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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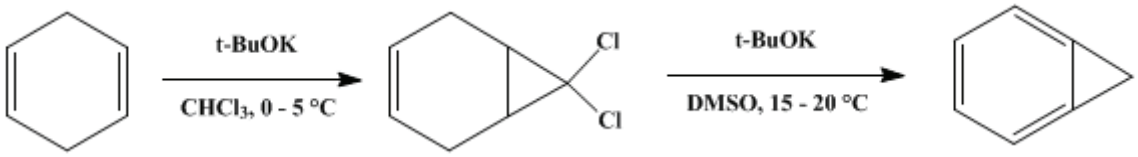
BENZOCYCLOPROPENE

[Bicyclo [4.1.0]hepta-1,3,5-triene]



Submitted by W. E. Billups[1], A. J. Blakeney, and W. Y. Chow[1].
Checked by Nobuo Nakamura and S. Masamune.

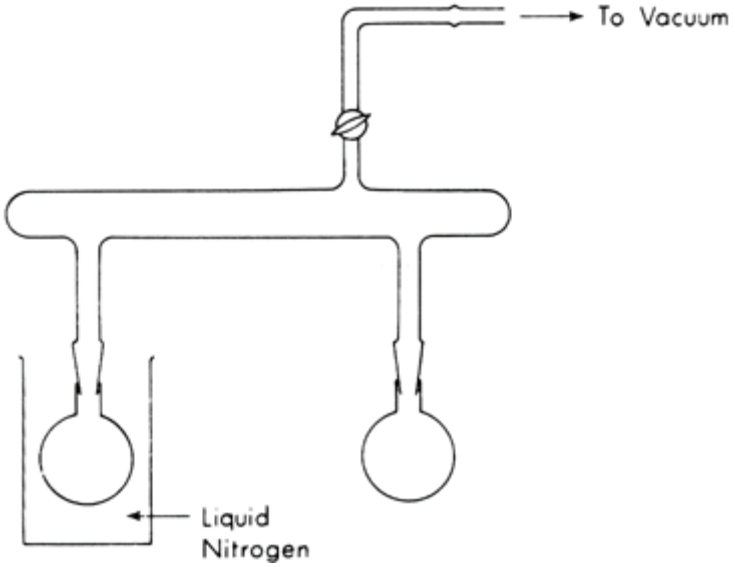
1. Procedure

Caution! Benzocyclopropene is characterized by an extremely unpleasant (foul) odor, and use of a good hood is recommended for the preparation.

A. *7,7-Dichlorobicyclo*[4.1.0]*hept-3-ene*.[2] A 2-l., three-necked, round-bottomed flask is equipped with a sealed mechanical stirrer, a reflux condenser, and a pressure-equalizing dropping funnel. The system is flushed with nitrogen with a gas-inlet tube attached to the top of the condenser before 126 g. (1.123 moles) of potassium *tert*-butoxide (Note 1) and 1.2 l. of pentane are added. The stirred suspension is cooled to 0–5° with an ice bath and 90 g. (1.12 moles) of 1,4-cyclohexadiene (Note 2) is introduced rapidly through the dropping funnel; 135 g. (1.131 moles) of chloroform (Note 3) is then added dropwise over a period of 1.5–2 hours. The resulting mixture is stirred for an additional 30 minutes before 300 ml. of cold water is added to dissolve all of the precipitated salts. The organic phase is separated, and the aqueous phase is extracted with one 50-ml. portion of pentane. The extract is combined with the original pentane solution and dried over approximately 20 g. of anhydrous sodium sulfate. The solvent is removed on a rotary evaporator, and the product is distilled through a 15-cm. Vigreux column, giving 69–72 g. (38–39%) of 7,7-dichlorobicyclo[4.1.0]hept-3-ene, b.p. 50–51° (0.8 mm.) (Note 4).

