



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.

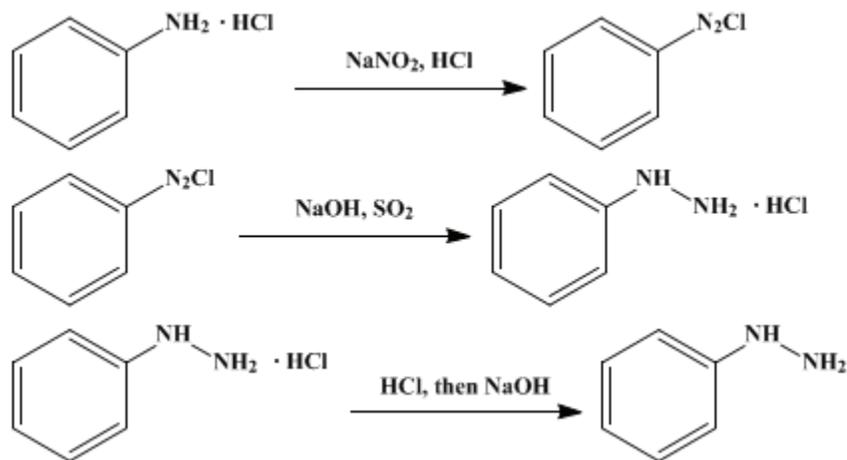
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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. 1, p.442 (1941); Vol. 2, p.71 (1922).

PHENYLHYDRAZINE

[Hydrazine, phenyl-]



Submitted by G. H. Coleman

Checked by J. B. Conant and H. R. Thompson.

1. Procedure

In a 12-l. round-bottomed flask, fitted with a mechanical stirrer, is placed 1045 cc. of concentrated commercial [hydrochloric acid](#) (sp. gr. 1.138). The flask is surrounded with a freezing mixture of ice and salt, and, when the contents are at 0° , stirring is started and 500 g. of cracked ice is added, or more ice can be added and the external cooling dispensed with; then 372 g. (364 cc., 4 moles) of [aniline](#), also cooled to 0° , is run in during five minutes. The mixture is treated with 500 g. more of cracked ice, and a cold solution (0°) of 290 g. (4 moles) of technical [sodium nitrite](#) dissolved in 600 cc. of water is allowed to run in slowly (twenty to thirty minutes) from a separatory funnel, the end of which is drawn to a small tip and reaches nearly to the bottom of the flask. During this addition, the stirrer is operated rather vigorously, and the temperature is kept as near 0° as possible by the frequent addition of cracked ice (about 1 kg.).

In the meantime, a [sodium sulfite](#) solution is prepared by dissolving 890 g. (20 moles) of [sodium hydroxide](#), of about 90 per cent purity, in about 1 l. of water and then diluting to 6 l. A few drops of [phenolphthalein](#) solution are added and [sulfur dioxide](#) passed in, first until an acid reaction is indicated and then for two or three minutes longer. During the addition of the [sulfur dioxide](#), the solution is cooled with running water. On account of the strong alkaline solution, the original color produced by the [phenolphthalein](#) is very faint, but this slowly increases until it becomes deep just before the acid point is reached. It is best to remove a small sample of the liquid from time to time, dilute with three or four volumes of water, and add a drop more of [phenolphthalein](#) ([Note 1](#)).

The [sodium sulfite](#) solution is placed in a 12-l. flask and cooled to about 5° . Approximately 500 g. of cracked ice is added, and then, with mechanical stirring, the diazonium salt solution is run in as rapidly as possible ([Note 2](#)). The mixture becomes a bright orange-red. The flask is now warmed to about 20° on a steam bath, until the solid [sodium sulfite](#), which has separated while cooling, redissolves. The total amount of liquid is now about 10 l. One-half of this is poured into another 12-l. flask, and both halves are warmed on the steam bath to $60\text{--}70^\circ$, until the color becomes quite dark (thirty to sixty minutes). Sufficient [hydrochloric acid](#) (300–400 cc.) is now added ([Note 3](#)) to each flask to make the solutions acid to litmus. The heating is continued and the color gradually becomes lighter until, after four to six hours, the solutions have become nearly colorless; they may be heated overnight, if desired.

To the hot solutions is now added about one-third of their volume of concentrated [hydrochloric acid](#)

(2 l. to each portion), and the mixtures are cooled, first in running water, then in a freezing mixture, to 0° (Note 4). The phenylhydrazine hydrochloride precipitates in the form of slightly yellowish or pinkish crystals which may be filtered off and dried (Note 5).

