



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](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.

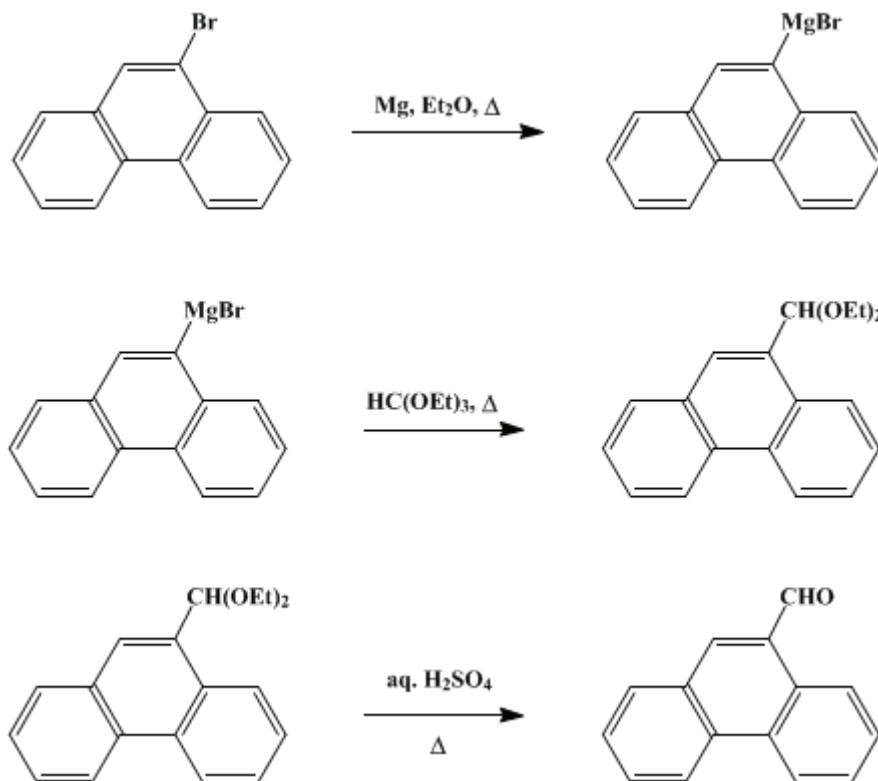
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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## PHENANTHRENE-9-ALDEHYDE

### [9-Phenanthrenecarboxaldehyde]



Submitted by Clinton A. Dornfeld and George H. Coleman<sup>1</sup>.

Checked by Robert E. Carnahan and Homer Adkins.

### 1. Procedure

A dry 5-l. three-necked flask is provided with a stirrer (Note 1), a nitrogen inlet tube, a 500-ml. Pyrex separatory funnel, and a large Allihn reflux condenser. To the upper end of the condenser are attached an outlet tube and a 1-l. separatory funnel. Both separatory funnels and the outlet tube are provided with calcium chloride drying tubes. To the flask is added 50.3 g. (2.07 gram atoms) of magnesium turnings (Note 2). Nitrogen gas, dried by bubbling through concentrated sulfuric acid, is passed in to displace the air in the flask. The nitrogen atmosphere is maintained until the hydrolysis of the Grignard addition product is completed. Five hundred and fourteen grams (2 moles) of crude 9-bromophenanthrene (p. 134) (Note 3) is melted and poured into the Pyrex separatory funnel (Note 4). One liter of anhydrous ether (dried over sodium wire) is placed in the upper separatory funnel. About 200 ml. of the ether and 10 ml. of the melted bromophenanthrene are allowed to run into the reaction flask. The reaction of the bromophenanthrene with magnesium is initiated by the addition of a few crystals of iodine and 1 ml. of ethyl bromide; the reaction begins after the mixture is stirred for a few minutes without external heating. As the reaction proceeds, the ether and the bromo compound are added at rates sufficient to maintain gentle refluxing. The relative rates of addition should be such that the two separatory funnels will be emptied at about the same time. After the additions are complete, but while the reaction is still in progress, the Grignard reagent begins to precipitate on the sides of the flask. One liter of dry, thiophene-free benzene is added from the Pyrex separatory funnel at such a rate as to keep the Grignard reagent in solution. When refluxing due to the exothermic reaction stops, the mixture is heated at gentle reflux with stirring for 4 hours.

The mixture is allowed to cool until refluxing ceases, and 296.4 g. (2 moles) of ethyl orthoformate

(Note 5) is added from the lower separatory funnel over a period of about 30 minutes. The mixture is then refluxed gently for 6 hours.

The reaction mixture is cooled with stirring in an ice bath, and 1 l. of cold 10% hydrochloric acid (Note 6) is added from the separatory funnel; the acid is added dropwise at first and more rapidly after the reaction subsides. The benzene-ether layer is separated from the aqueous layer and concentrated under reduced pressure in a 5-l. round-bottomed flask on a steam bath. One liter of 25% sulfuric acid is added to the residue, and the mixture is refluxed gently for 12 hours.

The mixture is then cooled in an ice bath, the acid is decanted, and the residue is washed twice by decantation with water. The residue is dissolved in 1 l. of benzene in the same flask, and 1.5 l. of water and 1.2 kg. of sodium bisulfite are added. The flask is fitted with a stirrer, and the mixture is stirred vigorously overnight. The mixture is filtered through an 8-in. Büchner funnel, and the bisulfite addition product is washed on the funnel with 500 ml. of benzene.

