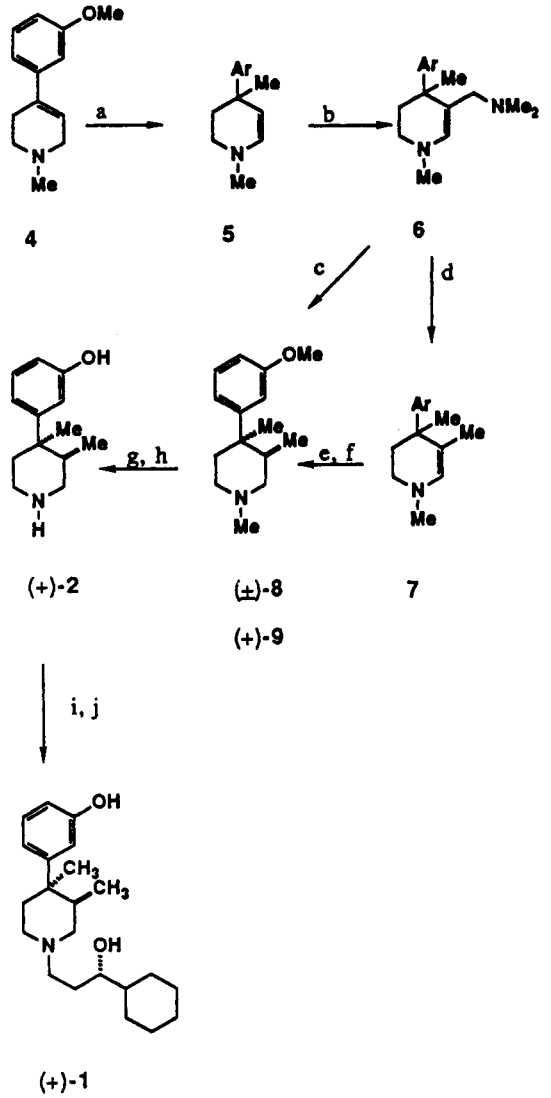
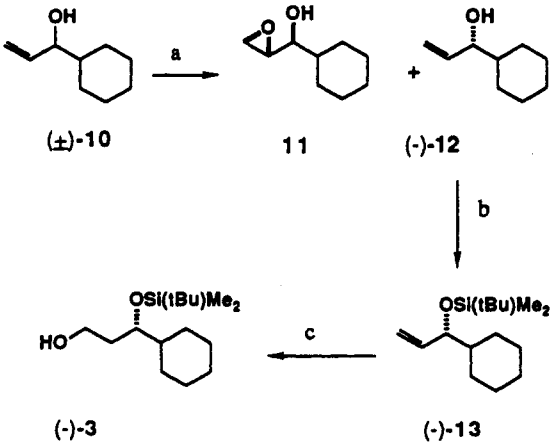
Scheme I[a]



[a] (a) *n*-BuLi, MeI; (b) CH_2O, $HNMe_2$; (c) H_2/Pt–C; (d) H_2/$BaSO_4$; (e) $NaBH_3CN$; (f) dibenzoyl L-tartrate; (g) vinyl chloroformate; HCl, MeOH; (h) HBr, AcOH; (i) (–)-3 + MsCl; (j) HF.

Scheme II[a]



[a] (a) Ti(O-*i*-Pr)$_4$, diisopropyl L-tartrate; (b) ClSi(*t*-Bu)Me_2; (c) BH_3–THF.

1 mmHg) afforded 16.7 g (94%) of (–)-13 having a rotation of $[\alpha]^{25}_{365}$ = –37° (*c* = 1.0, MeOH): ^{1}H NMR ($CDCl_3$) δ 5.74 (m, 1 H), 5.12 (m, 2 H), 4.81 (m, 1 H), 0.92 (s, 9 H), 0.05 (s, 3 H), 0.00 (s, 3 H). Anal. Calcd for $C_{15}H_{30}OSi$: C, 70.80; H, 11.88. Found: C, 70.59; H, 11.68.

(–)-(1*S*)-1-Cyclohexyl-1,3-dihydroxypropane ((–)-3). To a 0 °C solution of 10.8 g (42.4 mmol) of (–)-13 in 100 mL of THF was slowly added 64 mL (64 mmol) of 1 M BH_3·THF complex. After 2 h, the reaction mixture was carefully quenched by slow addition of 50 mL of water. Seventy milliliters of 3 N NaOH was added followed by 70 mL of 30% hydrogen peroxide. The mixture was stirred vigorously for 3 h and then extracted three times with 250 mL of Et_2O. The combined extracts were washed with brine, dried, and evaporated under vacuum. Purification on a Waters Prep 500 apparatus using 10% EtOAc/hexane as eluent afforded 6.2 g (54%) of (–)-3: $[\alpha]^{25}_{365}$ = –67° (*c* = 1.0, MeOH): ^{1}H NMR ($CDCl_3$) δ 3.74 (m, 1 H), 0.91 (s, 9 H), 0.09 (s, 3 H), 0.06 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 74.97, 59.91, 43.35, 35.04, 28.87, 28.04, 26.63, 26.44, 26.35, 25.81, 17.93, –4.54, –4.58; MS *m/z* calcd for $C_{15}H_{32}O_2Si$ $(M + H)^+$ 273.2250, found 273.2251.

