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.

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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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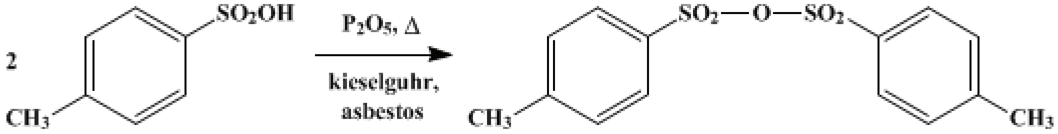
p-TOLUENESULFONIC ANHYDRIDE



Submitted by L. Field and J. W. McFarland[1].
Checked by William S. Johnson, Raymond R. Hindersinn, and A. G. Fisher.

1. Procedure

A mixture of 213 g. (1.5 moles) of phosphorus pentoxide and 14 g. of kieselguhr (Note 1) is prepared by shaking in a dry, stoppered 1-l. Erlenmeyer flask. About one-half of the mixture is then added to a mixture of 7 g. of asbestos (Note 1) and 190 g. (1.0 mole) of *p*-toluenesulfonic acid monohydrate (Note 2) in a 1-l. round-bottomed flask with one standard-taper neck protected from atmospheric moisture with a drying tube containing calcium chloride. The mixture, which soon becomes quite hot, is allowed to stand for 1 hour with occasional swirling. It is then heated in an oil bath held at about 125° for 9 hours, the remainder of the phosphorus pentoxide mixture being added in four portions during the first 3 hours. During this total 9-hour period the mass is mixed as well as possible with a metal spatula from time to time.

The drying tube is replaced by a condenser, and 400 ml. of ethylene chloride (Note 3) is added. The mixture is heated under reflux for several minutes. The flask is closed with a glass stopper and shaken well (Note 4). A thin pad of glass wool is then inserted into the lower part of the flask neck, and the extract is decanted. This extraction and decantation process is repeated with three 100-ml. portions of ethylene chloride. The extracts are combined in a 1-l. round-bottomed flask, the solvent is removed by distillation under reduced pressure, and the molten solid is swirled briefly at 3 mm. pressure until cessation of bubbling indicates complete removal of solvent. The dark oily solid, which is formed on cooling, amounts to 138–143 g. and melts in the range 80–124° (sealed tube) (Note 5). This material is purified by dissolving it in the minimum amount (about 200 ml.) of boiling anhydrous benzene (Note 6) and (Note 7) and, after cooling to about 50°, adding 300 ml. of anhydrous ether (Note 7). After crystallization is well advanced, the mixture is stored at −5° overnight. The solvent is removed by forcing it under nitrogen pressure either through a 6-mm. glass tube packed with glass wool up to a constriction about 1 in. from the bottom or through a sintered-glass filter stick. Residual solvent is removed at 3-mm. pressure through a stopcock which is then closed to permit storage of the anhydride at low pressure (Note 8). The yield is 77–114 g. (47–70%) of light brown or gray prisms. The product, which softens at about 90° and melts at 110–127° (sealed tube) (Note 5), is sufficiently pure for most purposes (Note 9).

2. Notes

1. It is satisfactory to use the Super-Cel brand of kieselguhr supplied by Johns-Manville Company and asbestos of the type used in Gooch crucibles. Inclusion of these inert materials facilitates mixing and extraction of the product.
2. A good commercial grade of *p*-toluenesulfonic acid monohydrate, m.p. 104–106°, was used.
3. A good commercial grade of ethylene chloride, b.p. 83–84°, was used. It is dried by distilling a portion.
4. If shaking is too violent, the gummy residue that clings to the flask may be dislodged, and the flask may break. After extraction is complete, the phosphorus pentoxide residue can be removed from the flask by adding water and replacing this by fresh water as the mixture becomes hot.
5. Even brief exposure to moist air causes a lowering of the melting point. The melting-point tube is therefore best filled by inserting it into material ground against the flask bottom or by using a dry box; the tube is then quickly sealed. The melting point of pure *p*-toluenesulfonic anhydride is 129.5–131.5°, with softening about 120° (sealed tube).[2]

6. Commercial grades of anhydrous ether and benzene which have been allowed to stand over sodium are satisfactory. Dry glassware should be used for transferring the solvents.
7. Usually a small amount of material remains undissolved. This material does not affect the melting point significantly but can be removed if desired by forcing the solution, kept hot by an electric heating mantle, through the filter arrangement described above into a dry flask protected from moisture by a calcium chloride tube.
8. In order to open the flask, air is admitted slowly through a calcium chloride tube. The melting point of the anhydride drops somewhat during prolonged storage with occasional opening, but the purity does not seem to be affected appreciably.[2]
9. The broad melting range apparently results from an unusual sensitivity of this property to small amounts of impurities.[2] The melting point can be raised by further recrystallizations.

3. Discussion

p-Toluenesulfonic anhydride has been prepared from the acid salt by the use of thionyl chloride[3] and phosphorus pentoxide,[2] and from the acid or sodium salt by treatment with a mixture of phosphorus pentachloride and phosphorus oxychloride.[4] It also has been obtained by heating oxime *p*-toluenesulfonates,[5] by reaction of *p*-toluenesulfonic acid with di-*p*-tolylcarbodiimide,[6] and by the interaction of methoxyacetylene and *p*-toluenesulfonic acid.[7]

References and Notes

1. Vanderbilt University, Nashville **4**, Tennessee.
2. Field, *J. Am. Chem. Soc.*, **74**, 394 (1952).
3. Meyer and Schlegl, *Monatsh.*, **34**, 573 (1913); Meyer, *Ann.*, **433**, 335 (1923).
4. Lukashevich, *Doklady Akad. Nauk S.S.S.R.*, **114**, 1025 (1957) [*C. A.*, **52**, 3717 (1958)].
5. Oxley and Short, *J. Chem. Soc.*, **1948**, 1524.
6. Khorana, *Can. J. Chem.*, **31**, 585 (1953).
7. Eglinton, Jones, Shaw, and Whiting, *J. Chem. Soc.*, **1954**, 1860.

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

oxime p-toluenesulfonates

calcium chloride (10043-52-4)

Benzene (71-43-2)

ether (60-29-7)

phosphorus pentachloride (10026-13-8)

thionyl chloride (7719-09-7)

ethylene chloride (107-06-2)

nitrogen (7727-37-9)

Phosphorus Oxychloride (21295-50-1)

sodium (13966-32-0)

methoxyacetylene (6443-91-0)

p-toluenesulfonic acid (104-15-4)

phosphorus pentoxide (1314-56-3)

p-toluenesulfonic acid monohydrate (6192-52-5)

p-Toluenesulfonic anhydride (4124-41-8)

di-p-tolylcarbodiimide