



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.

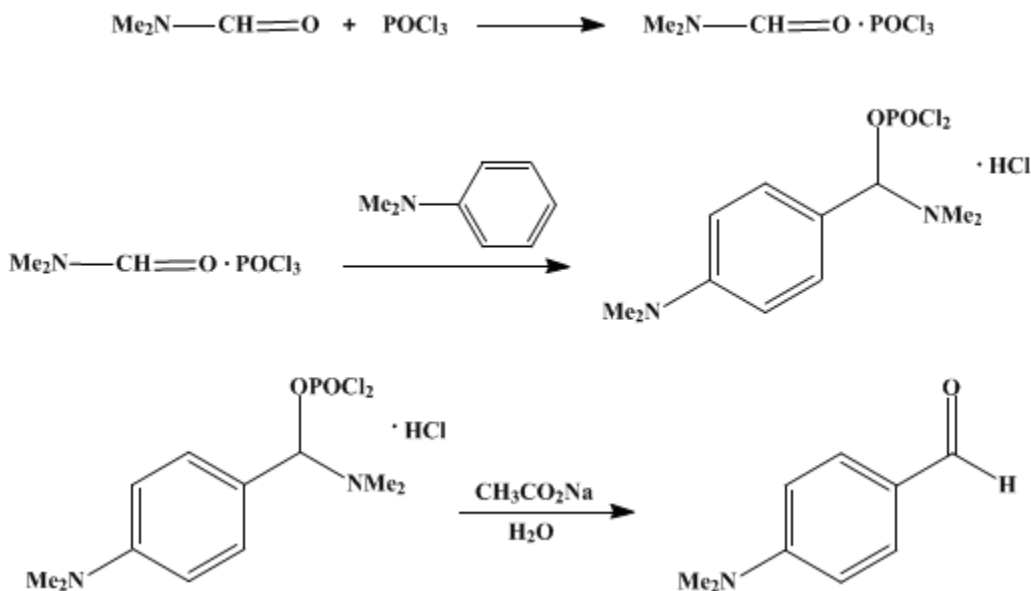
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.331 (1963); Vol. 33, p.27 (1953).

***p*-DIMETHYLAMINOBENZALDEHYDE**

[Benzaldehyde, *p*-dimethylamino-]



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1. Procedure

In a 2-l. three-necked round-bottomed flask, equipped with a sealed stirrer, dropping funnel, and a reflux condenser topped by a calcium chloride tube, is placed 440 g. (6 moles) of [dimethylformamide](#) ([Note 1](#)). While the flask is carefully cooled in an ice bath, 253 g. (1.65 moles) of [phosphorus oxychloride](#) is added dropwise with stirring. An exothermic reaction occurs with the formation of the phosphorus oxychloride-dimethylformamide complex. When all the [phosphorus oxychloride](#) has been added, and the heat of the reaction has subsided, 200 g. (1.65 moles) of [dimethylaniline](#) ([Note 2](#)) is added dropwise with stirring. When the addition of the [dimethylaniline](#) is complete, a yellow-green precipitate begins to form. The reaction mixture is heated on a steam bath, and stirring is continued for 2 hours. The yellow-green precipitate redissolves when heating is begun. The mixture is then cooled and poured over 1.5 kg. of crushed ice in a 5-l. beaker. Any precipitate that remains in the flask may be washed into the ice mixture with cold water. The solution is neutralized to pH 6–8 (Universal Test Paper) by the dropwise addition of approximately 1.5 l. of saturated aqueous [sodium acetate](#) with vigorous stirring ([Note 3](#)). *p*-Dimethylaminobenzaldehyde begins to precipitate soon after the addition of the [sodium acetate](#) is begun. The neutral mixture (total volume about 4.5 l.) is stored in the refrigerator overnight ([Note 4](#)). The greenish-tinted crystalline precipitate is filtered by suction, with the aid of a rubber dam, and washed several times with water on the filter. The green color is readily removed during the washing. The very light-yellow to nearly colorless product, after air-drying, weighs 198–208 g. (80–84%) and melts at 73–74°. It is essentially pure and useful for most purposes as obtained ([Note 5](#)).

2. Notes

1. The [dimethylformamide](#) is available as technical grade DMF from the Grasselli Chemicals Department of E. I. du Pont de Nemours and Company. [Dimethylformamide](#) can be prepared by the method of Mitchell and Reid² from [dimethylamine](#) and [formic acid](#).

2. [Dimethylaniline](#) free from [monomethylaniline](#) (Eastman Kodak Company) is used.

3. It is possible to neutralize the acid solution partially with [sodium hydroxide](#) before the [sodium acetate](#) is added, but it is more difficult to avoid localized heating by this method. It is important to keep the reaction mixture below 20° during the neutralization, by the addition of ice if necessary, since any excessive increase in temperature of the aqueous solution leads to the formation of greenish blue dyestuffs, which are very difficult to remove from the product.
4. The mixture may turn orange-colored when allowed to stand overnight.
5. If a purer product is desired, the aldehyde may be purified by the method described by Adams and Coleman.³

3. Discussion

[p-Dimethylaminobenzaldehyde](#) has been prepared from [dimethylaniline](#), [formaldehyde](#), and [p-nitrosodimethylaniline](#) in 56–59% yield,³ by the formylation of [dimethylaniline](#) with [N-methylformanilide](#) in approximately 50% yield,⁴ by the formylation of [dimethylaniline](#) with [dimethylformamide](#),⁵ and by the condensation of [methyl formate](#) with [p-dimethylaminophenyl chloride](#) in [tetrahydrofuran](#).⁶

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 4, 539](#)
- [Org. Syn. Coll. Vol. 4, 831](#)

References and Notes

1. Indiana University, Bloomington, Indiana.
 2. Mitchell and Reid, *J. Am. Chem. Soc.*, **53**, 1879 (1931).
 3. *Org. Syntheses Coll. Vol. 1*, 214 (1941).
 4. Vilsmeier and Haack, *Ber.*, **60**, 119 (1927).
 5. Brit. pat. 607,920 [*C. A.*, **43**, 2232 (1949)].
 6. Ramsden (to Metal & Thermit Corp.), Brit. pat. 806,710 [*C. A.*, **54**, 2264 (1960)].
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Appendix

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

phosphorus oxychloride-dimethylformamide complex

[sodium acetate](#) (127-09-3)

[sodium hydroxide](#) (1310-73-2)

[formaldehyde](#) (50-00-0)

[formic acid](#) (64-18-6)

[Phosphorus Oxychloride](#) (21295-50-1)

[dimethylaniline](#) (121-69-7)

[dimethylamine](#) (124-40-3)

methyl formate (107-31-3)

monomethylaniline (100-61-8)

Tetrahydrofuran (109-99-9)

N-methylformanilide (93-61-8)

dimethylformamide (68-12-2)

p-Dimethylaminobenzaldehyde,
Benzaldehyde, p-dimethylamino- (100-10-7)

p-nitrosodimethylaniline (138-89-6)

p-dimethylaminophenylmagnesium chloride