Organic Syntheses

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.

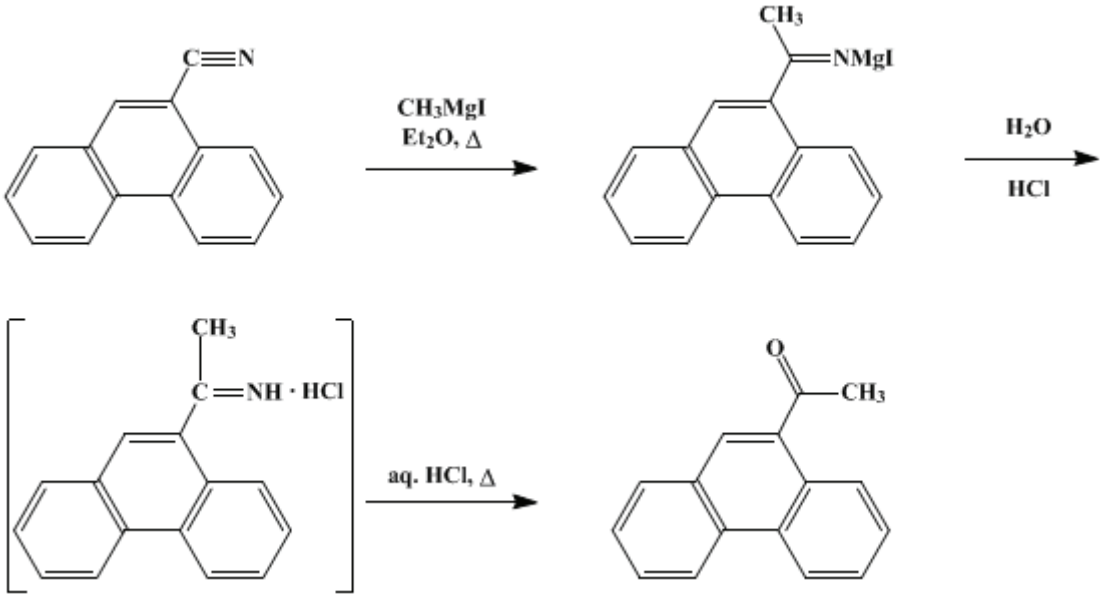
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.028.0006

Organic Syntheses, Coll. Vol. 3, p.26 (1955); Vol. 28, p.6 (1948).

9-ACETYLPHENANTHRENE

[Ketone, methyl 9-phenanthryl]



Submitted by Joseph E. Callen, Clinton A. Dornfeld, and George H. Coleman[1].
Checked by Robert E. Carnahan and Homer Adkins.

1. Procedure

A dry 12-l. three-necked flask is equipped with an efficient motor-driven stirrer (Note 1), a nitrogen inlet tube, a large Allihn condenser, and a 1-l. separatory funnel. Both the condenser and the funnel are provided with calcium chloride drying tubes. To the flask is added 146 g. (6 gram atoms) of magnesium turnings (Note 2), and nitrogen gas, first bubbled through concentrated sulfuric acid, is passed in to displace the air. During the reaction the nitrogen atmosphere is maintained. The magnesium is covered with 200 ml. of anhydrous ether, and a few milliliters of a solution of 852 g. (6 moles) of methyl iodide in 1 l. of anhydrous ether is added from the separatory funnel. The reaction starts spontaneously, and then the remainder of the methyl iodide solution is added slowly. When the reaction is complete (Note 3), 4 l. of dry benzene is added, a condenser is arranged for downward distillation, and about 1.2 l. of solvent is distilled (Note 4). The condenser is changed to a reflux position, 609 g. (3 moles) of 9-cyanophenanthrene (p. 212) is added quickly through a powder funnel, and the mixture is heated and stirred under reflux for 3 hours. It is then cooled in an ice bath to 0°, 3 l. of cold 6 *N* hydrochloric acid is slowly added (*Caution!*) from a separatory funnel with stirring, and the mixture is refluxed for 6 to 8 hours (Note 5).

After cooling, the layers are separated, the organic layer is washed with dilute sodium bicarbonate solution and placed in a flask equipped for distillation, and the solvent is distilled The oily residue is transferred while still warm to a 1-l. Claisen flask, and the product is distilled under reduced pressure; b.p. 190–200°/2.5 mm. (168–170°/1 mm.). The yield is 400–430 g. (61–65%). The distilled ketone is recrystallized once from ethanol (1.5–2 l.) to yield 345–390 g. (52–59%) of 9-acetylphenanthrene of m.p. 73–74°.

2. Notes

1. If a 12-l. three-necked flask is not available, a three-way adapter tube may be used in making the necessary connections. Although a mercury seal may be used, a glycerol-rubber tube seal is adequate.

2. The checkers operated on one-tenth the scale specified.
3. In several runs the Grignard reagent was filtered at this point, but the improvement in yield was not appreciable.
4. The addition of benzene and distillation of part of the solvent raises the reaction temperature.
5. The oily layer of ketimine hydrochloride usually dissolves during 6 hours' refluxing.

3. Discussion

The method described above is a modification of that of Bachmann and Boatner.[2] 9-Acetylphenanthrene has also been obtained by a Claisen condensation of methyl phenanthrene-9-carboxylate with ethyl acetate followed by scission of the resulting phenanthroylacetic ester,[3] by the reaction of 9-phenanthrylmagnesium bromide with acetyl chloride,[4] and by dehydrogenation of 9-acetyl-1,2,3,4-tetrahydrophenanthrene by heating with sulfur.[5]

References and Notes

1. Work done under contract with the Office of Scientific Research and Development.
2. Bachmann and Boatner, *J. Am. Chem. Soc.*, **58**, 2098 (1936).
3. Mosettig and van de Kamp, *J. Am. Chem. Soc.*, **55**, 3445 (1933).
4. Miller and Bachman, *J. Am. Chem. Soc.*, **57**, 768 (1935).
5. Bachmann and Struve, *J. Org. Chem.*, **4**, 476 (1939).

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

ethanol (64-17-5)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

ethyl acetate (141-78-6)

ether (60-29-7)

acetyl chloride (75-36-5)

sodium bicarbonate (144-55-8)

magnesium,
magnesium turnings (7439-95-4)

nitrogen (7727-37-9)

sulfur (7704-34-9)

Methyl iodide (74-88-4)

9-Acetylphenanthrene,
Ketone, methyl 9-phenanthryl (2039-77-2)

9-Cyanophenanthrene (2510-55-6)

methyl phenanthrene-9-carboxylate

9-phenanthrylmagnesium bromide

9-acetyl-1,2,3,4-tetrahydrophenanthrene

ketimine hydrochloride