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.

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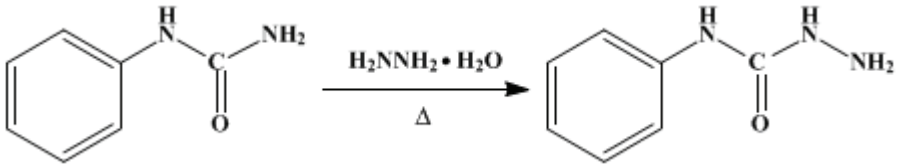
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.006.0074

Organic Syntheses, Coll. Vol. 1, p.450 (1941); Vol. 6, p.74 (1926).

4-PHENYLSEMICARBAZIDE

[Semicarbazide, 4-phenyl-]



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1. Procedure

In a 500-cc. round-bottomed flask fitted with a reflux condenser are placed 68 g. of phenylurea (0.5 mole) (Note 1) and 120 cc. (1 mole) of 42 per cent hydrazine hydrate solution (Note 2). The flask is heated on a steam bath for about twelve hours. The hot mixture is treated with a small amount of decolorizing charcoal (Norite) and filtered. The charcoal is washed with two 15-cc. portions of warm water, and the filtrate and washings are then concentrated on a steam bath to about 100 cc. On cooling in an ice bath a crop of crystals separates which is collected on a filter and washed with two 15-cc. portions of cold water. The filtrate and washings are concentrated to about 25 cc., and another crop of crystals is obtained as before. The total yield of crude compound is 47–52 g. It is white at first but sometimes turns brown on drying. It usually melts below 115° because of some unchanged phenylurea.

The product is purified (Note 3) by conversion to the hydrochloride, which is then changed into the free base.

A filtered solution of the crude product in 200 cc. of hot absolute alcohol is treated with 250 cc. of concentrated hydrochloric acid. Most of the hydrochloride precipitates at once and is filtered, washed with alcohol, and dried. The filtrate is cooled in an ice-salt bath and again filtered, and the precipitate is washed, dried, and added to the previous portion. The yield is 46–48 g. of material melting at about 215° (Note 4). The hydrochloride is dissolved in three times its weight of water, previously heated nearly to boiling (Note 5). The solution is filtered if necessary and then treated with sodium hydroxide solution (2.2 g. of 10 per cent sodium hydroxide solution for each gram of hydrochloride used). The free base separates at once, and the solution is cooled in an ice bath and filtered. This product melts at 120–123°. The yield of pure base is 28–30 g. (37–40 per cent of the theoretical amount) (Note 6).

2. Notes

1. The phenylurea was prepared as described on p. 453 and melted at 146–147°.
2. An equivalent amount of hydrazine sulfate (p. 309) and sodium hydroxide in 80 per cent alcohol may be used in place of the hydrazine hydrate solution without greatly diminishing the yield.
3. The crude product contains about 9–10 g. of unchanged phenylurea which cannot be satisfactorily removed by crystallization from benzene or water. When the hydrochloride of the phenylsemicarbazide is formed, the phenylurea may be recovered from the alcoholic filtrates.
4. Inasmuch as the melting point of the salt varies somewhat with the rate of heating, this temperature is not particularly significant.
5. The salt should not be boiled with water any longer than is necessary, as some decomposition occurs, and diphenylurea, melting at about 235–240°, is produced.
6. It is suggested that an improved yield is obtainable by heating 34 g. of phenylurea, 25 cc. of 100 per cent hydrazine hydrate, and 25 cc. of absolute alcohol for twenty-four hours on a steam bath. This procedure would eliminate the need of purification by passing through the hydrochloride and back to the base (A. S. Wheeler, private communication).

3. Discussion

4-Phenylsemicarbazide can be prepared by the action of hydrazine hydrate on phenylurea;[1] and by hydrolysis of benzal-4-phenylsemicarbazone[2] and of α-benzoyl β-phenylcarbamyl hydrazine.[3]

References and Notes

1. Curtius, J. prakt. Chem. (2) **58**, 216 (1898).
2. Curtius and Hofmann, ibid. (2) **53**, 526 (1896).
3. Bailey and McPherson, J. Am. Chem. Soc. **39**, 1333 (1917).

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

benzal-4-phenylsemicarbazone

α-benzoyl β-phenylcarbamyl hydrazine

alcohol (64-17-5)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

sodium hydroxide (1310-73-2)

hydrazine hydrate (7803-57-8)

Hydrazine sulfate (10034-93-2)

4-PHENYLSEMICARBAZIDE,
Semicarbazide, 4-phenyl- (537-47-3)

Phenylurea (64-10-8)

phenylsemicarbazide (103-03-7)

diphenylurea (603-54-3)