Organic Syntheses

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.

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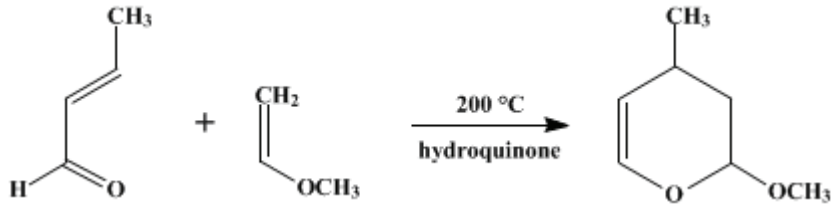
Organic Syntheses, Coll. Vol. 4, p.311 (1963); Vol. 34, p.29 (1954).

3,4-DIHYDRO-2-METHOXY-4-METHYL-2H-PYRAN

[2H-Pyran, 3,4-dihydro-2-methoxy-4-methyl-]



Submitted by Raymond I. Longley, Jr., William S. Emerson, and Albert J. Blardinelli[1].
Checked by T. L. Cairns and T. E. Young.

1. Procedure

In a high-pressure autoclave, arranged for agitation by shaking or rocking, are placed 286 g. (336 ml., 4.08 moles) of crotonaldehyde, 294 g. (5.06 moles) of methyl vinyl ether, and 1.1 g. of hydroquinone (Note 1) and (Note 2). The autoclave is heated to 200° (Note 3) and held there for 12 hours. The autoclave is cooled and vented, and the black product is distilled through a 1 by 60 cm. helix-packed column. The yield of 3,4-dihydro-2-methoxy-4-methyl-2H-pyran is 270–297 g. (52–57%), b.p. 42–50° /19 mm., n_D^{25} 1.4349–1.4374 (Note 4), (Note 5), and (Note 6).

2. Notes

1. The purer grade of crotonaldehyde supplied by the Eastman Kodak Company was used. Methyl vinyl ether was obtained from the Matheson Chemical Company.
2. The submitters condensed the methyl vinyl ether in the aldehyde cooled to 0° and then charged this mixture to a precooled autoclave. The checkers cooled the autoclave containing the crotonaldehyde to −70°, evacuated, and condensed the required amount of methyl vinyl ether directly into the autoclave.
3. The autoclave should be capable of withstanding a pressure of 3000 p.s.i. This provides a margin of safety, since at 220° the pressure is about 2600 p.s.i.
4. Pure 3,4-dihydro-2-methoxy-4-methyl-2H-pyran boils at 135–138° /760 mm. and at 79–80° /100 mm. and has n_D^{25} 1.4370.
5. The submitters used approximately three times the quantities reported here and obtained yields of 82–83%.
6. Under comparable conditions the submitters found that the corresponding dihydropyran derivatives were similarly obtained by the condensation of acrolein with methyl vinyl ether in 80–81% yield, with ethyl vinyl ether (77–85% yield), with *n*-butyl vinyl ether (82% yield), with ethyl isopropenyl ether (50% yield), and with *n*-butyl cyclohexenyl ether (40% yield). Other α,β-unsaturated carbonyl compounds that have thus been condensed with ethyl vinyl ether are crotonaldehyde (87% yield), methacrolein (40% yield), α-ethyl-β-*n*-propylacrolein (54% yield), cinnamaldehyde (60% yield), β-furylacrolein (85% yield), methyl vinyl ketone (50% yield), benzalacetone (75% yield), and benzalacetophenone (74% yield).

3. Discussion

3,4-Dihydro-2-methoxy-4-methyl-2H-pyran has been prepared only by the addition of methyl vinyl ether to crotonaldehyde.[2,3,4,5]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 660
- Org. Syn. Coll. Vol. 4, 816

References and Notes

1. Monsanto Chemical Company, Dayton 7 Ohio.
2. Longley and Emerson, *J. Am. Chem. Soc.*, **72**, 3079 (1950).
3. Smith, Norton, and Ballard, *J. Am. Chem. Soc.*, **73**, 5267 (1951).
4. Smith, Norton, and Ballard, U. S. pat. 2,514,168.
5. N. V. de Bataafsche Petroleum Maatschappij, Brit. pat. 653,764 [*C. A.*, **47**, 5452 (1953)].

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

Acrolein (107-02-8)

hydroquinone (123-31-9)

Benzalacetophenone (94-41-7)

Benzalacetone (122-57-6)

cinnamaldehyde

crotonaldehyde (123-73-9)

methyl vinyl ketone (78-94-4)

3,4-Dihydro-2-methoxy-4-methyl-2H-pyran,
2H-Pyran, 3,4-dihydro-2-methoxy-4-methyl- (53608-95-0)

methyl vinyl ether (9003-09-2)

ethyl vinyl ether (109-92-2)

ethyl isopropenyl ether (926-66-9)

methacrolein (78-85-3)

β-furylacrolein (623-30-3)

n-butyl vinyl ether (111-34-2)

n-butyl cyclohexenyl ether

α-ethyl-β-n-propylacrolein