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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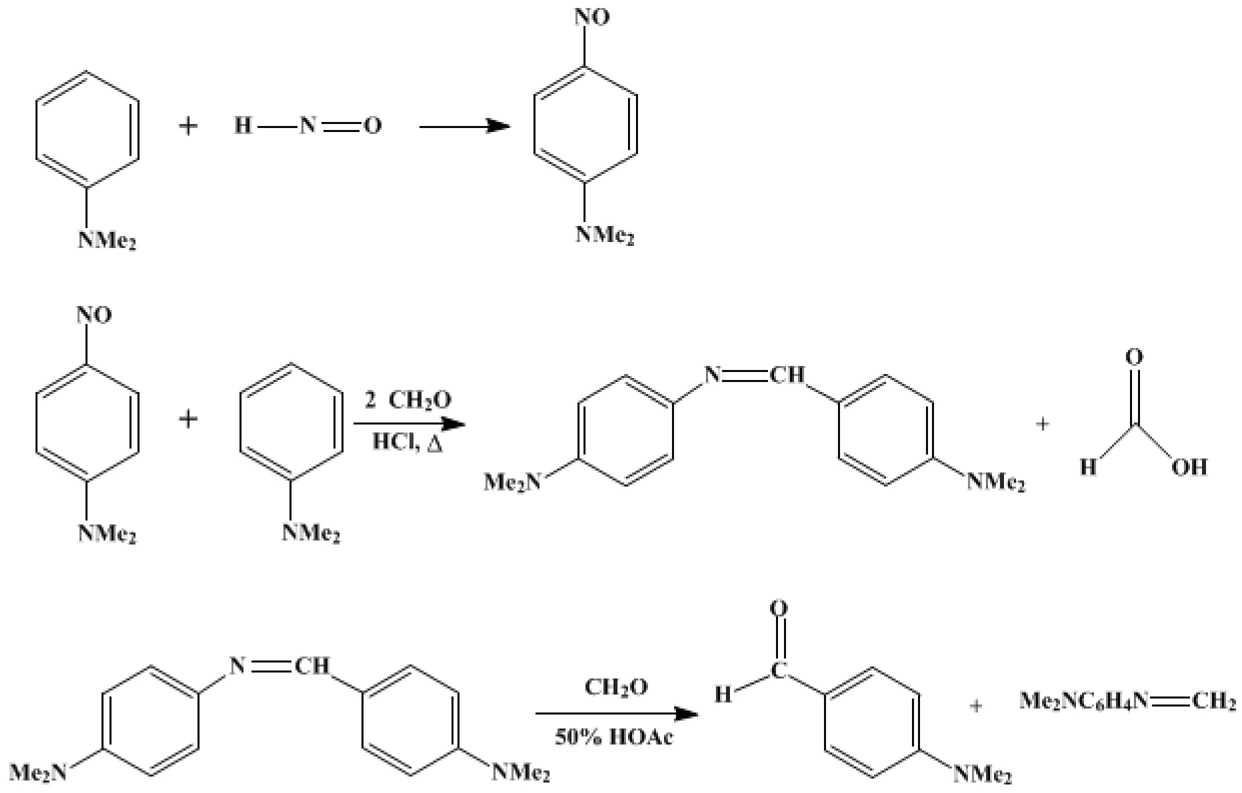
p-DIMETHYLAMINOBENZALDEHYDE

[Benzaldehyde, *p*-dimethylamino-]



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1. Procedure

In a 3-l. round-bottomed flask fitted with a mechanical stirrer 150 g. (1.24 moles) of technical dimethylaniline is dissolved in 750 cc. of dilute hydrochloric acid (1 part concentrated acid to 1 part water). This solution is now cooled to 0°, and a solution (previously cooled to 0°) of 90 g. (1.24 moles) of technical sodium nitrite in 150 cc. of water is added through a separatory funnel. During the addition of the nitrite solution, mechanical stirring should be employed and the flask cooled well with ice and salt, or the contents can be cooled directly by the addition of ice. The addition is made at such a rate (thirty to forty minutes) that the temperature does not rise above 5°. The precipitate of *p*-nitrosodimethylaniline hydrochloride is filtered off with suction, then washed with about 300 cc. of dilute (1:1) hydrochloric acid.

In a 2-l. beaker, 180 g. (1.5 moles) of technical dimethylaniline, 125 cc. of formaldehyde (technical 40 per cent) (see Note 1 on p. 378), and 300 cc. of concentrated hydrochloric acid are mixed and heated for ten minutes on a steam bath. The mixture is now placed in a hood and the *p*-nitrosodimethylaniline hydrochloride added all at once, or as rapidly as possible. The beaker is then covered with a watch glass. A vigorous reaction soon occurs and is complete in about five minutes. The resulting solution is transferred to a 5-l. flask and diluted to 4 l.; stirring is started, and a 25 per cent solution of sodium hydroxide is added until the red color disappears (about 650 cc. is required). The yellow benzylidene compound separates, is filtered with suction, and washed with water. The moist precipitate is transferred to a 4-l. glass jar, covered with 1 l. of 50 per cent acetic acid and 250 cc. of formaldehyde, and stirred until twenty minutes after the benzylidene compound has gone into solution. While the mixture is being stirred vigorously (Note 1) to prevent lumping of the precipitate, 400 cc. of water and 200 g. of cracked ice are added during the course of five minutes. The dimethylaminobenzaldehyde generally separates gradually in fifteen to twenty minutes, but in some cases does not. If the precipitate does not form, the solution is placed in a refrigerator for a few hours or overnight. The mixture is filtered with suction and washed at least ten times with 300-cc. portions of water (Note 2). The precipitate is sucked as dry as possible for fifteen to thirty minutes (Note 3).

