



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](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.

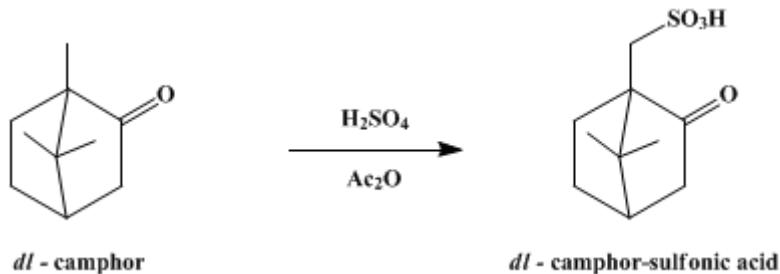
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 5, p.194 (1973); Vol. 45, p.12 (1965).*

## D,L-10-CAMPHORSULFONIC ACID (REYCHLER'S ACID)



Submitted by Paul D. Bartlett and L. H. Knox<sup>1</sup>.

Checked by John D. Roberts and Dinshaw Patel.

### 1. Procedure

In a 3-l., three-necked, round-bottomed flask fitted with a powerful slow-speed stirrer having a Teflon<sup>®</sup> blade, a 500-ml. dropping funnel, and a thermometer arranged to dip into the liquid is placed 588 g. (366 ml., 6 moles) of concentrated **sulfuric acid**. The flask is surrounded by an ice-salt mixture, the stirrer started, and 1216 g. (1170 ml., 12 moles) of **acetic anhydride** (Note 1) is added at such a rate that the temperature does not rise above 20° (Note 2). The separatory funnel is removed and 912 g. (6 moles) of coarsely powdered D,L-**camphor** is added (Note 3). The flask is then closed with a stopper and stirring is continued until the **camphor** is dissolved. The stirrer is replaced by a stopper, the ice bath allowed to melt, and the mixture left to stand for 36 hours (Note 4). The **camphorsulfonic acid** is collected on a suction filter and washed with **ether** (Note 5). After being dried in a vacuum desiccator at room temperature, the nearly white crystalline product weighs 530–580 g. (38–42%). It melts at 202–203° with rapid decomposition and is relatively pure (Note 6).

### 2. Notes

1. If the **acetic anhydride** is of a good commercial grade, it need not be redistilled.
2. When the temperature is allowed to rise above 20°, the acetic-sulfuric anhydride mixture acquires a yellow to orange color from which discolored crystals are subsequently deposited. The addition, which must be slow at first, requires 1–1.5 hours depending on the efficiency of the cooling bath.
3. The **camphor** employed is of the synthetic variety supplied by Howe and French, Boston. If an optically active product is desired, active natural **camphor** may be used.
4. The yields vary with the length of the crystallization period. After 16 hours the yield is 470 g. (34%). When the crystallization period is extended to 2 weeks, the yield is 615–655 g. (44–47%).
5. The checkers found the product to be very hygroscopic, in fact deliquescent, in a reasonably humid atmosphere. In such circumstances, it was preferable to decant the mother liquor from the crystals in the flask and to wash the solid by stirring it up with four 250-ml. portions of anhydrous **ether**, each washing being removed by decantation. The well-drained residual solid can then be transferred to a crystallizing dish and the **ether** removed by pumping under reduced pressure before the final drying in a vacuum desiccator over **sulfuric acid**.
6. The product can be purified with some loss by recrystallization from glacial **acetic acid**. About 60 g. of crude product dissolves in 90 ml. of **acetic acid** at 105° and gives a recovery of about 40 g. of purified material.

### 3. Discussion

The procedure described is that of Reychler.<sup>2</sup>

### 4. Merits of the Preparation

D,L-10-Camphorsulfonic acid is used for the preparation of the corresponding chloride (p. 196). The optically active acid has been used widely for the resolution of basic compounds into optical antipodes.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 196](#)

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## 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); H. E. Armstrong and T. M. Lowry, *J. Chem. Soc.*, **1441** (1902); B. Rewald, *Ber.*, **42**, 3136 (1909); F. Girault, *J. Pharm. Chim.*, [8] **20**, 207 (1934) [*C. A.*, **29**, 144 (1935)]; Y. Asahina and K. Yamguti, *Proc. Imp. Acad. (Tokyo)*, **13**, 38 (1937) [*C. A.*, **31**, 4305 (1937)]; R. Poggi and A. Polverini, *Ann. Chim. Appl.*, **30**, 284 (1940) [*C. A.*, **35**, 1395 (1941)]; R. Poggi and A. Pasquarelli, *Ann. Chem. Appl.*, **37**, 321 (1947) [*C. A.*, **42**, 8788 (1948)].

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## Appendix

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

REYCHLER'S ACID

[sulfuric acid](#) (7664-93-9)

[acetic acid](#) (64-19-7)

[ether](#) (60-29-7)

[acetic anhydride](#) (108-24-7)

[camphor](#) (21368-68-3)

[10-CAMPHORSULFONIC ACID](#),  
[camphorsulfonic acid](#),  
[D,L-10-CAMPHORSULFONIC ACID](#) (5872-08-2)