



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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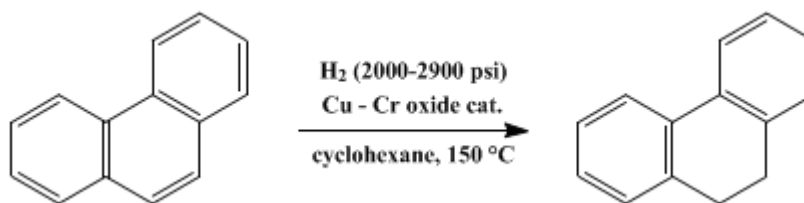
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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9,10-DIHYDROPHENANTHRENE

[Phenanthrene, 9,10-dihydro-]



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1. Procedure

A. *Purification of phenanthrene.* 1. By azeotropic distillation.² A mixture of 300 g. of commercial phenanthrene (Note 1), 90 g. of maleic anhydride, and 600 ml. of xylene, contained in a 2-l. round-bottomed flask, is heated under reflux for 20 hours (Note 2). The initially yellow solution rapidly turns to a dark brown on heating. This solution is cooled to room temperature and filtered by suction to remove any insoluble adduct. The filtrate is then extracted with two 100-ml. portions of dilute sodium hydroxide, and the basic extracts are discarded. The organic phase is next washed with water and saturated sodium chloride solution, and finally is filtered through a layer of anhydrous magnesium sulfate. The excess xylene is removed by distillation, first at atmospheric pressure; then the final portions are removed at reduced pressure. The residue, while still hot, is poured into a large mortar and, after solidification, is powdered to a convenient size. The yield of crude phenanthrene is 230–240 g.

A solution of 52 g. of the crude phenanthrene in 400 ml. of diethylene glycol (Note 3) is azeotropically distilled through a small column (Note 4). A fore-run of approximately 50 g. is collected at 155–165°/100 mm., followed by the main fraction of 390–400 g., b.p. 140–141°/21 mm. (Note 5). The fore-run contains considerable fluorene and should be discarded. The main fraction is added to five times its volume of water, and the precipitated hydrocarbon is collected by suction filtration and washed well with water to remove the last traces of diethylene glycol. The colorless product (41–43 g.) is heated under reflux for 3 hours with about 450 ml. of 95% ethanol containing approximately 9 g. of Raney nickel catalyst. The hot solution is filtered with slight suction through a sintered-glass funnel. On being concentrated to about 250 ml. and cooled, the filtrate deposits 33–35 g. (63–67%) of colorless phenanthrene, m.p. 97.5–98°.

2. By sodium treatment.³ Commercial phenanthrene (Note 1) is treated with maleic anhydride as described above (part 1), and 170 g. of the residue is added to a 1-l. three-necked flask equipped with a Hershberg mercury-sealed Nichrome stirrer,⁴ an air condenser, and a thermometer. Ten grams of sodium is added, and the mixture is vigorously stirred at 190–200° for 6 hours. The dark residue is cooled to about 80°, and 300 ml. of benzene is added. The mixture is brought to reflux with stirring and, while still hot, is cautiously filtered through a coarse sintered-glass funnel with gentle suction (Note 6). The benzene is removed by distillation at atmospheric pressure, and the residual phenanthrene is distilled through a small column (Note 4) adapted to the distillation of solids to give 125–130 g. (74–76%) of colorless phenanthrene, b.p. 183–183.5°/15 mm. This product is heated under reflux for 3 hours with about 1.2 l. of 95% ethanol containing approximately 9 g. of Raney nickel catalyst, and the hot solution is filtered as described under paragraph 1. The filtrate on cooling deposits 115–120 g. (68–71%) of colorless phenanthrene, m.p. 97–98°.

B. *Catalytic reduction.* A hydrogenation bomb of approximately 300 ml. total capacity is charged with 29.5 g. (0.17 mole) of purified phenanthrene (Note 7); then 70 ml. of cyclohexane (Note 8) and 1.5 g. of copper chromium oxide catalyst (Note 9) are added. The bomb is filled with hydrogen to an initial pressure of 2000 p.s.i. at 20° and heated with shaking to 150° (maximum pressure about 2900 p.s.i.).

