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POTENTIAL ROUTES TO CYCLOBUTA[1,2-C] CYCLOPROPABENZENE

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Abstract—The $CpCo(CO)_2$-catalyzed cyclization of 1-trimethylsilyl-1, 5-hexadiyne (4) with propargyltetrahydropyranylether (5 leads to the formation of both possible regioisomers of the benzocyclobutene product: 3-trimethylsilyl-4-tetrahydropyranyloxymethylbenzocyclobutene (6) and the corresponding 5-tetrahydropyranyloxymethyl-isomer 7. On the other hand, cyclization of the same diyne with 3-(trimethylsilyloxy) propyne (10) gave only the 3,4-disubstituted product as the free alcohol 11. Compound 6 was iododesilylated, the ether hydrolyzed, and the alcohol tosylated to give 4-iodo-5-tosyloxymethylbenzocyclobutene 13, also obtainable more directly from 11 by treatment with ICl and tosylation. Iodide 13 could be reacted with *n*-butyllithium to give a variety of products incorporating the *n*-butylgroup and derived from crosscoupling of the carbon skeleton of starting material. The title compound 1 may be an intermediate en route to the observed products, but was not detected. Several thermal elimination routes to 1 from appropriately 4,5-substituted benzocyclobutenes were unsuccessful. Flash vacuum thermolysis of 11 furnished the silyloxyderivative 21 through elimination of methane.

Cyclopropaarenes[1] are gaining increasing synthetic attention as possible structures within which the elusive property of aromatic bond fixation might be detected.[2] The first member of this class of compounds was isolated in 1964[3] and the parent cyclopropabenzene shortly thereafter.[4] Preparative methods consist of: photolysis of 3H-indazoles,[3,5] retrocyclization of 1,6-methano [10] annulene cycloadducts,[4,6] base-mediated dehydrohalogenation of bicyclo [4.1.0] heptene dichlorides,[7-9] and 1,3-elimination of *o*-lithiobenzylethers[10] and tosylates.[11] These methods furnish, in addition to the parent compound, a variety of even more highly strained systems.[12]

One of the more intriguing structures in this series is cyclobuta[1,2-*c*] cyclopropabenzene (1) since, in contrast to its linear isomer 2,[9a,10b] this compound contains two fused rings which should augment each other in their bond fixation effect on the benzene nucleus. For this reason, it appeared of interest to us to develop effective and efficient synthetic routes to 1. At the outset of our

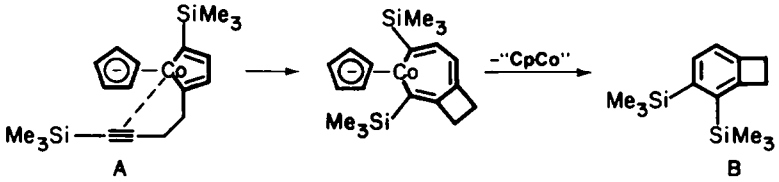
1 2 3

efforts we had succeeded to effect an (unfortunately low yielded) 1,3-elimination of lithium methoxide from lithiated 3 to provide a relatively fast synthesis (3 steps) of 2,[10d] relying on a recently developed cobalt mediated general synthesis of benzocyclobutenes[13] for the preparation of 3. We had hoped that the latter synthesis might also provide access to the angular series by the appropriate use of starting materials ultimately furnishing an analog of 3 but with the necessary substituents at positions 4 and 5. This indeed proved to be the case although attempted 1,3-eliminations did not allow the isolation of 1, but rather (as described below) furnished a variety of other compounds. The strained benzene 1 has recently been synthesized in a synthetic sequence employing the dehydrohalogenation route,[9c] and was found to contain an aromatic (diatropic) benzene ring seemingly devoid of appreciable bond fixation.

RESULTS AND DISCUSSION

The synthesis of 4,5-disubstituted benzocyclobutenes by the cobalt route requires regiospecific cyclization of 1-substituted 1,5-hexadiynes with monosubstituted alkynes. We had observed earlier[13] such specificity in the reaction of 4 with trimethylsilylacetylene and had explained it by postulating a mechanism in which the (sterically or electronically dictated) kinetic preference for the formation of metallacycle A provides a rationale for the exclusive isolation of product B (Scheme 1). Further support for this mechanism was found in the experiments to be described.

