Organic Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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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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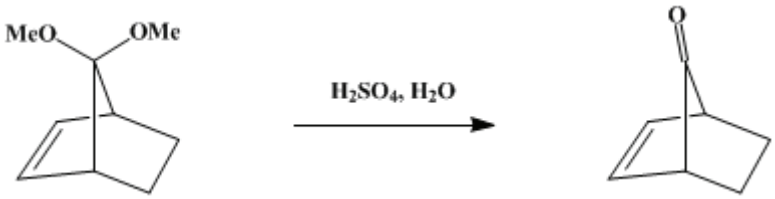
BICYCLO[2.2.1]HEPTEN-7-ONE

[2-Norbornen-7-one]



Submitted by P. G. Gassman and J. L. Marshall[1].
Checked by William G. Dauben and James L. Chitwood.

1. Procedure

Into a 250-ml. Erlenmeyer flask are placed 45.9 g. (0.298 mole) of 7,7-dimethoxybicyclo[2.2.1]heptene (Note 1), 75 ml. of 5% aqueous sulfuric acid, and a Teflon-coated magnetic stirring bar. The flask is stoppered, and the mixture is stirred vigorously with a magnetic stirrer for 20 hours. The mixture is extracted with three 40-ml. portions of pentane, and the combined extracts are dried over anhydrous magnesium sulfate. The drying agent is removed by filtration, and the solvent is distilled through a 12-in. Vigreux column. Fractional distillation of the residual oil yields 28.9 g. (90%) of colorless bicyclo[2.2.1]hepten-7-one, b.p. 96–100° (115 mm.), n^{25}D 1.4786 (Note 2) and (Note 3).

2. Notes

1. The preparation of 7,7-dimethoxybicyclo[2.2.1]heptene is described on p. 424.
2. The checkers, working at half-scale, obtained an 85% yield of product, b.p. 93–97° (118 mm.).
3. This material is extremely volatile and should be handled with care.

3. Discussion

Bicyclo[2.2.1]hepten-7-one has been prepared by the oxidation of *anti*-7-hydroxybicyclo[2.2.1]heptene with chromic acid in acetone[2] and with aluminum *t*-butoxide in benzene with benzoquinone as the hydrogen acceptor.[3] The procedure described here is essentially that of Gassman and Pape.[4]

4. Merits of the Preparation

Bicyclo[2.2.1]hepten-7-one is a useful intermediate in the synthesis of a variety of norbornane derivatives. The present procedure involves a four-step synthesis from hexachlorocyclopentadiene with a 39% overall yield. The next best method[3] involves a four-step synthesis from norbornadiene with a 15% overall yield.

References and Notes

1. Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.
2. C. J. Norton, Ph.D. Thesis, Harvard University, 1955.
3. R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28**, 3165 (1963).
4. P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).

Appendix

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

sulfuric acid (7664-93-9)

Benzene (71-43-2)

hydrogen (1333-74-0)

acetone (67-64-1)

chromic acid (7738-94-5)

Pentane (109-66-0)

benzoquinone (106-51-4)

magnesium sulfate (7487-88-9)

Bicyclo[2.2.1]hepten-7-one,
2-Norbornen-7-one (694-71-3)

7,7-Dimethoxybicyclo[2.2.1]heptene (875-04-7)

hexachlorocyclopentadiene

norbornadiene

anti-7-hydroxybicyclo[2.2.1]heptene

aluminum t-butoxide

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