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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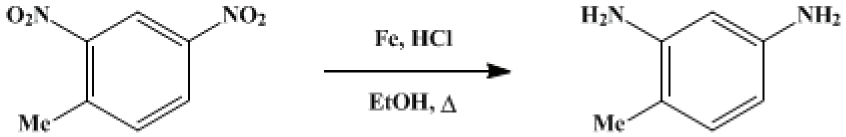
2,4-DIAMINOTOLUENE

[2,4-Toluenediamine]



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1. Procedure

In a 500-cc. three-necked flask, fitted with a reflux condenser and a mechanical stirrer (Note 1), are placed 45.5 g. (0.25 mole) of 2,4-dinitrotoluene (Note 2), 85 g. (1.5 moles) of iron (Note 3), and 100 cc. of 50 per cent (by weight) ethyl alcohol (Note 4). The mixture is heated to boiling on a water bath, the stirrer is started (Note 5), and a solution of 5.2 cc. (0.06 mole) of concentrated hydrochloric acid in 25 cc. of 50 per cent (by weight) ethyl alcohol is added slowly (Note 6). The mixture is refluxed for two hours after addition of the acid is complete. At the end of this time the apparatus is disconnected and the hot mixture is made just alkaline to litmus by the addition of the calculated amount of 15 per cent alcoholic potassium hydroxide solution (Note 7). Without allowing the mixture to cool, the iron is removed by filtration and the reaction flask is rinsed with two 50-cc. portions of 95 per cent ethyl alcohol; the same alcohol is used to wash the iron residue. To the filtrate is added 84 cc. of 6 *N* sulfuric acid; the normal sulfate of 2,4-diaminotoluene precipitates. The mixture is cooled to 25° and filtered by suction. The product is washed with two 25-cc. portions of 95 per cent ethyl alcohol, dried in the air for two hours (Note 8) and then dried to constant weight at 110°. The yield is 49 g. (89 per cent of the theoretical amount) of a product which melts with decomposition at 249–251° (Note 9).

A solution of 20 g. of 2,4-diaminotoluene sulfate in 200 cc. of water at 60° is cooled to 40° (Note 10), and made alkaline to litmus with saturated sodium hydroxide solution (Note 11). To this solution is added 15 g. of the sulfate, which is dissolved by raising the temperature of the mixture to 55°. The solution is cooled to 40° and made slightly alkaline to litmus with saturated sodium hydroxide solution. The mixture is then cooled to 30° and filtered by suction. The remainder of the diaminotoluene sulfate (14 g.) is then dissolved in the filtrate by heating the mixture to 55°. The solution is cooled to 40° and again made alkaline to litmus with saturated sodium hydroxide solution. The mixture is cooled to 25°, and the diaminotoluene crystals are collected on a Büchner funnel. The entire product is dried to constant weight in a desiccator over calcium chloride. The yield is 26.5 g. (95 per cent of the theoretical amount based on the diaminotoluene sulfate used) of a product melting at 97–98.5°.

The crude diaminotoluene (Note 12) is dissolved in eight times its weight of benzene (212 g.) at 70°, and the solution is filtered quickly through a hot Büchner funnel (Note 13) with moderate suction (Note 14). The filtrate is cooled to 25°, and the mother liquor is decanted from the brown crystals. The mother liquor is concentrated to a volume of 25 cc. by distillation under atmospheric pressure and then cooled to 25°. The mother liquor is decanted from the diaminotoluene, and the entire product is dried in the air. The yield is 22.5 g. (81 per cent of the theoretical amount based on the diaminotoluene sulfate used; 74 per cent based on the dinitrotoluene used) of a product which melts at 98° (Note 15).