The $CpCo(CO)_2$ catalyzed cyclization of 1-trimethylsilyl-1,5-hexadiyne (4) with propargyltetrahydropyranylether (5) lead to the formation of both possible regioisomers of the benzocyclobutene product: 3-trimethylsilyl-4-hydroxymethylbenzocyclobutene tetrahydropyranylether (6) in 13% yield, and 3-trimethylsilyl-5-hydroxymethylbenzocyclobutene tetrahydropyranyl-



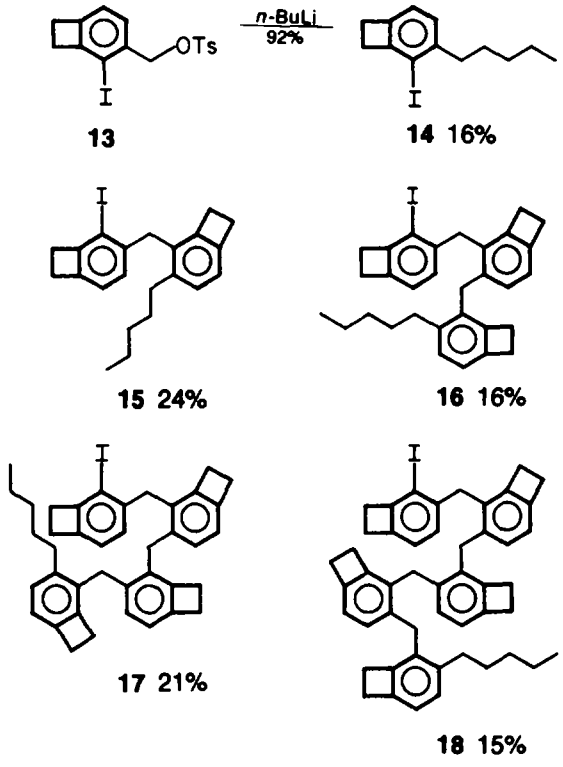
Scheme 1.

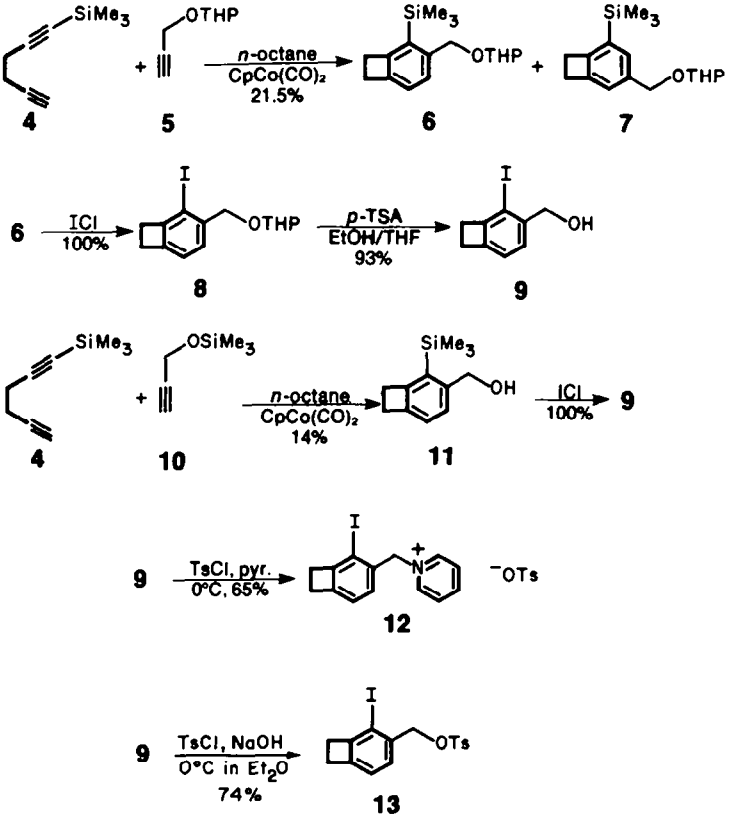
ether (7) in 8.5% yield. These isomers are separable by careful column chromatography on silica gel. There is no apparent hydrolysis of the THP-protecting group during the synthesis or isolation of these compounds—any of the alcohol so produced would have been isolated during chromatography.

The $CpCo(CO)_2$ catalyzed cyclization of 1-trimethylsilyl-1,5-hexadiyne (4) with 3-trimethylsilyloxypropyne (10), in contrast, afforded after silica gel chromatography *exclusively* 3-trimethylsilyl-4-hydroxymethylbenzocyclobutene (11) in 14% yield. Neither the anticipated 3-trimethylsilyl-4-hydroxymethylbenzocyclobutene trimethylsilylether nor any 3-trimethylsilyl-5-hydroxymethylbenzocyclobutene were isolated. From both cyclizations very little other material was obtained, and column chromatography to elute the presumably also formed higher cooligomers of the starting alkynes was not continued beyond the isolation of the desired products. It is tempting to associate the greater selectivity in the reaction of 4 with 10 with the increased steric bulk of the trimethylsilyloxymethyl- when compared with the tetrahydropyranyloxymethyl group. The latter evidently is not significantly distinguishable from a hydrogen to lead to improved preference of 6 over 7.

