



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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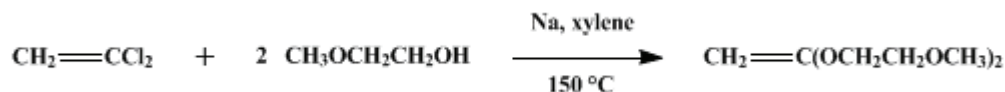
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.684 (1973); Vol. 47, p.78 (1967).

KETENE DI(2-METHOXYETHYL) ACETAL

[Ketene bis(2-methoxyethyl) acetal]



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Checked by Earl M. Levi and Peter Yates.

1. Procedure

In a dry 1-l. five-necked flask equipped with a mechanical stirrer, a reflux condenser (Note 1), a thermometer, a nitrogen inlet, and a stoppered port (Note 2) are placed 152 g. (2.00 moles) of 2-methoxyethanol (Note 3) and 50 g. of xylene (Note 4). A constant dry nitrogen purge is maintained on the apparatus throughout the following operations (Note 5). Metallic sodium (46.0 g., 2.00 moles) is added in small chunks through the stoppered port to the stirred reaction mixture over a 2-hour period at a temperature of 130–150°. After all the sodium has reacted (Note 6), heating is discontinued, and 120 g. (1.24 moles) of vinylidene chloride (Note 7) is added dropwise to the stirred reaction mixture over a 20-minute period. During the addition of vinylidene chloride the reaction mixture becomes dark, and its temperature increases rapidly from an initial 140° to a maximum of 170–175°. It then decreases as addition continues, and concomitant precipitation of sodium chloride is noted. Stirring is continued for an additional 10 minutes after completion of the addition of vinylidene chloride. Anhydrous diethyl ether (100 ml.) is slowly added, serving both to reduce the viscosity and to cool the reaction mixture to about 60°. This mixture is then filtered through a medium-grade fritted-glass funnel, and the sodium chloride cake is washed with several 20-ml. portions of fresh ether (Note 8).

The ethereal filtrate and washings are distilled under reduced pressure (Note 9) with the use of a 6-in. Vigreux column, and pure ketene di(2-methoxyethyl) acetal (Note 10) is obtained; b.p. 81–84° (2.0 mm.), n_D^{25} 1.4411, yield 98–132 g. (56–75%). The infrared spectrum of the product shows a very strong C=C absorption band at 1640 cm^{-1} .

2. Notes

1. A dry ice type of condenser has been found to be the most satisfactory because of the low boiling point (32°) of the vinylidene chloride. An efficient water-cooled condenser is satisfactory, however.
2. An addition funnel is fitted in this port after the sodium addition is complete.
3. 2-Methoxyethanol (methyl Cellosolve) from Union Carbide Corporation, Chemicals Division, was used.
4. Xylene (analytical reagent grade) from Mallinckrodt Chemical Works was distilled from sodium before use.
5. This is essential to avoid both the excessive oxidation of the reactants and the danger of a sodium-sparked fire.
6. Small amounts of metallic sodium, such as a few very small spheres floating in the reaction mass, are tolerable as long as dry nitrogen is being continuously passed through the reaction flask. A slow nitrogen purge is also maintained on the apparatus during the addition of the vinylidene chloride. The checkers found that appreciable amounts of sodium remained unconsumed after 3.5 hours; they added more 2-methoxyethanol (10–12 g.) to complete the reaction (significant loss of this reagent appeared to occur from the port during addition of the sodium).
7. Vinylidene chloride (inhibited grade) from Dow Chemical Company was used.
8. The sodium chloride cake is washed with as many 20-ml. portions of ether as are required to make the filtrate essentially colorless (usually four or five).
9. The diethyl ether is collected directly into traps cooled in dry ice-acetone.
10. The directions of McElvain and Kundiger² regarding the storage of ketene acetals should be

followed. The submitters have found that storage at 0°, in a bottle which was previously washed with a hot concentrated caustic solution, is satisfactory.

3. Discussion

Ketene di(2-methoxyethyl) acetal has been obtained by the present method with the use of diethylene glycol dimethyl ether as solvent.³ Other methods for the preparation of ketene acetals include the dehydrohalogenation of a halo acetal with potassium *t*-butoxide^{2,4} and the reaction of an α -bromo orthoester with metallic sodium.⁵

4. Merits of the Preparation

This synthetic process is applicable to the preparation of other ketene acetal derivatives of β -alkoxy alcohols. Examples include the ketene acetal derivatives of tetrahydrofurfuryl alcohol and 1-methoxy-2-propanol.³ There are a number of advantages in its use, including a simple, time-saving procedure, readily available and inexpensive reagents, and good yields of ketene acetal obtained by a *one-step* method.

References and Notes

1. Union Carbide Corporation, Technical Center, Research and Development Department, South Charleston, West Virginia.
 2. S. M. McElvain and D. Kundiger, *Org. Syntheses*, Coll. Vol. **3**, 506 (1955).
 3. W. C. Kuryla and D. G. Leis, *J. Org. Chem.*, **29**, 2773 (1964).
 4. F. Beyerstedt and S. M. McElvain, *J. Am. Chem. Soc.*, **58**, 529 (1936).
 5. P. M. Walters and S. M. McElvain, *J. Am. Chem. Soc.*, **62**, 1482 (1940).
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Appendix

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

ketene acetal derivatives of tetrahydrofurfuryl alcohol and 1-methoxy-2-propanol

ether,
diethyl ether (60-29-7)

sodium chloride (7647-14-5)

nitrogen (7727-37-9)

sodium (13966-32-0)

xylene (106-42-3)

methyl Cellosolve,
2-methoxyethanol (109-86-4)

diethylene glycol dimethyl ether (111-96-6)

vinylidene chloride (75-35-4)

KETENE DI(2-METHOXYETHYL) ACETAL,
Ketene bis(2-methoxyethyl) acetal (5130-02-9)

potassium t-butoxide (865-47-4)

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