crystallization from monoglyme solvent has already found a number of useful applications in organic chemistry. These applications include the regiospecific, quantitative hydroboration of alkenylsilanes,[7] the preparation of molecular addition compounds,[8] detailed kinetic studies on the hydroboration reaction[9] as well as provide the basis for the commercial preparation of the reagent.[10]

Thus with this new route to high-purity 9-BBN dimer the fascinating chemistry of this most remarkable reagent can be more conveniently and efficiently explored.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere, using oven-dried glassware (4 h, at 110 °C). Monoglyme and 1,5-cyclooctadiene were distilled from lithium aluminum hydride prior to use. Borane–methyl sulfide complex (Aldrich-Boranes) was used without prior purification. The ^{11}B NMR spectra were obtained on a Varian FT-80A instrument.

9-Borabicyclo[3.3.1]nonane (1). A 2-L round-bottom flask containing a magnetic stirring bar and surmounted by an addition funnel and a distillation assembly was charged, under a nitrogen atmosphere, with 1,2-dimethoxyethane (monoglyme, 500 mL) and borane–methyl sulfide complex (153 mL, 1.53 mol), using a double-ended needle. The addition funnel was similarly charged with 1,5-cyclooctadiene (164 g, 1.52 mol). To the stirred borane solution 1,5-COD was added dropwise over ca. 1 h (reaction temperature, 50–60 °C) during which time, dimethyl sulfide (bp 38 °C) distills slowly from the reaction mixture. After the addition was complete, approximately 300 mL of the solution was distilled to reach a distillation temperature of 83–85 °C, which indicated the removal of the dimethyl sulfide from the reaction mixture.[11] The distillation assembly was replaced with a rubber septum and monoglyme was added to bring the volume to ca. 1 L. The mixture was allowed to cool slowly to 0 °C, which results in the formation of crystalline (needles) 9-BBN.[12] The supernatant liquid was decanted with a double-ended needle and the residue was dissolved in fresh monoglyme (1 L). After cooling slowly to 0 °C, the supernatant liquid was removed as above, and the large needles were dried in vacuo (60 °C for 16 h, at 100 μmHg) to give 162 g (88%) of product mp 153–155 °C, sealed capillary).[13]

Solubility Determination. With purified reagent-grade solvents, saturated solutions of 9-BBN dimer were allowed to equilibrate for several hours in a constant temperature bath. Aliquots were hydrolyzed in a 50:50 methanol–tetrahydrofuran mixture, and the hydride molarity was determined from the corrected volume of hydrogen evolved.[14] The values so determined for dimeric 9-BBN are presented in Table II.

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Registry No. 1, 21205-91-4; borane methyl sulfide, 13292-87-0; 1,5-cyclooctadiene, 111-78-4; 9-BBN·THF, 76422-63-4; 9-BBN·S-$(CH_3)_2$, 64045-91-6; 9-BBN·NC_5H_5, 64045-95-0.

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(11) Failure to remove the dimethyl sulfide lowers the overall yield to ca. 65%. The high solubility 9-BBN in dimethyl sulfide (see Table II), which is likely to be due to the formation of 9-BBN·SMe_2 (see Table I), probably accounts for this yield diminution.
(12) These crystals can be dried as described to give 91% of product (mp 152–154 °C).
(13) The 9-BBN so prepared is reasonably air stable so that exposure to the atmosphere for 1 month lowered the melting point to 146–151 °C. We were unable to detect any significant (<2%) loss of hydride activity or selectivity for the exposed sample.
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1-Substituted Benzocyclobutenes via Parham Cyclialkylation[1]

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The discovery that certain 1-substituted benzocyclobutenes can undergo intramolecular cycloaddition through isomerization to a derivative of *o*-quinodimethane was one of the important synthetic advances of the past decade.[2] While such cycloadditions frequently occur stereospecifically and in excellent yield, the preparation of the desired 1-substituted benzocyclobutenes (**4**) has frequently been less satisfactory. Of the many[2] available, the most versatile preparative scheme for **4** has involved a Bunnett[3] cyclization of an *o*-halodihydrocinnamonitrile (**1** → **2**, Scheme I) followed either by elaboration of the nitrile group[4,5] or by alkylation[6,7] at the tertiary carbon α to it (**2** → **3**) with subsequent reductive decyanation (**3** → **4**).

