^{13}C–^{1}H Coupling Constants in Carbocations. 6.[1] Generation and Trapping of the (1aα,7aα)-1a,2,7,7a-Tetrahydro-1*H*-cyclopropa[*b*]naphthalen-2-yl Cation

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New synthetic routes to (1aα,2β,7bα)-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalen-2-ol (**4b**) and (1aα,2α,7aα)-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalen-2-ol (**6b**) have been established involving dichlorocarbene addition to the appropriate dihydronaphthalene as the key step. Ionization of either alcohol **4b** or **6b** in FSO_3H/SO_2ClF at −130 °C produces the title cation **5b**, in which the positive charge is stabilized by the adjacent benzo and cyclopropyl moieties. This is the same cation as that obtained previously by protonation of 1,6-methano[10]annulene (**1**). Generation of the cation **5b** by protonation of C11-^{13}C-enriched **1** has shown that the C11 bridge methylene carbon is incorporated into both benzylic positions (C2 and C7) and not the apical cyclopropyl carbon (C1). Application of the ΔJ equation shows that **5b** adopts an anti-boat conformation in this superacid medium.

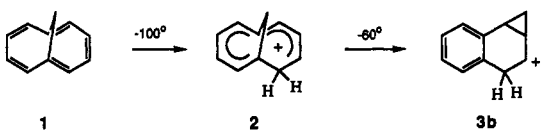
Protonation of 1,6-methano[10]annulene (**1**) in superacid at −100 °C has been proposed to yield a monoprotonated cation **2**[2] which rearranges to an internal cyclopropylcarbinyl cation **3b** when warmed to −60 °C (Scheme I).[3] Subsequently, we showed that cations related to **3b** rearrange spontaneously (are not observed) to the benzylic cations by way of a cyclopropylcarbinyl rearrangement.[4] For example, ionization of (1aα,2β,7bα)-3,3-dimethyl-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalen-2-ol (**4a**) in FSO_3H/SO_2ClF at −130 °C gave the rearranged cation **5a** as the only observable species. This was shown by comparison of the ^{1}H and ^{13}C NMR chemical shifts with those of other cations of unambiguous structure and by application of the ΔJ equation for one-bond ^{13}C–^{1}H coupling constants.[5] The structure of **5a** was confirmed by isolation of the *syn*-methyl ether **7a** from the cation solution following quenching in methoxide/methanol. Product **7a** was identical in all respects with authentic material prepared from alcohol **6a**. Furthermore, under the same conditions used to ionize **4a**, alcohol **6a** yields the identical cation **5a** (Scheme II).[4] These results clearly suggested that the observed cyclopropylcarbinyl cation derived from protonation of **1** has structure **5b** and not **3b**. Nevertheless, this conclusion relied on the assumption that the tetrahydro-1*H*-cyclopropanaphthalene skeleton was not perturbed significantly by the presence of the *gem*-dimethyl group. The latter was necessitated by the synthetic route used to generate the precursor alcohol **4a** from β-naphthol.[4]

We have now developed synthetic routes to the parent alcohols (1aα,2β,7bα)-1a,2,7,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalen-2-ol and (1aα,2α,7aα)-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalen-2-ol (**4b** and **6b**, respectively) and have demonstrated that on ionization in FSO_3H/SO_2ClF at −130 °C both compounds yield the same cation, namely, **5b**, the spectroscopic data for which is identical with that previously reported[3a] for **3b**.

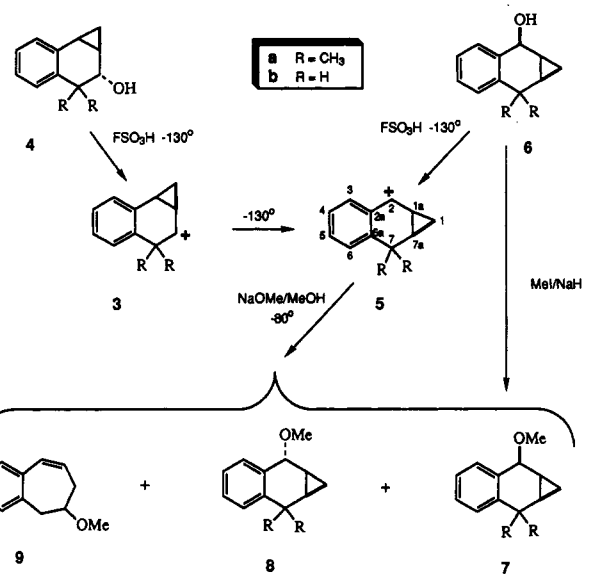
Results and Discussion

Synthesis. Alcohol **4b** was obtained in 4% overall yield in six steps from 1,4-dihydronaphthalene[6] (Scheme III).

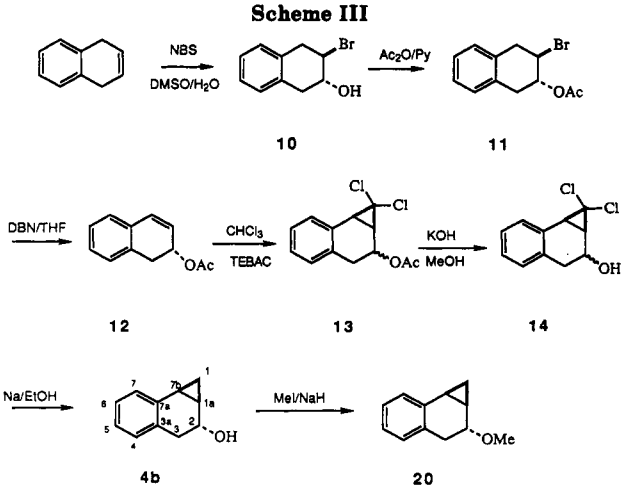
Scheme I



Scheme II



Scheme III



Thus, treatment of 1,4-dihydronaphthalene with *N*-bromosuccinimide in wet dimethyl sulfoxide[7] gave the

(1) Part 5: Kelly, D. P.; Giansiracusa, J. J.; Leslie, D. R.; McKern, I. D.; Sinclair, G. C. *J. Org. Chem.* **1988**, *53*, 2497–2504.
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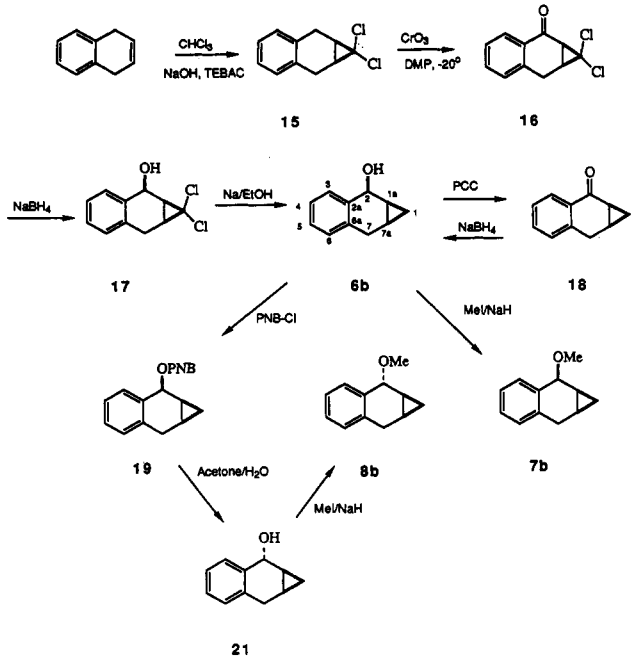
Scheme IV