Iodination of the ether 6 with ICl in CCl_4, followed by acid catalyzed hydrolysis of the protecting group yielded 3-iodo-4-hydroxymethylbenzocyclobutene 9 in 93% yield from 6. Alternatively, the alcohol 11 could be quantitatively iodinated with ICl/CCl_4 to compound 9. An indication of the unusual benzylating capacity of the desired ester 13 was obtained in the attempted tosylation of alcohol 9 by the usual method (TsCl, pyridine, 0°), which furnished the solvolyzed pyridinium salt 12 as colorless crystals in 65% yield.

Formation of the tosylate 13 was finally achieved by reaction of 9 with a twofold excess of recrystallized tosyl chloride, after stirring over NaOH pellets for 3 hr at room temperature. Although we had used an elimination

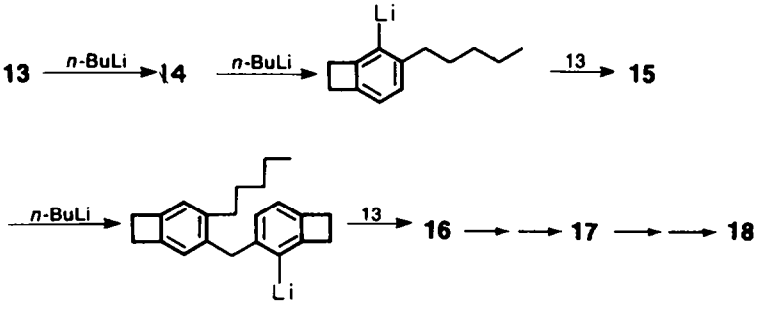




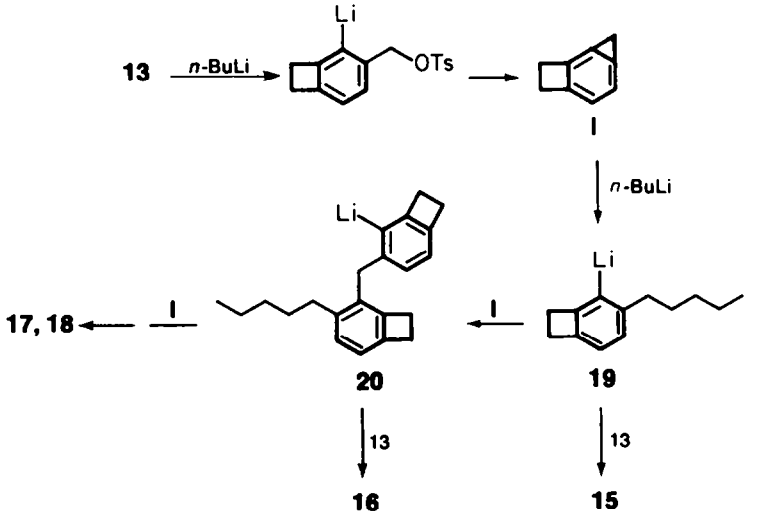
from a benzylmethylether to obtain **2**, the ester **13** appeared more desirable as a starting material from which conversion to angular cyclobutacyclopropabenzene **1** might be attempted. As noted by us,[10b,15] and others,[11,14] *o*-lithiobenzylmethylethers are disadvantageous starting materials in the synthesis of cyclopropabenzenes. On the other hand, *o*-lithiobenzyl tosylates have been suggested as suitable alternatives in this approach.[11]