(+)-1-[(3*S*)-3-Hydroxy-3-cyclohexylpropyl]-(3*R*,4*R*)-3,4-dimethyl-4-(3-hydroxyphenyl)piperidine ((+)-1). To a 0 °C solution of 2.73 g (10 mmol) of (–)-3 and 2.1 mL (15 mmol) of triethylamine in 50 mL of CH_2Cl_2 was added 0.85 mL (11 mmol) of methanesulfonyl chloride. After 30 min the solution was concentrated under vacuum. The residue was taken up in 50 mL of DMF, 2.05 g (10 mmol) of (+)-2 and 8.4 g of $NaHCO_3$ were added, and the mixture was heated at reflux for 1 h. After cooling to room temperature, 500 mL of EtOAc was added and the solution was extracted three times with 200 mL of brine. The organic phase was then dried and evaporated under vacuum. The residue was taken up in 100 mL of acetonitrile and 5 mL of 48% aqueous HF was added. After being stirred for 2 h at room temperature, an additional 5 mL of 48% HF was added. After a total reaction time of 4 h, the solution was basified to approximately pH 10 with 50% NaOH. The mixture was concentrated under vacuum and diluted with 100 mL of water. The solution was extracted with three 250-mL portions of EtOAc, and the combined extracts were washed with brine, dried, and evaporated under vacuum. HPLC analysis (eluent: 800 mL of hexane, 400 mL of EtOAc, 6 mL of MeOH, 2 mL of water, and 1 mL of triethylamine; silica gel column) showed that the unpurified material was free of possible diastereomers to the limits of detection (>99%). Preparative chromatography (1:1 EtOAc/hexane, 1% triethylamine as eluent) followed by recrystallization from EtOAc/hexane gave 1.0 g (29%) of (+)-1 as needles: mp 154–155 °C and $[\alpha]^{25}_{365}$ = +229° (*c* = 1.0, MeOH); ^{1}H NMR ($CDCl_3$) δ 7.18 (m, 5 H), 3.55 (m, 1 H), 1.24 (s, 3 H), 0.58 (d, 3 H, *J* = 7 Hz). Anal. Calcd for $C_{22}H_{35}NO_2$: C, 76.48; H, 10.21; N, 4.05. Found: C, 76.64; H, 10.48; N, 4.17.

Acknowledgment. We wish to thank Professor K. Barry Sharpless of MIT and Dr. Charles J. Barnett of the Lilly Research Laboratories for helpful discussions.

Supplementary Material Available: ^{1}H NMR and ^{13}C NMR data for compounds 6, 7, and (–)-3 and details of the crystal structure determination for compound (+)-1, including tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, H-atom coordinates, isotropic displacement parameters, and an ORTEP drawing of the structure showing the numbering scheme used in the tables (12 pages). Ordering information is given on any current masthead page.

Single Atom, *peri*-Bridged Arenes: 1-Alkylidene-1*H*-cyclobuta[*de*]naphthalenes and $\Delta^{1,1}$-Bi-1*H*-cyclobuta[*de*]naphthalene

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The abilities of naphthalenes to adjust to enormous strain are impressively illustrated upon preparing stable *peri* derivatives (1 and 2) in which bridging by single atoms

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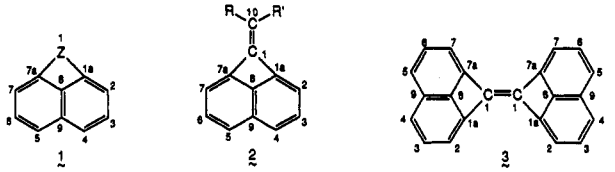
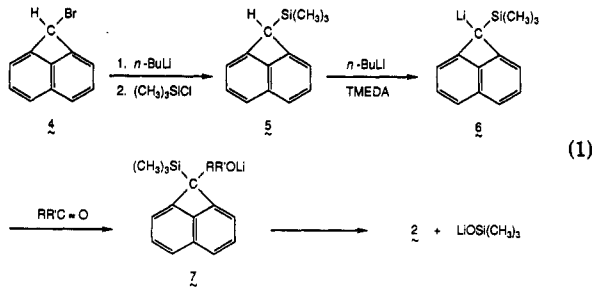
is effected with sulfur,[1] silicon,[2] or carbon.[3] Of present interest are synthesis and the structural accommodations in naphthalenes **2** bridged in 1,8-positions by alkylidene moieties.[3h] Study is now reported of (1) improved methodology for preparing 1-alkylidene-1*H*-cyclobuta[*de*]naphthalenes **2**,[3h] (2) the detailed structure of crystalline 1-(diphenylmethylene)-1*H*-cyclobuta[*de*]naphthalene (**2d**),[3h] and (3) synthesis of $\Delta^{1,1}$-bi-1*H*-cyclobuta[*de*]naphthalene (**3**).



