Glycidyl Vinyl Ether
[1-(Vinyloxy)-2,3-epoxypropane]

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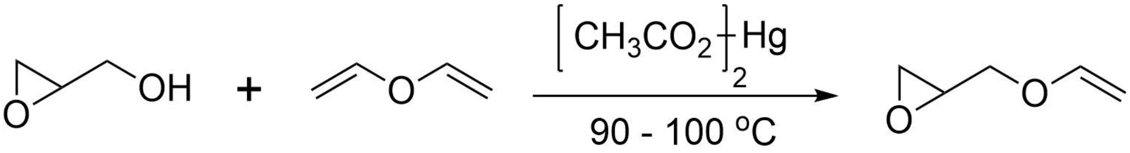

1. Procedure

Caution! Vinyl ethers react violently with acidic materials. Care should be taken to maintain neutral or slightly alkaline conditions during the reaction and product isolation.

In a 3 l pressure vessel (Note 1), cooled externally with ice water (Note 2), are sealed under nitrogen a cold solution of 127 g (0.4 mol) of reagent-grade mercuric acetate in 297 g (4.0 mol) of glycidol (Notes 3) and 1120 g (16.0 mol) of vinyl ether (Note 4). The vessel is heated rapidly with agitation to 90-100° and maintained at this temperature for 8 h. The vessel is cooled to below room temperature with ice water, vented in an efficient hood and discharged.

The solution (Note 5) is distilled from a 500 ml flask (Note 6) without fractionation at a pressure less than 10 torr until the temperature in the distillation flask reaches 90°; the distillate is collected in a 3 l receiver (Note 7) cooled in a Dry Ice bath. The residue (Note 8) can be discarded. The cooled distillate is washed with three 400 ml portions of an ice-cold 20% sodium chloride solution and then with two 300 ml portions of ice water. The organic layer is dried over molecular sieves (Note 9), and 2 g of *N*-phenyl-1-naphthylamine is added (Note 10). The drying agent is removed by gravity filtration through a coarse-grade sintered-glass funnel and washed with 175 ml of *p*-*t*-butyltoluene (Note 11).

The combined filtrates are distilled through a 45 cm, vacuum-jacketed column filled with Heli-pak packing (Note 12) from a 500 ml distillation flask (Note 6). Initially, vinyl ether is collected to a bp of 35° (Note 13). The product, collected at 132-133°, n_D^{25} 1.4329 (Note 14), is a colorless liquid weighing 280-310 g (70-77%, Note 15).

2. Notes

1. A stainless steel, water-jacketed autoclave equipped with a mechanical stirrer was used.
2. Cooling is advisable to prevent excessive losses of vinyl ether.
3. Glycidol is available from several suppliers. A supply obtained from the Ott Chemical Company was used in developing the synthesis. Because it decomposes slowly, even at room temperature, glycidol, bp 49-51° (7 torr), should be distilled before use.
4. Vinyl ether is sold under the trade-name of "Vinethene" by Merck, Sharp & Dohme. As supplied, it contains *N*-phenyl-1-naphthylamine and alcohol as stabilizers. Vinyl ether, bp 28-29°, should therefore be distilled through a Vigreux column just before use.
5. A small amount of flocculent precipitate is usually present in the solution. It need not be removed, because it remains in the residue from the first distillation.