Reaction of **13** with *n*-butyllithium in ether at $-100°$ followed by warming to room temperature (16 hr) gave a mixture of compounds. None of the desired **1** was detected either spectroscopically or through its pungent smell[9c] characteristic of cyclopropabenzene and its derivatives. Separation by preparative thin layer chromatography gave five compounds **14–18** in a total yield of 92%, the structures of which are suggested on the basis of spectral and analytical data. A mechanistic rationale for this rather remarkable array of compounds is suggested in Schemes 2 and 3. It is possible that the alkylating power of tosylate **13** leads to butylation at the benzylic carbon (and hence **14**) rather than to the ordinarily rather rapid transmetallation at either benzylic or phenylic carbon.[16] Alternatively, transmetallation to a benzyllithium derivative and subsequent nucleophilic[17] displacement of the butyltosylate function might furnish **14**. Compound **14** in turn could function as an electron acceptor with additional *n*-butyllithium, transmetallation resulting in a phenyllithium derivative capable of further reaction with **13** to give **15**, the latter in turn providing **16** by an analogous sequence, **16** producing **17**, and **17** ultimately yielding **18**. The efficiency of this process appears unusual considering the absence of side products of this type in the synthesis of **2** by a similar route,[10b] and in the attempted preparation of cyclopropa [*a*]-naphthalene and cyclopropa[*l*]phenanthrene.[14] Moreover, *o*-bromobenzyl tosylate undergoes halogen lithium exchange with *n*-butyllithium.[11] Considering that transmetallation should occur in an even more facile manner with a phenyl iodide moiety such as the one encountered in **13**, particularly in view of the stabilizing effect exerted by the four ring on adjacent negatively charged centers,[18] and considering that the above *o*-bromobenzyl tosylate yields cyclopropabenzene, it appears appropriate to consider an alternative mechanism for the formation of the coupling products **15–18**.

In light of the above comments one could propose a mechanism (see Scheme 3) incorporating the desired cyclopropacyclobutabenzene **1** as a reactive intermediate. Reaction of this compound with *n*-butyllithium in a regiospecific manner such as to place the lithium α to the strained ring as in **19** followed by further reaction with **13** to give **15**, or with **1** to provide **20**, provides a mechanistic rationale for the formation of the observed products except **14**. Compound **13** might be intercepted by **13** to give **16** or continue to form new more extended systems by further reaction with **1** ultimately resulting in **17** and **18**. Therefore it is possible that **1** is formed in the reaction of **13** with *n*-butyllithium, however, subsequent



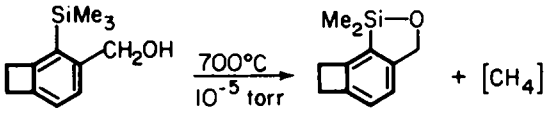
Scheme 2.



Scheme 3.

reactions prevent its isolation.[19] This suggests, as has been previously pointed out,[10b,11,14] that the 1,3-elimination route[10a] to cyclopropabenzene is inferior to the Billups procedure.[7]

In an alternative approach to **1** a series of experiments was carried out to possibly effect flash pyrolytical elimination of Me_3SiOH from alcohol **11**. When the latter was vacuum transferred through a hot quartz tube at 700° and 10^{-5} torr a new product was formed quantitatively to which structure **21** was assigned on the basis of the spectral data, particularly the diagnostic ^{13}C-NMR spec-



11 **21**

trum. This unusual product is formally derived by methane elimination from **11**, a possible mechanism being nucleophilic attack of the hydroxyl group on the silicon followed by methane extrusion. Pyrolysis at higher temperatures led to decomposition. Similar flash pyrolysis experiments were carried out on 4-trimethylsilyl-5-chloromethylcyclobutabenzene (**22**) (synthesized from **11** by treatment with $SOCl_2$-pyridine in quantitative yield) to give complex mixtures of uncharacterized products. Finally, treatment of **22** with sodium fluoride in DMF did not furnish **1**.

EXPERIMENTAL

M. and b.ps are uncorrected. M.ps were measured on a Thomas Hoover Unimelt apparatus. NMR spectra were recorded on a Varian T-60, Hitachi Perkin–Elmer R-24B (60 MHz), and a home-built 180 MHz instrument. Spectra are reported in τ-values from TMS. Unless otherwise stated CCl_4 was used as solvent. CMR spectra were obtained either on the 180 MHz machine described above or on a Nicolet TT-23 instrument at 25.14 MHz, and chemical shifts are reported in ppm downfield from TMS, referenced to the central peak of the deuterochloroform triplet (77.0 ppm downfield from TMS). IR spectra were obtained with a Perkin–Elmer Model 137 spectrometer. Mass spectra and elemental analyses were provided by the Mass Spectral Service and the Microanalytical Laboratory, respectively, of the University of California, Berkeley, California. Analyses are within 0.3% of theoretical values unless mentioned otherwise. Gas chromatography was performed on two instruments: a Hewlett–Packard 5710A gas chromatograph with a (20' × 1/8" 10% UCW 98 on 80-100 WAW-DMCB) column, and a Varian Aerograph Model 920 with a (10' × 3/8" 20% UCW 98 on ChromW DMCS/AW 60/80 conditioned at 200°C) column. All chromatography was carried out on E.M. Reagents silica gel (70–230 mesh ASTM), all p.t.l.c. on commerical silica gel plates (Merck) or on plates prepared with E.M. Reagents Silica Gel-PF 254 containing $CaSO_4$ and fluorescent indicator. Solvents were dried by distillation over an appropriate drying agent under nitrogen atmosphere and stored under nitrogen and over Linde Molecular Sieves (4A).

