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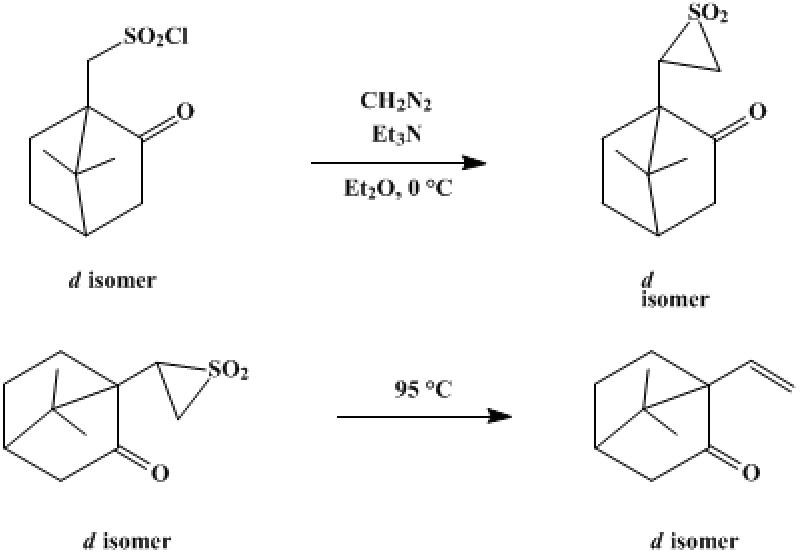
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.048.0106

Organic Syntheses, Coll. Vol. 5, p.877 (1973); Vol. 48, p.106 (1968).

D-2-OXO-7,7-DIMETHYL-1-VINYLBICYCLO[2.2.1]HEPTANE

[2-Norbornanone, 7,7-dimethyl-1-vinyl-, D-]



Submitted by Nikolaus Fischer[1] and G. Opitz[2].
Checked by Hermann Ertl, Ian D. Rae, and Peter Yates.

1. Procedure

Caution! Diazomethane is both explosive and poisonous, and all operations involving its preparation and use must be carried out in a hood. Follow the directions for its handling given in earlier volumes.[3,4]

In a 500-ml. three-necked flask equipped with a mechanical stirrer, a dropping funnel, and a reflux condenser fitted with a potassium hydroxide drying tube are placed 7.0 g. (0.069 mole) of triethylamine (Note 1) and a solution of 3.15 g. (0.075 mole) of diazomethane in 200 ml. of ether (Note 2). The flask is cooled in an ice bath, and a solution of 13.0 g. (0.052 mole) of D-camphor-10-sulfonyl chloride (Note 3) in 75 ml. of anhydrous ether is added dropwise over a period of 1 hour. Triethylamine hydrochloride slowly precipitates. The reaction mixture is stirred for an additional 30 minutes and then concentrated to *ca.* 150 ml. under reduced pressure (water aspirator) with continued stirring to remove the excess of diazomethane. The mixture is filtered under reduced pressure; the precipitate is washed with 50 ml. of anhydrous ether, giving 6.7 g. (94%) of triethylamine hydrochloride. The combined filtrate and washings are freed of solvent on a rotary evaporator at room temperature to give 10.7 g. (90%) of crude episulfone, m.p. 76–85° (dec.) (Note 4). This is used without purification in the next step; it can be purified by crystallization from a little methanol at −20°. This gives colorless episulfone, m.p. 83–85° (dec.), $[\alpha]^{24}\text{D}$ −6.72° (methanol, *c* = 3.20); infrared bands at 3070, 1300, and 1170 cm.$^{-1}$ (Note 5).

The crude episulfone (3.0 g.) is placed in a 10-ml. round-bottomed flask fitted with a reflux condenser and is heated at 95° for 30 minutes, when it decomposes with loss of sulfur dioxide. The reflux condenser is replaced with a distillation head (Note 6), and the yellow residue is distilled under reduced pressure (water aspirator). D-2-Oxo-7,7-dimethyl-1-vinylbicyclo[2.2.2]heptane (1.7 g., 71% based on sulfonyl chloride), b.p. 95–96° (10 mm.), distills at a bath temperature of 110–120°. Sublimation at 60° (0.01 mm.) gives the olefin as colorless, waxy crystals, m.p. 64–65°, $[\alpha]^{25}\text{D}$ +16.35° (methanol, *c* = 2.16); infrared band at 1650 cm.$^{-1}$.