known[8] bromohydrin **10**, which was converted into the corresponding acetate (**11**) by standard methods. On treatment with the weakly nucleophilic base 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), compound **11** afforded a ca. 7:3 mixture of the allylic acetate **12** and naphthalene. Compound **12** is extremely acid sensitive and gave naphthalene almost instantaneously on exposure to a trace of trifluoroacetic acid. Dichlorocarbene addition to the double bond of allylic acetate **12** could be accomplished under phase-transfer conditions[9] (using chloroform, sodium hydroxide, and benzyltriethylammonium chloride) and afforded an epimeric mixture of the dichlorotetrahydrocyclopropa[*a*]naphthalen-2-ol acetates **13**, which were not isolated but immediately subjected to hydrolysis with KOH in methanol. The resulting 1:6 mixture of alcohols **14** could not be separated chromatographically. However, a pure sample of the major isomer was obtained by fractional crystallization of the derived benzoates and subsequent hydrolysis of the purified ester derivative. Reductive dechlorination of the mixture of alcohols **14** did not proceed cleanly, but after chromatographic purification and recrystallization, an epimerically pure tetrahydrocyclopropa[*a*]naphthalen-2-ol was obtained. Since the yield (24%) of this product is greater than could be expected from reduction of the minor epimer of **14**, it must be derived from the major epimer. On the basis that dichlorocarbene should add preferentially to the sterically less hindered face in alkene **12**, thereby producing a predominance of the adduct **13** with anti stereochemistry, the crystalline product derived from the reductive dechlorination reaction is assigned as the anti alcohol **4b**. O-Methylation of compound **4b** was achieved under standard conditions (NaH, methyl iodide) and provided ether **20**, which was required for characterization of cation quenching products (see below).

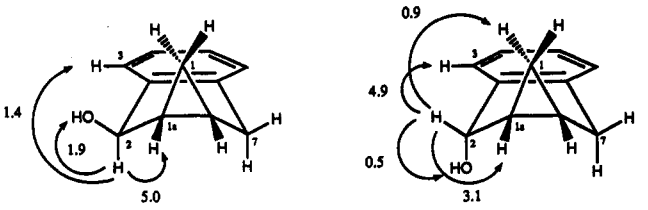


Figure 1. Nuclear Overhauser enhancements for epimeric alcohols **6b** and **21**.

The isomer of **4b**, alcohol **6b**, was obtained by similar methods (Scheme IV). Thus, dichlorocarbene addition to 1,4-dihydronaphthalene gave the previously reported[11] adduct **15** (35%). Benzylic oxidation of this latter compound using the 3,5-dimethylpyrazole/chromium trioxide complex[12] afforded the crystalline ketone **16** (78%), which upon reduction with sodium borohydride in methanol delivered alcohol **17** (77%) as a single stereoisomer. Reductive dechlorination[10] of **17** then afforded the required alcohol **6b** (63%) as a crystalline solid. This syn alcohol **6b** could be converted into the corresponding *O*-methyl ether **7b** under standard conditions (NaH, methyl iodide). Attempts to prepare alcohol **21** and thence the epimeric *anti*-methyl ether **8b** [required for identification of cation quench products (see below)] by subjecting alcohol **6b** to an oxidation (to give known[13] ketone **18**)/reduction sequence returned only the starting alcohol. However, on the basis of work by Ohkata et al.,[14] the *p*-nitrobenzoate, **19**, of alcohol **6b** was solvolyzed in aqueous acetone at 35 °C for 80 h and thereby afforded a ca. 10:1 mixture of alcohols **21** and **6b**. O-Methylation of this mixture then provided the corresponding mixture of methyl ethers **7b** and **8b** (70%), which were not separated.

The assigned stereochemistries in the epimeric alcohols **6b** and **21** were established by homonuclear NOE experiments at 400 MHz (Figure 1). Thus, irradiation of H2 (in isomer **21**) at δ 5.06 resulted in enhancements of 0.5% to OH, 3.1% to H1a, 4.9% to H3, and most importantly, 0.9% to $H1_{endo}$. The latter was identified unequivocally by its two (equal) small couplings to $H1_{exo}$ and H1a, H7a ($J_{gem} = J_{cis} = 4.9$ Hz). Similar experiments on alcohol **6b** gave enhancements of 1.9% to OH, 5% to H1a, and 1.4% to H3 and no enhancements to either of the geminal cyclopropyl protons (H1). These experiments confirm the configurational assignments for these epimeric alcohols **21** and **6b** as anti and syn, respectively. These assignments are opposite to those reported[14] earlier by Ohkata and co-workers but are consistent with the notion that hydride should add preferentially to the sterically less hindered face of the carbonyl moiety in ketone **16** thereby establishing the proposed syn stereochemistry in compound **17** and, ultimately, in its dechlorinated counterpart **6b**.

Consideration of the NOE data has also allowed us to propose that **6b** and **21** exist predominantly in anti-boat conformations (Figure 1). In **6b**, the NOE between H2 and H1a (5.0%) is much greater than that between H2 and H3 (1.4%). This is consistent with an anti-boat conformation where there is a greater distance between H2 and H3 as

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gauged from Dreiding molecular models. The corresponding distances in a syn-boat conformation (H1a–H2 and H2–H3) are approximately equal and would be expected to result in an equivalence of the NOEs. In **21** the NOE between H2 and H1a (3.1%) is much greater than that between H2 and $H1_{endo}$ (0.9%). Again, this is consistent with the greater distance between the latter pair and not consistent with a syn-boat conformation in which the distances are reversed ($r_{2,1endo} < r_{2,1a}$).

Ion Generation. Dissolution of **4b** in either dichloromethane or sulfuryl chloride fluoride and addition to FSO_3H/SO_2ClF at −130 °C gave dark red-brown solutions, the ^{13}C NMR spectra of which displayed chemical shifts closely similar to those reported for **3b**, in particular a cationic carbon shift of 221.7 ppm.[3a] Treatment of the isomeric alcohol **6b** under similar conditions yielded an identical spectrum (Scheme II).

Quenching of both the cationic solutions in methoxide/methanol at −80 °C yielded mixtures, shown by ^1H and ^{13}C NMR to contain predominantly the *anti*-methyl ether **8b**, small amounts of the *syn*-methyl ether **7b**, and in some cases, quantities of the ring-opened cycloheptenyl methyl ether **9**. (The precise composition of the quench mixture varied from run to run.) This was confirmed by chromatographic isolation of **8b** and **9** from the quench mixture and, in the case of **8b**, comparison with authentic material prepared above. None of the isomeric *anti*-methyl ether **20** could be detected in the mixture derived from the cation quenching experiments.

