56-23-5)

cyclohexane (110-82-7)

iodine (7553-56-2)

palladium (7440-05-3)

Phenyllithium (591-51-5)

aluminum oxide (1344-28-1)

Triphenylethylene (58-72-0)

1-phenyl-1,3-butadiene (31915-94-3)

9-Phenylphenanthrene,
Phenanthrene, 9-phenyl- (844-20-2)

9-chlorophenanthrene (947-72-8)

2-biphenylylmagnesium iodide

2-phenoxyacetophenone

α-Styrylnaphthalene

chrysene (218-01-9)

β-styrylnaphthalene

1,2-di-α-naphthylethylene

picene (213-46-7)

benzo[c]phenanthrene (195-19-7)

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