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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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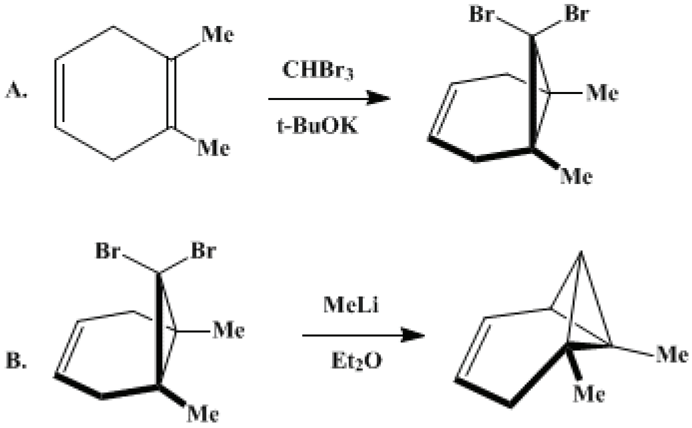
1,6-DIMETHYLTRICYCLO[4.1.0.0^{2,7}]HEPT-3-ENE



Submitted by R. T. Taylor and L. A. Paquette[1].
Checked by David A. Cortes and M. F. Semmelhack.

1. Procedure

A. *7,7-Dibromo-1,6-dimethylbicyclo*[4.1.0]*hept-3-ene.* Into a 3-L, three-necked flask equipped with an overhead stirrer, 1-L addition funnel, and reflux condenser capped with a nitrogen-inlet tube are introduced 44.8 g (0.4 mol) of powdered potassium *tert*-butoxide (Note 1) and 1 L of olefin-free petroleum ether (bp 35–55°C; (Note 2)). To this stirred mixture is added a solution containing 38.0 g (0.35 mol) of 1,2-dimethyl-1,4-cyclohexadiene (Note 3) in 200 mL of the same solvent. With external cooling from an ice bath and under nitrogen, 102.4 g (0.4 mol) of bromoform in 400 mL of petroleum ether is added dropwise during 1 hr. The ice bath is removed and the resultant slurry is stirred at room temperature under nitrogen for 6 hr. Water (500 mL) is added and the mixture is poured into a 3-L separatory funnel containing 300 mL of benzene. The organic layer is washed with four 500-mL portions of water, dried over anhydrous magnesium sulfate, and concentrated on a rotary evaporator (Note 4). Further evacuation at 0.5 mm produces a solid that is recrystallized from ether–petroleum ether (1 : 3) to afford 55–62 g (56.5–63.5%) of colorless solid, mp 95–98°C (Note 5).

B. *1,6-Dimethyltricyclo*[4,1.0.0^{2,7}]*hept-3-ene*. A solution of 20.95 g (0.075 mol) of 7,7-dibromo-1,6-dimethylbicyclo[4.1.0]hept-3-ene in 500 mL of anhydrous ether is placed in a 1-L, three-necked flask equipped with a magnetic stirring bar, reflux condenser, addition funnel, and nitrogen-inlet tube. With stirring under nitrogen and external cooling in an ice bath, 50 mL of 1.6 *M* ethereal methyllithium (Note 6) in 70 mL of ether (0.08 mol) is introduced by dropwise addition during 30 min. The ice bath is removed and the mixture is stirred at room temperature for 1 hr. After 100 mL of water has been cautiously introduced, the mixture is transferred to a separatory funnel and the organic layer is separated. This solution is washed with water (3 × 100 mL), dried over anhydrous sodium sulfate (Note 7), and carefully concentrated by slow distillation through a 40-cm Vigreux column at atmospheric pressure, heating at <60°C (Note 8). The residual liquid is distilled through a short, unpacked column to give 4.2–4.4 g (46–49%) of colorless oil, bp 48–49°C (23 mm) (Note 9). Under the proper conditions, this hydrocarbon can be stored for 2 weeks at −5°C without deterioration.

2. Notes

1. Potassium *tert*-butoxide can be obtained commercially from MSA Research Corporation, Callery, Pennsylvania. The checkers used a sample from Aldrich Chemical Company, Inc.
2. A liter of technical grade petroleum ether was treated in a separatory funnel with 200 mL of concentrated sulfuric acid, washed with water, and dried over anhydrous magnesium sulfate.
3. This diene was prepared by the procedure of Paquette and Barrett;[2] satisfactory results can be realized with material of 70–85% purity (15–30% contamination by *o*-xylene) since the aromatic impurity does

not react subsequently and is easily removed.

