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.

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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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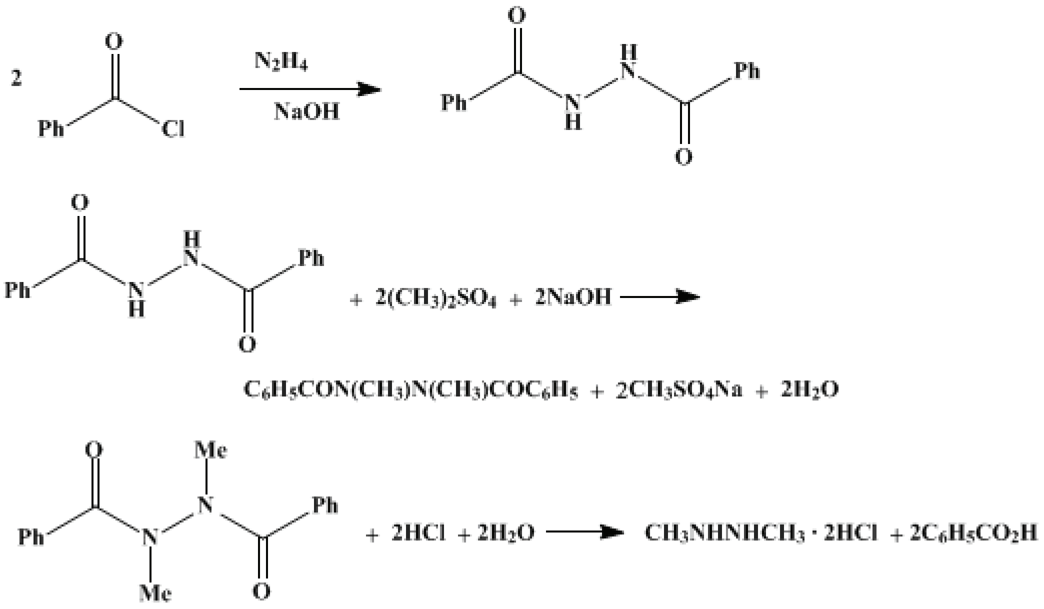
sym.-DIMETHYLHYDRAZINE DIHYDROCHLORIDE

[Hydrazine, 1,2-dimethyl-, dihydrochloride]



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1. Procedure

(*A*) *Dibenzoylhydrazine*.—In a 2-l. flask, provided with a mechanical stirrer (Note 1) and cooled in a bath of cold water, are placed a solution of 48 g. (1.2 moles) of sodium hydroxide in 500 cc. of water and 65 g. (0.5 mole) of hydrazine sulfate (Org. Syn. Coll. Vol. I, **1941**, 309). With stirring, 145 g. (120 cc., 1.03 moles) of freshly distilled benzoyl chloride and 120 cc. of an aqueous solution containing 45 g. (1.1 moles) of sodium hydroxide are added slowly from separate dropping funnels. The benzoyl chloride is added over a period of one and one-half hours; the alkali is added slightly faster. After both additions are completed the mixture is stirred for two hours longer and then saturated with carbon dioxide (Note 2). The dibenzoylhydrazine is filtered with suction, pressed thoroughly, and ground to a paste with 50 per cent aqueous acetone. The material is filtered with suction, washed with water, and pressed as dry as possible. The crude product is dissolved in about 650 cc. of boiling glacial acetic acid, from which, on cooling, the dibenzoylhydrazine separates as a mass of fine white needles. These are filtered with suction, washed with cold water, and dried by heating under reduced pressure on a water bath, in a slow current of air. This first fraction, m.p. 234–238°, amounts to 80–90 g. (66–75 per cent of the theoretical amount) and is practically pure. Small quantities of less pure material can be obtained by concentration of the mother liquor.

(*B*) *Dibenzoyldimethylhydrazine*.—The following operations should be performed under a hood. In a 2-l. three-necked flask, provided with a mechanical stirrer, a thermometer, and two dropping funnels, are placed 80 g. (0.33 mole) of dibenzoylhydrazine, 10 g. (0.25 mole) of sodium hydroxide, and 600 cc. of water. The mixture is maintained at about 90° (Note 3) by heating on a water bath. With stirring, 320 g. (240 cc., 2.54 moles) of methyl sulfate (Note 4) and 250 cc. of an aqueous solution containing 125 g. (3.1 moles) of sodium hydroxide are added from separate dropping funnels. The methyl sulfate is added in 10-cc. portions at five-minute intervals, the sodium hydroxide solution at a rate that maintains the reaction mixture slightly alkaline. When markedly alkaline the mixture has a distinctly yellow color; it is best to maintain a degree of alkalinity slightly less than that required to produce this color.

During the additions, which require about two hours, the dibenzoyldimethylhydrazine separates as a supernatant liquid (Note 5); the semisolid material thrown up on the sides of the flask must be washed down from time to time. After being heated for one-half hour longer the mixture is allowed to cool. The solid dibenzoyldimethylhydrazine is collected, crushed with water, filtered, and dissolved in 100 cc. of chloroform. The solution is filtered from insoluble impurities and dried over sodium sulfate; the chloroform is removed by heating on a water bath, finally under reduced pressure. The solid residue melts at 77–84° and is sufficiently pure for further use. The yield is 77–83 g. (86–93 per cent of the theoretical amount) (Note 6).