Vacuum line operations were carried out on a high vacuum (mercury diffusion) multiple line apparatus. Solvents and reagents to be used in the presence of $CpCo(CO)_2$ were degassed on the vacuum line and purged with dried, air free (MnO tower) nitrogen.

The reported IR figures are ν_{max} values (cm^{-1}). Only the strongest and/or structurally most important fragmentation peaks are reported in the mass spectra of new compounds. Peaks due to higher silicon isotopes are omitted.

3-Trimethylsilyl-4-hydroxymethylbenzocyclobutene tetrahydropyranylether (**6**). Compounds **4**[13b] (1.85 g, 12.3 mmoles), **5** (3.34 g, 23.9 mmoles) and $CpCo(CO)_2$ (30 μl) were dissolved in dry degassed octane (12 ml). This soln was added over a 4.5 day period (using a syringe pump) to refluxing octane (30 ml) containing $CpCo(CO)_2$ under dry N_2. After cooling and vacuum transfer of volatile materials a dark brown oil remained which was separated into its components by column chromatography on 150 g of silica gel (100 ml fractions). Gradually raising the solvent polarity from pentane to pentane/ether (9:1) gave the desired **6**, isolated from the nineteenth fraction as a light yellow oil. Microdistillation (5×10^{-3} torr, T_{bath} = 105°C) gave pure material as a colorless liquid (451 mg, 13%): mass *m/e* 290 (M^+, 0.4%), 190 (75%), 189 (83%), 175 (35%); NMR 2.82 (d, J = 8Hz, 1H), 3.10 (d, J = 8Hz, 1H), 5.30 (d, J = 12Hz, 1H), 5.40 (bs, 1H), 5.60 (d, J = 12Hz, 1H), 6.30 (m, 2H), 6.85 (m, 4H), 8.37 (m, 6H), 9.68 (s, 9H), IR spectrum (neat) 2940, 1385, 1250, 1200, 1155, 1035; Anal. ($C_{17}H_{26}O_2Si$) C, H.

The twentieth fraction gave a light yellow oil which was identified as **7** (301 mg, 8.5%): mass *m/e* 290 (M^+, 0.7%), 217 (1.5%), 191 (29%), 190 (75%), 189 (96%), 175 (34%); NMR 2.93 (bs, 1H), 3.10 (bs, 1H), 5.53 (m, 3H), 6.40 (m, broad, 2H), 6.92 (bs, 4H), 8.40 (m, 6H), 9.80 (s, 9H); IR spectrum (neat) 2940, 1370, 1240, 1190, 1110, 1025; Anal. ($C_{17}H_{26})_2Si$) C, H.

3-Trimethylsilyl-4-hydroxymethylbenzocyclobutene (**11**). Compounds **4** (2.35 g, 15.6 mmoles), **10** (3.56 g, 27.8 mmoles) and $CpCo(CO)_2$ (50 μl) were dissolved in octane to give 20 ml of soln. This was added over 4.5 days (syringe pump) to refluxing octane (40 ml) containing $CpCo(CO)_2$ (30 ml), under dry N_2. Vacuum transfer of octane was followed by column chromatography (150 g silica gel, 75 ml fractions). Gradually raising the solvent polarity from pentane to pentane/ether (3:1) gave **11** in the 39th to 44th fractions as a light yellow oil. Attempted recystallization from pentane yielded no solid, even at −78°. Microdistillation (T_{bath} = 74 β, 0.005 torr) gave a clear liquid which upon slow sublimination (49°, 0.005 torr, overnight) gave white crystals (414 mg, 14%): m.p. 43–44°; mass *m/e* 206 (M^+, 2%), 191 (65%), 189 (7%), 175 (15%), 173 (50%), 115 (26%), 75 (100%), 73 (22%); NMR 2.93 (d, J = 8Hz, 1H), 3.18 (d, J = 8Hz, 1H), 5.47 (s, broad, 2H), 6.90 (m, 4H), 9.67 (s, 9H); IR spectrum (microdistilled liquid, neat) 3300, 2930, 1370, 1240; Anal. ($C_{12}H_{18}OSi$) C, H.

