



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.

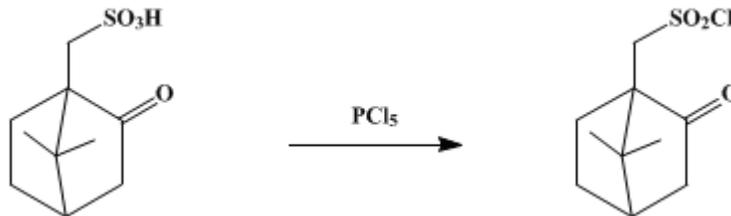
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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.

Organic Syntheses, Coll. Vol. 5, p.196 (1973); Vol. 45, p.14 (1965).

D,L-10-CAMPHORSULFONYL CHLORIDE



Submitted by Paul D. Bartlett and L. H. Knox¹.
Checked by John D. Roberts

1. Procedure

In a 2-l., three-necked, round-bottomed flask (Note 1) fitted with a sealed stirrer having a Teflon[®] blade and, on the two side necks, with gas-outlet tubes connected by rubber or plastic tubing to an efficient hydrogen chloride absorption trap (Note 2), 464 g. (2 moles) of D,L-10-camphorsulfonic acid (Note 3) is mixed with 416 g. (2 moles) of phosphorus pentachloride (Note 4). The flask is immersed in ice water and, as soon as the mixture has liquefied sufficiently, the stirrer is started but must be run slowly at first because of lumps. When the vigorous reaction has subsided, the cooling bath is removed and stirring continued until the chloride is completely dissolved (Note 5). The mixture is then allowed to stand for 3 or 4 hours. It is poured (*Hood!*) onto 500 g. of crushed ice contained in a 2-l. beaker. This mixture is immediately poured into a second beaker containing a similar quantity of crushed ice. The mixture is then poured back and forth between the two beakers until all evidence of reaction has disappeared (Note 6). The fine white product is collected on a suction filter and washed several times with cold water. The yield is essentially quantitative (500 g.) of moist sulfonyl chloride which is pure enough to be used for the preparation of D,L-ketopinic acid (p. 55). When carefully dried, the crude material has m.p. 81–83° (Note 7) and (Note 8) and may be preserved in a desiccator.

2. Notes

1. The checker found it expedient to carry on the reaction in a 2-l. Pyrex[®] reaction kettle (Corning 6947), the large closure making the initial mixing of the solid reactant and the removal of the product much simpler.
2. The type of trap described in *Org. Syntheses, Coll. Vol. 2, p.4*, is particularly useful.
3. The D,L-10-camphorsulfonic acid employed is the unrecrystallized product described on p. 194.
4. The initial mixing is conveniently made by turning the stirrer back and forth by hand.
5. The mixture does not usually become a clear solution because the product begins to crystallize. It is not difficult, however, to recognize yellow lumps of unreacted phosphorus pentachloride.
6. 10-Camphorsulfonyl chloride is rather rapidly hydrolyzed by warm water. The procedure here provides for complete hydrolysis of phosphorus oxychloride and excess phosphorus pentachloride without local heating and loss of product due to hydrolysis. For best results, the whole hydrolysis operation should be carried out quickly and steadily. It is well to have additional quantities of crushed ice on hand because the mixture may become quite hot if all of the ice added initially melts.
7. If the crude moist sulfonyl chloride is to be preserved, it must be thoroughly and reasonably rapidly dried. The checker found it very convenient to use a "freeze-drying" apparatus to remove the bulk of the moisture.
8. The submitters report that crystallization of the crude product from ligroin produces material of m.p. 83–84°. The sulfonyl chloride from (+)-camphorsulfonic acid has m.p. 67–68°.

3. Discussion

The procedure described here is adapted from that of Reychler.² The chloride may also be made from treatment of the acid with thionyl chloride.³

4. Merits of the Preparation

D,L-10-Camphorsulfonyl chloride may be oxidized to ketopinic acid (p. 690). The optically active forms of the sulfonyl chloride are useful for resolving alcohols and amines into optical antipodes.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 194
- Org. Syn. Coll. Vol. 5, 689
- Org. Syn. Coll. Vol. 5, 877

References and Notes

1. Converse Memorial Laboratory, Harvard University, Cambridge, Massachusetts. Preparation was submitted November 1, 1939.
2. A. Reychler, *Bull. Soc. Chim.*, [3] **19**, 120 (1898).
3. S. Smiles and T. P. Hilditch, *J. Chem. Soc.*, **91**, 519 (1907); H. Sutherland and R. L. Shriner, *J. Am. Chem. Soc.*, **58**, 62 (1936); J. Read and R. A. Storey, *J. Chem. Soc.*, 2761 (1930).

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

ligroin

D,L-ketopinic acid

ketopinic acid

phosphorus pentachloride (10026-13-8)

thionyl chloride (7719-09-7)

Phosphorus Oxychloride (21295-50-1)

D,L-10-CAMPHORSULFONIC ACID (5872-08-2)

10-CAMPHORSULFONYL CHLORIDE,
D,L-10-CAMPHORSULFONYL CHLORIDE (6994-93-0)

(+)-camphorsulfonic acid (3144-16-9)