(*C*) *Dimethylhydrazine Dihydrochloride*.—In a 2-l. flask, a mixture of 67 g. (0.25 mole) of dibenzoyldimethylhydrazine and 250 cc. of 32 per cent hydrochloric acid (sp. gr. 1.16) is refluxed gently for two hours under a hood. To remove the benzoic acid, the mixture is steam-distilled until 10 l. of distillate has collected (Note 7); the residual liquor is evaporated to dryness under reduced pressure on a water bath. The crystalline dihydrochloride is treated with 25 cc. of absolute ethyl alcohol, and the mixture is evaporated to dryness under reduced pressure. This treatment is repeated, and the dihydrochloride is crushed with a mixture of 25 cc. of absolute alcohol and 2–3 cc. of concentrated hydrochloric acid, filtered, and washed with 10–15 cc. of cold absolute alcohol. The first fraction of dimethylhydrazine dihydrochloride, after being dried in a vacuum desiccator, weighs 22–23 g. By evaporation of the mother liquors and further treatment with 5–6 cc. of absolute alcohol and a little hydrochloric acid, a second fraction of 3 g. of the hydrochloride is obtained. Repetition of this procedure yields a third fraction amounting to about 0.5 g. (Note 8). The total yield is 25–26 g. (75–78 per cent of the theoretical amount).

2. Notes

1. The reaction flask need neither be corked nor placed under a hood if a glass tube, connected to a filter pump, is passed a short way into the neck of the flask.
2. Most of the dibenzoylhydrazine separates during the reaction as a white precipitate; if the mixture is not saturated with carbon dixoide, about 3 g. of the product remains in solution.
3. The temperature may be determined by a thermometer sheathed in a glass tube, which passes through the stopper and dips into the liquid. A section of rubber tubing slipped over the upper end of the thermometer serves to hold it in place. This device also provides a convenient method of testing the alkalinity of the solution.
4. Since methyl sulfate is very toxic, care should be exercised to avoid spilling the liquid or inhaling the vapor of the reaction mixture. Ammonia is a specific antidote.
5. The stated quantities of methyl sulfate and sodium hydroxide are merely approximations of the amounts actually required. The methyl sulfate is added at the stated rate until all the solid dibenzoylhydrazine has disappeared, and then another 25 cc. is added. Usually less than the stated amount of alkali is required.
6. The dibenzoyldimethylhydrazine can be obtained in a purer state by treating the cold, filtered chloroform solution with a 1 : 1 mixture of ether and petroleum ether (b.p. 40–60°) until crystallization begins and then adding slowly a moderate excess of petroleum ether. The hydrazine separates in small white needles, m.p. 84–87°.
7. It is found that this treatment removes the benzoic acid almost completely. Alternatively, the benzoic acid can be extracted with a 1 : 1 benzene-ether mixture.
8. The mono- and dihydrochlorides are very hygroscopic and should not be exposed to air for any length of time. Solutions of the dihydrochloride lose hydrochloric acid on evaporation, and the dihydrochloride obtained from solutions so treated tends to be oily. In recrystallization a little concentrated hydrochloric acid is added to the alcoholic solution.

The dihydrochloride may be crystallized by dissolving in boiling absolute ethyl alcohol (1 g. requires 20 cc. of alcohol), then adding a little concentrated hydrochloric acid and, after cooling slightly, about one-fifth of the volume of ether. The dimethylhydrazine dihydrochloride separates as a white crystalline powder, melting at 165–167°.

3. Discussion

Symmetrical dimethylhydrazine has been obtained by heating the methiodide of 1-methylpyrazole with potassium hydroxide.[1] It has usually been prepared by methylation of diformylhydrazine and subsequent hydrolysis with hydrochloric acid.[2] The present method is based on the observation of Folpmers that dibenzoylhydrazine may be similarly employed.[3]

References and Notes

1. Knorr and Köhler, Ber. **39**, 3257 (1906).
2. Harries and Klamt, ibid. **28**, 503 (1895); Harries and Haga, ibid. **31**, 56 (1898); Thiele, ibid. **42**, 2575 (1909).
3. Folpmers, Rec. trav. chim. **34**, 34 (1915).

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

petroleum ether

carbon dixoide

Symmetrical dimethylhydrazine

methiodide of 1-methylpyrazole

sym.-DIMETHYLHYDRAZINE DIHYDROCHLORIDE

ethyl alcohol,
alcohol (64-17-5)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

ammonia (7664-41-7)

Benzene (71-43-2)

ether (60-29-7)

sodium hydroxide (1310-73-2)

chloroform (67-66-3)

sodium sulfate (7757-82-6)

Benzoic acid (65-85-0)

carbon dioxide (124-38-9)

acetone (67-64-1)

benzoyl chloride (98-88-4)

potassium hydroxide (1310-58-3)

methyl sulfate (75-93-4)

Hydrazine sulfate (10034-93-2)

DIMETHYLHYDRAZINE DIHYDROCHLORIDE

Hydrazine, 1,2-dimethyl-, dihydrochloride (306-37-6)

Dibenzoylhydrazine

Dibenzoyldimethylhydrazine

diformylhydrazine