The hydrogenation proceeds rapidly under these conditions, and about 85% of the theoretical uptake is complete within 1.75–2 hours. The reaction is interrupted at this point (Note 10), and the catalyst is removed by centrifugation or filtration. The cyclohexane is evaporated, and the residue is distilled through a small column (Note 4). After a small fore-run (0.2–0.3 g.) distilling below 182°, there is collected 21–23 g. (70–77% yield) of 9,10-dihydrophenanthrene, b.p. 183–184°/25 mm., n_D^{25} 1.6401–1.6416. The residue consists of 4.5–5.0 g. (15–17%) of phenanthrene, m.p. 96.5–98°, which may be recycled.

2. Notes

1. Technical grade phenanthrene (80–90%) is satisfactory for this preparation.
2. An electric heating mantle is convenient for this operation.
3. Technical diethylene glycol may be used with satisfactory results.
4. The submitter used a 65-cm. Podbielniak type column equipped with partial reflux head.⁵ For distillation of the sodium-treated phenanthrene the checkers employed a 6-in. Vigreux column. For the fractionation of the dihydrophenanthrene, the checkers employed a 15-cm. spinning-band column obtainable from Nester and Faust, Exton, Pennsylvania.
5. At these concentrations, the azeotrope is solid and adequate heating of the condenser and receivers must be provided by an infrared lamp or similar device. The use of twice this amount of diethylene glycol is reported² to give a liquid azeotrope but requires the distillation of proportionately larger amounts, for the azeotrope has nearly the same boiling point as diethylene glycol.
6. The finely divided sodium presents a serious fire hazard, and as much of it as possible should be retained in the flask. This may be accomplished by careful decantation. The material that is collected on the funnel should always be covered with a layer of solvent and should not be allowed to become dry. The residues may be safely destroyed by placing the funnel and flask in a large pail and adding about 1 l. of isopropyl alcohol. This operation is best conducted out-of-doors.
7. Phenanthrene purified by the sodium treatment was found superior to that from the azeotropic distillation, but both products gave satisfactory results. A good grade of commercially available phenanthrene ("white label" grade supplied by the Eastman Kodak Company), although recrystallized and treated with Raney nickel, resisted hydrogenation under the described conditions.
8. Cyclohexane as supplied by Matheson Company was used without further purification. The use of ethanol as solvent⁶ gave inconsistent results, and the yield of 9,10-dihydrophenanthrene never exceeded 50%. Erratic results were also obtained when the solvent was omitted.
9. Copper-chromium oxide (HJS2) was prepared as reported by Adkins and coworkers.⁷
10. If the hydrogenation is allowed to proceed to completion, the product is contaminated with considerable polyhydrogenated material, as indicated by its low refractive index. The optimum time for obtaining about 85% hydrogenation may vary with the purity of the phenanthrene and activity of the catalyst. The purest 9,10-dihydrophenanthrene is obtained when the lower limits of hydrogen uptake are realized, although the yield is correspondingly lower.

3. Discussion

9,10-Dihydrophenanthrene has been prepared from 2,2'-bis(bromomethyl)biphenyl and sodium;⁸ from the reduction of 2,2'-diiodobiphenyl in the presence of 1% palladium on barium carbonate catalyst;⁹ by the hydrogenation of phenanthrene in the presence of nickel⁸ or copper-chromium oxide catalyst;^{3,6,10} by the coupling of 2,2'-bis(bromomethyl)biphenyl with lithium phenyl;¹¹ and by the thermal decomposition of 1,1-(*o,o'*-biphenylenebismethylene)-2-*p*-toluenesulfonylhydrazine.¹²

References and Notes

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

sodium-treated phenanthrene

lithium phenyl

1,1-(o,o'-biphenylenebismethylene)-2-p-toluenesulfonylhydrazine

ethanol (64-17-5)

Benzene (71-43-2)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

sodium chloride (7647-14-5)

cyclohexane (110-82-7)

nickel,
Raney nickel (7440-02-0)

sodium (13966-32-0)

isopropyl alcohol (67-63-0)

palladium (7440-05-3)

barium carbonate (513-77-9)

xylene (106-42-3)

magnesium sulfate (7487-88-9)

Copper-Chromium Oxide

fluorene (86-73-7)

phenanthrene (85-01-8)

maleic anhydride (108-31-6)

diethylene glycol (111-46-6)

9,10-Dihydrophenanthrene,
Phenanthrene, 9,10-dihydro- (776-35-2)

copper chromium oxide

dihydrophenanthrene

2,2'-bis(bromomethyl)biphenyl

2,2'-diiodobibenzyl