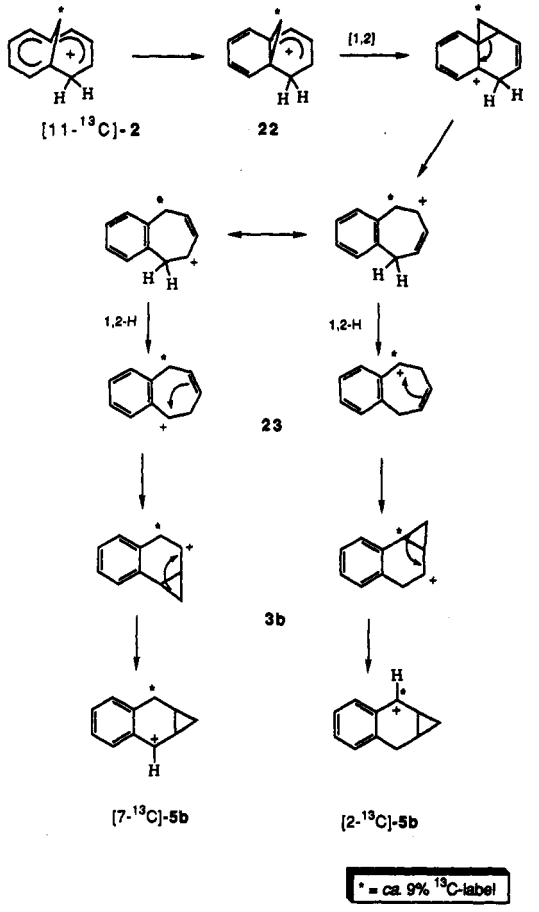
The conclusion is inescapable: the rearranged cation from monoprotonated 1,6-methano[10]annulene is the benzylic cation **5b** rather than the cation **3b**. If the latter is formed, it must rearrange spontaneously to **5b** as suggested previously for the conversion of **3a** into **5a**.[4] In addition, application of the ΔJ equation[5] using the appropriate $^1J_{CH}$ values for the cation (190 Hz) and the model ketone **18** (171 Hz) shows that the cation **5b** exists in the same conformation as **5a**, that is, an anti-boat conformation in which the C–H1a bond is perpendicular to the adjacent vacant pπ orbital at the cationic carbon.[4] This validates our previous assumption that the conformation of the tetrahydro-1*H*-cyclopropa[*b*]naphthalene skeleton is not perturbed by the presence of a *gem*-dimethyl unit.

The mechanism previously proposed to account for the formation of **3b** from **2** involved firstly ring closure between C1 and C6 "after which the bridge methano group wanders over the 'naphthalenium' skeleton probably via [1,2] and subsequent [1,4] sigmatropic shift...".[3a]

In order to investigate this proposal we prepared 1,6-methano[10]annulene enriched with ^{13}C at the bridging carbon (C11, ca. 9% ^{13}C). Dissolution of labeled **1** in FSO_3H/SO_2ClF at −110 °C produced a beautiful clear orange-red solution, the ^1H NMR spectrum of which was consistent with that previously reported for **2**, the H2 protons appearing as a pair of doublets at δ 3.23 and 3.77 and the bridge protons (H11) at 0.88 and 1.53 ppm. The latter two signals showed enhanced ^{13}C satellites consistent with the label being located at C11. The corresponding carbon signal appeared as an intense line at 39.7 ppm.

Warming of the solution of **2** to −70 °C caused the color to turn to red and the ^{13}C NMR spectrum to change completely (2–3 h) to that previously considered to be the spectrum of **3b**, but herein shown to be that of **5b**. The intensity of two resonances at δ 220.4 and 30.4 demonstrated that the label is distributed approximately equally between the cationic carbon (C2) and a methylene carbon (C?). If the bridge methano group "wanders" over the skeleton, it may be anticipated that C11 would be located in the cyclopropyl group when it finally comes to rest. That this is *not so* is demonstrated unequivocally by the one-bond J_{CH} value of 132 Hz for the intense triplet at δ 30.4 and a value of ca. 170 Hz for the normal intensity triplet at 62.5 ppm. These two methylene resonances are thus assigned to C7 and C1, respectively.

Scheme V



A possible mechanism for the rearrangement of **2**, which accommodates these observations and includes the postulated norcaradiene intermediate[3a] **22** and the unobserved cation **3b**, is shown in Scheme V. Thus, a [1,2] shift in **22** would produce firstly an allylic cation and secondly, after a 1,2-hydride shift, the stabilized (benzylic) homoallylic cations **23**. A homoallyl–cyclopropylcarbinyl rearrangement (to **3b**) followed by a cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement would produce the required ^{13}C-labeled cations **5b**.

Finally, quenching of ^{13}C-labeled **5b** in methoxide/methanol yields a mixture of *syn*- and *anti*-methyl ethers **7b** and **8b**, characterized by relatively intense ^{13}C signals at δ 75.9 (syn-C2), 80.2 (anti-C2), 28.8 (anti-C7), and 29.0 (syn-C7) ppm.

Experimental Section

General Procedures. Analytical TLC was conducted on aluminum-backed 2-mm silica gel 60 F_{254} plates (Merck) by using an anisaldehyde/H_2SO_4/EtOH (2:5:93 v/v/v) spray reagent or 254-nm UV irradiation. Preparative TLC was conducted on 20 × 20 cm glass plates loaded with Merck Kieselgel 60 GF_{254} (35 g/plate). Gas chromatograms (GC) were obtained from a 4 mm (o.d.) × 2 m glass column containing 3% Dexil on Chromasorb W, by using a nitrogen carrier gas flow rate of 16 mL min^{-1} and a standard temperature program 70 °C (5 min)/heat 10 °C min^{-1}/300 °C (10 min). Retention times (t_R) are quoted in seconds. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from benzophenone ketyl immediately prior to use. Dichloro-

methane (CH_2Cl_2) was distilled from CaH_2. All other solvents and reagents were purified by literature procedures.[15] All reactions requiring anhydrous conditions were run under a nitrogen atmosphere in oven-dried glassware. Aqueous solutions were extracted with CH_2Cl_2, Et_2O, or a combination thereof. The extracts were dried with anhydrous $MgSO_4$.

NMR Spectra. Deuteriochloroform was used as the solvent for ^1H and ^{13}C NMR spectra unless otherwise stated. Chemical shifts of cation solutions were measured from external Me_4Si or internal CH_2Cl_2 (taken as 54.8 ppm from Me_4Si), and field stabilization was provided by a concentric capillary (2 mm) of acetone-d_6 containing Me_4Si. Proton-coupled spectra were recorded under standard gated decoupling conditions. J values (±1 Hz) were checked by hand from expanded plots where necessary. Temperatures were measured with a calibrated platinum resistance thermometer or by the internal probe thermometer of the spectrometer. NOE difference spectra were obtained by using a standard pulse program NOEDIF, 128 scans, 8-s irradiation, and 10-s pulse delay.

(2α,3β)-2-Hydroxy-3-bromo-1,2,3,4-tetrahydronaphthalene (10). 1,4-Dihydronaphthalene[6] was treated with *N*-bromosuccinimide in wet DMSO[7] at 5 °C for 45 min and worked up in the prescribed[7] fashion to give **10** (73%): mp 107–107.5 °C (lit.[8] mp 106 °C); ^1H NMR (400 MHz) δ 7.13–7.20 (complex m, 2 H), 7.11 (complex m, 1 H), 7.06 (m, 1 H), 4.30 (ddd, J = 10.5, 9.8, 5.6 Hz, 1 H), 4.07–4.15 (complex m, 1 H), 3.53 (dd, J = 16.6, 5.6 Hz, 1 H, H4), 3.37 (dd, J = 16.6, 10.8 Hz, 1 H), 3.33 (dd, J = 16.6, 5.9 Hz, 1 H), 2.88 (dd, J = 16.6, 9.5 Hz, 1 H), 2.65 (s, 1 H, OH); ^{13}C NMR (22.5 MHz) δ 133.5, 133.3, 129.0, 127.8, 126.6, 126.4, 71.4, 56.5, 39.0, 36.2; IR ν_{max} (KBr) 3389 cm^{-1}; MS, m/z (70 eV) 228 (3), 226 (M^+, 3), 129 (100); HRMS calcd for M^+ 225.9993, obsd 225.9993.

