

55% yield: mp 42–43° (lit.⁶ mp 42–43°); ir (CCl₄) 1710 cm⁻¹ (C=O); nmr (CCl₄) δ 1.15 (s, 6), 2.9 (s, 2), 7.3 (m, 4).

1-*tert*-Butylethynyl-2,2-dimethylindan-1-ol was prepared as described earlier³ for the general synthesis of tertiary propargyl alcohols by addition of *tert*-butylethynyllithium to 2,2-dimethyl-1-indanone. Distillation afforded the alcohol in 82% yield (99–100° at 0.5 mm): ir (neat) 3460 cm⁻¹ (O—H), 2250 cm⁻¹ (C=C); nmr (CCl₄) δ 1.0 (s, 3), 1.15 (s, 3), 1.23 (s, 9), 2.02 (s, 1), 2.55 (s, 1), 2.78 (s, 1), 7.05 (m, 4).

1-(*tert*-Butylchlorovinylidene)-2,2-dimethylindan (2) was prepared according to the general procedure for the preparation of chloroallenes by Jacobs and Fenton.⁷ After three successive distillations from a small amount of sodium borohydride to remove unreacted alcohol, the desired chloroallene was obtained in 23% yield: bp 96–100° at 0.3 mm; ir (neat) 1945 cm⁻¹ (C=C); nmr (CCl₄) δ 1.22 (s, 9), 1.29 (s, 6), 2.86 (s, 2), 7.08 (m, 4).

Anal. Calcd for C₁₇H₂₃Cl: C, 78.31; H, 8.06; Cl, 13.63. Found: C, 78.40; H, 8.12; Cl, 13.46.

Kinetic Procedure.—The rate of appearance of HCl was measured conductometrically as described earlier.^{2,3} All rates are the average of triplicate determinations. Acetone was purified according to Denoon.⁸ Kinetic solvent solutions exhibited initial measured conductances of less than 2 μmho.

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Registry No.—2, 40548-49-0; 2,2-dimethyl-1-indanone, 10489-28-8; 1-*tert*-butylethynyl-2,2-dimethylindanol, 40548-50-3; *tert*-butylethynyllithium, 37892-71-0.

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A New Synthesis of Benzocyclobutene¹

ANDREA SANDERS² AND WARREN P. GIERING*

Department of Chemistry, Boston University,
Boston, Massachusetts 02215

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In connection with current studies of transition metal complexes of strained cyclic olefins, we required a supply of benzocyclobutene. The preparations of benzocyclobutene (2) previously reported in the literature are inconvenient for large-scale synthesis. Hydrogenation of 1,2-diiodobenzocyclobutene with palladium on carbon³ requires a specially aged sodium ethoxide catalyst and involves lengthy purifications. High temperature pyrolyses *in vacuo* (without or with uv irradiation) of 1,3-dihydroisothianaphthene 2,2-dioxide^{4,5} require special apparatus. A recent synthetic route to 2 involves the dissolving metal reduction of benzocyclobutenyl acetate⁶ which is prepared

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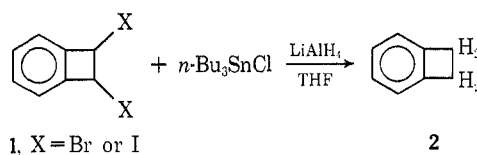
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by the cycloaddition of vinyl acetate to benzene-diazonium-2-carboxylate, an explosive benzync⁷ precursor requiring special handling.

We devised a convenient reduction of the mixture of 1,2-dibromo- and 1,2-diiodobenzocyclobutene^{3b} (1) which is readily prepared in 90% yields from the commercially available α,α,α',α'-tetrabromo-*o*-xylene (Columbia Organic Chemicals, Co., Inc.). Reduction of 1 with lithium aluminum hydride in refluxing tetrahydrofuran gave 2 in 20% yields. This method was inconvenient since large quantities of lithium aluminum hydride were required and much polymeric material was formed, thus making purification tedious. A more expeditious method involved the reduction of 1 with tri(*n*-butyl)tin hydride generated *in situ* from tri(*n*-butyl)tin chloride with lithium aluminum hydride. Since the reduction of 1 with the hydride gives



2 and tri(*n*-butyl)tin halide (which can be reduced to the hydride), only a limited amount of tri(*n*-butyl)tin chloride is needed. Thus this route is convenient for a large-scale synthesis since the reaction is carried out in one reaction vessel with no special apparatus required, the course of the reaction is readily monitored by nmr spectroscopy, and the purification procedures are straightforward. Assuming the reactants to be pure 1,2-dibromobenzocyclobutene, yields of >50% of 2 have been realized.

Experimental Section

Benzocyclobutene (2).—To a 1000-ml round-bottom flask fitted with a magnetic stirrer, heating mantle, and reflux condenser was added tetrahydrofuran (200 ml), tri(*n*-butyl)tin chloride (70 g, 0.22 mol), and 100 g of a mixture of 1,2-dibromo- and 1,2-diiodobenzocyclobutene.^{3b} Lithium aluminum hydride (10 g, 0.26 mol) was added in 0.5-g portions over a period of 6 hr. while a gentle reflux was maintained. The mixture was allowed to cool to room temperature, transferred to a 1000-ml erlenmeyer flask, treated sequentially with 10 ml of H₂O, 10 ml of 15% NaOH, and 30 ml of H₂O, and shaken after each addition. The resulting mixture was filtered through a large sintered-glass filter, and the residue was washed with two 50-ml portions of THF. The filtrate was rapidly distilled under reduced pressure (12 mm) into a trap cooled in liquid nitrogen until 202 ml of volatile material had been collected and the pot temperature reached 60°. While at 60°, the residue was placed under high vacuum (10⁻³ mm) and an additional 6 ml of volatile material collected. The nmr spectrum of the residue showed no remaining benzocyclobutene. The volatile fractions were combined (208 ml) and poured into 1250 ml of water in a large separatory funnel. The lighter organic layer was separated from the aqueous layer and then extracted three times with 50-ml portions of water, dried over MgSO₄, and filtered through a sintered-glass funnel. The remaining solvent was removed by distillation through a 25-cm Vigreux column until the head temperature reached 80°. The product (2) was collected *via* short-path distillation of the residue: 20 g, ~50% yield; bp 143°; uv max (95% EtOH) 260, 265.5, 271.5 nm; nmr (CCl₄) τ 6.88 (s, 4), 3.03 (m, 4).

Registry No.—1 (X = Br), 22250-72-2; 1 (X = I), 6639-21-0; 2, 694-87-1; tri(*n*-butyl)tin chloride, 1461-22-9.

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