1; Z = S, SO, SO_2, SiR_2,
1; Z = CXY, CO, $CP(C_6H_5)_3$

2a; R = C_6H_5, R' = H
2b; R and R' = CH_3
2c; R = C_6H_5, R' = CH_3
2d; R and R' = C_6H_5

peri-Bridged naphthalenes **2** have been previously prepared by Wittig reactions of (1*H*-cyclobuta[*de*]naphthalen-1-ylidene)triphenylphosphorane (**1**, Z = C=$P(C_6H_5)_3$) with aldehydes and ketones.[3h] In the present investigation, 1-alkylidene-1*H*-cyclobuta[*de*]naphthalenes **2a–d** are obtained advantageously by Peterson condensations (eq 1) of 1-lithio-1-(trimethylsilyl)-1*H*-cyclobuta[*de*]naphthalene (**6**) with benzaldehyde, acetone, acetophenone, and benzophenone, respectively, in ethyl ether at ca. −70 °C. Generation of **6** (eq 1) is effected efficiently



(1)

from (1) 1-bromo-1*H*-cyclobuta[*de*]naphthalene (**4**)[3a,g] and *n*-butyllithium and then trimethylsilyl chloride in ethyl ether at −100 °C to 25 °C to give 1-(trimethylsilyl)-1*H*-cyclobuta[*de*]naphthalene (**5**) and (2) reaction of **5** with *n*-butyllithium and tetramethylethylenediamine (TMEDA) in ethyl ether at −60 °C. The syntheses of **2a–d** in excellent purity are convenient and rapid.

The structure of crystalline **2d** has been determined by X-ray diffraction methods (see Experimental Section). Figure 1, an ORTEP drawing, illustrates the numbering system used in designating atom positions, selected bond distances, and selected bond angles in **2d** and reveals many

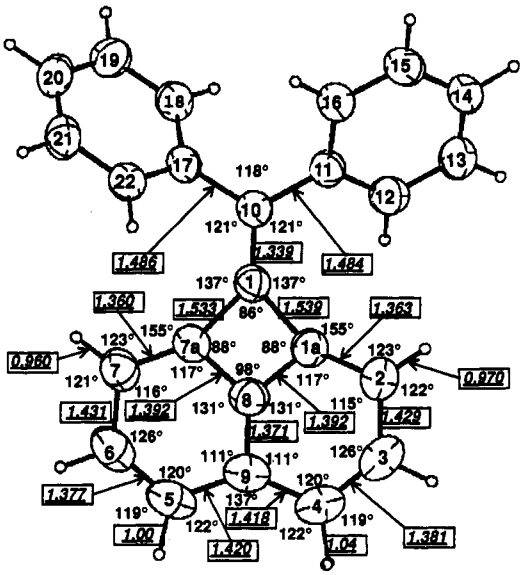


Figure 1.

of the important general features of the highly strained *peri*-bridged naphthalene.[4] Crystalline **2d** has pseudo C_{2v} symmetry with a 2-fold axis through its C(1), C(8), and C(9) atoms and its 1-methylene-1*H*-cyclobuta[*de*]naphthalene unit is essentially planar.[5] The two phenyl groups in **2d**, however, are significantly twisted. The dihedral angle between the planes of the two phenyl rings is 66.8° and those for the phenyl groups with the 1*H*-cyclobuta[*de*]naphthalene section are 40.4° and 47.8°, respectively.