(2α,3β)-2-Acetoxy-3-bromo-1,2,3,4-tetrahydronaphthalene (11). A solution of bromohydrin **10** (17.23 g, 0.076 mol) in dry pyridine (120 mL) was stirred with acetic anhydride (18.3 mL, 0.2 mmol, 0 °C) for 24 h, quenched (H_2O), extracted (CH_2Cl_2), washed (2 M HCl, 0 °C; $NaHCO_3$, NaCl), dried, filtered, and concentrated to give a pale yellow oil, which crystallized on standing. Recrystallization (*n*-hexane) gave **11** as white needles (18.26 g, 90%): mp 65.7–66.0 °C; ^1H NMR (400 MHz) δ 7.16–7.20 (complex m, 2 H), 7.07–7.11 (complex m, 2 H), 5.34 (ddd, J = 5.9, 5.9, 7.1 Hz, 1 H, H2), 4.41 (ddd, J = 7.3, 7.3, 5.1 Hz, 1 H, H3), 3.58 (dd, J = 17.3, 5.1 Hz, 1 H, H4), 3.46 (dd, J = 17.3, 5.9 Hz, 1 H, H1), 3.29 (dd, J = 17.3, 7.3 Hz, 1 H, H4), 2.91 (dd, J = 17.3, 6.2 Hz, 1 H, H1); ^{13}C NMR (22.5 MHz) δ 170.0 (C=O), 132.6, 132.0 (C4a, 8a), 128.9, 128.4, 126.7, 126.5 (C5,6,7,8), 71.9 (C2), 47.1 (C3), 36.9, 32.7 (C1,4), 21.0 (CH_3); IR ν_{max} (KBr), 1737 cm^{-1}; MS, m/z (70 eV) 129 (100), 43 (23).

2-Acetoxy-1,2-dihydronaphthalene (12). A solution of the bromoacetate **11** (11.37 g, 42 mmol) in THF (35 mL) was stirred with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (5.5 mL, 44.5 mmol) for 16 h at room temperature, diluted (CH_2Cl_2, H_2O), separated, dried, filtered, and concentrated to give a ca. 7:3 mixture of **12** and naphthalene as an unstable pale yellow oil (7.80 g, 69% yield of **12**): ^1H NMR (90 MHz) δ 7.18 (m, 4 H, H5,6,7,8), 6.65 (d, J = 10 Hz, 1 H, H4), 6.03 (dd, J = 10, 5 Hz, 1 H, H3), 5.50 (m, 1 H, H2), 3.10 (m, 2 H, H1), 2.00 (s, 3 H); ^{13}C NMR (22.5 MHz) δ 170.3 (C=O), 132.4, 131.9, 130.9, 128.0, 127.6 (coincident with signal due to naphthalene), 126.6, 125.5 (coincident with signal due to naphthalene), 124.7, 66.7 (C2), 32.9 (C1), 20.9 (CH_3); IR ν_{max} 1731, 1242 cm^{-1}; MS (CI, CH_4, 50 eV), 188 (M^+, 14), 129 (100), 128 (99).

(1aα,2β,7bα)- and (1aα,2α,7bα)-1,1-Dichloro-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalen-2-ol (14). The mixture of **12** and naphthalene (12.5 g, 46 mmol) and triethylbenzyl ammonium chloride (0.23 g, 1.0 mmol) in $CHCl_3$ (40 mL) was treated with aqueous NaOH (50% w/v, 35 mL) with vigorous stirring at 5 °C. The mixture was stirred for 40 h at room temperature, quenched (H_2O), separated, and extracted (CH_2Cl_2). The combined organic phases were washed (H_2O) (small amounts of methanol were added to disperse the emulsions that formed), then dried, filtered, and concentrated to give acetates **13** as a dark brown oil. The oil was dissolved in methanol (230 mL) and the solution stirred for 3h at room temperature with NaOH (4.71 g, 0.12 mol). The reaction mixture was diluted (H_2O), extracted (CH_2Cl_2), washed (H_2O), dried, filtered, and concentrated to yield a brown oil. Chromatographic filtration (SiO_2, CH_2Cl_2) and flash chromatography[16] (80:20 CH_2Cl_2/Et_2O) gave a ca. 6:1 mixture of epimeric alcohols **14** (8.22 g, 77%): GC, t_R 1290 s; ^1H NMR (400 MHz) δ (major isomer) 7.37 (m, 1 H), 7.22 (m, 2 H), 7.11 (m, 1 H), 4.26 (ddd, J = 7.0, 5.1, 3.4 Hz, 1 H, H2), 2.98 (dd, J = 15.6, 5.1 Hz, 1 H, H3) 2.90 (d, J = 10.5 Hz, 1 H, H7b), 2.84 (dd, J = 15.6, 7.0 Hz, 1 H, H3), 2.34 (ddd, J = 10.5, 3.5, 0.5 Hz, 1 H, H1a); ^1H NMR (400 MHz) δ (minor isomer) diagnostic signals were observed at 4.39 (ddd, 1 H), 3.15 (dd, 1 H), and 2.50 (dd, 1 H); the remaining signals were coincident with or obscured by those due to the major isomer; ^{13}C NMR (100 MHz) δ (major isomer) 133.9, 130.3, 129.7, 129.4, 127.9, 126.9, 64.2 (C2), 63.9 (C1), 36.6, 36.6, 32.4; ^{13}C NMR (100 MHz) δ (minor isomer) 130.2, 129.2, 129.1, 127.5, 126.5 (one aromatic resonance obscured), 64.7, 63.5, 37.0, 35.7, 35.6; IR ν_{max} (KBr) 3292, 1035 cm^{-1}; MS, m/z (15 eV), 232 (1), 230 (9), 228 (M^+, 15), 214 (3), 212 (21), 210 (33), 193 (71), 175 (44), 157 (42), 132 (46), 129 (100), 128 (20), 127 (12); HRMS calcd for M^+ 228.0109, obsd 228.0108. Benzoylation of this mixture (benzoyl chloride, pyridine) gave a yellow solid, which after recrystallization (MeOH × 3) afforded the epimerically pure ester **(1aα,2β,7bα)-1,1-dichloro-2-(benzoyloxy)-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalene**: mp 107.5–108.0 °C; ^1H NMR (400 MHz) δ 8.04 (dm, J = 7 Hz, 2 H), 7.57 (tt, J = 7.6, 1.2 Hz, 1 H), 7.44 (m, 3 H), 7.28 (m, 2 H), 7.14 (m, 1 H), 5.51 (ddd, J = 7.3, 5.2, 3.7 Hz, 1 H, H2), 3.18 (dd, J = 16.0, 5.2 Hz, 1 H, H3), 3.03 (dd, J = 16.0, 7.3 Hz, 1 H, H3), 2.99 (d, J = 10.5 Hz, 1 H, H7b), 2.53 (ddd, J = 10.5, 3.7, 0.5 Hz, 1 H, H1a); ^{13}C NMR (100 MHz) δ 165.7 (C=O), 133.5, 133.2, 130.3, 129.9, 129.7, 129.6, 129.2, 128.4, 128.0, 127.1, 67.1 (C2), 63.5 (C1), 34.0, 33.4, 32.4; IR ν_{max} (KBr) 1712, 1274 cm^{-1}; MS, m/z (15 eV) 334 (1), 332 (M^+, 2.5), 214 (10), 212 (57), 210 (100); HRMS calcd for M^+ 332.0371, obsd 332.0370. Hydrolysis of this material using potassium hydroxide in methanol afforded an epimerically pure alcohol (**14**) as an oil. This material was identical in all respects with the major component of the mixture of alcohols obtained above.