4. Any residual *o*-xylene should be removed prior to crystallization because the dibromide is exceedingly soluble in aromatic solvents.

5. Further recrystallization is not necessary, but pure crystals, mp 107–108°C, can be obtained in the manner described by Vogel and co-workers.[3]

6. The ethereal methyllithium solutions were purchased from Alfa Inorganics. The concentration of methyllithium in such solutions may be conveniently determined by a procedure described elsewhere[4,5] in which the lithium reagent is titrated with *sec*-butyl alcohol, utilizing the charge transfer complex formed from bipyridyl or *o*-phenanthroline and the lithium reagent as indicator.

7. Anhydrous magnesium sulfate is too acidic for this purpose and promotes rearrangement of the hydrocarbon.

8. All glassware that is to contain the cyclized product should be washed in base and dried (where necessary) prior to use.

9. The checkers found bp 55–56°C/30 mm. Attempted distillation at ca. 50 mm (bp 75°C) led to significant rearrangement to a dimethylcycloheptatriene. The product exhibits the following ^{1}H NMR spectrum ($CDCl_3$) δ: 1.08 (s, 3 H, CH_3), 1.33 (d, 1 H, $J = 2$, methine C-*H*), 1.52 (s, 3 H, CH_3), 2.15–1.80 (m, 3 H, allylic methylene and methine), 5.50–5.15 (m, 1 H, olefinic C-*H*), 6.10–5.70 (m, 1 H, olefinic C-*H*).

3. Discussion

The tricyclo[4.1.0.0^{2,7}]hept-3-ene ring system, with its conjugated bicyclobutane ring and double bond and its isomeric relationship to cycloheptatriene, has recently commanded attention as a precursor of yet more highly strained molecules. However, the preparation of the parent hydrocarbon by reaction of 7,7-dibromo-3-norcarene with methyllithium at 0°C, first reported by Klummp and Vrielink,[6] does not proceed in yields above 1–5%.[6,7] Placement of a single methyl group at a ring juncture position of the transient norcarenylidene intermediate is, however, adequate to promote efficient ring closure through C-H alpha insertion.[7,8] The procedure described above is exemplary. Although two alternative routes to tricyclo[4.1.0.0^{2,7}]hept-3-enes are currently available,[6,9] alkyllithium-promoted cyclization of readily available 7,7-dibromobicyclo[4,1.0]hept-3-enes constitutes the most direct and efficient approach. In addition, this procedure illustrates an entirely general method for converting norcarane derivatives to *endo,endo*-1,3-bridged bicyclobutanes.[10,11,12]

Exposure of tricyclo[4.1.0.0^{2,7}]hept-3-enes to catalytic amounts of Ag^+ leads instantaneously and quantitatively to cycloheptatriene derivatives.[7] Promise of their usefulness as synthetic intermediates is growing rapidly.[13,14]

References and Notes

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

petroleum ether

olefin-free petroleum ether

bipyridyl or o-phenanthroline

7,7-dibromobicyclo[4,1.0]hept-3-enes

endo,endo-1,3-bridged bicyclobutanes

sulfuric acid (7664-93-9)

Benzene (71-43-2)

ether (60-29-7)

sodium sulfate (7757-82-6)

nitrogen (7727-37-9)

bromoform (75-25-2)

lithium (7439-93-2)

magnesium sulfate (7487-88-9)

Methyllithium (917-54-4)

cycloheptatriene (544-25-2)

1,2-Dimethyl-1,4-cyclohexadiene (17351-28-9)

sec-butyl alcohol (78-92-2)

1,6-Dimethyltricyclo[4.1.0.0^{2,7}]hept-3-ene (61772-32-5)

7,7-Dibromo-1,6-dimethylbicyclo[4.1.0]hept-3-ene (38749-43-8)

dimethylcycloheptatriene

7,7-dibromo-3-norcarene

norcarenylidene

o-Xylene (95-47-6)

potassium tert-butoxide (865-47-4)