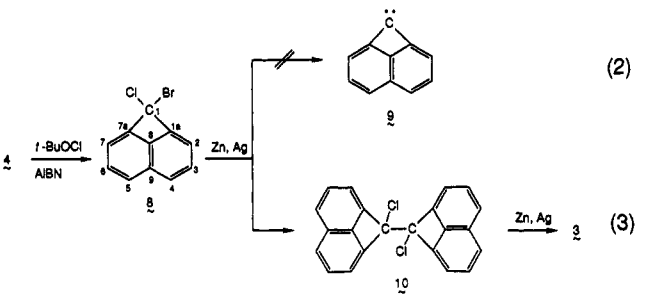
The most interesting features in **2d** arise from the strain in its 1-methylene-1*H*-cyclobuta[*de*]naphthalene system. The bond angles in its 1-methylene-1*H*-cyclobuta unit at C(1a)–C(1)–C(7a) and C(1a)–C(8)–C(7a) are ca. 86° and 98°, respectively.[6] The cyclobuta bond distances for C(1)–C(1a) and C(1)–C(7a) are only 1.53–1.54 Å and thus are similar to those of usual C–C single bonds and shorter (~0.03 Å) than those for such bonds in planar cyclobutanes.[7] The bond distances in the bridged naphthalene unit alternate impressively: C(1a)–C(2) and C(7a)–C(7), 1.36 Å; C(2)–C(3) and C(6)–C(7), ~1.43 Å; C(3)–C(4) and C(5)–C(6), ~1.38 Å; and C(4)–C(9) and C(9)–C(5), ~1.42 Å. *The most revealing feature in* **2d** *is its bond angle at C(4)–C(9)–C(5) of 137°*. It is thus clear in **2d** that (1) the front end of the 1-methylene-1*H*-cyclobuta[*de*]naphthalene system is highly compressed, (2) there is major alternating single and double bond character and bond fixation in its naphthalene nucleus, and (3) much of the strain in the *peri*-bridged portion is accommodated by adjustments in the bond angles and distances in the aft-end of the naphthalene section. The fact that the C–C bond distance at C(1)–C(10) is ~1.34 Å and therefore that of a typical carbon–carbon double bond is further indication of bond fixation and presumably depressed π-electron delocaliza-

(1) (a) Hoffman, R. W.; Seiber, W. *Justus Liebigs Ann. Chem.* **1967**, *706*, 93. (b) Meinwald, J.; Knapp, S. *J. Am. Chem. Soc.* **1974**, *96*, 6353.
(2) Yang, L. S.; Shechter, H. *J. Chem. Soc., Chem. Commun.* **1976**, 775.
(3) (a) Bailey, R. J.; Shechter, H. *J. Am. Chem. Soc.* **1974**, *96*, 8116. (b) Chapman, O. *Chem. Eng. News* **1978**, Sept. 18, 17. (c) Gessner, M.; Card, P.; Shechter, H.; Christoph, G. *J. Am. Chem. Soc.* **1977**, *99*, 2371. (d) Gessner, M. A. M.S. Thesis, The Ohio State University, Columbus, OH, 1977. (e) Becker, J.; Wentrup, C. *J. Chem. Soc., Chem. Commun.* **1980**, 190. (f) Engler, T. A.; Shechter, H. *Tetrahedron Lett.* **1982**, 2715. (g) Bailey, R. J.; Card, P. J.; Shechter, H. *J. Am. Chem. Soc.* **1983**, *105*, 6096. (h) Card, P. J.; Friedli, F. E.; Shechter, H. *Ibid.* **1983**, *105*, 6104. (i) Yang, L. S.; Engler, T. A.; Shechter, H. *J. Chem. Soc., Chem. Commun.* **1983**, 866. (j) Hayes, R. A.; Hess, T. C.; McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1983**, *105*, 7786. (k) McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H.-P. *Ibid.* **1985**, *107*, 7597.

(4) The detailed crystallographic information for **2d** and the ^1H NMR and the mass spectrum of **3** are available as supplementary material.
(5) The buckling in the 1-methylene-1*H*-cyclobuta[*de*]naphthalene portion in **2d** is within experimental error.
(6) (a) In 1-bromo-1*H*-cyclobuta[*de*]naphthalene (**4**) the bond angles and standard deviations at C(1a)–C(1)–C(7a), C(1a)–C(8)–C(7a), and C(4)–C(9)–C(5) are 83.7 (4)°, 99.0 (6)°, and 137.8 (6)°, respectively, and the bond distances and standard deviations at C(1)–C(1a), C(1a)–C(2), C(2)–C(3), C(3)–C(4), and C(4)–C(9) are 1.565 (9), 1.352 (8), 1.442 (10), 1.368 (9), and 1.420 (9) Å, respectively.[3c,d] (b) In naphthalene the C(1a)–C(8)–C(7a) bond angle is 121.5 (2)° and the C(1)–C(2) and the C(2)–C(3) bond distances are 1.361 (4) and 1.421 (4) Å, respectively.[3c]
(7) Adman, E.; Margulis, T. N. *J. Am. Chem. Soc.* **1968**, *90*, 4517.

tion in the front-end of the 1-methylene-1*H*-cyclobuta-[*de*]naphthalene section in **2d**.