The purpose of the present preliminary investigation was to determine whether the Parham cyclialkylation[8-10] reaction might offer a useful alternate route to 1-substituted benzocyclobutenes. For the preparation of the requisite model dihalides **8**, (2-bromophenyl)acetonitrile (**5**)[11] appeared to be a convenient starting material, since it was known that at −100 °C it reacts with butyllithium selectively by hydrogen–lithium exchange.[11] Further, Kaiser and Hauser[12] had shown that the anion derived from phenylacetonitrile in essentially this way could be monoalkylated in good yield.[13] Good results were obtained in the alkylation of **5** (75–92%) by using benzyl bromide, 1-bromobutane, or 5-bromo-1-butene.

The usual route from (2-bromophenyl)acetonitrile (**5**) to 2-(*o*-bromophenyl)ethanol (**7**, R = H) is via hydrolysis of the nitrile to the (2-bromophenyl)acetic acid, followed by reduction.[16] The alkylated nitriles **6** proved so difficult to hydrolyze that it was found more effective to reduce

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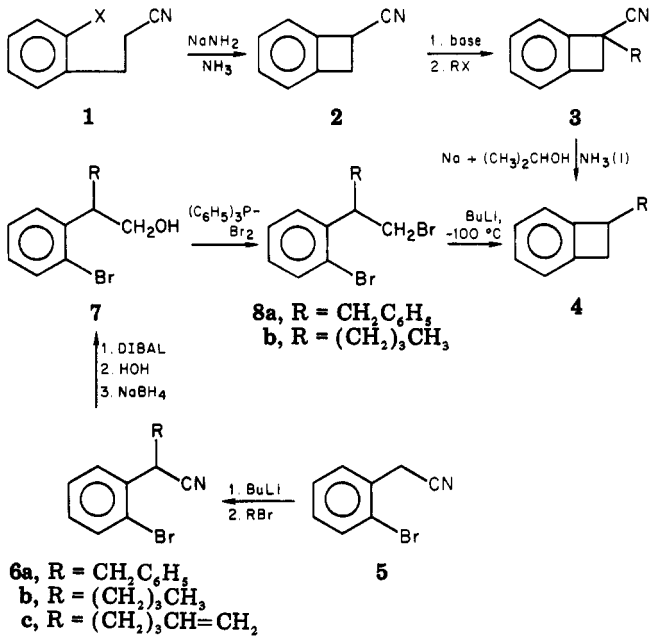
0022-3263/81/1946-4600$01.25/0

Scheme I



6a, R = $CH_2C_6H_5$
b, R = $(CH_2)_3CH_3$
c, R = $(CH_2)_3CH{=}CH_2$

them with diisobutylaluminum hydride (DIBAL),[17] to hydrolyze the resulting imine to the aldehyde, and finally to reduce the aldehyde. In this way the benzylated (**6a**) and butylated (**6b**) nitriles were converted to the alcohols (**7a,b**) 99% and 58% yields, respectively. Conversion to the bromides **8** was accomplished by action of the $Ph_3P{\cdot}Br_2$ complex,[18] both in a yield of 64%. The aryl halogen of **8a** underwent preferential bromine–lithium exchange at −100 °C with butyllithium, and as the solution was allowed to warm to room temperature, cyclialkylation occurred, affording 1-benzylbenzocyclobutene **4a** in 78% yield. In the same way **8b** afforded an 86% yield of 1-butylbenzocyclobutene (**4b**). From these preliminary results it appears likely that the Parham cyclialkylation may serve as a useful alternative to the methods hitherto employed for the synthesis of 1-alkylbenzocyclobutenes.

Experimental Section

General Methods. Precautions and procedures for work with butyllithium at −100 °C have been recorded earlier.[20] ^{13}C NMR were obtained by using a JEOL FX-60 15-MHz Fourier transform spectrometer with a $CDCl_3$ lock. ^1H NMR spectra were obtained by using a JEOL Model JNM-MH-100 instrument at 100 MHz or a Varian Model EM-360 instrument at 60 MHz.