The slightly moist aldehyde is distilled under diminished pressure from an oil bath, by means of a 1-l. Claisen flask (Note 4). A small amount of water comes over first, then the thermometer rises rapidly to the boiling point of the aldehyde (180°/22 mm.). In changing receivers between the water fraction and the aldehyde, care should be taken to keep the side arm of the distilling flask warm; otherwise, on starting the distillation again, the aldehyde will solidify in the side arm and cause trouble. It is advisable not to collect the very last portion of the distillate with the main portion, as the former is frequently quite red. This is best added to crude material from another run. The main distillate is dissolved in 100 cc. of alcohol in a 2-l. beaker, then 1 l. of water is gradually added with vigorous mechanical stirring to prevent lumping. The aldehyde separates, and is filtered with suction. The product, when dry, weighs 125–130 g. (56–59 per cent of the theoretical amount) and melts at 73°.

The aldehyde prepared in this way is in the form of small granular crystals, which vary in different runs from a flesh color to a lemon yellow. For practically all purposes, this slightly colored product is entirely satisfactory and is essentially pure, as can be judged by the melting point. For reagent purposes it is desirable to remove the color completely, particularly since the product obtained as just described has a tendency to take on a reddish tinge on exposure to light. Further purification can be accomplished by dissolving the aldehyde (it dissolves slowly) in dilute hydrochloric acid (1 part of concentrated acid, sp. gr. 1.19, to 6 parts of water), 125 g. of aldehyde requiring 700 cc. of the acid (Note 5). The solution is placed in a jar and diluted with half its volume of water, and dilute sodium hydroxide solution (15–20 per cent) (Note 6) is added slowly with mechanical stirring. At the beginning, the aldehyde comes down slightly colored. After about 10–30 g. are precipitated, however, the product appears white (Note 7); this point can be readily seen. The first precipitate is filtered off and added to the next run of crude material or fractionally precipitated again from hydrochloric acid (Note 2). The rest of the aldehyde is now precipitated by means of more sodium hydroxide solution, and comes down almost white. At the very end of the neutralization, particularly if the original product was quite yellow, the last 4–5 g. of aldehyde should be precipitated separately, as this is inclined to be slightly colored. If too much alkali is added towards the end of the neutralization, a brown color appears, but the addition of a little hydrochloric acid will destroy this color. The main portion of the precipitate is filtered and dried; it weighs 95–100 g. and melts at 73°. The succeeding runs yield 115–128 g. of finished product, on account of the extra crude material obtained from the distillation and reprecipitation of the previous run (Note 8).

2. Notes

1. Vigorous mechanical stirring must be employed during the precipitation of the crude aldehyde, as otherwise large lumps are formed which make washing difficult.
2. Thorough washing of the crude aldehyde is particularly desirable, as it removes a reddish impurity which tends to distil over and color the product lemon yellow or sometimes even brownish yellow. When such a brownish product is obtained, it is quite necessary to make a second precipitation later, as well as to observe the directions mentioned in the purification of the crude aldehyde, namely, to precipitate the first few grams and the last few grams of the aldehyde separately. The precaution of rejecting the first and last portions of the precipitate is unnecessary in the reprecipitation. In the reprecipitation of a deeply colored product, the portion of aldehyde at the end may be even purplish in color, and particular care must be taken to keep this separate.
3. A previous investigator has mentioned that the crude product must be dried before distilling. This, however, is unnecessary.
4. If the aldehyde is dried before distilling, a 500-cc. distilling flask may be used.
5. In purifying the aldehyde by dissolving in acid and reprecipitating, it is essential not to use stronger acid than that specified (1:6), as stronger acid causes a deepening of the color of the solution. If the concentrated acid, which is to be diluted and used in this procedure, does not have a sp. gr. of 1.19, it

will be necessary to add the equivalent amount of weaker acid in order to dissolve the *p*-dimethylaminobenzaldehyde.
6. Sodium carbonate may be used in place of sodium hydroxide for precipitation, but it causes much foaming.
7. The aldehyde that is obtained without reprecipitation gradually takes on a pinkish tinge on exposure to light. After the reprecipitation, however, this characteristic disappears.
8. When the apparatus for distilling, etc., is all set up, a run such as described requires about five to six hours for completion.

3. Discussion

The most satisfactory method for the preparation of *p*-dimethylaminobenzaldehyde is the condensation of dimethylaniline, formaldehyde and *p*-nitrosodimethylaniline, followed by hydrolysis,[1] a method for which details have been perfected.[2]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 331

References and Notes

1. Ullmann and Frey, Ber. **37**, 858 (1904).
2. Ingvaldsen and Bauman, J. Biol. Chem. **41**, 146 (1920).

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

acid

alcohol (64-17-5)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

sodium hydroxide (1310-73-2)

formaldehyde (50-00-0)

sodium carbonate (497-19-8)

sodium nitrite (7632-00-0)

dimethylaniline (121-69-7)

benzylidene

dimethylaminobenzaldehyde

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

p-Nitrosodimethylaniline hydrochloride (42344-05-8)

p-nitrosodimethylaniline (138-89-6)