



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](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.

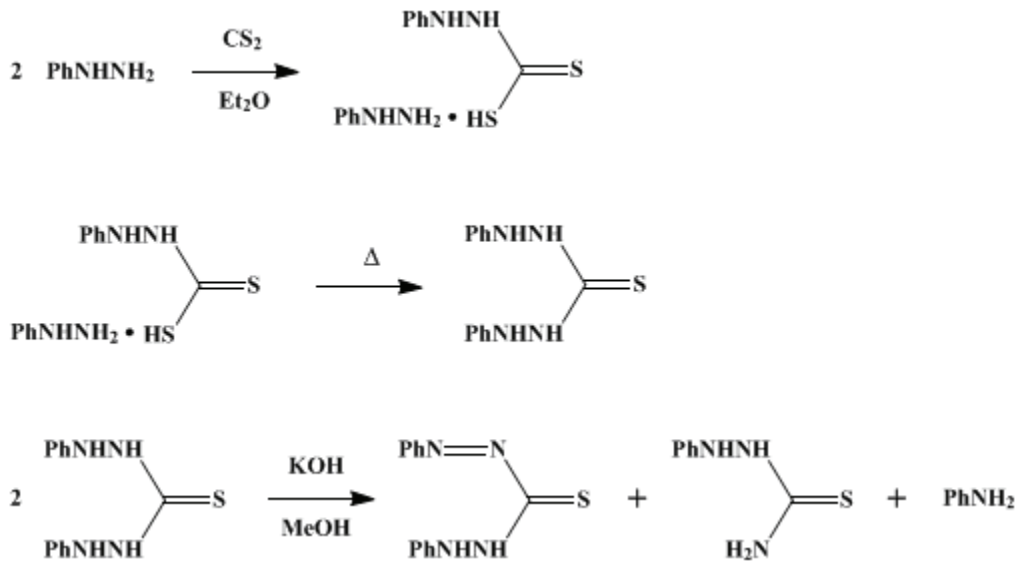
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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## DITHIZONE



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### 1. Procedure

A. *Phenylhydrazine salt of  $\beta$ -phenyldithiocarbamic acid.* In a 1-l. three-necked flask, fitted with a mechanical stirrer, a condenser, and a dropping funnel, is placed a solution of 128 ml. (1.3 moles) of pure redistilled phenylhydrazine in 600 ml. of ordinary ether. To the vigorously stirred mixture, 52 ml. (0.86 mole) of carbon disulfide is added in the course of 30 minutes (Note 1). After the mixture has been stirred for an additional 30 minutes, the precipitate is filtered with suction, washed with 50 ml. of ether, and spread on filter paper for 15–20 minutes to allow evaporation of the ether. The yield of the salt is 181–185 g. (96–98%).

B. *Diphenylthiocarbazide.* The above salt is transferred to a 1-l. beaker, and, while it is continuously stirred by hand (Note 2), it is heated (hood) in a water bath maintained at 96–98° (Note 3). After about 10–15 minutes the material softens to a taffylike mass, becomes yellow, foams, and evolves hydrogen sulfide. After about 20–30 minutes ammonia is evolved. When a distinct odor of ammonia is first detected (Note 4), the beaker is removed from the bath, placed in a pan of cold water for 1 minute (Note 5), and then surrounded immediately by cracked ice. About 150 ml. of absolute ethanol is added, the mixture is warmed slightly to loosen the mass, and the taffylike material is stirred until it is transformed into a granular precipitate. After the mixture has stood at room temperature for 1 hour, the precipitate is collected on a Büchner funnel and washed with 50 ml. of absolute ethanol (Note 6). The yield of crude diphenylthiocarbazide is 100–125 g. (60–75% based on phenylhydrazine) (Note 7).

C. *Dithizone.* The crude diphenylthiocarbazide is added to a solution of 60 g. of potassium hydroxide in 600 ml. of methanol in a 1-l. round-bottomed flask. The flask is immersed in a boiling water bath, and the mixture is refluxed for exactly 5 minutes (Note 8). The red solution is cooled with ice water and filtered by gravity. Ice-cold 1 N sulfuric acid (900–1100 ml.) is added to the filtrate, which is stirred vigorously by means of a mechanical stirrer, until the solution is just acid to Congo red paper (Note 9). The blue-black precipitate is filtered with suction and washed with 50 ml. of cold water (Note 10). The crude carbazone is dissolved in 500 ml. of 5% sodium hydroxide solution, the mixture is filtered with suction, and the filtrate is cooled in an ice bath and acidified immediately with ice-cold 1 N sulfuric acid (about 650 ml. is required) until it is just acid to Congo red paper. The precipitate is filtered with suction and then washed by transferring it to a 2-l. beaker and stirring it thoroughly with 1.6–1.8 l. of cold water. The mixture is filtered, and the process of washing is repeated until there is no trace of