(1aα,2β,7bα)-1a,2,3,7b-Tetrahydro-1*H*-cyclopropa[*a*]naphthalen-2-ol (4b). Reductive dechlorination of alcohol **14** was carried out according to the procedure of Lap and Paddon-Row.[10] Thus, sodium metal (5.3 g, 0.23 mol) was added over 2 h to a refluxing solution (EtOH) of **14** (2.03 g, 8.84 mmol). After a further 3 h at reflux, the mixture was cooled, quenched (ice, 200 mL), extracted (CH_2Cl_2), dried, filtered, and concentrated. Chromatographic filtration (CH_2Cl_2, R_f 0.3) through silica gel gave a yellow solid. Recrystallization (pentane/CH_2Cl_2) gave **4b** (345 mg, 24%) as fine white crystals: mp 87–87.5 °C; GC t_R 1020 s; ^1H NMR (400 MHz) δ 7.28 (dd, J = 7.3, 1.5 Hz, 1 H, H4), 7.16 (m, 1 H), 7.11 (m, 1 H), 7.05 (br d, J = 7.3 Hz, 1 H, H7) 4.50 (m, 1 H, H2), 2.81 (dt, J = 16.6, 2.2 Hz, 1 H, H3), 2.68 (dd, J = 16.6, 3.7 Hz, 1 H, H3), 2.05 (ddd, J = 8.5, 8.5, 4.6 Hz, 1 H, H7b), 1.75 (m, 1 H, H1a), 1.48 (s, 1 H, OH), 1.10 (ddd, J = 8.5, 8.5, 5.1 Hz, 1 H, $H1_{exo}$), 0.76 (ddd, J = 10.0, 5.1, 51. Hz, 1 H, $H1_{endo}$); ^{13}C NMR (100 MHz) δ 137.8, 130.2, 129.3, 128.0, 126.3, 125.4, 63.8 (C2), 34.2 (C3), 21.3, 15.4, 11.6; IR ν_{max} (KBr) 3300, 1604, 1494, 1462, 1045 cm^{-1}; MS, m/z (70 eV) 160 (M^+, 66), 145 (100), 142 (79), 115 (84); HRMS calcd for M^+ 160.0888, obsd 160.0888.

(1aα,2β,7bα)-2-Methoxy-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalene (20). To **4b** (0.02 g, 0.12 mmol) in THF (0.6 mL) was added methyl iodide (0.12 mL, 1.83 mmol) followed by sodium hydride (100%, 0.045 g, 1.83 mmol). The mixture was stirred at room temperature for 17 h, cooled (0 °C), quenched (H_2O), extracted (Et_2O), washed (NaCL), dried, filtered, and concentrated to give a yellow oil. Preparative TLC (CH_2Cl_2, R_f 0.5) afforded **20** (7.0 mg, 32%) as a viscous yellow oil: ^1H NMR (90 MHz) δ 7.0–7.3 (complex m, 4 H) 4.1 (m, 1 H, H2), 3.4 (s, 3 H, OCH_3), 3.0 (dm, J = 17 Hz, 1 H, H3), 2.8 (dd, J = 17, 4 Hz, 1 H, H3), 2.0 (m, 1 H, H7b), 1.6–1.8 (complex m, 1 H), 1.1 (m, 1 H, $H1_{exo}$, 0.6–0.8 (complex m, 1 H, $H1_{endo}$); ^{13}C NMR (22.5 MHz) δ 138.0, 130.1 (C3a,7a), 129.3, 128.0, 126.1, 125.3, 73.2 (C2), 56.2 (OCH_3), 30.2, 18.2, 15.8, 10.7; MS, m/z (70 eV) 174 (M^+, <1), 107 (11), 91 (100); HRMS calcd for M^+ 174.1045, obsd 174.1044.

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(1aα,7aα)-1,1-Dichloro-1a,2,7,7a-tetrahydro-1H-cyclopropa[b]naphthalene (15). Dichlorocarbene addition was affected as in the preparation of **13**, by using aqueous NaOH (50% w/v, 30 mL), 1,4-dihydronaphthalene (7.5 g, 57.6 mmol), and triethylbenzyl ammonium chloride (0.19 g, 0.8 mmol) in chloroform (35 mL). Similar workup gave an oil, which was filtered (silica gel, CH_2Cl_2), concentrated, and distilled to give a pale yellow oil (bp 116–118 °C/1 mmHg), which crystallized on standing. Recrystallization (methanol) gave **15** (4.41 g, 35%) as white needles: mp 56.5–57 °C (lit.[11] mp 55–57 °C); ^{13}C NMR (22.5 MHz) δ 133.6 (C2a,6a), 128.4, 126.0, 66.2 (C1), 27.2, 24.7; MS, *m/z* (70 eV) 216 (5), 214 (29), 212 (M^+, 47), 179 (29), 177 (93), 142 (37), 141 (42), 129 (100); HRMS calcd for M^+ 212.0160, obsd 212.0160.

(1aα,7aα)-1,1-Dichloro-1a,2,7,7a-tetrahydro-1H-cyclopropa[b]naphthalen-2-one (16). To chromium trioxide (14.1 g, 141 mmol) suspended in CH_2Cl_2 (120 mL) at −20 °C under N_2 was added 3,5-dimethylpyrazole (13.5 g, 141 mmol), and the mixture was stirred for 15 min. Compound **15** (1.5 g, 7.04 mmol) was added and stirring continued at ca. −15 °C for 4 h. NaOH (20% w/v, 120 mL) and ether (200 mL) were added to the reaction mixture, and stirring was continued at 0 °C for 1 h. Extraction of the aqueous phase (Et_2O) was followed by washing (2 M HCl, water, aqueous NaCl), drying, filtering, and concentration to give a yellow solid. Recrystallization (ethanol) afforded **16** (1.25 g, 78%) as white needles: mp 139.5–140 °C; R_f (CH_2Cl_2) 0.5; ^1H NMR (100 MHz) δ 8.0 (d, *J* = 8 Hz, 1 H, H3), 7.3 (m, 3 H, H4,5,6), 3.45 (m, 2 H, H7α,7β), 2.9 (d, *J* = 10 Hz, 1 H, H1a), 2.6 (m, 1 H, H7a); ^{13}C NMR (100 MHz) δ 188.5 (s), 140.2 (s), 134.0 (d, *J* = 161 Hz), 130.8 (s), 128.3 (d), 127.0 (d), 126.8 (d), 60.7 (s), 37.8 (d, *J* = 172 Hz, C1a), 30.7 (dm, *J* = 169 Hz, C7a), 23.9 (t, *J* = 129 Hz, C7); IR (KBr) ν_{max} 1669, 1593, 784 cm^{-1}; MS, *m/z* (70 eV) 230 (3), 228 (20), 226 (M^+, 33), 193 (28), 191 (87), 163 (85), 128 (100), 127 (96); HRMS calcd for M^+ 225.9952, obsd 225.9951. Anal. Calcd for $C_{11}H_8Cl_2O$: C, 58.18; H, 3.55; Cl, 31.22. Found: C, 58.01; H, 3.39; Cl, 31.44.

