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.

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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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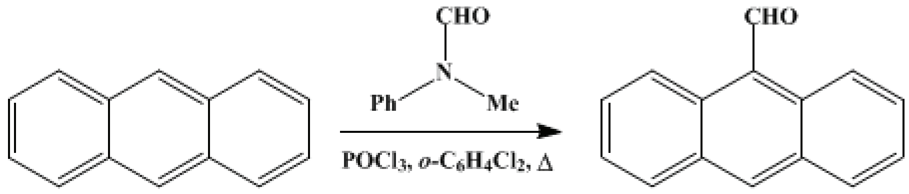
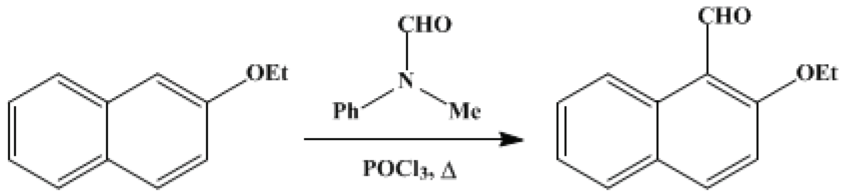
9-ANTHRALDEHYDE; 2-ETHOXY-1-NAPHTHALDEHYDE

A.



B.



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1. Procedure

A. *9-Anthraldehyde*. In a 2-l. round-bottomed flask fitted with a mechanical stirrer and reflux condenser are placed 35 g. (32 ml., 0.26 mole) of N-methylformanilide (p. 590), 35 g. (21 ml., 0.23 mole) of phosphorus oxychloride, 20 ml. of *o*-dichlorobenzene, and 22.5 g. (0.13 mole) of anthracene (Note 1). The flask is heated on the steam bath, with stirring, to 90–95° over a period of 20 minutes; the anthracene dissolves during this time to give a deep red solution, and hydrogen chloride is evolved (Note 2). The heating is continued for 1 hour (Note 3), after which a solution of 140 g. of crystalline sodium acetate in 250 ml. of water (Note 4) is added to the cooled mixture, and the *o*-dichlorobenzene and most of the methylaniline are rapidly distilled with steam (15–20 minutes). The residual reddish oil solidifies on cooling. The solid residue is broken up, and, after the aqueous liquor has been decanted through a Büchner funnel, it is washed by decantation with two 100-ml. portions of 6 *N* hydrochloric acid to remove amine, and then thoroughly with water (1–1.2 l.). The crude solid (22–24 g., m.p. 97–101°) is recrystallized from 50 ml. of hot glacial acetic acid; when cold, the bright yellow aldehyde is filtered by suction and washed on the filter with 30 ml. of methanol (Note 5). The yield is 20–22 g. (77–84%), and the melting point is 104.5–105° (Note 6).

B. *2-Ethoxy-1-naphthaldehyde*. A mixture of 45 g. (0.33 mole) of N-methylformanilide (p. 590), 51 g. (0.33 mole) of phosphorus oxychloride, and 43 g. (0.25 mole) of β-naphthyl ethyl ether in a 500-ml. round-bottomed flask provided with an air condenser (Note 2) is heated on a steam bath for 6 hours. The hot mixture is then poured in a thin stream into 700 ml. of cold water with very vigorous stirring to avoid the formation of large lumps (Note 7); the aldehyde separates in a granular condition. It is filtered by suction and washed thoroughly, using 1 l. of water. Without drying, the crude aldehyde is dissolved in 450 ml. of ethanol and decolorized by the addition of 4 g. of Norit, boiling for 15 minutes, and filtering hot (Note 8), using a double filter paper. The filtrate is cooled, and the product is collected on a filter and washed with 40 ml. of cold ethanol; it crystallizes in pale yellow needles, m.p. 111–112°. The yield is 37–42 g. (74–84%).

2. Notes

1. The yield and purity of the anthraldehyde depend on the quality of the hydrocarbon. The figures given are attained only if the anthracene melts at 213° or higher. With anthracene, m.p. 208–210°, the yield is 19–20 g., m.p. 103–104° (Note 6).
2. The reaction may be carried on in a hood, or a gas trap may be used.
3. When run on a fourfold scale, the time of heating should be extended to 2 hours. Prolonged heating leads to the formation of tars.

4. Sodium acetate appears to decompose a product of the condensation of methylaniline with phosphorus oxyhalides; substances other than the aldehyde are largely retained in the sodium acetate solution.
5. A brighter-colored product is secured by this wash.
6. The aldehyde also exists in a low-melting form, m.p. 98.5–99.5°, and occasionally this form is obtained from the reaction. It is less stable than the high-melting form, into which it is easily converted by seeding.
7. Care must be exercised to prevent the reaction product from lumping upon being poured into water. If this happens, decomposition by the water is slow and subsequent purification is more difficult. Any lumps that are formed should be broken up, and the reaction mixture should then be permitted to stand overnight in contact with the water. The flask in which the reaction is carried out is also filled with water to decompose the product adhering to the walls. This is purified with the rest.
8. A heated funnel is desirable. Some of the product usually crystallizes during the filtration.

3. Discussion

This aldehyde synthesis is applicable to compounds of the aromatic series having a labile hydrogen atom (phenyl ethers,[1] naphthols,[2] dialkylanilines,[3,4] naphthostyril,[2] anthrones[2]) and to certain hydrocarbons of requisite reactivity (anthracene,[5,6] 1,2-benzanthracene,[6] 3,4-benzpyrene,[3,7] pyrene,[8] styrene,[9] and α,α-diarylethylenes[9]). With polynuclear hydrocarbons the best results are secured by the use of a solvent such as *o*-dichlorobenzene. 9-Anthraldehyde has also been prepared by the action of hydrogen cyanide and aluminum chloride on anthracene in chlorobenzene.[10]

With liquid or low-melting ethers no solvent is required. 2-Ethoxy-1-naphthaldehyde has also been prepared by ethylation of the hydroxy compound,[11] and from β-naphthyl ethyl ether by the Gattermann reaction.[12]

It is possible to employ N,N-dimethylformamide in place of N-methylformanilide in some cases. A general method, applied to 9-anthraldehyde, has been described by Campaigne and Archer.[13]

References and Notes

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6. Fieser and Hartwell, *J. Am. Chem. Soc.*, **60**, 2556 (1938).
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11. Bartsch, *Ber.*, **36**, 1975 (1903).
12. Gattermann, *Ann.*, **357**, 367 (1907).
13. Campaigne and Archer, *J. Am. Chem. Soc.*, **75**, 989 (1953).

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

naphthostyril

3,4-benzpyrene

ethanol (64-17-5)

hydrogen chloride,
hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

methanol (67-56-1)

sodium acetate (127-09-3)

hydrogen cyanide (74-90-8)

Norit (7782-42-5)

chlorobenzene (108-90-7)

Phosphorus Oxychloride (21295-50-1)

aluminum chloride (3495-54-3)

anthracene (120-12-7)

styrene (100-42-5)

β-naphthyl ethyl ether (93-18-5)

methylaniline (100-61-8)

9-ANTHRALDEHYDE (642-31-9)

2-ETHOXY-1-NAPHTHALDEHYDE (19523-57-0)

N-methylformanilide (93-61-8)

anthraldehyde

1,2-benzanthracene (56-55-3)

pyrene (129-00-0)

N,N-dimethylformamide (68-12-2)

o-dichlorobenzene (95-50-1)