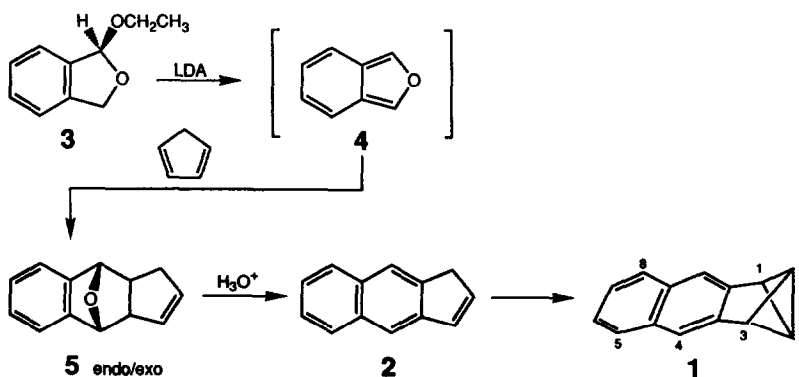


BENZ[F]INDENE AND ITS KATZ REACTION

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Summary. A novel and very short synthesis of the useful title hydrocarbon **2** is presented. Its key step is based on a *Diels-Alder* reaction of isobenzofuran **4**. The lithium salt of **2** gives a remarkably stable valence isomer of anthracene **1** in a reaction analogous to the indene → benzobenzvalene transformation.

For our continuing studies of the physical and chemical properties of bridged bicyclo[1.1.0]butanes^{2,3}, we needed preparative scale access to 1,2,3-metheno-2,3-dihydro-1H-cyclopenta[b]naphthalene (naphtho[2,3]benzvalene) **1**. Although this valence isomer of anthracene had been obtained previously as a byproduct of the reaction of dilithio-s-indacene with chlorocarbene⁴, a more economical approach was desired, and we considered the possibility of obtaining the bicyclobutane **1** from benz[f]indene **2** via a *Katz* reaction⁵. Curiously, prior to early 1990, no synthesis of benz[f]indene **2** could be found in the chemical literature. Only very recently we learned of an eight-step procedure giving compound **2** in 11% o.a. yield⁷. This synthesis starts from 2-methyl naphthalene, and uses a *Friedel-Crafts* cyclization as its key step.



In view of the increasing interest⁸ in benz[f]indene **2**, we wish to report an alternative shorter route to this useful hydrocarbon, and comment finally on its transformation into the bicyclobutane derivative **1**. The skeleton of **2** was assembled, in our approach, by a *Diels-Alder* reaction of isobenzofuran **4**⁹ with cyclopentadiene.

To this purpose, we treated a 0.6M solution of the readily available 1-ethoxy-1,3-dihydrobenzofuran **3**¹⁰ in benzene with 2.5 equivalents of LDA, hydrolyzed with sat. aqueous NH₄Cl, and intercepted the ensuing diene **4** by addition of 1.5 equivalents of cyclopentadiene. After reflux for 2h, the solvent was removed and the products purified by flash chromatography (silica gel, hexane/ether 9:1). This procedure gave a 1:5 mixture of *exo*, and *endo*-4,9-epoxy-3a,4,9,9a-tetrahydro-1H-benz[*f*]indene **5** in 69% isolated yield. The ring opening and dehydration of this isomeric mixture was achieved by boiling its solution in ethanol/conc. hydrochloric acid (15:1) for 5h under reflux. Flash chromatography (silica gel, hexane), or alternatively crystallization from ethanol, gave the colorless benz[*f*]indene **2** in 83 % yield, with m.p.160-162 °C (lit.⁷ 163-164 °C), identical by ¹H and ¹³C-NMR with the compound described in lit.⁷.

The transformation **2** → **1** followed closely the original protocol for the synthesis of benzobenzvalene from indene¹¹. To this purpose, a 0.7M solution of the lithium salt of **2** in ether was combined slowly at -50 °C under N₂ with four equivalents of *n*-BuLi in hexane followed by a 10-fold molar excess of methylene chloride. After warming to 0 °C, the mixture was hydrolyzed with sat. aqueous NH₄Cl, washed with brine and dried over K₂CO₃. Medium pressure chromatography (silica gel, pentane) gave the crystalline bicyclobutane **1**¹² (R_f=0.42, m.p. 108-109 °C) in 12 % yield, and anthracene (R_f=0.32, 63 % yield).

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¹² For the photoelectron spectrum of **1** see ref.¹³. For ¹H-NMR of **1** see ref.⁴. ¹³C-NMR of **1** (CDCl₃, 50 MHz): 36.54 (C(1)/C(3), ¹J_{CH}=170 Hz); 37.17 (C(2)/C(10), ¹J_{CH}=216.5 Hz); 117.3, 124.6, and 127.2 (3-CH_{arom} of double intensity); 132.1, and 146.6 (2-C_{arom} of double intensity). The explicit assignment and the ¹J values are based on an INEPT spectrum.

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