of 4 and 6; ^{1}H NMR ($CDCl_3$) δ 5.16 (0.29 H, d, J = 4 Hz), 4.48 (0.71 H, d, J = 3 Hz), 3.04 (1 H, br s), 2.5–1.2 (7 H, m). Since these isomers could not be readily separated, the mixture was used in the dehydrobromination step.

A solution of 52.9 g of the mixture of 4 and 6 in 100 mL of *tert*-butyl alcohol was added dropwise over a 4-h period to a solution of 22 g (1.2 equiv) of potassium *tert*-butoxide in 150 mL of *tert*-butyl alcohol. The reaction mixture was refluxed for 8 h, cooled to 25 °C, and poured into 300 mL of water. The aqueous solution was extracted with three 100-mL portions of ether. The combined extracts were washed with brine, dried over anhydrous magnesium sulfate, and filtered, and the filtrate was concentrated. Fractional distillation gave 20.4 g (51%) of 2,3-dibromobicyclo-[2.2.1]hept-2-ene (1): bp 58–60 °C (1.5 mm); ^{1}H NMR ($CDCl_3$) δ 2.92 (2 H, t, J = 2 Hz), 1.8–1.0 (6 H, m); ^{13}C NMR ($CDCl_3$) 125.37 (s), 51.42 (d), 46.80 (t), 25.53 (t) ppm; exact mass calcd for $C_7H_8{}^{79}Br_2$ 249.8993, found 249.9004. An analytical sample was prepared by preparative VPC on 10 ft × 0.25 in. 10% SE-30 on 60/80 Chromosorb W at 170 °C.

Anal. Calcd for $C_7H_8Br_2$: C, 33.37; H, 3.20; Br, 63.43. Found: C, 33.46; H, 3.24; Br, 63.53.

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A Convenient and Unambiguous Synthesis of 1-Bromoindene

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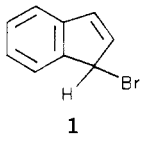
The literature on 1-bromoindene (1) is sparse and inconclusive. It was first reported in 1944[1] as the product (24% yield) of the reaction of indene and *N*-bromosuccinimide. Later, Crofts and Williamson found this method gave them only low and variable yields.[2] However, they did describe a new route to 1 involving dehydrobromination of *trans*-1,2-dibromoindane (3). This reaction



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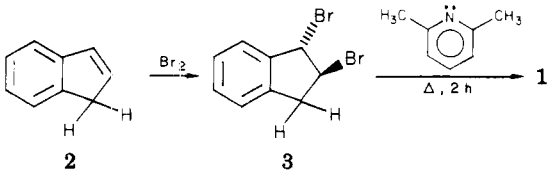
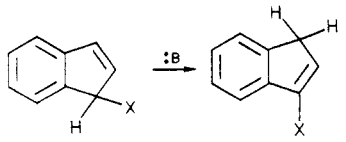


2 3

gave a single product (24% yield) that had a boiling point and infrared spectrum similar to that reported earlier.[1] It was further argued[2] that 1 should be the exclusive product because the reaction conditions favored the E2 mechanism, i.e., strong base, high temperature, and nonpolar solvent.

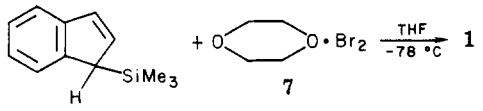
In light of a recent study by Freidrich and Taggart,[3] however, in which it was shown that 1-substituted indenes (4) isomerize rapidly and quantitatively to derivatives of structure 5 in the presence of even weakly basic amines,



4 5

the earlier assignments became questionable. Since other work in our laboratories required ready access to 1-bromoindene and the published methods[1,2] gave us low yields of complex mixtures, we looked for a simple and unambiguous synthetic procedure.

The successful cleavage of silicon–carbon bonds by electrophilic reagents[4] led us to consider that approach as a route to 1. We found that 1-(trimethylsilyl)indene (6), when treated with a 10% excess of dioxane dibromide (7) in tetrahydrofuran at −78 °C, gave 1 in 66% yield. All



6 7

of silane 6 was consumed and 1-bromoindene (1) was detected as the sole product. The yield corresponded to pure product after column chromatography. The ^{1}H NMR spectrum permitted an unambiguous structural assignment, eliminating the possibility that the isomer 5, X = Br, was the product. The complexation of bromine by dioxane is essential to the success of this preparation. When bromine was substituted for 7, 1 could be detected by ^{1}H NMR but not isolated.

Experimental Section

1-(Trimethylsilyl)indene (6) was prepared by the method of Rakita and Davison.[5] Dioxane dibromide (7) was prepared by the method of Billimoria and Maclagen.[6] Tetrahydrofuran was purified by distillation from sodium benzophenone ketyl immediately before use. Pentane was stirred over H_2SO_4 and distilled. NMR spectra were recorded on a Varian EM-390 spectrometer, using tetramethylsilane as the internal standard.

1-Bromoindene (1). A 100-mL three-neck flask fitted with an addition funnel and a nitrogen inlet was dried and purged with nitrogen. The entire apparatus was covered with aluminum foil to exclude light. The flask was charged with (trimethylsilyl)indene (2.00 g, 10.7 mmol) and THF (25 mL). Dioxane dibromide (2.92 g, 11.8 mmol) was placed in the addition funnel to which 10 mL of THF was added to form a homogeneous solution. The flask was cooled in a bath of acetone–dry ice and the contents of the addition funnel were slowly added. Upon completion of this addition, the flask was allowed to warm to room temperature and the solvent was removed by rotary evaporation. The remaining oil was placed on top of 14 × 3.5 cm column of Florisil, 60–100 mesh, and eluted with 200 mL of pentane. Removal of solvent left 1.38 g (7.1 mmol, 66%) of pure 1 as a pale yellow liquid: NMR ($CDCl_3$) δ 5.48 (br s, 1 H, CHBr), 6.6 (d of d, J = 2, 6 Hz, 1 H, C=CHCHBr), 6.82 (d, J = 6 Hz, 1 H, HC=CHCHBr), 7.67–7.13 (m, 4 H, aromatic).

Anal. Calcd for C_9H_7Br: C, 55.38; H, 3.59. Found: C, 55.16; H, 3.74.

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