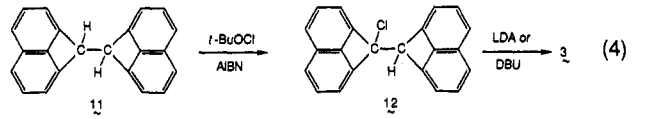
The synthetic utility of 1-bromo-1-chloro-1*H*-cyclobuta[*de*]naphthalene (**8**)[3a,h,8] as prepared by chlorination of **4** with *tert*-butyl hypochlorite in carbon tetrachloride in the presence of azobis(isobutyronitrile) has been investigated. In efforts to generate the carbene, 1*H*-cyclobuta[*de*]naphthalen-1-ylidene (**9**, eq 2), reaction of **4** with



(2)

(3)

zinc/silver in refluxing tetrahydrofuran is found to result in coupling–elimination (primarily as in eq 3) to give **3**, a highly strained ethylene in which each of the ethylene carbon atoms is fused into the *peri* positions of a naphthalene moiety. An alternate synthesis of **3** (eq 4) involves (1) chlorination of 1,1′-bi-1*H*-cyclobuta[*de*]naphthalene (**11**)[3h] with *tert*-butyl hypochlorite and azobis(isobutyronitrile) in refluxing carbon tetrachloride and (2) elimination of the resulting 1-chloro-1,1′-bi-1*H*-cyclobuta[*de*]-naphthalene (**12**) with lithium diisopropylamide (LDA) at



(4)

0 °C or with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in refluxing tetrahydrofuran. Olefin **3** is stable at room temperature and is assigned from its spectral properties, exact mass, and combustion analysis and its synthesis origins. Various addition, isomerization, and substitution reactions of **3** are to be investigated.

Experimental Section

1-(Trimethylsilyl)-1*H*-cyclobuta[*de*]naphthalene (5). To 1-bromo-1*H*-cyclobuta[*de*]naphthalene (**4**; 1.10 g, 0.05 mol)[3a,g] in anhydrous ethyl ether (100 mL) at −100 °C under argon was slowly added *n*-butyllithium (6.41 g, 0.10 mol, 2 equiv) in hexane. The bright red solution obtained was stirred at −100 °C for 40 min and chlorotrimethylsilane (6.90 g, 0.64 mol) was added. The mixture was allowed to warm to 20–25 °C, washed successively with water, hydrochloric acid (2 N), and saturated aqueous sodium bicarbonate, and then dried ($MgSO_4$). Evaporation of the solvents at reduced pressure yielded **5** (1.04 g, 0.049 mol, 98%), a pale yellow oil >95% pure spectroscopically (^1H NMR). Kugelrohr distillation (90 °C/1.5 mm) of the product gave **5** (0.87 g, 85% isolated yield) as a white semisolid identical (^1H NMR, ^{13}C NMR, and exact mass) with that prepared from **4**, magnesium, and chlorotrimethylsilane.[3h]

1-Benzylidene-1*H*-cyclobuta[*de*]naphthalene (2a). *n*-Butyllithium (384 mg, 0.60 mmol in hexane) was added to **5** (107 mg, 0.5 mmol) and tetramethylethylenediamine (118 mg, 1.0 mmol, 2 equiv) in ethyl ether (20 mL) at −70 °C under argon, and the stirred solution was gradually warmed to room temperature. After 1 h, the bright red mixture was cooled to −60 °C, benzaldehyde (53 mg, 0.5 mmol) was added, and the red color was discharged instantly. The solution was gradually warmed to 20–25 °C, stirred for 6 h, and poured into saturated aqueous ammonium chloride. The organic layer was washed with water, dried ($MgSO_4$), and concentrated to give **2a** (110 mg, 0.48 mmol, 98%) as a pale yellow oil, which has the proper NMR and does not separate on thin-layer chromatography. Column chromatography of the product on silica gel with pentane yielded **2a** (79 mg, 0.35 mmol, 70%) as a white solid identical with a prior sample:[3h] mp 56–57 °C (lit.[3h] mp 54–56 °C); ^1H NMR ($CDCl_3$) δ 6.76 (s, 1 H, vinyl), 7.06–7.77 (m, 11 H, aromatic).