The free base is liberated by adding to the phenylhydrazine hydrochloride 1 l. of a 25 per cent solution of sodium hydroxide. The phenylhydrazine separates and is taken up with benzene (two 300-cc. portions). The combined extractions are well dried with 200 g. of solid sodium hydroxide (Note 6), poured off, and distilled. Most of the benzene may be distilled under ordinary pressure, and the remainder, and any low-boiling impurities, under diminished pressure. The pure phenylhydrazine boils at 137–138°/18 mm., and is obtained as a pale yellow liquid (Note 7). It can be crystallized on cooling in an ice bath; the crystals melt at 23°. The crude phenylhydrazine from two lots of aniline (744 g.) is best distilled at one time and gives 695–725 g. of pure product (80–84 per cent of the theoretical amount).

2. Notes

1. If the sodium sulfite solution contains an excess of alkali, a black tar tends to form when the solution is warmed, and very little phenylhydrazine is obtained. Great care must be taken in determining the end point in the neutralization of the sodium hydroxide by the sulfur dioxide.

It is best to use freshly prepared sodium sulfite for the reduction, since the commercial quality is poor and gives a lower yield of phenylhydrazine. A cylinder of liquid sulfur dioxide should, of course, be available.

2. The rapid addition of the diazonium salt solution to the sodium sulfite seems to be advantageous.

3. If the sodium sulfite-diazonium salt mixture is acidified before warming or before becoming dark, the red color of the solution does not disappear on heating, and the precipitated phenylhydrazine hydrochloride obtained is colored red.

Most published directions for the preparation of phenylhydrazine specify the use of zinc dust and acetic acid following the reduction with sodium sulfite. No improvement in the quality or quantity of the product was obtained by using zinc and acetic acid.

4. In order to obtain the maximum yield, it is necessary to cool the hydrochloric acid solution of the phenylhydrazine hydrochloride from 20° to 0°, before filtration. From 5 to 10 per cent of product separates between these two temperatures. When this is done, no more phenylhydrazine hydrochloride is obtained by concentration of the mother liquor. An increase in the amount of hydrochloric acid above 2 l. for the precipitation of the hydrochloride produces no increase in yield of product.

5. The phenylhydrazine hydrochloride may be purified by crystallizing from water. A 600-cc. portion of water is used for 100 g. of crude hydrochloride, and the solution boiled a short time with a few grams of animal charcoal. After filtering, 200 cc. of concentrated hydrochloric acid is added, and the mixture cooled to 0°. Pure white crystals in a yield of 85–90 g. are obtained.

6. The benzene solution of phenylhydrazine should be well dried before distilling, since the presence of moisture causes an increased amount of foaming to take place just after the benzene has distilled off. When the distillation is carried out carefully, practically no phenylhydrazine distills with the benzene or other low-boiling impurities.

Care should be taken that the free base contains no trace of hydrochloride, for this compound catalyzes the decomposition of phenylhydrazine above 100°.

7. Pure phenylhydrazine dissolves in dilute acetic acid to yield a perfectly clear solution.

Care should be taken when working with large quantities of phenylhydrazine, since the product may cause serious injury to the skin. The vapors of phenylhydrazine should not be inhaled.

3. Discussion

Phenylhydrazine can be prepared by the reduction of benzenediazonium salts by means of a miscellany of reducing agents, of which sodium sulfite¹ is preferred. Although this method is given in several laboratory manuals, the results were not found entirely satisfactory. The present directions provide for a lengthy but essential heating of the diazonium-sulfite mixture, omit the useless zinc dust reduction, and supply exact details for preparation on a fairly large laboratory scale. The electrolytic reduction of benzenediazonium salts has been reported to furnish a quantitative yield of phenylhydrazine.²

References and Notes

1. Fischer, Ann. **190**, 79 (1878); Reychler, Ber. **20**, 2463 (1887). Thompson, J. Soc. Dyers Colourists **37**, 7 (1921) [C. A. **15**, 1513 (1921)].
 2. Takayanagi, J. Chem. Soc. Japan **53**, 427 (1932) [C. A. **27**, 233 (1933)].
-

Appendix

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

sodium sulfite-diazonium salt

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

Benzene (71-43-2)

aniline (62-53-3)

sodium sulfite (7757-83-7)

sodium hydroxide (1310-73-2)

sulfur dioxide (7446-09-5)

sodium nitrite (7632-00-0)

Phenylhydrazine,
Hydrazine, phenyl- (100-63-0)

zinc (7440-66-6)

phenolphthalein (77-09-8)

phenylhydrazine hydrochloride (59-88-1)