Unless otherwise specified, the drying agent used for solutions containing organic residues was magnesium sulfate. Melting points were observed in capillaries by using a Thomas-Hoover apparatus and are uncorrected. Elemental analyses were performed by MHW Laboratories.

2-(2-Bromophenyl)-3-phenylpropionitrile (6a). 2-(2-Bromophenyl)acetonitrile[21] (**5**; 20.0 g, 102 mmol) was dissolved in 480 mL of tetrahydrofuran (THF) and 160 mL of hexane, and the mixture was cooled to −100 °C and was stirred while butyllithium (102 mmol) was added at such a rate that the temperature did not exceed −90 °C. The resulting slurry was stirred for 1 h at −100 °C, benzyl bromide (19.19 g, 112.2 mmol) in 20 mL of hexane was added over 15 min, and stirring was continued at −100 °C for 1.5 h. The stirred suspension was warmed to 25 °C, was allowed to stir at that temperature for 18 h, and was then poured into water. The organic layer was separated, and the aqueous layer was extracted three times with ether. The combined organic solution was washed with saturated NaCl solution, dried, and concentrated to afford a quantitative yield of yellow crystals with the odor of benzyl bromide. The crystals were recrystallized from hexane, affording 26.93 g (92%) of colorless prisms: mp 80–84 °C [mp(pure material) 82.5–84 °C]; ^1H NMR ($CDCl_3$) δ 2.83–3.34 (ABX m, 2, $PhCH_2$), 4.34–4.60 (ABX unsym q, 1, CHCN), 6.80–7.75 (m, 9, ArH); IR ($CHCl_3$) 2251 cm^{-1} (C≡N).

Anal. Calcd for $C_{15}H_{12}BrN$: C, 62.96; H, 4.23; Br, 27.92; N, 4.89. Found: C, 63.11; H, 4.29; Br, 28.00; N, 4.74.

2-(2-Bromophenyl)hexanenitrile (6b). 2-(2-Bromophenyl)acetonitrile (**5**; 15.0 g, 76.51 mmol) was metalated with butyllithium (76.51 mmol) essentially as in the preparation of **6a** and alkylated at −100 °C with butyl bromide (10.48 g, 76.51 mmol). Worked up as for **6a**, it afforded 18.47 g of orange oil which by VPC (10% SE-30 on 50/60 Chromsorb W, AW, DMCS, 6 ft × 0.25 in. column, 175 °C, 30 mL of He/min) consisted of a major peak and only two extremely minor (total ≤5%) peaks due to impurities. The oil was twice distilled (short path), giving pure **6b**: 76% yield: bp 92.5–94.0 °C (0.19 torr); ^1H NMR ($CDCl_3$) δ 0.92 (t, J = 7 Hz, 3, CH_3), 1.08–2.20 (m, 6, $CH_2CH_2CH_2$), 4.28 (unsym t, 1, CHCN), 7.06–7.74 (m, 4, Ar H); IR (neat) 2247 cm^{-1} (C≡N).

Anal. Calcd for $C_{12}H_{14}BrN$: C, 57.16; H, 5.60; Br, 31.69; N, 5.55. Found: C, 57.30; H, 5.69; Br, 31.96; N, 5.44.

2-(2-Bromophenyl)-6-heptenenitrile (6c). 2-(2-Bromophenyl)acetonitrile (**5**; 10 g, 51 mmol) was converted to the anion by the action of butyllithium, and 5-bromo-1-pentene[22] (8.5 g, 57.0 mmol) in 20 mL of hexane was added at −100 °C. The resulting yellow suspension was stirred for 1 h at −100 °C, allowed to warm to 25 °C (4 h), and stirred at that temperature for an additional 2 h. Worked up as was **6a**, **6c** was obtained first as a reddish brown oil (13.2 g) which was purified by short-path distillation, affording 10.4 g (77%) of **6c** as a colorless oil: bp 95.5–98.0 °C (0.05 torr); ^1H NMR ($CDCl_3$) δ 1.40–2.41 (m, 6, $(CH_2)_3$), 4.24 (unsym t, 1, CHCN), 4.77–5.14 (m, 2, $CH{=}CH_2$), 5.37–5.97 (m, 1, $CH{=}CH_2$), 6.89–7.81 (m, 4, Ar H); IR (neat) 2250 (CN), 1642 cm^{-1} (C=C).

