



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.

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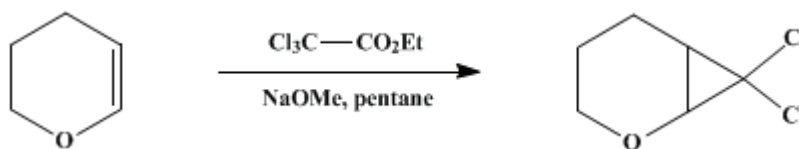
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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2-OXA-7,7-DICHLORONORCARANE

[7,7-Dichloro-2-oxabicyclo[4.1.0]heptane]



Submitted by William E. Parham, Edward E. Schweizer, and Sigmund A. Mierzwa Jr¹.
Checked by William G. Dauben and Richard Ellis.

1. Procedure

In a 1-l. three-necked flask (Note 1) is placed 50 g. (0.92 mole) of sodium methoxide (Note 2) and (Note 3). The flask is temporarily stoppered and then fitted with a nitrogen inlet tube, a sealed stirrer, and a 250-ml. pressure-equalized dropping funnel carrying a calcium chloride tube.

The dropping funnel is removed, and 67.4 g. (0.8 mole) of dihydropyran (Note 4) and 600 ml. of dry, olefin-free pentane (Note 5) are added successively. The light-yellow solution is stirred for 15 minutes in an ice-water bath, and then 164.8 g. (0.86 mole) of ethyl trichloroacetate (Note 6) is added from the dropping funnel over a period of 3–4 minutes. The dropping funnel is removed and replaced by a calcium chloride tube.

The reaction mixture is stirred for 6 hours (Note 7) at the ice-bath temperature and then is allowed to warm to room temperature overnight while the stirring is continued. During this period the color of the mixture changes from yellow-orange to brown.

Water (200 ml.) is added, the mixture is transferred to a 2-l. separatory funnel and shaken. The layers are separated and the aqueous layer is extracted twice with 100-ml. portions of petroleum ether (b.p. 60–68°). The organic layers are combined and dried over anhydrous magnesium sulfate.

The solvent is removed at a maximum water-bath temperature of 60° and a minimum pressure of 30 mm. (Note 8). The residual liquid is distilled through a 25-cm. Vigreux column, and the fraction boiling at 74–76/8 mm. is collected (Note 9). The yield of 2-oxa-7,7-dichloronorcarane is 91–100 g. (68–75%), n_D^{25} 1.4974–1.4983.

2. Notes

- All the glassware used is dried in an oven at 120°. The reaction vessel is arranged so that all the steps prior to hydrolysis are carried out under a constant positive pressure of dry nitrogen.
- The sodium methoxide was obtained from Matheson, Coleman and Bell Co. The submitters carried out all operations with this reagent in a dry-box under a stream of dry nitrogen. Sodium ethoxide and potassium *tert*-butoxide have been successfully substituted for sodium methoxide;² the choice of sodium methoxide is here principally one of convenience. With other olefins, the choice of alkoxide depends upon the boiling points of the dichlorocarbene adduct and the corresponding dialkyl carbonates.
- The checkers did not use a dry-box but simply rapidly weighed the sodium methoxide on a balance which was constantly swept with a stream of dry nitrogen from a large inverted funnel and then transferred the solid directly to the reaction flask.
- The dihydropyran (Matheson) is dried over sodium carbonate and distilled once prior to use.
- Technical grade pentane (Eastman Kodak) is freed of olefins by five successive washes each with 100 ml. of concentrated sulfuric acid per liter of pentane. The olefin-free pentane is then washed with an equal amount of water, dried over magnesium sulfate, distilled, and stored over sodium wire.
- Ethyl trichloroacetate (Eastman Kodak) is distilled prior to use.
- The nitrogen flow must be slow enough to prevent significant loss of the pentane by evaporation.

8. A rotary evaporator is a convenient apparatus for this operation.
9. Distillation at significantly higher pressures results in increased decomposition.

3. Discussion

The present procedure is that described by the submitters.³

4. Merits of the Preparation

The generation of dichlorocarbene for addition to olefins has been realized by the use of chloroform and alkali metal alkoxides^{4,5} (preferably potassium *tert*-butoxide), sodium trichloroacetate,⁶ butyllithium and bromotrichloromethane,⁷ phenyl(trichloromethyl)mercury,⁸ and the reaction of an ester of trichloroacetic acid with an alkali metal alkoxide.^{2,3} The latter method, which is here illustrated by the preparation of 2-oxa-7,7-dichloronorcarane, and procedures using phenyl-(trichloromethyl)mercury generally give higher yields of adducts.

References and Notes

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Appendix

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

petroleum ether

2-Oxa-7,7-dichloronorcarane

butyllithium

sulfuric acid (7664-93-9)

chloroform (67-66-3)

sodium carbonate (497-19-8)

nitrogen (7727-37-9)

sodium methoxide (124-41-4)

sodium (13966-32-0)

sodium ethoxide (141-52-6)

Pentane (109-66-0)

magnesium sulfate (7487-88-9)

trichloroacetic acid (76-03-9)

dihydropyran

ethyl trichloroacetate (515-84-4)

7,7-Dichloro-2-oxabicyclo[4.1.0]heptane (7556-13-0)

sodium trichloroacetate (650-51-1)

bromotrichloromethane (75-62-7)

Phenyl(trichloromethyl)mercury,
phenyl-(trichloromethyl)mercury (3294-57-3)

potassium tert-butoxide (865-47-4)