



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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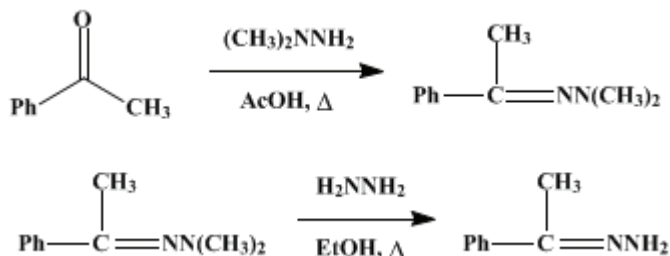
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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PREPARATION OF HYDRAZONES: ACETOPHENONE HYDRAZONE

[Ethanone, 1-phenyl-, hydrazone]



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1. Procedure

Caution! Hydrazines are toxic and should be handled in a hood. Anhydrous hydrazine is extremely reactive with oxidizing agents (including air) and should always be used behind a protective screen.

A. *Acetophenone N,N-dimethylhydrazone*. A mixture of acetophenone (12.0 g., 0.100 mole), anhydrous *N,N*-dimethylhydrazine (18.0 g., 0.300 mole) (Note 1), absolute ethanol (25 ml.), and glacial acetic acid (1 ml.) (Note 2) is heated at reflux for 24 hours. During this period the colorless solution becomes bright yellow. The volatile reactants and solvent are removed under reduced pressure and the residual oil is fractionally distilled through a 10-cm. Vigreux column, giving a small forerun of unreacted acetophenone, b.p. 30–40° (0.15 mm.), followed by 14.6–15.2 g. (90–94%) of acetophenone *N,N*-dimethylhydrazone, b.p. 55–56° (0.15 mm.), n_D^{25} 1.5443 (Note 3) and (Note 4).

B. *Acetophenone hydrazone*. A mixture of acetophenone *N,N*-dimethylhydrazone (8.1 g., 0.050 mole) and anhydrous hydrazine (6.4 g., 0.20 mole) (Note 5) in absolute ethanol (15 ml.) is heated at reflux until the reaction mixture turns colorless (Note 6). The volatile materials are removed on a rotary evaporator without allowing the flask temperature to rise above 20° (Note 7). The colorless residual acetophenone hydrazone, which solidifies as the last traces of solvent are removed, weighs 6.5–6.6 g. (97–99%) and is sufficiently pure for most purposes, m.p. 24–25° (Note 8) and (Note 9).

2. Notes

1. Anhydrous *N,N*-dimethylhydrazine obtained from Matheson, Coleman and Bell is used directly. It can also be prepared by the method in *Org. Synth., Coll. Vol. 2*, 213 (1943).
2. It is not necessary to use glacial acetic acid as a catalyst, but without it the reaction time required for completion is prolonged.
3. Physical constants previously reported:³ b.p. 100.5–102° (10 mm.), n_D^{25} 1.5455.
4. This method has been used to prepare various *N,N*-dimethylhydrazones in 70–99% yield.⁴
5. A good commercial grade of anhydrous hydrazine (Eastman Organic Chemicals) is satisfactory.
6. The reaction time for complete conversion is usually less than 24 hours. A convenient "end point" is the visual color change from bright yellow to colorless or very pale yellow.
7. It is of utmost importance that the flask temperature during the removal of the volatile materials be kept below 20° to minimize possible azine formation by decomposition of the hydrazone.
8. The reported melting points are 16–20°,⁵ 22°,⁶ 24–25°,^{4,7} and 26°.⁷
9. Acetophenone hydrazone can be stored at temperatures below 0° for indefinite periods of time.

3. Discussion

The formation of acetophenone hydrazone has been accomplished by heating acetophenone with hydrazine or hydrazine hydrate,^{7,8,9,10} by heating acetophenone azine with anhydrous hydrazine,^{6,11} by the reaction of α -dimethylaminoacetophenone with hydrazine,⁵ and by the present method.⁴

This synthetic process is applicable to the preparation of most hydrazones from aldehydes and ketones. The two-step preparation offers several distinct advantages over the one-step method:^{6,9} (1) The yield of both steps is high; (2) the product is not contaminated with azine; (3) the isolated product is pure enough to be used in subsequent reactions without further purification. This method excels in the preparation of unstable liquid or low-melting hydrazones over the common methods of preparation.

References and Notes

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Appendix

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

ethanol (64-17-5)

acetic acid (64-19-7)

Acetophenone (98-86-2)

hydrazine hydrate (7803-57-8)

hydrazine (302-01-2)

N,N-dimethylhydrazine (57-14-7)

Acetophenone hydrazone,
Ethanone, 1-phenyl-, hydrazone (13466-30-3)

acetophenone azine (729-43-1)

α -dimethylaminoacetophenone (3319-03-7)

Acetophenone N,N-dimethylhydrazone (13466-32-5)

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