sulfate in the washings (Note 11). After air has been drawn through the precipitate on the Büchner funnel for 20–30 minutes, the solid is dried in an oven at 40°. The product at this stage weighs 63–85 g. For purification, a portion of 5–10 g. of the carbazone is placed in the thimble of a Soxhlet extractor (Note 12), covered with ether, allowed to stand for 1 hour, and then extracted for 1.5 hours. The material in the thimble is transferred immediately to a beaker, stirred with 50 ml. of ether, and the mixture is filtered with suction until most, but not all, of the liquid is removed. The wet product is then dried by pressing it between filter papers. The yield of pure dithizone (diphenylthiocarbazon) which decomposes sharply at a temperature between 165° and 169° is 43–54.8 g. (50–64% based on phenylhydrazine) (Note 13).

## 2. Notes

1. A precipitate is formed immediately upon addition of the carbon disulfide; the mixture becomes warm, and the temperature soon approaches the boiling point. The temperature is maintained just below the boiling point; cooling with ice water may be necessary to keep it there. As the carbon disulfide is added, the mixture soon becomes pasty, then more fluid, and finally pasty again.
2. A heavy glass rod, bent or flattened at the bottom, serves as an efficient stirrer.
3. Care must be taken that the temperature of the bath does not exceed 98°. If the material remains above 98° for a long period of time and/or if it is not immediately cooled after removal from the water bath, the product decomposes violently after standing for 10–15 minutes.
4. Ammonia can be detected by means of litmus paper before the odor is noticeable, but the heating should be continued until there is a distinct odor of ammonia (but no longer). The yield depends upon the rapidity with which the heating is stopped after the first sign of ammonia is detected.
5. The mass may be olive-green or brown while hot, but it becomes light brown on cooling.
6. The precipitate is almost pure white. More diphenylthiocarbazide crystallizes from the red alcoholic filtrate and washings, if they are allowed to evaporate slowly. When the mixture is allowed to stand for some time before it is filtered, the amount of precipitate is increased and that of the material left in the filtrate is decreased.
7. Diphenylthiocarbazide does not have a sharp melting point. The compound is reported to become green at 130° and melt at 150° to a dark green liquid which decomposes on further heating.
8. The solution is heated until it is definitely boiling; then it is allowed to boil for 5 minutes only. If the solution is boiled for a longer time, the yield of product is decreased.
9. When the end point is reached, the mother liquor is no longer red but colorless.
10. Care should be exercised in handling this precipitate or suspensions of it. If any of it is spilled or splashed, it should be removed at once, for it dries to a light, fine powder which is readily scattered; it dyes the skin black and other material pink.
11. Four or five washings are usually necessary.
12. The Soxhlet extractor used by the submitters had a capacity of 85 ml. to the top of the siphon tube. The size of the thimble was 33 by 80 mm.
13. The pure compound is completely soluble in chloroform.

## 3. Discussion

This method of preparation is a modification of the method used by Emil Fischer.<sup>1</sup> Similar methods have been described by H. Fischer,<sup>2</sup> Wertheim,<sup>3</sup> and Grummitt and Stickle.<sup>4</sup>

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## References and Notes

1. E. Fischer, *Ann.*, **190**, 118 (1878); **212**, 316 (1882).
  2. H. Fischer and Leopoldi, *Wiss. Veröffentl. Siemens-Konzern*, **12**, 44 (1933) [*C. A.*, **27**, 3418 (1933)].
  3. Wertheim, *Organic Chemistry Laboratory Guide*, 2nd ed., p. 504, P. Blakiston's Son & Co.
  4. Grummitt and Stickle, *Ind. Eng. Chem., Anal. Ed.*, **14**, 953 (1942).
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**Appendix**  
**Chemical Abstracts Nomenclature (Collective Index Number);**  
**(Registry Number)**

ethanol (64-17-5)

sulfuric acid (7664-93-9)

ammonia (7664-41-7)

methanol (67-56-1)

ether (60-29-7)

sodium hydroxide (1310-73-2)

chloroform (67-66-3)

hydrogen sulfide (7783-06-4)

Phenylhydrazine (100-63-0)

potassium hydroxide (1310-58-3)

carbon disulfide (75-15-0)

Dithizone (60-10-6)

diphenylthiocarbazide (622-03-7)

diphenylthiocarbazone

Phenylhydrazine salt of  $\beta$ -phenyldithiocarbazic acid