(1aα,2α,7aα)-1,1-Dichloro-1a,2,7,7a-tetrahydro-1H-cyclopropa[b]naphthalen-2-ol (17). Ketone **16** (0.30 g, 1.3 mmol) in methanol (20 mL) was stirred under N_2 at 0 °C with $NaBH_4$ (75 mg, 2 mmol) until dissolution was complete (ca. 0.5 h). The mixture was diluted (H_2O), extracted (Et_2O), dried, filtered, and concentrated to give a white solid that dissolved in CH_2Cl_2/Et_2O (4:1), filtered through TLC grade silica gel, and concentrated to give a white solid. Recrystallization (hexane) gave **17** (230 mg, 77%) as white needles: mp 127.5–128 °C; R_f (CH_2Cl_2) 0.4; ^1H NMR (100 MHz) δ 7.6 (m, 1 H, H3), 7.2 (m, 3 H, H4,5,6), 5.1 (br t, 1 H, H2), 3.2 (m, 2 H, H7α,7β), 2.4 (m, 3 H, H1a, H7a, OH); ^{13}C NMR (22.5 MHz) δ 136.2, 132.7, 127.7, 127.2, 126.6, 126.4, 65.2, 61.7, 33.2, 28.7, 24.8; IR (KBr) ν_{max} 3450, 1028, 771, 728 cm^{-1}; MS, *m/z* (70 eV) 230 (7), 228 (M^+, 11), 193 (21), 157 (37), 129 (48), 128 (46), 119 (100); HRMS calcd for M^+ 228.0109. Anal. Calcd for $C_{11}H_{10}Cl_2O$: C, 57.67; H, 4.40; Cl, 30.95. Found: C, 57.56; H, 4.39; Cl, 31.06.

(1aα,2α,7aα)-1a,2,7,7a-Tetrahydro-1H-cyclopropa[b]naphthalen-2-ol (6b). Reductive dechlorination of alcohol **17** was performed as for **14**.[10] Preparative TLC (CH_2Cl_2, R_f 0.3) followed by recrystallization (hexane/THF) gave **6b** (211 mg, 67%) as fine white needles: mp 85–87 °C; ^1H NMR (400 MHz) δ 7.62 (d, *J* = 7.6 Hz, 1 H, H3), 7.25 (dd, *J* = 7.6, 7.6 Hz, 1 H), 7.18 (dd, *J* = 7.3, 7.3 Hz, 1 H), 7.03 (d, *J* = 7.6 Hz, 1 H, H6), 5.06 (dd, *J* = 8.5, 4.3 Hz, 1 H, H2), 3.07 (dd, *J* = 16.4, 3.9 Hz, 1 H, H7), 2.98 (dd, *J* = 16.4, 1.7 Hz, 1 H, H7), 1.82 (br d, *J* = 8 Hz, 1 H, OH), 1.62–1.68 (complex m, 1 H, H1a), 1.40–1.47 (complex m, 1 H, H7a), 0.41 (dt, *J* = 8.0, 4.9 Hz, 1 H, $H1_{exo}$), 0.23 (dt, *J* = 4.9, 4.9 Hz, 1 H, $H1_{endo}$); ^{13}C NMR (100 MHz) δ 137.1, 132.8 (C2a,6a), 128.3 (C6), 127.1, 126.5, 125.5 (C3), 67.7 (C2), 28.9 (C7), 18.3, 9.5, 1.7 (C1); IR (KBr) ν_{max} 3330 (br), 1453, 1034, 737 cm^{-1}; MS, *m/z* (70 eV) 160 (M^+, 100), 159 (56), 158 (12), 142 (82), 141 (64), 131 (81), 129 (80), 128 (60), 116 (59), 115 (60); HRMS calcd for M^+ 160.0888, obsd 160.0888. Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.56; H, 7.44.

(1α,2α,7aα)-2-Methoxy-1a,2,7,7a-tetrahydro-1H-cyclopropa[b]naphthalene (7b). Alcohol **6b** (102 mg, 0.64 mmol) was added to a stirred suspension of sodium hydride (225 mg, 9.15 mmol) in THF (3.0 mL) under N_2 at room temperature. The mixture was treated with methyl iodide (0.6 mL, 9.15 mmol), stirred for 16 h, cooled to 0 °C, quenched (H_2O), extracted (Et_2O), dried, filtered, and concentrated to give a light yellow oil. Preparative TLC (CH_2Cl_2, R_f 0.6) gave **7b** (88 mg, 79%) as a clear, colorless oil: ^1H NMR (400 MHz) δ 7.53 (d, *J* = 7.6, 1 H), 7.22 (m, 1 H), 7.15 (m, 1 H), 7.03 (d, *J* = 7.4 Hz, 1 H), 4.77 (d, *J* = 4.4 Hz, 1 H, H2), 3.59 (s, 3 H, OCH_3), 3.03 (dd, *J* = 16, 4.0 Hz, 1 H, H7β), 2.95 (dd, *J* = 16, 2.2 Hz, 1 H, H7α), 1.61–1.67 (complex m, 1 H), 1.34–1.41 (complex m, 1 H), 0.45 (dt, *J* = 5, 8 Hz, 1 H, $H1_{exo}$), 0.27 (dt, *J* = 5, 5 Hz, 1 H, $H1_{endo}$); ^{13}C NMR (100 MHz) δ 135.1, 133.3 (C2a,6a), 128.5, 127.0, 126.4, 125.6, 75.9 (d, *J* = 142 Hz), 55.7 (q, *J* = 141 Hz), 29.0 (t, *J* = 127 Hz, C7), 13.6 (d, *J* = 161 Hz), 8.7 (d, *J* = 161 Hz), 2.76 (t, *J* = 161 Hz, C1); IR (NaCl) ν_{max} 1454, 1092, 742 cm^{-1}; MS, *m/z* (70 eV) 174 (M^+, 61), 173 (54), 143 (91), 142 (66), 129 (67), 128 (81), 116 (100), 115 (50); HRMS calcd for M^+ 174.1045, obsd 174.1044.