1-Isopropylidene-1*H*-cyclobuta[*de*]naphthalene (2b). Reaction of *n*-butyllithium (2.15 M in hexane, 38 mg, 0.6 mmol), **5** (106 mg, 0.5 mmol), and tetramethylethylenediamine (118 mg, 1.0 mmol, 2 equiv) in ethyl ether at −70 °C to ~25 °C for 8 h, cooling the mixture to −78 °C, addition of acetone (29 mg, 0.5 mmol), storage for 8 h, and product isolation as for **2a** gave **2b** (89 mg, 0.5 mmol, 99%), a pale yellow oil, which does not separate on column chromatography and whose spectra are identical (^1H NMR and IR) with an authentic sample:[3h] ^1H NMR ($CDCl_3$) δ 2.02 (s, 6 H, $2CH_3$), 7.04 (dd, 2 H, J = 5 and 2 Hz, ortho) and 7.40–7.55 (m, 4 H, meta and para).

1-(Methylphenylmethylene)-1*H*-cyclobuta[*de*]-naphthalene (2c). Acetophenone (68 mg, 0.56 mmol) was added at −60 °C to a solution prepared under argon from *n*-butyllithium (2.15 M, 0.7 mmol in hexane), **5** (120 mg, 0.56 mmol), and tetramethylethylenediamine (118 mg, 1.0 mmol). The mixture was allowed to warm to room temperature and then stirred for 8 h. Product isolation as for **2a** yielded an oil, which was chromatographed on silica gel using hexane as eluent to give **2c** (99 mg, 0.41 mmol, 73%) as a white powder: mp 59–61 °C; ^1H NMR ($CDCl_3$) δ 2.54 (s, 3 H, CH_3), 7.2 (dd, 2 H, J = 2 and 4 Hz, ortho H in naphthalene unit), 7.3–7.86 (m, 9 H, aromatic); exact mass for $C_{19}H_{14}$, m/e (calcd) 242.3196, m/e (obsd) 242.3199. Anal. Calcd for $C_{19}H_{14}$: C, 94.18; H, 5.82. Found: C, 94.27; H, 5.72.

1-(Diphenylmethylene)-1*H*-cyclobuta[*de*]naphthalene (2d). With use of the preparative and the isolation procedures for **2a**, reaction of benzophenone (102 mg, 0.56 mmol) with **5** (120 mg, 0.56 mmol), *n*-butyllithium (0.60 mmol in hexane), and tetramethylethylenediamine (141 mg, 1.19 mmol) in ethyl ether (20 mL) yielded **2d** (155 mg, ~0.56 mmol, ~100%) as a yellow solid (mp 140–144 °C; lit.[3h] mp 144–146 °C) in >95% purity (^1H NMR) with spectral properties [^1H NMR ($CDCl_3$) δ 6.93 (dd, 2 H, J = 2 and 4 Hz, ortho H in naphthalene ring), 7.14–7.80 (m, 14 H, aromatic)] essentially identical with an authentic sample.[3h] Crystals obtained from purification of the above sample of **2d** were used for the X-ray analysis reported.

1-Bromo-1-chloro-1*H*-cyclobuta[*de*]naphthalene (8). A mixture of 1-bromo-1*H*-cyclobuta[*de*]naphthalene (**4**, 220 mg, 1 mmol), *tert*-butyl hypochlorite (1 mL), and azobis(isobutyronitrile) (20 mg, 0.12 mmol) in carbon tetrachloride (15 mL) was refluxed 16 h. Volatiles were removed under reduced pressure and the residue was chromatographed on silica gel and eluted with hexane to give (1) **4** (10 mg, ~5%) and (2) **8** (225 mg, 0.89 mmol, 89%): a colorless solid; mp 104–106 °C; IR (KBr, cm^{-1}) 1460, 1190, 1010, 990, 834, 782, and 724; ^1H NMR ($CDCl_3$) δ 7.20 (dd, 2 H, J = 5 and 5 Hz, ortho), 7.54–7.62 (m, 4 H, meta and para); ^{13}C NMR ($CDCl_3$, δ) 70.30 (1 C, C_1), 113.52 (2 C, $C_{2,7}$), 123.99 (2 C, $C_{4,5}$), 126.95 (1 C, C_9), 131.67 (2 C, $C_{3,6}$), 140.95 (1 C, C_8), 149.13 (2 C, $C_{1a,7a}$); exact mass for $C_{11}H_6BrCl$, m/e (calcd 251.9342, m/e (obsd) 251.9346. Anal. Calcd for $C_{11}H_6BrCl$: C, 52.11; H, 2.39. Found: C, 51.79; H, 2.40.

Base-Catalyzed Hydrolysis of 8. A mixture of **8** (200 mg, 0.8 mmol), potassium hydroxide (50 mg, 0.86 mmol), water (150 mg, 8.4 mmol), and tetrahydrofuran (15 mL) was refluxed for 48 h, poured into ethyl ether, and then acidified with hydrochloric acid. After the ethereal layer had been dried ($MgSO_4$) and concentrated, the residue was chromatographed on silica gel to give (1) **8** (60 mg, 30% recovery) identical with initial **8** and (2) 1-naphthoic acid (80 mg, 0.46 mmol, 58% conversion; mp 162 °C) identical with an authentic sample (IR, mixed mp, and ^1H NMR).

