

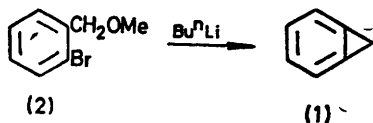
## Synthesis and Birch Reduction of Benzocyclopropene

By PHILLIP RADLICK\* and HERSCHEL T. CRAWFORD

(Department of Chemistry, University of California, Riverside, California 92502)

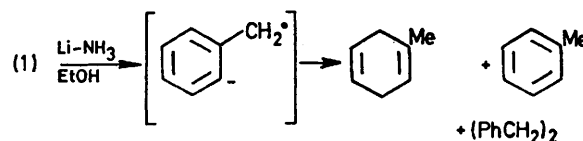
**Summary** *o*-Bromobenzyl methyl ether reacts with *n*-butyl-lithium to give benzocyclopropene, Birch reduction of which gives only products related to cyclopropene ring opening.

SEVERAL reports of the preparation of benzocyclopropene (1) have appeared and are well documented by Billups.<sup>1</sup> We have found that (1) may also be prepared *via* a 1,3-elimination from the readily available *o*-bromobenzyl methyl ether (2). Treatment of (2) with Bu<sup>n</sup>Li in tetrahydrofuran (initially at -40 °C for 30 min, then heated at reflux for 1 h) followed by aqueous work up and extraction



into ether gives (1) in 30% yield. A sample of (1) purified by g.l.c. gave n.m.r., u.v., and i.r. spectra in complete accord with those published.<sup>1</sup> The reaction no doubt proceeds by an initial exchange reaction to form the *o*-lithiobenzyl methyl ether followed by elimination of LiOMe to give (1). This synthesis opens up the possibility of preparing a large variety of benzocyclopropenes which are substituted in the aromatic ring, provided that the substituent is stable to Bu<sup>n</sup>Li. Since direct attempts at

electrophilic substitution on benzocyclopropene lead to cyclopropene ring opening, this synthesis may be of great importance. Leaving groups other than methoxy may give better yields of (1) and we are investigating this.



SCHEME

We also investigated the Birch reduction of (1). Treatment of (1) in liquid NH<sub>3</sub>-Et<sub>2</sub>O with Li (2.5 mol. equiv.) and EtOH gave (93% total yield) a mixture of toluene, 2,5-dihydrotoluene, and 1,2-diphenyl ethane (62:28:10). It is clear that under these conditions cleavage of the cyclopropene ring takes place most readily. We could not detect any bicyclic materials of the usual variety found in the Birch reduction of other benzocycloalkenes.<sup>2</sup> We suggest that this reaction takes place as in the Scheme.

We are grateful for support from a Public Health Service Research Career Development Award from the Institute of General Medical Sciences.

(Received, 12th November, 1973; Com. 1560.)

<sup>1</sup> W. Billups, A. Blakeney, and W. Chow, *Chem. Comm.*, 1971, 1461.

<sup>2</sup> H. House, 'Modern Synthetic Reactions', 2nd edn., Benjamin, New York, 1972, pp. 145-227.