Anal. Calcd for $C_{13}H_{14}BrN$: C, 59.11; H, 5.34; N, 5.30. Found: C, 59.10; H, 5.59; N, 5.22.

2-(2-Bromophenyl)-3-phenylpropanal. 2-(2-Bromophenyl)-3-phenylpropionitrile (**6a**; 12.00 g, 41.93 mmol) in 300 mL of toluene in an apparatus protected from oxygen and moisture was cooled to −72 °C, and diisobutylaluminum hydride (DIBAL, 50.3 mmol) in hexane was added dropwise over 20 min so that the temperature did not rise above −65 °C. When the addition was complete, the temperature was allowed to rise to 25 °C and remain there for 36 h. Next the mixture was poured into a saturated solution of ammonium chloride and the mixture stirred vigorously for 30 min, after which 100 mL of tetrahydrofuran and 150 mL of 5% hydrochloric acid were added, and stirring was continued for an additional 3 h. The layers were separated, and the aqueous layer was extracted with ether (3 × 100 mL). The combined organic solutions were washed with saturated NaCl solution, dried, and concentrated to 12.52 g of yellow oil. This oil was nearly pure aldehyde: ^1H NMR ($CDCl_3$) δ 2.85–3.17 (AMX q, J_{MX} = 14 Hz, J_{AX} = 7 Hz, 1, $CH_2C_6H_5$), 3.29–3.61 (AMX q, J_{MX} = 14 Hz, J_{AM} = 7 Hz, 1, $CH_2C_6H_5$), 4.44 (AMX t, J_{AM} = J_{AX} = 7 Hz, 1, CHCHO, 6.85–7.40 (m, 8, Ar H), 7.43–7.71 (m, 1, Ar H), 9.71 (s, 1, CHO); IR (neat) 1728 cm^{-1} (C=O).

The aldehyde was pure enough for reduction to **7a**, but a sample was converted to the **dinitrophenylhydrazone**:[23] orange prisms; mp 166.0–168.5 °C.

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(19) Although both **8a** and **8b** were pure enough for further reactions only **8b** was obtained in analytical purity by distillation. Attempts to purify **8a** by preparative VPC were thwarted, apparently by dehydrobromination.

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Anal. Calcd for $C_{21}H_{17}BrN_4O_4$: C, 53.75; H, 3.65; N, 11.94. Found: C, 53.55; H, 3.68; N, 11.85.

2-(2-Bromophenyl)-3-phenyl-1-propanol (7a). Crude 2-(2-bromophenyl)-3-phenylpropanal (3.83 g, 13.2 mmol) was dissolved in 50 mL of 2-propanol and stirred while 500 mg (13.2 mmol) of sodium borohydride was added all at once. Stirring was continued for an additional 21 h at 25 °C. The reaction mixture was quenched by the dropwise addition of acetic acid (ca. 10 mL) and then was concentrated (rotary evaporator). Ether (50 mL) and water (100 mL) were added to the residue, and the water layer was extracted repeatedly with ether (3 × 50 mL). The combined organic solution was washed with sodium bicarbonate solution and saturated sodium chloride solution and finally was dried and concentrated to 3.82 g (99%) of pale yellow oil. This material gave a single peak on VPC analysis: ^{1}H NMR ($CDCl_3$) δ 1.79 (br s, 1, OH, exchangeable with D_2O), 2.80–3.16 (m, 2, $ArCH_2$), 3.73 (br s, 3, CH_2OH and Ar H), 6.80–7.40 (m, 8, Ar H), 7.40–7.68 (br d, 1, *o*-BrAr H); IR (neat) 3375 (OH).[24] The analytical sample was prepared by distillation; bp 140.5–143.5 (0.09 torr).