The filter cake is broken up and returned to the same 5-l. flask. A saturated solution of sodium bicarbonate is added slowly (Note 7) with stirring until there is no further evidence of decomposition. The mixture is stirred for 2 hours longer. The solution is kept alkaline to litmus throughout by the addition of more sodium bicarbonate if necessary. The crude aldehyde is collected on an 8-in. Büchner funnel, washed with water, and allowed to dry as completely as possible. The product is dissolved in 1 l. of chloroform, the small aqueous layer is separated (Note 8), and the solution is dried with Drierite or another suitable drying agent.

A 250-ml. modified Claisen flask, equipped with a dropping funnel, a thermometer, a water-cooled condenser, and a receiver, is arranged for distillation. The chloroform solution is filtered into the dropping funnel, from which it is admitted to the flask slowly as the solvent is distilled (Note 9). When the solvent has been removed, the dropping funnel is replaced by a stopper and the condenser by a 250-ml. distilling flask as a receiver. The residue is distilled at 160–170°/1 mm. The distillate weighs 206–216 g. (50–52%). This material is recrystallized once from glacial acetic acid (approximately 1 g. to 0.9 ml.) and then from ethanol (about 1 g. to 3 ml.) to give 166–174 g. (40–42% over-all yield) of phenanthrene-9-aldehyde melting at 100–101°.

## 2. Notes

1. A mercury seal may be used, but a glycerol-rubber tube seal is adequate.
2. The checkers operated on one-fifth the scale specified.
3. Crude bromophenanthrene prepared by the bromination of technical (90%) phenanthrene and purified by distillation only was used by the submitters in this preparation. The anthracene-9-aldehyde, which may be formed from the anthracene present as an impurity in "90% phenanthrene," does not form a sodium bisulfite addition product and so will not contaminate the phenanthrene-9-aldehyde. The checkers used 9-bromophenanthrene, m.p. 54–56° (p. 134), exclusively, but without any advantage in yield. The submitters report yields of 55–60% from pure 9-bromophenanthrene.
4. It is not feasible to add the 9-bromophenanthrene as an ether solution because of the limited solubility of the substance in this solvent. Since the melting point of the crude 9-bromophenanthrene is about 50° it is desirable to heat the melted material to 70° in order to prevent crystallization in the funnel. If the bromo compound begins to solidify in the funnel it may be melted again by careful heating with a microburner.
5. The ethyl orthoformate should be freshly distilled with rejection of the fraction boiling below 140°.
6. If this procedure is used for the preparation of the acetal instead of the aldehyde, it may be preferable to use ammonium chloride solution for hydrolysis instead of 10% hydrochloric acid.
7. The alkaline solution must be added carefully to avoid excessive foaming.
8. The water in the filter cake is removed with difficulty by drying in air or even in an oven under reduced pressure. If the water is not removed as indicated in the procedure, difficulty may be encountered in the early part of the distillation.
9. The distillation of the solvent may be carried out at reduced pressure if desired.

## 3. Discussion

Phenanthrene-9-aldehyde has been obtained by the Sonn and Müller synthesis from 9-phenanthroyl chloride,<sup>2</sup> by the Rosenmund reduction of 9-phenanthroyl chloride,<sup>3</sup> by the Gattermann hydrogen cyanide synthesis from phenanthrene,<sup>4</sup> and by the reaction of 9-phenanthrylmagnesium bromide with ethyl formate.<sup>5</sup> The procedure described above is an adaptation of the method of Miller and Bachman.<sup>6</sup> This Grignard method has also been used by others.<sup>7</sup>

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## References and Notes

1. Work done under contract with the Office of Scientific Research and Development.
  2. Shoppee, *J. Chem. Soc.*, **1933**, 40.
  3. Mosettig and van de Kamp, *J. Am. Chem. Soc.*, **55**, 2996 (1933).
  4. Hinkel, Ayling, and Beynon, *J. Chem. Soc.*, **1936**, 344.
  5. Bergmann and Israelashwili, *J. Am. Chem. Soc.*, **67**, 1955 (1945).
  6. Miller and Bachman, *J. Am. Chem. Soc.*, **57**, 768 (1935).
  7. Hewett, *J. Chem. Soc.*, **1938**, 195; Weizmann, Bergmann, and Berlin, *J. Am. Chem. Soc.*, **60**, 1332 (1938).
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## Appendix

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

ethanol (64-17-5)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

Benzene (71-43-2)

ether (60-29-7)

ammonium chloride (12125-02-9)

chloroform (67-66-3)

sodium bicarbonate (144-55-8)

magnesium,  
magnesium turnings (7439-95-4)

Ethyl bromide (74-96-4)

nitrogen (7727-37-9)

sodium bisulfite (7631-90-5)

iodine (7553-56-2)

sodium (13966-32-0)

anthracene (120-12-7)

Ethyl orthoformate

ethyl formate (109-94-4)

phenanthrene (85-01-8)

9-phenanthrylmagnesium bromide

anthracene-9-aldehyde (642-31-9)

9-Bromophenanthrene (573-17-1)

bromophenanthrene

Phenanthrene-9-aldehyde,  
9-Phenanthrenecarboxaldehyde (4707-71-5)

9-phenanthroyl chloride