



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.

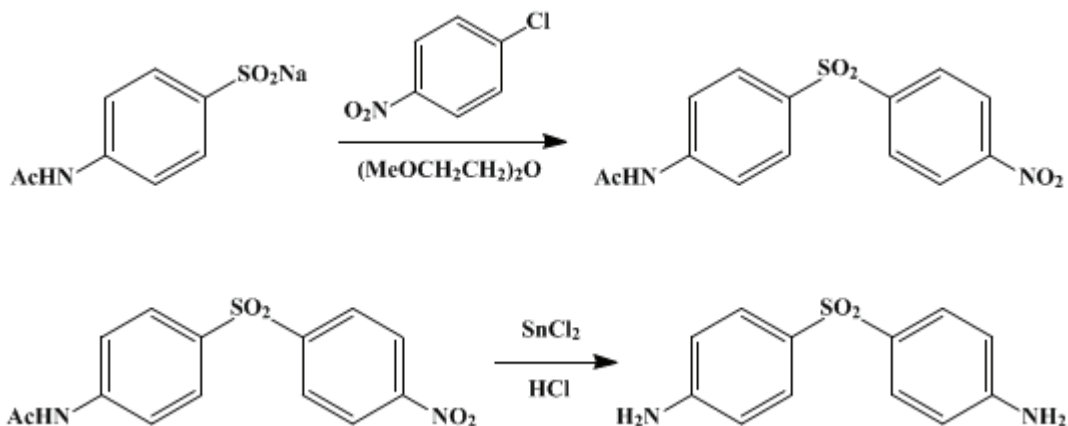
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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4,4'-DIAMINODIPHENYLSULFONE

[Aniline, 4,4'-sulfonylbis-]



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1. Procedure

In a 1-l. beaker on a steam bath, 155 g. (0.78 mole) of *p*-acetaminobenzenesulfinic acid is suspended in 310 ml. of water. The suspension is stirred by hand and warmed gently while it is neutralized by the addition of a solution of 31.5 g. of sodium hydroxide in 125 ml. of water (Note 1). The solution is then transferred to a 2-l. flask and the bulk of the water is removed under the vacuum of a good water pump; 330–350 ml. of water is removed during 1.5 hours. During this time, the solid salt begins to separate. When bumping becomes severe, the flask is cooled by immersion in an ice bath for 30 minutes, and the salt is filtered with suction. The filtrate is concentrated as before, the product being added to the first crop. The second filtrate, on concentration, yields a less pure salt which may be worked up separately. The yields are 107–124 g. (63–73%) of the first crop, 25–34 g. (15–20%) of the second crop, and 12–17 g. (7–10%) of material of inferior grade.

In a 500-ml. three-necked round-bottomed flask fitted with a reflux condenser, a mechanical stirrer, and a thermometer are placed 48.5 g. (0.22 mole) of the sodium sulfinate and 60 ml. of a mixture of 75 ml. of ethylene glycol and 120 ml. of carbitol or methyl carbitol. The mixture is stirred and heated in an oil bath until solution is complete, after which 31.5 g. (0.2 mole) of 4-chloronitrobenzene (m.p. 76–78°) is added. The mixture is heated for 3.5 hours at 141–143° (thermometer in the mixture), with continued stirring, and then is allowed to cool overnight. After the addition of 20 ml. of water, the pasty lumps are broken up, and the solid is filtered with suction and washed with 50–75 ml. of hot water. The solid is then transferred to a 1-l. flask and refluxed with 250 ml. of 95% ethanol for 15 minutes. After cooling, the *p*-nitro-*p*'-acetylamino-diphenylsulfone is filtered with suction and washed on the funnel, first with 25 ml. of ethanol and then with 25 ml. of ether. After drying in the air, the tan-colored solid weighs 32–33 g. (50–52%) and melts at 226–228° (Note 2).

To a solution of 300 g. of stannous chloride dihydrate in 300 ml. of concentrated hydrochloric acid (sp. gr. 1.19) in a 1-l. beaker there is added 96 g. of the sulfone, and the mixture is stirred occasionally. Evolution of heat is sufficiently great so that, after 10–15 minutes, external cooling is necessary to prevent violent boiling with possible loss of material (Note 3). After nearly all the solid has dissolved, the mixture is heated on the steam bath for 2 hours. The solution is then cooled and added to 1.35 l. of 40% sodium hydroxide solution contained in a 3-l. beaker; it is necessary to stir mechanically and to add about 1.5 kg. of ice during the operation. The final temperature should be about 10°. After standing for 30 minutes the crude amine is filtered with suction (Note 4) and washed with water (200–250 ml.) until free from alkali.