Base-Catalyzed Methanolysis of 8. A mixture of **8** (125 mg, 0.5 mmol), methanol (10 mL), and sodium methoxide (100 mg, 2.44 mmol) was refluxed 6 days. Vacuum removal of the solvent, chromatography on silica gel, and elution with hexane and benzene yielded (1) **8** (50 mg, 0.2 mmol, 40%) identical with initial **8** and (2) methyl 1-naphthoate (37 mg, 0.2 mmol; 40% conversion)

(8) 1-Bromo-1-chloro-1*H*-cyclobuta[*de*]naphthalene (**8**) is converted by (1) aqueous potassium hydroxide and acidification to 1-naphthoic acid and (2) methanolic sodium methoxide and chromatography on silica gel or methanolic silver nitrate to methyl 1-naphthoate (see Experimental Section).

identical with an authentic sample.

Reaction of 8 with Methanolic Silver Nitrate. A solution of 8 (130 mg, 0.5 mmol) and methanolic (150 mL) silver nitrate (300 mg, 1.8 mmol) was stirred vigorously. After 30 min the methanol was removed under reduced pressure and the organic product was dissolved in ethyl ether. Filtration and concentration of the solution yielded methyl 1-naphthoate (80 mg, 0.43 mmol, 86%) of proper spectral properties.

$\Delta^{1,1}$-Bi-1*H*-cyclobuta[*de*]naphthalene (3). Procedure A. Zinc (50 mg, 0.77 mmol) activated with silver was suspended in a solution of 8 (256 mg, 1.0 mmol) in tetrahydrofuran (15 mL). The mixture was refluxed for 10 h, cooled, filtered, and concentrated under reduced pressure. Column chromatography of the residue on silica gel using hexane as eluent led to (1) 1*H*-cyclobuta[*de*]naphthalene[3a,g] (20 mg, 0.14 mmol, 14%) and (2) 3 (40 mg, 0.145 mmol, 34% conversion): a white solid; mp 191-195 °C; IR (KBr, cm^{-1}) 1560, 1460, 1380, 1140, 1060, 1005, 910, 740; ^1H NMR ($CDCl_3$) δ 7.31 (dd, 4 H, J = 2 and 4 Hz, ortho), 7.55-7.7 (m, 8 H, *meta and para*); ^{13}C NMR ($CDCl_3$) δ 114.6 (2 C, $C_{2,7}$), 122.3 (2 C, $C_{4,5}$), 125.7 (1 C, C_9), 131.15 (2 C, $C_{3,6}$), 143.7 (1 C, C_8), 144.2 (2 C, $C_{1a,7a}$), 149.7 (1 C, C_1); exact mass for $C_{22}H_{12}$, m/e (calcd) 276.0939, m/e (obsd) 276.0943. Anal. Calcd for $C_{22}H_{12}$: C, 95.62; H, 4.38. Found: C, 95.07; H, 4.37.[4]

Procedure B. 1,1'-Bi-1*H*-cyclobuta[*de*]naphthalene[3h] (11; 278 mg, 1 mmol), *tert*-butyl hypochlorite (110 mg, 1 mmol), and azobis(isobutyronitrile) (10 mg, 0.6 mmol) in carbon tetrachloride (15 mL) were refluxed 6 h. Removal of the volatiles left crude 1-chloro-1,1'-bi-1*H*-cyclobuta[*de*]naphthalene [12; ^1H NMR ($CDCl_3$) δ 5.80 (s, 1 H, bridge H), 6.8-7.6 (m, 12 H, aromatic); mass calcd for $C_{22}H_{13}Cl$ 312.5, found 312-314] that was used for conversion to 3.

Lithium diisopropylamide [1.0 mmol, prepared from *n*-butyllithium (1.1 mmol, 1.1 equiv) and diisopropylamine (100 mg, 1.0 mmol) at -78 °C] was added to crude 12 (~310 mg, 1.0 mmol) in tetrahydrofuran (15 mL) at 0 °C. After the mixture had been stirred for 3 h at room temperature and the volatiles were removed under reduced pressure, chromatography of the residue on silica gel with hexane yielded 3 (65 mg, 24%) identical with previous 3.

Elimination of 12 (310 mg, 1.0 mmol) was also effected with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU, 150 mg, 1.0 mmol) in refluxing tetrahydrofuran (10 mL) for 8 h. Isolation and purification of the product as above gave 3 (57 mg, 21%).