2. Notes

1. The triethylamine was purified by treatment with naphthyl isocyanate and distilled; the distillate was stored over sodium wire.
2. The ethereal diazomethane was prepared from N-nitrosomethylurea and aqueous potassium hydroxide and dried over potassium hydroxide pellets for 2–3 hours. The solid potassium hydroxide was replaced once or twice to ensure complete dryness. The checkers used the procedure of Arndt[5] for this preparation and for the estimation of the diazomethane.
3. D-Camphor-10-sulfonyl chloride can be prepared from commercially available D-camphor-10-sulfonic acid and phosphorus pentachloride[6] or thionyl chloride.[7] The checkers used the following procedure. D-Camphor-10-sulfonic acid (50.0 g.) was added slowly to 50 g. of thionyl chloride. The mixture was boiled under reflux until homogeneous and then for a further 2 hours. The solution was cooled and poured onto *ca.* 500 g. of crushed ice. The crude product (51.1 g., 95%) was filtered and crystallized twice from hexane to give the sulfonyl chloride, m.p. 65–67.5°; yield, 35.5 g. (66%).
4. The checkers obtained higher yields (94–97%) of less pure material [m.p. 50–78° (dec.)].
5. The checkers observed that the episulfone decomposed slowly at room temperature and, on one occasion, during evaporation at 15°.
6. The checkers found it advisable to use an apparatus with a wide-bore side arm (18 mm.) without a condenser.

3. Discussion

The only method reported for the preparation of D-2-oxo-7,7-dimethyl-1-vinylbicyclo[2.2.1]heptane is that of the present procedure.[8,9]

4. Merits of the Preparation

The method is of general applicability[8,9] for the synthesis of olefins. Other sulfonyl chlorides, RCH_2SO_2Cl, have been used where R = H, C_2H_5, C_6H_5, and $C_6H_5CH_2$; other diazoalkanes that have been used are diazoethane and 1-diazo-2-methyl-propane. In all cases the olefins form without double-bond migration. A review[9] of the method is available.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 231

References and Notes

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2. Chemisches Institut der Universität, Tübingen, Germany.
3. T. J. de Boer and H. J. Backer, *Org. Syntheses*, Coll. Vol. **4**, 250 (1963).
4. J. A. Moore and D. E. Reed, this volume, p. 351.
5. F. Arndt, *Org. Syntheses*, Coll. Vol. **2**, 165 (1943).
6. P. D. Bartlett and L. H. Knox, this volume, p. 196.
7. S. Smiles and T. P. Hilditch, *J. Chem. Soc.*, **91**, 519 (1907).
8. G. Opitz and K. Fischer, *Angew. Chem.*, **77**, 41 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4**, 70 (1965) [Correction: Compounds (**1f**) and (**2i**) were obtained from 1-diazo-2-methylpropane (R^2=H, R^3=$CH(CH_3)_2$) and not from 2-diazobutane (R^2=CH_3, R^3=C_2H_5)].
9. N. H. Fisher, *Synthesis*, 393 (1970).

Appendix

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

episulfone

D-2-Oxo-7,7-dimethyl-1-vinylbicyclo[2.2.2]heptane

methanol (67-56-1)

ether (60-29-7)

phosphorus pentachloride (10026-13-8)

thionyl chloride (7719-09-7)

sulfur dioxide (7446-09-5)

potassium hydroxide (1310-58-3)

sodium wire (13966-32-0)

Triethylamine hydrochloride (554-68-7)

Diazomethane (334-88-3)

N-nitrosomethylurea

hexane (110-54-3)

naphthyl isocyanate (86-84-0)

triethylamine (121-44-8)

D-camphor-10-sulfonyl chloride (6994-93-0)

D-2-Oxo-7,7-dimethyl-1-vinylbicyclo[2.2.1]heptane,
2-Norbornanone, 7,7-dimethyl-1-vinyl-, D- (53585-70-9)

diazoethane

1-diazo-2-methyl-propane

D-camphor-10-sulfonic acid (3144-16-9)