



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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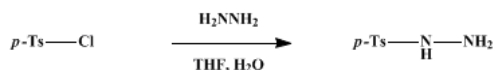
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

***p*-TOLUENESULFONYLHYDRAZIDE**

[*p*-Toluenesulfonic acid, hydrazide]



Submitted by Lester Friedman, Robert L. Little¹, and Walter R. Reichle.
Checked by Alan Black and Henry E. Baumgarten.

1. Procedure

Caution! See the discussion in Org. Synth. 1973, Coll. Vol. 5, 976 with regard to potential hazards associated with the purification of THF described in this procedure.

Into a 1-l. round-bottomed three-necked flask fitted with a thermometer, a mechanical stirrer, and a dropping funnel are placed 200 g. (1.05 moles) of *p*-toluenesulfonyl chloride and 350 ml. of tetrahydrofuran (Note 1). The stirred mixture is cooled in an ice bath to 10–15°; then a solution of hydrazine in water (135 ml. of 85% hydrazine hydrate, 2.22 moles; (Note 2)) is added at such a rate that the temperature is maintained between 10° and 20° (Note 3). Stirring is continued for 15 minutes after the addition is complete. The reaction mixture is transferred to a separatory funnel. The lower layer is drawn off, and discarded. The upper tetrahydrofuran layer is filtered with suction through a bed of Celite to remove suspended particles and foreign matter (if any). The Celite is washed with a little tetrahydrofuran to remove any absorbed tosylhydrazide. The clear, colorless filtrates are stirred vigorously during the slow addition of two volumes of distilled water. *p*-Toluenesulfonylhydrazide separates as fluffy white crystalline needles (Note 4). The product is filtered through a Büchner funnel; washed several times with distilled water, and air-dried. A yield of 175–185 g. (91–94%) is obtained; m.p. 109–110° (Note 5).

2. Notes

1. According to the submitters, commercial tetrahydrofuran (DuPont) is washed several times with 40% aqueous sodium hydroxide to remove peroxides and organic stabilizers and then dried over solid sodium hydroxide. The clear supernatant liquid is used without further purification. This procedure is no longer regarded as being free from hazard as several serious accidents have occurred during attempts to purify tetrahydrofuran in this fashion. The checkers used a good grade of commercially available tetrahydrofuran taken from a freshly opened bottle (without washing or drying) as recommended in this volume (see p. 976).

2. The submitters diluted 74 ml. of 95% hydrazine with 74 ml. of water. The dilution of hydrazine with water is exothermic. Hydrazine hydrate (50–100%) may be substituted if the volume of water is adjusted so that the resulting solution contains 50% hydrazine.

3. The addition is complete in 20–25 minutes.

4. Celite analytical filter aid, a product of the Johns-Manville Company, was used.

5. In some runs the checkers found it necessary to chill the mixture in the refrigerator for several hours or to stir the mixture in an ice bath until the product crystallized.

6. The product may be contaminated with trace amounts of *N,N'*-di-*p*-toluenesulfonylhydrazide. A more nearly pure product may be obtained by dissolving the crude product in hot methanol (4 ml. per gram of hydrazide), filtering through a bed of Celite, and reprecipitating the purified material by addition of 2 to 2.5 volumes of distilled water. This purification step is not necessary for most uses.

The submitters obtained the same yields with quantities as much as ten times those specified here.

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3. Discussion

p-Toluenesulfonylhydrazide has been prepared by shaking 50% hydrazine hydrate and *p*-toluenesulfonyl chloride in benzene for several hours.^{2,3} Ammonia has been used as an agent for removing the hydrogen chloride evolved.⁴ The present procedure is a modification of one previously published in *Organic Syntheses*.⁵

A number of hydrazides have been prepared in comparable yields from their respective sulfonyl chlorides by the procedure cited.⁵ These include *p*-bromobenzenesulfonylhydrazide, *p*-chlorobenzenesulfonylhydrazide, *p*-methoxybenzenesulfonylhydrazide, *m*-nitrobenzenesulfonylhydrazide, *p*-nitrobenzenesulfonylhydrazide, *o*-nitrobenzenesulfonylhydrazide, benzenesulfonylhydrazide, and methanesulfonylhydrazide.

p-Toluenesulfonylhydrazide has been found to be an exceptionally useful reagent in the synthesis of diazo compounds, olefins, and acetylenes and in the generation of diimide, carbenes, and carbenoid intermediates. Examples are too numerous to cite here; however, leading references may be found in *Reagents for Organic Synthesis*.⁶

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 258
- Org. Syn. Coll. Vol. 6, 62
- Org. Syn. Coll. Vol. 6, 172
- Org. Syn. Coll. Vol. 6, 293

References and Notes

1. Department of Chemistry, Case Institute of Technology, Cleveland, Ohio.
 2. A. Albert and R. Royer, *J. Chem. Soc.*, 1148 (1949).
 3. K. Freudenberg and F. Bluemmel, *Ann.*, 440, 51 (1924).
 4. N. K. Sundholm, U.S. pat. 2,640,853 (1953) [*C.A.*, **48**, 6464 (1954)].
 5. L. Friedman, R. L. Little, and W. R. Reichle, *Org. Syntheses*, **40**, 93 (1960).
 6. L. F. and M. Fieser, *Reagents for Organic Synthesis*, **1**, 257, 1185 (1967); **2**, 417 (1969); **3**, 293 (1972).
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Appendix

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

Celite

N,N'-di-p-toluenesulfonylhydrazide

hydrogen chloride (7647-01-0)

ammonia (7664-41-7)

Benzene (71-43-2)

methanol (67-56-1)

sodium hydroxide (1310-73-2)

hydrazine hydrate (7803-57-8)

hydrazine (302-01-2)

Tetrahydrofuran (109-99-9)

benzenesulfonylhydrazide (80-17-1)

tosylhydrazide

methanesulfonylhydrazide (10393-86-9)

p-Toluenesulfonyl chloride (98-59-9)

o-nitrobenzenesulfonylhydrazide (5906-99-0)

p-Toluenesulfonylhydrazide,

p-Toluenesulfonic acid, hydrazide (1576-35-8)

p-bromobenzenesulfonylhydrazide

p-chlorobenzenesulfonylhydrazide

p-methoxybenzenesulfonylhydrazide (1950-68-1)

m-nitrobenzenesulfonylhydrazide

p-nitrobenzenesulfonylhydrazide