2. Notes

1. The mechanical stirrer should extend well to the bottom of the flask in order to prevent caking of the iron during the reduction.
2. The 2,4-dinitrotoluene used must be free from oil and have the correct melting point of 71°.
3. The iron used may be either iron powder or iron filings, but it should pass a 100-mesh sieve in order to give invariable results. If iron particles of larger size are used the reduction may be incomplete,

although complete reduction was obtained with a sample of iron powder contaminated with filings.

4. The concentration of the alcoholic solution is important. Incomplete reduction was obtained with 95 per cent alcohol, as well as with methylated spirit, as suggested by West.[1] Complete reduction may be obtained in aqueous solution, but the product is difficult to isolate and is not always pure.

5. The stirrer should be run at such a speed that the iron particles do not settle or the iron will cake during the reduction. A speed of about 750 r.p.m. is satisfactory.

6. The reaction between the iron and hydrochloric acid is very vigorous, especially with iron powder, and the hydrochloric acid must be added very slowly at first. About one drop every ten seconds for the first ten minutes is satisfactory, and this may be increased to one drop every four seconds after this length of time has elapsed. The addition of the hydrochloric acid should require about thirty minutes.

7. The exact amount of alcoholic potassium hydroxide is determined previously by titration of a separate sample of 5.2 cc. of concentrated hydrochloric acid with the alcoholic potassium hydroxide.

8. Most of the alcohol and any aldehyde must be removed by evaporation at room temperature since heating the wet product at once to 110° always causes the formation of orange-colored impurities.

9. The same percentage yields of the sulfate were obtained using six times the amounts of materials.

10. The solution is cooled before addition of the alkali, as this is accompanied by a rise in temperature.

11. Saturated sodium hydroxide solution is used rather than more dilute solutions since dilution of the diaminotoluene solution is to be avoided as much as possible.

12. The diaminotoluene obtained by neutralizing the sulfate contains varying amounts of sodium sulfate and possibly some diaminotoluene sulfate, both of which are insoluble in benzene.

13. A hot Büchner funnel (70° or above) is used to prevent crystallization of the diaminotoluene in the funnel.

14. Moderate suction is used to prevent boiling of the benzene since this causes crystallization of the diaminotoluene in the funnel.

15. In an attempt to prepare a pure white product, the dry recrystallized material was distilled rapidly at atmospheric pressure using a short air condenser. A yellow product distilling at 292° was obtained. On distilling the recrystallized material at 148–150°/8 mm., a white product was obtained.

3. Discussion

2,4-Diaminotoluene has been prepared by reduction of 2,4-dinitrotoluene with iron and acetic acid,[2] electrolytically,[3] or with hydrogen and Raney nickel;[4] and by reduction of 4-nitro-*o*-toluidine[5] or 2,4-dinitrobenzoyl chloride[6] with tin and hydrochloric acid.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 63

References and Notes

1. West, J. Chem. Soc. **127**, 494 (1925).
2. Hofmann, Jahresber. **1861**, 512.
3. Hofer and Jakob, Ber. **41**, 3192 (1908).
4. Albert and Ritchie, J. Proc. Roy. Soc. N. S. Wales **74**, 74 (1940) [C. A. **34**, 7286 (1940)].
5. Nölting and Collin, Ber. **17**, 268 (1884).
6. Krasusky, J. Russ. Chem. Soc. **27**, 337 (1896) [Bull. soc. chim. (3) **16**, 370 (1896)].

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

ethyl alcohol,

alcohol (64-17-5)

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

Benzene (71-43-2)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

iron,
iron filings,
iron powder (7439-89-6)

sodium sulfate (7757-82-6)

tin (7440-31-5)

Raney nickel (7440-02-0)

potassium hydroxide (1310-58-3)

4-nitro-o-toluidine (99-52-5)

2,4-Diaminotoluene,
2,4-Toluenediamine,
diaminotoluene (95-80-7)

2,4-dinitrotoluene,
dinitrotoluene (121-14-2)

2,4-diaminotoluene sulfate,
diaminotoluene sulfate

2,4-dinitrobenzoyl chloride

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