Anal. Calcd for $C_{15}H_{15}BrO$: C, 61.87; H, 5.19; Br, 27.44. Found: C, 61.68; H, 5.27; Br, 27.38.

2-(2-Bromophenyl)-1-hexanol (7b). The butylated nitrile **6b** (14.0 g, 55.52 mmol) was subjected to reduction by DIBAL (66.62 mmol) in 200 mL of toluene and worked up as in the reduction of **6a**. The product was a yellow oil (13.8 g, 54.08 mmol) which showed but a single peak on VPC analysis: ^{1}H NMR ($CDCl_3$) δ 0.60–2.48 (m, 9, $CH_2CH_2CH_2CH_3$), 4.14 (unsym t, 1, CHCHO, 6.96–7.82 (m, 4, Ar H), 9.70 (s, 1, CHO); IR (neat) 1738 cm^{-1} (C=O). This material was used without purification in the sodium borohydride reduction. The yellow oil (14.17 g, 15.52 mmol) was dissolved in 50 mL of 2-propanol and reduced with sodium borohydride as in the preparation of **7a**. The crude alcohol (**7b**, 13.37 g) was subjected to distillation in a short-path apparatus, affording 8.34 g (58% from **6b**) of a colorless oil: bp 93–99 °C (0.04 torr); ^{1}H NMR ($CDCl_3$) δ 0.60–2.20 (m, 9, $CH_2CH_2CH_2CH_3$), 1.92 (br s, 1, OH), 3.29–3.6 (m, 1, $CHCH_2OH$), 3.6–4.0 (m, 2, $CHCH_2OH$), 6.98–7.90 (m, 4, Ar H); IR (neat) 3340 cm^{-1} (OH).

Anal. Calcd for $C_{12}H_{17}BrO$: C, 56.04; H, 6.66. Found: C, 55.67; H, 6.60.

1-Benzylbenzocyclobutene (4, R = $PhCH_2$). The triphenylphosphine–bromine complex[18b] was prepared from 3.45 g (13.15 mmol) of triphenylphosphine in 60 mL of dry acetonitrile, and 3.82 g (13.12 mmol) of alcohol **7a** in 25 mL of acetonitrile was added over 5 min. The resulting pale yellow solution was stirred for 4 h at 25 °C and then was concentrated with a rotary evaporator having Teflon seals. The resulting orange syrup was vacuum distilled via short path to afford the bromide as 2.96 g (64%) of a colorless oil: bp 146.5–152.5 °C (0.08 torr); ^{1}H NMR ($CDCl_3$) δ 2.92–3.21 (m, 2, CH_2Ar), 3.48–3.7 (m, 2, CH_2Br), 3.7–4.13 (m, 1, $ArCHCH_2Br$), 6.88–7.92 (m, 9, Ar H), IR (neat) 1601 cm^{-1} (C=C).[19] To the colorless oil (5.66 g, 16.0 mmol) in 200 mL of tetrahydrofuran and 50 mL of hexane stirred and cooled to −100 °C was added 16.0 mmol of butyllithium at such a rate that the temperature did not exceed −95 °C. After 30 min at −100 °C the mixture was warmed to −78 °C and maintained at that temperature for 2 h. It was then allowed to warm to 25 °C and to remain at that temperature overnight. The reaction mixture was poured into 100 mL of water, the layers were separated, and the aqueous layer was extracted with ether (3 × 75 mL). The combined organic layers were washed with saturated sodium chloride solution, dried, and concentrated to afford 3.57 g of a pale yellow oil. The oil which by VPC appeared to be >90% homogeneous was subjected to chromatography on silica gel (200 g) with CH_2Cl_2–petroleum ether as the eluant and afforded 2.42 g (78%) of 1-benzylbenzocyclobutene as a colorless oil: ^{1}H NMR δ 2.67–3.58 (m, 4, $ArCH_2$), 3.58–3.99 (m, 1, methine proton), 6.57–7.83 (m, 9, Ar H); ^{13}C NMR ($CDCl_3$) δ 36.20, 40.56, 44.47, 122.33, 123.24, 126.33, 126.69, 127.54, 128.52, 128.97, 141.08, 143.75, 149.35.