3-Iodo-4-hydroxymethylbenzocyclobutene (**9**). Compound **6** (384 mg, 1.32 mmoles) was dissolved in CCl_4 (5 ml) and cooled to 0°, under dry N_2. ICl (214 mg, 1.32 mmoles—in 3.5 ml CCl_4 soln) was added with magnetic stirring in one portion. This mixture was allowed to warm to room temp. The soln was then poured into ether (50 ml) and extracted with sat $Na_2S_2O_3$ aq (50 ml), water (2 × 50 ml), brine (50 ml) and dried over $MgSO_4$. Evaporation of the ether left crude **8** (460 mg, quantitative conversion): mass *m/e* 344 (M^+, 2%), 260 (42%), 243 (93%), 116 (56%), 115 (96%), 105 (83%); NMR 2.97 (d, J = 8Hz, 1H), 3.27 (d, J = 8Hz, 1H), 5.48 (d, J = 13Hz, 1H), 5.55 (m, 1H), 5.82 (d, J = 13Hz, 1H), 6.50 (m, 2H), 7.13 (s, 4H), 8.48 (m, 6H); IR spectrum (neat) 2920, 1580, 1430, 1330, 1250, 1195, 1120, 1030.

The iodo-THP ether **8** was hydrolyzed directly with *p*-toluenesulfonic acid (0.05 g of the monohydrate, 0.2 mmoles) in 25 ml refluxing THF/95% EtOH (2:3) for 1 hr. After cooling, the solvent was removed at reduced pressure to yield a thick, light yellow semisolid. Recrystallization from pentane/ether (3:2) afforded **9** as colorless crystals (320 mg, 93%): m.p. 93–94°; mass *m/e* 260 (M^+, 36%), 243 (92%), 133 (33%), 116 (50%); NMR 2.80 (d, J = 8Hz, 1H), 3.08 (d, J = 8Hz, 1H), 5.43 (bs, 2H), 6.93 (s, 4H); IR spectrum (KBr pellet) 3210, 2905, 1575, 1415, 1340, 1095; Anal. (C_9H_9IO) C, H.

Compound **9** may alternatively be obtained from **11** by quantitative iodination with ICl:

Compound **11** (104 mg, 0.51 mmole) was dissolved in CCl_4(5 ml) and cooled to 0°, under dry N_2. ICl (82 mg, 0.51 mmole in 0.56 ml CCl_4 soln) was added from a syringe in one portion as the soln was agitated rapidly with magnetic stirring. The walls of the flask were rinsed with an additional aliquot of CCl_4(5 ml). Gradual warming to room temp. over 30 min was followed by normal aqueous work-up (30 ml sat $Na_2S_2O_3$ aq; 2 × 3 ml water) isolating the organic material in ether (75 ml). The resulting clear soln, after drying over $MgSO_4$ and evaporation of solvent, gave the crude **9** as slightly yellow crystals. Recrystallization from ether/pentane (2:3) gave colorless crystals, (133 mg, 100%), m.p.

93–94°. Mixed m.p. with analytically pure material prepared by the first method gave no m.p. depression.

Pyridinium salt **12**. Alcohol **9** (250 mg, 0.96 mmole) and pyridine (3 ml) were cooled to −10° under dry N_2 and *p*-toluenesulfonyl chloride (199 mg, 1.04 mmole) added in one portion. After stirring for 1 hr the soln was stored at −10° for an additional 12 hr. A white ppt formed which was dissolved by addition of 5N H_2SO_4 (7.2 ml). The mixture was extracted with $CHCl_3$, the extracts dried with $MgSO_4$ and the solvent evaporated to give colorless crystals. Recrystallization from ether-THF (4:1) gave pure **12** (310 mg, 65%): m.p. 161–163°; mass *m/e* no M^+ observed, 414 (5%), 287 (12%), 259 (32%), 243 (100%), 172 (13%), 79 (100%); NMR ($CDCl_3$) 1.17 (bd, J = 5Hz, 2H), 2.13 (m, 5H), 3.02 (m, 4H), 4.13 (s, 2H), 7.07 (s, 4H), 7.73 (s, 3H); IR spectrum (KBr pellet) 3000, 1640, 1470, 1435, 1190, 1160, 1110, 1060, 1020; Anal. ($C_{21}H_{20}INO_3S$) C, H, N, S.

3-Iodo-4-hydroxymethylbenzocyclobutene tosylate **13**. Compound **9** (373 mg, 1.44 mmoles) was dissolved in abs ether (70 ml, distilled directly from LAH). To this soln were added NaOH pellets (Mallinckrodt Analytical Reagent, 98% NaOH minimum, 4g) and freshly purified tosyl chloride (532 mg, 2.79 mmoles) and the entire soln was then stirred under dry N_2 for 3 hr at 23°.

