



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

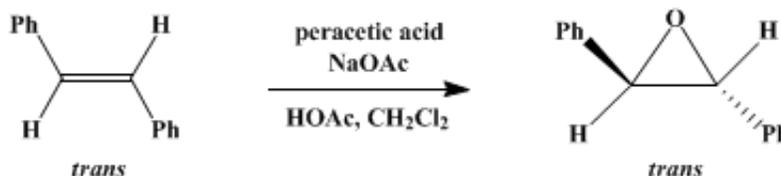
Working with Hazardous Chemicals

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.

trans-STILBENE OXIDE[Bibenzyl, α,α' -epoxy-]

Submitted by Donald J. Reif and Herbert O. House¹.
 Checked by Melvin S. Newman and Donald K. Phillips.

1. Procedure

*Caution! Reactions and subsequent operations involving peracids and peroxy compounds should be run behind a safety shield. Peroxy compounds should be added to the organic material, never the reverse. For relatively fast reactions, the rate of addition of the peroxy compound should be slow enough so that it reacts rapidly and no significant unreacted excess is allowed to build up. The reaction mixture should be stirred efficiently while the peroxy compound is being added, and cooling should generally be provided since many reactions of peroxy compounds are exothermic. New or unfamiliar reactions, particularly those run at elevated temperatures, should be run first on a small scale. Reaction products should never be recovered from the final reaction mixture by distillation until all residual active oxygen compounds (including unreacted peroxy compounds) have been destroyed. Decomposition of active oxygen compounds may be accomplished by the procedure described in Korach, M.; Nielsen, D. R.; Rideout, W. H. *Org. Synth.* 1962, 42, 50 (*Org. Synth.* 1973, Coll. Vol. 5, 414). [Note added January 2011].*

In a 1-l. three-necked flask equipped with stirrer, dropping funnel, and thermometer is placed a solution of 54 g. (0.3 mole) of *trans*-stilbene (Note 1) in 450 ml. of methylene chloride. The methylene chloride solution is cooled to 20° with an ice bath, and then the cooling bath is removed. A solution of peracetic acid (0.425 mole) in acetic acid (Note 2) containing 5 g. of sodium acetate trihydrate is added dropwise and with stirring to the reaction mixture during 15 minutes. The resulting mixture is stirred for 15 hours, during which time the temperature of the reaction mixture is not allowed to rise above 35° (Note 3) and (Note 4). The contents of the flask are poured into 500 ml. of water, and the organic layer is separated. The aqueous phase is extracted with two 150-ml. portions of methylene chloride, and the combined methylene chloride solutions are washed with two 100-ml. portions of 10% aqueous sodium carbonate and then with two 100-ml. portions of water. The organic layer is dried over magnesium sulfate, and the methylene chloride is distilled, the last traces being removed under reduced pressure. The residual solid is recrystallized from methanol (3 ml./g. of product) to yield 46–49 g. (78–83%) of crude *trans*-stilbene oxide, m.p. 66–69° (Note 5). An additional recrystallization from hexane (3 ml./g. of product) sharpens the melting point of the product to 68–69°. The yield is 41–44 g. (70–75%).

2. Notes

- trans*-Stilbene (Eastman Kodak Company) may be used directly. A slightly higher yield is obtained if the stilbene is crystallized once from alcohol.
- Approximately 40% peracetic acid in acetic acid is available (Becco Chemical Division, Food Machinery and Chemical Corporation, Buffalo 7, New York). Sodium acetate is added to neutralize a small amount of sulfuric acid which is present in the commercial product. The peracetic acid concentration should be determined by titration.² The peracetic acid solution used by the submitters

contained 0.497 g. (0.00655 mole) of peracid per milliliter. Consequently 65 ml. (0.425 mole) of this solution was used in the reaction.

3. Without further cooling, the temperature of the reaction mixture usually rises to 32–35° after 1–2 hours and then gradually falls.

4. The progress of the epoxidation can be followed by measuring periodically the optical density of the reaction mixture at 295 m μ . The reaction time and temperature specified in the procedure were found to reduce the optical density of the reaction mixture at 295 m μ (and, accordingly, the *trans*-stilbene concentration) to less than 3% of its initial value. If more than this amount of unchanged *trans*-stilbene remains in the crude product, it cannot be removed by recrystallization from either *methanol* or *hexane*. Even after repeated crystallization the melting point of the product does not rise above 66–67°. Pure *trans*-stilbene oxide can be isolated from such a mixture if the mixture is treated with additional *peracetic acid* to convert the remaining *trans*-stilbene to *trans*-stilbene oxide.

5. This melting point and yield are obtained after the crystalline product which separates from *methanol* has been dried under reduced pressure for 12 hours. This drying process is unnecessary if the product is subsequently to be recrystallized from *hexane*.

3. Discussion

trans-Stilbene oxide has been prepared by the reaction of *silver oxide* with the methiodide of 1,2-diphenyl-2-dimethylaminoethanol,^{3,4} by the reaction of *hydrazine* with *hydrobenzoin*,⁵ and by the reaction of *peracetic acid*^{6,7} or *perbenzoic acid*⁸ with *trans*-stilbene. The procedure described illustrates the use of a commercially available *peracetic acid* solution for the epoxidation of carbon double bonds. Since the reaction of *trans*-stilbene and other olefins conjugated with aromatic nuclei with peracids is slow, the procedure for the epoxidation of unconjugated olefins should be modified by the use of a lower reaction temperature, a shorter reaction time, and a longer period of time for the addition of the peracid.

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 4*, 375
- *Org. Syn. Coll. Vol. 6*, 312

References and Notes

1. Massachusetts Institute of Technology, Cambridge, Massachusetts.
2. Greenspan and MacKellar, *Anal. Chem.*, **20**, 1061 (1948).
3. Read and Campbell, *J. Chem. Soc.*, **1930**, 2377.
4. Rabe and Hallensleben, *Ber.*, **43**, 884 (1910).
5. Müller and Kraemer-Willenberg, *Ber.*, **57B**, 575 (1924).
6. Böeseken and Elsen, *Rec. trav. chim.*, **47**, 694 (1928).
7. Böeseken and Schneider, *J. prakt. Chem.*, **131**, 285 (1931).
8. Tiffeneau and Levy, *Bull. soc. chim. France*, [4]**39**, 763 (1926).

Appendix

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

peracid

methiodide of 1,2-diphenyl-2-dimethylaminoethanol

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

methanol (67-56-1)
sodium acetate (127-09-3)
silver oxide (20667-12-3)
sodium carbonate (497-19-8)
hydrazine (302-01-2)
methylene chloride (75-09-2)
magnesium sulfate (7487-88-9)
stilbene
peracetic acid (79-21-0)
sodium acetate trihydrate (6131-90-4)
hexane (110-54-3)
hydrobenzoin (52340-78-0)
Perbenzoic acid (93-59-4)
trans-Stilbene oxide (1439-07-2)
trans-Stilbene (103-30-0)
Bibenzyl, α,α' -epoxy-