Anal. Calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.61; H, 7.47.

1-Bromo-2-(2-bromophenyl)hexane (8b). To 31.11 mmol of triphenylphosphine–bromine complex[18b] was added 8.0 g (31.11 mmol) of alcohol **7b**, and the mixture was allowed to react as in the reaction of **7a**. After the usual workup involving concentration under reduced pressure, the residue was purified by two distillations under reduced pressure, affording 6.36 (64%) of a colorless oil: bp 92.5–95.0 °C 0.13 torr); ^{1}H NMR ($CDCl_3$) δ 0.60–2.50 (m, 9, Bu), 3.36–4.20 (m, 3, $ArCHCH_2Br$), 7.05–8.03 (m, 4, Ar H).

Anal. Calcd for $C_{13}H_{16}Br_2$: C, 45.03; H, 5.04; Br, 49.93. Found: C, 45.18; H, 5.07; Br, 49.94.

1-Butylbenzocyclobutene (4, R = Bu). The dibromide **8b** (2.5 g, 6.04 mmol) was subjected to halogen–metal exchange with butyllithium at −100 °C, cyclized essentially as described in the preparation of **4** (R = $PhCH_2$), and worked up in the usual way. The crude oil remaining after vacuum evaporation of the solvents was purified by column chromatography on silica gel with hexane as eluant, affording 2.07 g (86%) of 1-butylbenzocyclobutene as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.63–1.98 (m, 9, Bu), 2.32–3.61 (m, 5, benzylic H), 6.83–7.31 (m, 4, Ar H); ^{13}C NMR ($CDCl_3$) δ 14.13, 22.85, 30.60, 34.24, 36.20, 43.62, 122.07, 123.18, 126.75, 127.21, 144.14, 150.32.

Anal. Calcd for $C_{12}H_{16}$: C, 89.93; H, 10.06. Found: C, 89.89; H, 10.29.

Registry No. **4** (R = Bu), 78920-29-3; **4** (R = $PhCH_2$), 78920-30-6; **5**, 19472-74-3; **6a**, 78920-31-7; **6b**, 58830-40-3; **6c**, 78920-32-8; **7a**, 78920-33-9; **7b**, 78920-34-0; **8a**, 78939-71-6; **8b**, 78920-35-1; benzyl bromide, 100-39-0; butyl bromide, 109-65-9; 5-bromo-1-pentene, 1119-51-3; 2-(2-bromophenyl)-3-phenylpropanal, 78920-36-2; 2-(2-bromophenyl)-3-phenylpropanal DNP, 78920-37-3.

(24) There was no significant absorption at 1728 cm^{-1} (C=O) and in the ^{1}H NMR spectrum no evidence of the aldehyde proton at 9.71 ppm.

Sesquiterpene Lactones of *Eremanthus incanus* and *Porella japonica*. Crystal Structure and Stereochemistry of Eregoyazidin

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Eremanthus species (Compositae, Vernoniae) are rich sources of guaianolides which possess schistosomicidal properties.[1] In previous paper,[1,2] one of us reported isolation of schistosomicidal and cytotoxic heliangolides and eremanthanolides together with eregoyazin (1) and eregoyazidin (2) from *Eremanthus incanus* and *E. goyazensis*. The crystal structure and stereochemistry of eregoyazin (1) has recently been established by X-ray crystallographic analysis.[1] For eregoyazidin, and 11,13-dihydroderivative, structure **2** with C(4) and *C(11)*-methyl groups α was proposed on the basis of ^{13}C NMR and CD spectral data.[1,2] However, the stereochemistry at C(4) remained somewhat uncertain because of the seemingly enantiomeric nature of the CD curves of eregoyazin and eregoyazidin in the ketone n,π* region.[2]

Some liverworts belonging to the Jungermanniales and the Marchantiales elaborate strongly allergenic and cytotoxic sesquiterpene lactones.[3-12] In particular, a leafy

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