6. Because of the large volume of vinyl ether that must be carried through both distillations, it is advisable, in the interest of obtaining optimum yield, to use a small distillation flask and add the solutions to it with an addition funnel. (The checkers found it more convenient to use a 1 l flask to prevent flooding after removal of the low-boiling material.)
7. To obtain maximum recovery of vinyl ether the receiver should be fitted with a Dry Ice-cooled condenser at its outlet.
8. The residue, a viscous syrup, consists of mercuric salts and glycidyl polymers.
9. Type 3A molecular sieves, available from the Linde Company, were used in the form of 1/16 in pellets.
10. *N*-Phenyl-1-naphthylamine acts both as an antioxidant and inhibitor to maintain alkalinity. It can be used as it is supplied by any of several vendors, such as Matheson, Coleman and Bell.
11. In addition to washing product from the molecular sieves, *p*-*t*-butyl-toluene, bp 190-191°, acts as a distillation "chaser." It can be used as obtained from suppliers such as Eastman Organic Chemicals.
12. This kind of packing is supplied by Podbielniak, Inc. It was chosen because of its efficiency and low liquid retention. The particular packing used was made of "Hastelloy 'B'" in the dimensions of 0.092 x 0.175 x 0.175 in.
13. The recovered vinyl ether, which contains small amounts of acetaldehyde, can be recycled through the synthesis after redistillation. It should be stabilized with a small amount of *N*-phenyl-1-naphthylamine as soon as it is collected.
14. Glycidyl vinyl ether obtained in this way has a purity of 98-99% by vapor phase chromatography.
15. Redistillation of combined small fractions, bp 120-132° and 133-136°, affords an additional 16-24 g (4-6%) of product.

3. Methods of Preparation

Glycidyl vinyl ether has been prepared by dehydrochlorination of glycidyl 2-chloroethyl ether.[3] The method described here is a modification of the vinyl *trans*-esterification reaction.[4] The preparation of glycidyl vinyl ether from glycidol and vinyl ethers using mercuric acetate as catalyst, as well as polymerization to homo- and copolymer through the vinyl or epoxy groups, has been described.[5,6,7,8] Copolymers with pendent epoxy groups have been reported to be obtained from glycidyl vinyl ether.[9]

4. Merits of the Preparation

Because of the sensitivity of the epoxide ring to nucleophiles, glycidyl vinyl ether cannot be obtained by the base-catalyzed vinylation of glycidol with acetylene,[10] a method used for the preparation of most of the vinyl ethers of commerce. The same deterrent severely restricts the yield in the dehydrochlorination of glycidyl 2-chloroethyl ether with sodium hydroxide.[3]

Two factors limit the yield of glycidyl vinyl either to about 18% by the standard vinyl *trans*-esterification method.[4] Again, the sensitivity of epoxides, in this case to by-product alcohols, is a problem. In addition, the necessity of shifting the equilibrium prevailing in the process requires a slow distillation of the product at a reaction temperature near 160°. The elevated temperatures and prolonged contact permit competing reactions to destroy the epoxide ring to a considerable extent.

The method described here, though a vinyl *trans*-esterification, does not yield a by-product alcohol or involve shifting an equilibrium. It should find application in vinylating alcohols containing other reactive groups and in the preparation of vinyl ethers from high-boiling or solid alcohols.

Glycidyl vinyl ether can be copolymerized with many vinyl monomers, such as tetrafluoroethylene and other fluorinated olefins,[11] maleic anhydride, vinyl chloride, vinylidene chloride, and ethylene to yield polymers that can be crosslinked by the epoxide ring.

5. References

1. *Contribution No. 395 from the Organic Chemicals Department, E. I. DuPont de Nemours & Company, Wilmington, DE 19899.*
2. *Department of Chemistry, The University of Arizona, Tucson, AZ 85721.*
3. Kawai, W.; Tsutsumi, S. *J. Chem. Soc. Japan, Pure Chem. Sect.*, **1959**, *80*, 88; *Chem. Abst.*, **1961**, *55*, 4466a.
4. Watanabe, W. H.; Conlon, L. E. *J. Am. Chem. Soc.*, **1957**, *79*, 2828.
5. Tinsley, S. W.; Rick, E. A. U.S. Patent 3,203,939, August 31, 1965.
6. Sorkin, H. U.S. Patent 3,414,634, December 3, 1968.
7. Payne, G. B. Canadian Patent 820.339, August 12, 1969.
8. Wang, T. I.; Nakaguchi, G. M. U.S. Patent 3,699,131, October 17, 1972.
9. Vecellio, B. German Patent 1,520,584, April 10, 1969.
10. Copenhaver, J. W.; Bigelow, M. H. *Acetylene and Carbon Monoxide Chemistry*; Reinhold: New York, 1949; Chapter II.
11. Pascal, I. British Patent 948,998, February 5, 1964; *Chem. Abst.*, **1964**, *60*, 13408h; U.S. Patent 3,132,121, May 5, 1964.