The amine is recrystallized by dissolving it in 250 ml. of 95% [ethanol](#), boiling a few minutes with 5 g. of Norit, and filtering. The clear filtrate is either concentrated to a small volume or is diluted by the addition of 200–250 ml. of water ([Note 5](#)) and allowed to stand overnight in the icebox. The crystalline amine (m.p. 176°) is then filtered and air-dried. The yield is 55–57 g. (74–77%) ([Note 6](#)).

2. Notes

1. Frequently the solution develops a blue color. If this persists, a little additional [sodium hydroxide](#) solution is required.
2. The yield (per cent) is the same if twice the amounts given are used. It is convenient to combine several runs for the reduction.
3. Sometimes the reduction does not start readily. In this event the beaker may be cautiously heated, but provision for rapid cooling should be made.
4. Filtration is facilitated by use of a Pyrex glass or Vinyon filter fabric; a 30-cm. funnel is advisable.
5. A part of the amine usually crystallizes during the filtration. It is dissolved by warming, after which water is added until the solution is just cloudy.
6. If the melting point is low, a second recrystallization is needed.

3. Discussion

[4,4'-Diaminodiphenylsulfone](#) and/or [4,4'-diacetylamino](#)diphenylsulfone have been prepared by various procedures, starting with [4,4'-dinitrodiphenylsulfide](#);¹ or [4,4'-dichlorodiphenylsulfone](#).^{2,3} It has also been made from a sulfinic acid and a halonitrobenzene;⁴ from [4-acetylamino](#)benzenesulfonyl chloride and [acetanilide](#);⁵ from [acetanilide](#) and [thionyl chloride](#);⁶ from [4-nitro-4'-aminodiphenylsulfide](#);⁷ and by acetylation of [thioaniline](#) ([4,4'-diaminodiphenylsulfide](#)) followed by [hydrogen peroxide](#) oxidation.⁸ The [4,4'-diacetylamino](#)diphenylsulfone obtained by any of these procedures is readily deacetylated.^{7,8} A method somewhat similar to the one described above has been patented.⁹

References and Notes

1. Fromm and Wittmann, *Ber.*, **41**, 2270 (1908).
2. I. G. Farbenind. A-G., Brit. pat. 506,227 [*C. A.*, **33**, 9328 (1939)].
3. I. G. Farbenind. A-G., Fr. pat. 829,926 [*C. A.*, **33**, 1760 (1939)].
4. Schering A-G., Brit. pat. 510,127 [*C. A.*, **34**, 4079 (1940)].
5. Kereszty and Wolf, Hung. pat. 120,021 [*C. A.*, **33**, 4600 (1939)].
6. Sugasawa and Sakurai, *J. Pharm. Soc. Japan*, **60**, 22 (1940 [*C. A.*, **34**, 3704 (1940)]).
7. Raiziss, Clemence, Severac, and Moetsch, *J. Am. Chem. Soc.*, **61**, 2763 (1939).
8. Van Arendonk and Kleiderer, *J. Am. Chem. Soc.*, **62**, 3521 (1940).
9. Roblyn and Williams, U. S. pat. 2,227,400 [*C. A.*, **35**, 2531 (1941)].

Appendix

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

[carbitol](#) or methyl [carbitol](#)

[4,4'-diacetylamino](#)diphenylsulfone

[ethanol](#) (64-17-5)

[hydrochloric acid](#) (7647-01-0)

ether (60-29-7)

Acetanilide (103-84-4)

sodium hydroxide (1310-73-2)

4-acetylamino benzenesulfonyl chloride (121-60-8)

thionyl chloride (7719-09-7)

sulfone (7446-09-5)

ethylene glycol (107-21-1)

hydrogen peroxide (7722-84-1)

stannous chloride dihydrate (10025-69-1)

sodium sulfinate

4-chloronitrobenzene (100-00-5)

thioaniline

p-Acetaminobenzenesulfinic acid (710-24-7)

4,4'-dinitrodiphenylsulfide (1223-31-0)

4,4'-DIAMINODIPHENYLSULFONE,
Aniline, 4,4'-sulfonylbis- (80-08-0)

p-nitro-p'-acetylamino diphenylsulfone (1775-37-7)

4,4'-dichlorodiphenylsulfone

4-nitro-4'-aminodiphenylsulfide