(1aα,7aα)-1a,2,7,7a-Tetrahydro-1H-cyclopropa[b]naphthalen-2-one (18). A solution of **6b** (186 mg, 1.16 mmol) in CH_2Cl_2 (5 mL) containing sodium acetate (300 mg, 3.66 mmol) was stirred with pyridinium chlorochromate (600 mg, 2.78 mmol) for 4 h at room temperature, then diluted (Et_2O), filtered (TLC grade silica gel), and concentrated to give an orange oil. Preparative TLC (CH_2Cl_2, R_f 0.3) upon extraction (CH_2Cl_2/Et_2O, 1:1) gave **18**[13] (121 mg, 66%) as a light yellow oil: ^1H NMR (400 MHz) δ 7.86 (dd, *J* = 7.8, 1.4 Hz, 1 H, H3), 7.44 (dt, *J* = 7.3, 1.5 Hz, 1 H), 7.29 (t, *J* = 7.3 Hz, 1 H), 7.17 (d, *J* = 7.8 Hz, 1 H), 3.33 (dd, *J* = 17.5, 5.1 Hz, 1 H), 3.20 (d, *J* = 17.5 Hz, 1 H, H7β), 2.10–2.17 (complex m, 1 H), 1.90–1.97 (complex m, 1 H), 1.31 (ddd, *J* = 9.0, 8.0, 4.8 Hz, 1 H, $H1_{exo}$), 0.82 (ddd, *J* = 6.1, 6.1, 4.6 Hz, 1 H, $H1_{endo}$); ^{13}C NMR (100 MHz) δ 198.1, 138.4, 132.9, 131.0, 128.7, 126.8, 126.7, 27.8 (t, *J* = 129 Hz, C7) 25.2 (d, *J* = 171 Hz, C1a), 13.8 (d, *J* = 169 Hz, C7a), 12.7 (t, *J* = 167 Hz, C1); IR (NaCl) ν_{max} 1666, 1604 cm^{-1}; MS, *m/z* (70 eV) 158 (M^+, 100), 129 (52), 115 (28).

Ketone **18** (100 mg, 0.63 mmol) in methanol (4 mL) was treated with $NaBH_4$ (25 mg) and stirred at room temperature for 0.75 h. Standard workup (CH_2Cl_2 extraction) gave alcohol **6b** (97%), identical in all respects with material obtained earlier.

(1aα,2a,7aα)-1a,2,7,7a-Tetrahydro-1H-cyclopropa[b]naphthalen-2-ol p-Nitrobenzoate (19). The procedure of Ohkata et al.[14] was used to convert alcohol **6b** into the corresponding *p*-nitrobenzoate (**19**) (75%): mp 113–114 °C (lit.[14] mp 110–111 °C); ^1H NMR (400 MHz) δ 8.20–8.40 (complex m, 4 H), 7.10–7.30 (complex m, 4 H), 6.56 (d, *J* = 4.9 Hz, H2), 3.17 (dd, *J* = 16.6, 4.2 Hz, H7), 3.08 (dd, *J* = 16.6, 1.7 Hz, H7), 1.81–1.88 (complex m, 1 H), 1.48–1.56 (complex m, 1 H), 0.56 (ddd, *J* = 8.0, 8.0, 5.1 Hz, $H1_{exo}$), 0.47 (ddd, *J* = 10.3, 5.1, 5.1 Hz, $H1_{endo}$); ^{13}C NMR (100 MHz) δ 164.7, 150.6 (s), 136.0, 133.6, 132.0, 130.9, 129.0, 127.8, 126.6, 125.4, 123.6, 72.8, 28.7, 14.8, 9.6, 3.1; IR (KBr) ν_{max} 1713, 1603, 1518, 1336, 1318, 1273 cm^{-1}; MS, *m/z* (70 eV) 309 (<1), 167 (5), 150 (11), 142 (100), 141 (62), 128 (23), 115 (17); HRMS calcd for M^+ 309.1001, obsd 309.1000.

(1aα,2β,7aα)-1a,2,7,7a-Tetrahydro-1H-cyclopropa[b]naphthalen-2-ol (21). Solvolysis of ester **19** according to Ohkata et al.[14] provided a ca. 10:1 mixture of alcohols **21** and **6b** (13 mg, 50%) as a light yellow oil: ^1H NMR (400 MHz) δ (major isomer) 7.06–7.26 (complex m, 4 H), 5.06 (d, *J* = 2.9 Hz, H2), 3.31 (dd, *J* = 16.1, 3.9 Hz, H7), 2.98 (d, *J* = 16.1 Hz, H7), 1.72 (br s, OH), 1.49–1.56 (complex m, 1 H, H1a), 1.34–1.41 (complex m, 1 H, H7a), 0.54 (ddd, *J* = 8.5, 8.5, 5.1, Hz, $H1_{exo}$), −0.04 (ddd, *J* = 10.0, 4.9, 4.9 Hz, $H1_{endo}$); ^{13}C NMR (100 MHz) δ (major isomer) 135.7, 134.0, 129.6, 129.4, 128.6, 126.8, 71.3, 28.5, 17.3, 8.1, 4.8; IR (film) ν_{max} 3341, 1453, 1433, 1064, 1034, 1022, 737 cm^{-1}; MS, *m/z* (70 eV) 160 (M^+, 16), 159 (14), 158 (13), 142 (100), 141 (68), 129 (56), 128 (48), 115 (47); HRMS calcd for M^+ 160.0888, obsd 160.0885.

(1aα,2β,7aα)-2-Methoxy-1a,2,7,7a-tetrahydro-1H-cyclopropa[b]naphthalene (8b). The ca. 10:1 mixture of alcohols **21** and **6b** (8 mg, 0.050 mmol) in THF (1 mL) was converted into the corresponding mixture of methyl ethers **8b** and **7b** by using NaH (22.05 mg, 0.92 mmol) in THF (1 mL), and methyl iodide (58 mL, 0.92 mmol). The usual workup (Et_2O extraction) gave a ca. 1:10 mixture of **7b** and **8b** (6 mg, 70%) as a light oil: ^1H NMR (400 MHz) δ (major isomer) 7.25 (ddd, *J* = 7.6, 7.3, 1.7 Hz, 1 H), 7.18 (tm, *J* = 7.3 Hz, 1 H), 7.08 (dd, *J* = 7.2, 1.5 Hz, 2 H, H3, H6), 4.55 (d, *J* = 2.9 Hz, 1 H, H2), 3.28 (dd, *J* = 16.1, 3.6 Hz, 1 H, H7), 3.26 (s, 3 H, OCH_3), 2.93 (dd, *J* = 16.1, 1 Hz, 1 H, H7), 1.52–1.59 (complex m, 1 H), 1.35–1.42 (complex m, 1 H), 0.50 (ddd, *J* = 8.3, 8.3, 5.1 Hz, 1 H, $H1_{exo}$), −0.08 (ddd, *J* = 10, 4.9, 4.9 Hz, 1 H, $H1_{endo}$); ^{13}C NMR (100 MHz) δ (major isomer) 135.1, 132.6,

130.4, 129.6, 128.6, 125.8, 80.2 (C2), 55.6 (OCH_3), 28.8, 15.5, 8.1, 4.4; IR (film) ν_{max} 1455, 1082, 750 cm^{-1}; MS, m/z (70 eV), 174 (M^+, 8), 173 (12), 158 (16), 149 (25), 143 (80), 142 (100), 141 (55), 129 (52), 128 (87), 127 (22), 116 (39), 115 (61); HRMS calcd for M^+ 174.1045, obsd 174.1046.