Determination of the Crystal Structure of 1-(Diphenylmethylene)-1*H*-cyclobuta[*de*]naphthalene (2d). A plate-like prismatic, colorless crystal of 2d of approximate dimensions 0.20 × 0.45 × 0.50 mm was mounted on the tip of a thin glass fiber. The crystal 2d was examined by X-ray methods at room temperature, and data were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo K_α radiation (λ = 0.710 73 Å). The cell parameters and standard deviations were determined by least-squares fitting from 24 reflections well distributed in reciprocal space and lying in the 2θ range between >25° and 30°: Intensity data were collected by the ω-2θ scan mode [scan angle (ω) = 0.75 + 0.35 tan θ, scan speed (deg/min) = 0.65-5° (in ω)] with a 2θ range between 4° and 50°. A total of 3070 reflections was measured with 1768 unique data having $I > 3.0\sigma(I)$. The data were corrected for Lorentz and polarization effects and for decay but not for absorption. The crystal parameters of 2d at room temperature are space group $p2_{1/c}$, a = 12.085 (2) Å, b = 16.993 (1) Å, c = 8.134 (2) Å, β = 103.58 (1)°, V = 1623.66 Å^3, Z = 4.0, formula weight = 304.39, D_{calcd} = 1.2459 g cm^{-3}, and u = 0.655.

Solution and Refinement of Structure of 2d. Analytical forms of the scattering factors for neutral atoms were used throughout the analysis and Δf and $i\Delta f''$ terms were included for all atoms. All crystallographic computations were carried out on a PDP 11/44 computer using the structure determination package (SDP).

The space group, $p2_{1/c}$, for 2d was determined unambiguously from the systematic absences. The statistical distributions of the reflection intensities also suggest that the space group is likely centrosymmetric. The unit cell contains four molecules and thus there is one molecule per each crystallographic asymmetric unit. The structure of 2d was solved via a combination of MULTAN, difference Fourier, and least-squares refinements of the heavy atoms. All of the hydrogens appeared on the difference electron density map. The function minimized during the least-squares refinement process was $\Sigma w(|F_o| - |F_c|)^2$, where the assigned weighted are given as $w = [\sigma(I)^2 + (pI)^2]^{1/2}$ and p = 0.02 was chosen to make $\Sigma w \Delta F$ uniformly distributed in $|F_o|$. The final full-matrix least-squares refinement cycle with anisotropic thermal parameters for all non-hydrogen atoms, isotropic for hydrogens, gave R_f = 0.033 and R_{wf} = 0.040, where $R_f = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_{wf} = \Sigma w^{1/2}||F_o| - |F_c||/\Sigma_w{}^{1/2}|F_o|$, for the 1768 reflections having $I > 3.0\sigma(I)$ with 282 variables. The final difference Fourier map showed no significant features, with a maximum peak height of 0.115 e/Å^3. The bond angles and bond distances in 2d are summarized in Tables 1 and 2 (supplementary material).

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Supplementary Material Available: X-ray data for 1-(diphenylmethylene)-1*H*-cyclobuta[*de*]naphthalene and ^1H NMR spectra for $\Delta^{1,1}$-bi-1*H*-cyclobuta[*de*]naphthalene (15 pages). Ordering information is given on any current masthead page.

A Strategy for the Convergent Synthesis of Gilvocarcins via Chromium Carbene Benzannulation. 1-*O*-Methyldefucogilvocarcin V in Seven Steps†

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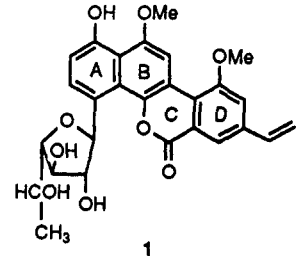
Of the *C*-aryl glycosides[1] which have been shown to have promising antitumor activity, members of the gilvocarcin group[2] (e.g. gilvocarcin V, 1) are particularly interesting because of their potency. Several approaches to the synthesis of the tetracyclic gilvocarcin "aglycons" have proven successful,[3] but there has been no report of the synthesis of a fully functionalized glycosylated natural product.[4]



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Our approach to the preparation of gilvocarcins is based on the elaboration of simple *C*-phenyl glycosides **5b** to the complex *C*-aryl glycoside structures **2b**. We imagined that this might be effected directly by a Dötz chromium carbene benzannulation[5] of the appropriately substituted phenyl acetylene 4 (Scheme I). The highly regioselective Dötz reaction tolerates numerous functional groups including the ester and olefin required for gilvocarcins.

In order to demonstrate the viability of this approach, we prepared phenyl acetylene 4 and employed this readily available intermediate in the conversion of *o*-bromoanisole to the known methyl ether **2a**[3c] of defucogilvocarcin V.[6] The intermediate required for this transformation is the

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