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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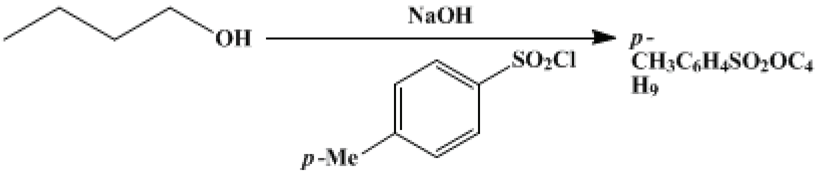
Organic Syntheses, Coll. Vol. 1, p.145 (1941); Vol. 9, p.28 (1929).

n-BUTYL *p*-TOLUENESULFONATE

[*p*-Toluenesulfonic acid, butyl ester]



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1. Procedure

In a 2-l., three-necked flask, fitted with a mechanical stirrer, a thermometer, and a 250-cc. separatory funnel, are placed 148 g. (2 moles) of *n*-butyl alcohol and 210 g. (1.1 moles) of pure *p*-toluenesulfonyl chloride (Note 1). From the separatory funnel 320 cc. (1.6 moles) of 5 *N* sodium hydroxide is run in at a rate that does not cause the temperature of the reaction mixture to exceed 15° (Note 2); the addition requires three to four hours.

Another portion of 210 g. (1.1 moles) of *p*-toluenesulfonyl chloride is added and then 320 cc. of 5 *N* sodium hydroxide solution is slowly introduced, again keeping the temperature below 15°. Stirring is continued for four hours longer, and the oily layer is separated from the water layer and any unchanged *p*-toluenesulfonyl chloride. Enough petroleum ether (b.p. 60–70°) or benzene is added to the oil to cause it to float on water; the solution is washed thoroughly with 50 cc. of 10 per cent sodium hydroxide and dried by standing overnight over 20 g. of anhydrous potassium carbonate. The solution is filtered, and the solvent is distilled. This is conveniently accomplished by adding the solution from a separatory funnel to a 500-cc. Claisen flask heated on a steam bath. The oily ester is then distilled under reduced pressure (Note 3), and, after a forerun boiling to 170°/10 mm., the pure ester distils at 170–171°/10 mm. The yield is 250–270 g. (50–54 per cent of the theoretical amount) (Note 4).

2. Notes

1. Technical *p*-toluenesulfonyl chloride is dissolved in benzene, washed with 5 per cent sodium hydroxide, dried by shaking with a small amount of potassium carbonate, and then distilled under reduced pressure. If the distillation must be interrupted, it is recommended that the liquid be allowed to cool before breaking the vacuum; otherwise, when distillation is resumed later, considerable decomposition takes place.
2. The cooling may be effected conveniently by immersing the flask in a water bath containing a small amount of ice, or by cold running water. If the bath is cooled to 0°, the time required for the completion of the reaction is appreciably longer.
3. It is best to distil the ester under greatly reduced pressure. Appreciable decomposition takes place even at 10-mm. pressure, and the distilled ester becomes quite dark after standing a week. To avoid superheating and consequent decomposition, it is recommended that the ester be distilled in small lots (from 250-cc. Claisen flasks when large runs are made). A sample of 100 g. distilled at 132–133°/3 mm. remained water-white after standing for two months.
4. Methyl *p*-toluenesulfonate may be prepared in a somewhat similar manner with good yields. One kilogram of methyl alcohol (90–95 per cent) is placed in a round-bottomed flask, contained in an ice-salt bath. One kilogram of powdered pure *p*-toluenesulfonyl chloride (crude material may be used but the yield of product drops to about 75 per cent) is added with mechanical stirring. From a separatory funnel 840 g. of 25 per cent sodium hydroxide solution is added drop by drop. The temperature must be held at about 23–27° for the best results. When all this alkaline solution is added the reaction mixture is tested with litmus; if not alkaline, more alkali is added until the neutral point is reached. Upon standing

several hours the ester sinks and the alcohol forms the top layer. The alcohol may be siphoned off and used in subsequent experiments; the methyl *p*-toluenesulfonate is washed with water to remove a little salt and then with 5 per cent hydrochloric acid to dissolve iron, if an iron stirrer was used. Finally it is washed with 5 per cent sodium carbonate and water. The ester is then distilled and boils at 161°/10 mm. (m.p. 27–28°). The yield is 90 per cent of the theoretical amount.
The spent alcohol is distilled from a steam bath, and alcohol of 84–91 per cent purity is obtained which is suitable for subsequent runs.

3. Discussion

Other alkyl esters have been prepared by this general method.[1] The *n*-butyl ester can be prepared by treating an ethereal solution of *p*-toluenesulfonyl chloride and butyl alcohol with powdered potassium hydroxide,[2] by refluxing the acid chloride with a 10 per cent excess of alcohol,[2] and by heating the acid chloride with the alcohol and anhydrous sodium carbonate.[3] By using pyridine as the condensing agent the yield can be increased to 86 per cent.[4]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 47
- Org. Syn. Coll. Vol. 3, 366

References and Notes

1. Krafft and Roos, Ber. **25**, 2255 (1892); Földi, Ber. **53**, 1836 (1920); Izmailskii and Razorenov, J. Russ. Phys. Chem. Soc. **52**, 359 (1920) [C. A. **18**, 1481 (1924)]; Slotta and Franke, Ber. **63**, 678 (1930).
2. Gilman and Beaber, J. Am. Chem. Soc. **47**, 518 (1925).
3. Slotta and Franke, Ber. **63**, 678 (1930).
4. Sekera and Marvel, J. Am. Chem. Soc. **55**, 345 (1933); Org. Syn. **20**, 50 (1940).

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

petroleum ether

n-butyl ester

alcohol (64-17-5)

potassium carbonate (584-08-7)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

methyl alcohol (67-56-1)

sodium hydroxide (1310-73-2)

iron (7439-89-6)

sodium carbonate (497-19-8)

butyl alcohol,
n-butyl alcohol (71-36-3)

pyridine (110-86-1)

potassium hydroxide (1310-58-3)

p-Toluenesulfonyl chloride (98-59-9)

n-BUTYL p-TOLUENESULFONATE,
p-Toluenesulfonic acid, butyl ester (778-28-9)

Methyl p-toluenesulfonate (80-48-8)