B. *Benzocyclopropene*. A dry, three-necked, round-bottomed flask fitted with a sealed mechanical stirrer, a reflux condenser, and a pressure-equalizing dropping funnel is flushed with nitrogen and charged with 35.0 g (0.312 mole) of potassium *tert*-butoxide (Note 1), followed by 200 ml. of dimethyl sulfoxide (Note 5). The stirred mixture is cooled to 15–20° (Note 6) with an ice bath before 24.5 g. (0.154 mole) of 7,7-dichlorobicyclo[4.1.0]hept-3-ene is added over a 7-minute period. The bath is removed, the mixture stirred an additional 25 minutes, and the reaction quenched by first cooling the flask with an ice bath and then adding 180 ml. of ice water. The crude product is pumped directly into an acetone–dry ice cold trap through a glass vacuum take-off adapter. The *tert*-butyl alcohol and dimethyl sulfoxide are removed by washing the distillate once with 400 ml. of ice water (Note 7) and (Note 8). The benzocyclopropene that separates as the lower layer is distilled from 1 g. of anhydrous sodium sulfate, using the apparatus shown in Figure 1. This procedure gives 4.35–5.48 g. (32–41%) of almost pure benzocyclopropene (Note 9).

Figure 1.



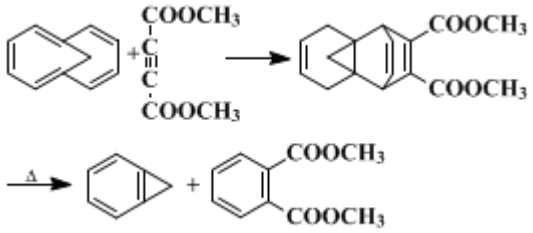
2. Notes

1. Potassium *tert*-butoxide was used from a freshly opened bottle supplied by the MSA Research Corporation.
2. The checkers purchased 1,4-cyclohexadiene from Aldrich Chemical Company, Inc., and distilled it prior to use.
3. Reagent grade chloroform was used without removal of stabilizer.
4. The product was shown to be approximately 95% pure by GC analysis, using a 180 cm. × 0.24 cm. column packed with UCW-98 and heated to 130°.
5. Dimethyl sulfoxide (supplied by the Aldrich Chemical Company, Inc.) was dried by distilling over calcium hydride at 5 mm.
6. Care should be taken not to freeze the dimethyl sulfoxide.
7. On one occasion the checkers observed that the mixture formed an emulsion and that centrifugation facilitated the separation of the layers.
8. An alternative procedure is to extract the product into pentane.
9. The ^{1}H NMR spectrum shows that the product is approximately 95% pure. The major impurities are toluene and styrene. The product has the following spectral properties; IR (neat) $cm.^{-1}$: 1666, 1380, 1060, 735; ^{1}H NMR ($CDCl_3$), δ (number of protons): 3.17 (2H), 7.21 (4H); ^{13}C NMR ($CDCl_3$ δ: 18.56, 115.07, 125.86, 129.15; UV (cyclohexane) nm. max. (log ε): 263 (3.88), 268 (3.96), 276 (3.90).

3. Discussion

Fusion of the smallest cycloalkene, cyclopropene, to benzene would be expected to result in accommodation of the aromatic sextet with consequent bond length alteration in the aromatic ring. Benzocyclopropene thus arouses theoretical interest, and the high strain energy (approximately 68 kcal./mole)[3] associated with the compound suggests unusual chemical reactivity. Two review articles have appeared.[4,5]

The first successful synthesis of benzocyclopropene was reported by Vogel and coworkers[6] and is illustrated below. Though elegant, this method does require the prior, lengthy synthesis of the commercially unavailable 1,6-methano[10]annulene.[7]



The procedure described here[8] is a convenient two-step reaction which relies on the base-induced elimination-isomerization reactions of *gem*-dichlorocyclopropanes.[9,10,11,12,13,14,15,16] The reaction mechanism has been studied.[17] The principal advantage of this method is the availability of reagents.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 6, 731

References and Notes

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

MSA Research Corporation

Benzene (71-43-2)

chloroform (67-66-3)

sodium sulfate (7757-82-6)

nitrogen (7727-37-9)

toluene (108-88-3)

Pentane (109-66-0)

styrene (100-42-5)

dimethyl sulfoxide (67-68-5)

tert-butyl alcohol (75-65-0)

calcium hydride (7789-78-8)

1,4-cyclohexadiene

Benzocyclopropene

Bicyclo [4.1.0]hepta-1,3,5-triene (4646-69-9)

7,7-dichlorobicyclo[4.1.0]hept-3-ene (16554-84-0)

Cyclopropene (2781-85-3)

1,6-Methano[10]annulene (2443-46-1)

potassium tert-butoxide (865-47-4)