1,6-Methano[10]annulene (1) enriched with 9% ^{13}C at the bridging carbon (C11) was prepared from naphthalene according to the method of Vogel et al.[17] but using 9% [^{13}C]chloroform during dichlorocarbene addition to 1,4,5,8-tetrahydronaphthalene: mp 27 °C (lit.[17] mp 27 °C); ^1H NMR (400 MHz) δ 7.44 (m, 4 H), 7.1 (m, 4 H), −0.45 (t, J_{CH} = 142.3 Hz, 2 H, H11); ^{13}C NMR (100 MHz) δ 128.8, 126.2, 114.9 (C1 and 6), 34.9 (C 11, ca. 9-fold enrichment); IR (KBr) ν_{max} 1445, 1397, 1245, 756 cm^{-1}; MS, m/z (70 eV) 143 (12), 142 (M^+, 70), 141 (100), 115 (33); HRMS calcd for $^{13}C_1{}^{12}C_{10}H_{10}$ 143.0816, obsd 143.0817.

Generation and Quenching of Cations. Alcohols **4b** and **6b** (ca. 22 mg) were dissolved in either CH_2Cl_2 (ca. 0.2 mL) or SO_2ClF cooled to <0 °C, and added dropwise to a mixture of FSO_3H/SO_2ClF (1:1 v/v) cooled to <−120 °C (pentane/liquid nitrogen slush) in a 5-mm NMR tube with vortex mixing. The resulting red/brown solutions from both **4b** and **6b** gave identical ^{13}C NMR spectra of **5b**: ^{13}C NMR (100 MHz, CH_2Cl_2, −80 °C) δ 221.9 (d, J = 166 Hz, C2), 147.3 (dd, J = 164, 7 Hz, C5), 146.8 (s, C6a), 140.6 (d, J = 168 Hz, C3), 134.3 (s, C2a), 132.7 (d, J = 166 Hz, C6), 131.3 (dd, J = 168, 7 Hz, C4), 64.1 (t, J = 172 Hz, C1), 52.2 (d, J = 190 Hz, C1a), 44.1 (dd, J = 176, 7 Hz, C7a), 31.7 (t, J = 132 Hz, C7). Larger sized samples (80 mg of **4b**, **6b**) were ionized in FSO_3H/SO_2ClF (1.5 mL) by using special reaction tubes as previously described.[18] These solutions were poured slowly into sodium methoxide/methanol (2.5 M solution, 5 mL) at −80 °C with rapid stirring. The mixtures were allowed to warm to room temperature, and water was added to give a clear solution, which was extracted with pentane. The pentane extracts were dried, filtered, and concentrated under a stream of nitrogen gas to give pale yellow oils. In some cases the oils were chromatographed on silica (CH_2Cl_2 elution) to yield small amounts of purified materials. In this way, 6,7-dihydro-6-methoxy-5*H*-benzocycloheptene (**9**) (6 mg) was isolated as a colorless oil: ^1H NMR (400 MHz) δ 7.13–7.23 (complex m, 4 H), 6.50 (dt, J = 11.7, 1.7 hz, 1 H, H5), 5.86 (dt, J = 11.7, 5.1 Hz, 1 H, H6), 3.73 (m, 1 H, H1), 3.39 (s, 3 H, OCH_3), 3.02 (dd, J = 13.7, 1 Hz, 1 H), 2.92 (dd, J = 13.7, 8.3 Hz, 1 H), 2.60 (dt, J = 17.3, 5.2 Hz, 1 H), 2.37 (dddd, J = 17.3, 7.5, 4.9, 1.7 Hz, 1 H); ^{13}C NMR (100 MHz) δ 136.8, 136.3, (C3,4) 130.3, 129.89, 129.87, 127.9, 127.0, 126.4, 81.6, 56.3, 40.7, 36.4.

Similarly, the *anti*-methyl ether **8b** was recovered.

^{13}C-Labeled 1,6-methano[10]annulene, [11-^{13}C]-**1** (24 mg, 1.7 mmol), was placed in a 5-mm NMR tube together with SO_2ClF (0.1 mL) and cooled in liquid nitrogen. FSO_3H/SO_2ClF (1:1 v/v 0.5 mL) was added to the frozen mixture, and the tube warmed to −120 °C with rapid vortex mixing. A clear orange-red solution was obtained, the ^1H NMR spectrum of which was consistent with that previously reported for **2**;[1] ^1H (400 MHz, −90 °C) δ 7.82 (d, J = 6.2 Hz, 1 H), 7.38 (m, 1 H), 7.21 (d, J = 8 Hz, 1 H), 7.12 (m, 1 H), 6.93 (m, 1 H), 6.79 (m, 1 H), 6.67 (m, 1 H), 3.77 (br d, J = 24.6 Hz, 1 H, h2), 3.23 (d, J = 24.6 Hz, 1 H, H2), 1.53 (d, J = 8.8 Hz, 1 H, H11), 0.88 (d, J = 8.8 Hz, 1 H, H11); ^{13}C NMR (100 MHz, −90 °C) δ 170.9, 160.1, 150.3, 147.4, 139.0, 133.0, 131.9, 126.8, 126.1, 45.8 (relative intensity 12, C2), 39.7 (relative intensity 100, C11).

After warming to −60 °C (2–3 h), the spectra of the solution prepared from ^{13}C-labeled **1** above were recorded and indicated the presence of only one cation [2,7-^{13}C]-**5b**: ^1H NMR (400 MHz, capillary, −60 °C) δ 9.54 (d, J = 7.3 Hz, 1 H) 7.37 (m, 1 H), 7.24 (d, J = 8 Hz, 1 H), 6.96 (m, 1 H), 6.90 (d, J = 7 Hz, 1 H), 3.63 (br s, 1 H) 3.19 (br m, 2 H), 3.05 (br s, 1 H), 2.83 (d m, J = 14 Hz, 1 H, H7), 1.17 (d, J = 9 Hz, H1); ^{13}C NMR (100 MHz, capillary, −60 °C δ (relative intensity, multiplicity, J, assignment) 220.4 (74, d, J = 166 Hz, C2), 146.0, (18, d, C5), 145.5 (s, C6a), 139.3 (25, d, C3), 133.0 (s, C2a), 131.33 (22, d, C6), 130.0 (25, d, C4), 62.5 (20, t, J = 170 Hz, C1), 50.7 (24, d, J = 188 Hz, C1a), 42.7 (18, dd, J = 176, 8 Hz, C7a), 30.4 (100, t, J = 132 Hz, C7).

Quenching of [2,7-^{13}C]-**5b** in NaOMe/MeOH afforded a mixture of **9** and ^{13}C-labeled **7** and **8**: ^1H NMR δ 3.3–3.6 (3 × s, 3 × OCH_3); ^{13}C NMR δ 80.3, 75.9 (2 × C2), 28.8, 29.0 (2 × C7).

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Supplementary Material Available: NMR spectra for compounds **4b**, **7b**, **8b**, **9**, **11**, **12**, and **14** (7 pages). Ordering information is given on any current masthead page.

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Benzyne Generation from Aryl Triflates

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The use of aryl triflates to form arynes as reactive intermediates is described. This allows the first general use of phenols as aryne precursors. Phenyl triflate reacts with LDA at −78 °C to form benzyne, which then reacts with diisopropylamine generating *N,N*-diisopropylaniline. Yields of diisopropylarylamines from aryne intermediates are superior to those previously reported. Regioisomeric ratios are similar to those obtained with use of other benzyne precursors.

Aryl electrophiles have become increasingly important as aryne precursors.[3,4] Classically, benzyne has been generated by the decomposition of diazocarboxylate salts,[5] by the oxidation of 1-aminobenzotriazole,[6] or by the base-catalyzed elimination of hydrogen halide from a halobenzene.[7] The ability to utilize phenols for benzyne

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