



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.

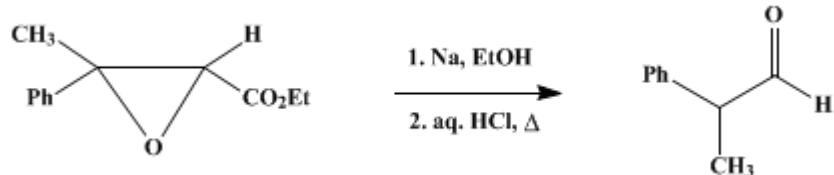
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.733 (1955); Vol. 24, p.87 (1944).

α -PHENYLPROPIONALDEHYDE

[Hydratropaldehyde]



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1. Procedure

An ethanolic solution of sodium ethoxide is prepared in a 1-l. round-bottomed flask from 15.5 g. (0.67 gram atom) of sodium and 300 ml. of absolute ethanol (Note 1). One hundred thirty-three grams (0.64 mole) of phenylmethylglycidic ester (p. 727) is added to this solution slowly and with shaking. The flask is then cooled externally to 15°, and 15 ml. of water is slowly added; considerable heat is evolved, and the sodium salt soon begins to separate. After the mixture has stood overnight, the salt is filtered by suction and rinsed with one 50-ml. portion of ethanol and a similar amount of ether. The dried salt weighs 102–108 g. (80–85%) and melts at 255–256° with decomposition.

The salt is added to a dilute solution of hydrochloric acid prepared by mixing 300 ml. of water and 56 ml. of concentrated acid (sp. gr. 1.18); the acid should be contained in a 1-l. flask under a reflux condenser. The mixture is warmed gently, whereupon carbon dioxide is evolved and an oil separates. The flask is heated on a steam bath for 1.5 hours, and the oil is then extracted from the cooled mixture with 150 ml. of benzene. The extract is washed once with 200 ml. of water and distilled under reduced pressure, using an ordinary 500-ml. Claisen flask. The hydratropaldehyde distils at 90–93°/10 mm. or 73–76°/4 mm. (oil bath at 120–130°), leaving only a slight residue (3–5 g.). The yield is 56–60 g. (65–70%) (Note 2) and (Note 3).

2. Notes

1. The metal is placed in the flask, and the ethanol is added through the condenser as fast as refluxing will allow (p. 215, Note 1).
2. The generality of this reaction is limited only by the availability of the glycidic esters.
3. The 2,4-dinitrophenylhydrazone forms yellow prisms that melt at 135°.

3. Discussion

Hydratropaldehyde has been prepared by hydrolysis of phenylmethylglycidic ester,^{1,2,3} by chromyl chloride oxidation of cumene,⁴ by the elimination of halogen acid or water from halohydrins or glycols,^{5,6,7} and by the distillation at ordinary pressure of methylphenylethylene oxide.^{8,9}

Hydratropaldehyde has also been prepared by the catalytic addition of hydrogen and carbon monoxide to styrene.¹⁰

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 727
- Org. Syn. Coll. Vol. 6, 1028

References and Notes

1. Claisen, *Ber.*, **38**, 703 (1905).
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 3. Dutta, *J. Indian Chem. Soc.*, **18**, 235 (1941) [*C. A.*, **36**, 161 (1942)].
 4. v. Miller and Rohde, *Ber.*, **24**, 1359 (1889).
 5. Bougault, *Ann. chim. phys.*, (7) **25**, 548 (1902).
 6. Tiffeneau, *Bull. soc. chim. France*, (3) **27**, 643 (1902); *Compt. rend.*, **134**, 846 (1902); **137**, 1261 (1903); **142**, 1538 (1906); *Ann. chim. phys.*, (8) **10**, 353 (1907).
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 9. Tiffeneau, *Compt. rend.*, **140**, 1459 (1905); *Ann. chim. phys.*, (8) **10**, 192 (1907).
 10. Adkins and Krsek, *J. Am. Chem. Soc.*, **70**, 383 (1948).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Phenylmethylglycidic ester

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

ether (60-29-7)

hydrogen (1333-74-0)

carbon monoxide (630-08-0)

carbon dioxide (124-38-9)

sodium (13966-32-0)

sodium ethoxide (141-52-6)

styrene (100-42-5)

cumene (98-82-8)

chromyl chloride

methylphenylethylene oxide (14212-54-5)

hydratropaldehyde,
 α -PHENYLPROPIONALDEHYDE (93-53-8)