The ether soln was then decanted from the white solid formed, the solid was washed with additional ether (25 ml), and the combined ether layers were washed with water (20 ml) followed by sat NaCl aq (20 ml). After drying over $MgSO_4$ the ether was stripped off leaving white crystals of the crude tosylate. Recrystallization from petroleum ether gave the pure material (442 mg, 74%): m.p. 103–104°; mass *m/e* 414 (M^+, 3%), 259 (23%), 244 (24%), 243 (45%), 115 (100%); NMR ($CDCl_3$) 2.30 (d, J = 8Hz, 2H), 2.80 (d, J = 8Hz, 2H), 2.92 (d, J = 8Hz, 1H), 3.18 (d, J = 8Hz, 1H), 5.10 (s, 2H), 7.03 (s, 4H), 7.57 (s, 3H); IR spectrum (KBr pellet) 2900, 1590, 1575, 1440, 1415, 1345, 1190, 1165, 1085, 925, 865; Anal. ($C_{16}H_{15}IO_3S$) C, H.

Reaction of 3-iodo-4-hydroxymethylbenzocyclobutene tosylate (**13**) *with n-butyllithium*. The starting tosylate **13** (555 mg, 1.34 mmole) was dissolved in abs ether (75 ml, distilled directly from LAH into reaction flask). This soln was cooled under dry N_2 to −100° (Et_2O/CO_2 bath) resulting in a cloudy precipitation of the tosylate. *n*-BuLi (2.55 M in hexane) was added (0.52 ml, 1.34 meq *n*-BuLi) from a syringe over roughly 1 min as the soln was magnetically stirred. This soln was kept at −100° for 45 min, generating a cloudy and somewhat yellow suspension. The temp. was brought to −78° (acetone/CO_2 bath). Stirring at this temp. for 30 min produced no apparent change. Raising bath temp. to 0° gave, after stirring for 45 min, a fine white ppt. The solution was warmed to room temp. (23°) and left to stir for 16 hr. The slightly yellow mixture was then washed with sat NH_4Cl aq (15 ml), followed by brine (20 ml), and then dried over Na_2SO_4. Distillation, under dry N_2, through a 4-inch vacuum jacketed Vigreaux column removed the ether, b.p. 34°. When distillation at this temp. appeared complete, N_2 was flushed slowly through the system for 30 min. This left 253 mg of a viscous yellow oil in the distilling flask. NMR of this material revealed absence of both the benzyloxy proton signal (at 5.10 τ) and the tosyl group's aromatic proton peaks.

An attempt to remove volatile components of this oil by vacuum transfer at 0.005 torr/23° for 1 hr resulted in the collection of 32 mg of colorless transferred material that exhibited the same features in the NMR spectrum as the less volatile residue, notably a large multiplet at *ca* 1.0 to 2.0 δ, indicating the presence of aliphatic protons.

The combined products were then separated by ptlc on silica. Eluting the plate twice with pentane gave five bands. At $R_f \simeq 0.7$, **14** was isolated as a faintly yellow oil (62 mg, 16%): mass *m/e* 300 (M^+, 45%), 243 (33%), 173 (4%), 117 (100%); NMR 3.07 (d, J = 8Hz, 2H), 3.23 (d, J = 8Hz, 2H), 7.02 (s, 4H), 7.50 (bt, J = 8Hz, 2H), 8.60 (m, 6H), 9.10 (bt, 3H); Anal. ($C_{13}H_{17}I$) C, H.

The next band, at $R_f \simeq 0.6$, yielded **15** as an off-white semi-solid (66 mg, 24%): mass *m/e* 416 (M^+, 25%), 345 (10%), 289 (32%), 243 (20%), 233 (100%), 219 (85%), 186 (15%), 117 (72%); NMR 3.15 (m, 4H), 6.12 (bs, 2H), 6.98 (s, 8H), 7.44 (m, 2H), 8.70 (m, 6H), 9.13 (bt, 3H); Anal. ($C_{22}H_{25}I$) C, H.

At $R_f \simeq 0.33$ compound **16** was isolated as a yellow oil (40 mg, 16%): mass *m/e* 532 (M^+, 33%), 461 (13%), 405 (35%), 289 (57%), 243 (41%), 231 (100%), 204 (29%), 167 (48%), 117 (66%); NMR 3.22 (m, 6H), 6.17 (bs, 2H), 6.30 (bs, 2H), 6.95 (m, 12H), 7.33 (m, 2H), 8.75 (m, 6H), 9.17 (bt, 3H).

At $R_f \simeq 0.3$, compound **17** was isolated as an amorphous white solid (47 mg, 21% yield): mass *m/e* 648 (M^+, 10%), 476 (29%), 461 (11%), 405 (25%), 359 (51%), 289 (32%), 243 (30%), 204 (30%), 173 (12%), 117 (47%); NMR 3.30 (m, 8H), 6.37 (m, 6H), 7.07 (m, 16H), 7.40 (m, 2H), 8.77 (m, 9H).

At $R_f \simeq 0.23$ compound **18** eluted as a yellow oil (30 mg, 15%): mass *m/e* 764 (M^+, 7%), 591 (8%), 521 (11%), 475 (8%), 461 (11%), 405 (19%), 359 (25%), 333 (31%), 289 (44%), 279 (30%), 263 (33%), 243 (69%), 231 (100%), 229 (30%), 217 (82%); NMR 3.30 (m, 10H), 6.33 (m, 8H), 7.03 (m, 20H), 7.40 (m, 2H), 8.78 (m, 9H).

Pyrolysis of 3-trimethylsilyl-4-hydroxymethylbenzocyclobutene (**11**) *to* **21**. Compound **11** (19 mg, 0.092 mmole) was vacuum-transferred through a quartz tube (inside diameter 15 mm, hot path length 30 cm, contact time *ca* 0.005 sec) at 700° and 10^{-5} torr vacuum. Starting material was sublimed from a flask at room temp., requiring 3 hr for total transfer. The product was collected as a white solid in a U-shaped trap at −196°, to which an NMR tube was attached. Vacuum distillation of solvent (CCl_4, 0.5 ml, 1% TMS) allowed dissolution of the pyrolysate and transfer into the NMR tube which was subsequently sealed under vacuum. This latter precaution proved unnecessary since pure and air stable **21** was formed in this experiment (yield undetermined): mass (*m/e* 190 (M^+, 46.6%), 189 (20.9%), 175 (100%), 145 (10.2%), 115 (16.1%); NMR 3.10 (bs. 2H), 5.05 (s, 2H), 6.87 (bs, 4H), 9.67 (s, 6H); ^{13}C-NMR 0.48, 29.7, 30.4, 71.8, 120.0, 123.4, 143.7, 149.3, the two remaining aromatic carbon signals could not be observed with certainty because of the small sample size and signal to noise problems; IR spectrum (neat, KCl plates) 2960, 2940, 2860, 1405, 1350, 1250, 1110, 1040, 815, 795.

3-Trimethylsilyl-4-chloromethylbenzocyclobutene (**22**). Compound **11** (343 mg, 1.67 mmole) was dissolved in CCl_4(10 ml) and cooled to 0° under dry N_2. Pyridine (0.135 ml = 0.132 g, 1.67 mmoles) was added, followed by $SOCl_2$ (0.119 ml = 0.198 g, 1.67 mmoles). White crystals of pyridinium hydrochloride formed immediately. After 5 min the cold bath was removed and the soln left to stir as it warmed to room temp. The course of the reaction was followed conveniently by NMR. 2.5 hr at room temp. followed by 1.5 hr at 40° gave clean conversion. The soln was treated with water (10 ml) and extracted with ether (50 ml). Washing the organic layer with water (50 ml) twice and brine (50 ml) once, followed by drying over $MgSO_4$ gave after evaporation of solvent the crude material (378 mg, 100% yield). Molecular distillation at 0.1 torr/T_{bath} = 73–75° affords pure **22** as a colorless liquid: mass *m/e* 224 (M^+, 8%), 209 (89%), 189 (9%), 173 (35%), 115 (19%), 93 (100%), 73 (15%); NMR 2.97 (d, J = 8Hz, 1H), 3.23 (d, J = 8Hz, 1H), 5.55 (s, 2H), 6.97 (m, 4H), 9.70 (s, 9H); IR spectrum (neat, KCl plates) 2990, 1465, 1395, 1260, 1225, 1148, 935, 869, 841, 739; Anal. ($C_{12}H_{17}SiCl$) C, H.

Pyrolysis of 3-trimethylsilyl-4-chloromethylbenzocyclobutene (**22**). Compound **22** was subjected to flash pyrolysis conditions as described above. At oven temps. of 455° and 585° the starting material was recovered unreacted. When the pyrolysis was carried out at 750° (48 mg of **22** transferred over a 6 hr period, starting material not heated beyond room temp.) a black residue covered the inside of the hot part of the quartz tube. The product collected was brown at liquid N_2 temp., but progressed through orange and then a violet color before melting and turning colorless, indicative of the presence of radicals. The NMR spectrum revealed the presence of starting material and complex new aromatic, olefinic, and saturated signals. This material was not investigated any further.

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[19]Dr. P. J. Garratt at the University College London has informed us that he has planned an experiment in which compound **1** will be treated with *n*-BuLi. This might corroborate or refute the speculation in Scheme 3.