of dichloromethane and acetonitrile, the picrate concentration in the organic phase was determined from its absorption at 375 nm. The molar extinction coefficients at 375 nm for sodium, potassium, rubidium, and cesium picrates are 18600, 19000, 18800, and 18500 M^{-1} cm^{-1}, respectively.

In the experiments to determine extraction equilibrium constants (K_{ex}), dichloromethane solution of a crown ether of various concentrations (1×10^{-3} to 2×10^{-2} M) and aqueous alkali metal picrates (3×10^{-3} M) were brought to equilibrium at 25.0 ± 0.1 °C by the same procedure. With 15- and 16-crown-5 and 18- and 19-crown-6, the K_{ex} values were determined at several temperatures between 10 and 25 °C.

The free crown ether concentration in the organic phase, $[CE]_{org}$, was calculated by eq 2, described in our preceding paper.[4] $[CE]_i$

$$[CE]_{org} = ([CE]_i - n[M(CE)nA_{org})/(1 + K_D) \quad (2)$$

is the initial concentration of crown ether dissolved in the organic phase, and K_D is the distribution coefficient of crown ether between the two phases ($K_D = [CE]_{aq}/[CE]_{org}$).

In control experiments, detectable amounts of picrates were not extracted into the organic phase in the absence of crown ethers.

Distribution of crown ethers was determined by the procedure in our preceding paper.[4] Equal volumes (10 mL) of dichloromethane solution of a crown ether (3×10^{-3} and 5×10^{-3} M) and demineralized water, which was saturated with distilled dichloromethane, were brought to equilibrium at 25.0 °C under the conditions used for extraction. The concentration of the crown ether in the organic phase was determined by gas chromatographic analysis using cyclododecane or bicyclohexyl as an internal standard. The average distribution coefficients, K_D, for 15-crown-5 (**5a**), 16-crown-5 (**3a**), 17-crown-5 (**3b**), 18-crown-6 (**5b**), 19-crown-6 (**3c**), and 20-crown-6 (**3d**) were determined in several runs to be 0.31, 0.18, 0.06, 0.10, 0.12, and 0.08, respectively. The value of K_D did not change significantly between 10 and 25 °C.

Acknowledgment. This work was partially supported by a grant from the Hyogo Foundation for the Promotion of Science and Technology, which is gratefully acknowledged.

Registry No. **1a**, 504-63-2; **1b**, 110-63-4; **1c**, 629-11-8; **1e**, 4792-15-8; **2a**, 7460-82-4; **2b**, 19249-03-7; **2c**, 37860-51-8; **2d**, 41024-91-3; **2e**, 4724-56-5; **3a**, 55471-28-8; **3b**, 62991-38-2; **3c**, 55471-27-7; **3d**, 62991-36-0; **3e**, 89144-63-8; **4a**, 54308-73-5; **4b**, 62708-71-8; **5a**, 33100-27-5; **5b**, 17455-13-9; **6a**, 143-24-8; **6b**, 1191-87-3; sodium picrate, 3324-58-1; potassium picrate, 573-83-1; rubidium picrate, 23296-29-9; cesium picrate, 3638-61-7; 1,8-dichloro-3,6-dioxaoctane, 112-26-5; ethylene glycol, 107-21-1; ethylene glycol monomethyl ether, 109-86-4.

Supplementary Material Available: ^1H NMR and ^{13}C NMR and IR spectra of glycol ditosylates and crown ethers (2 pages). Ordering information is given on any current masthead page.

Strained Aromatic Systems. Synthesis of Dicyclobuta[1,2:3,4]naphthalenes, Dicyclobuta[1,2:3,4]anthracene, and Tricyclobutabenzene

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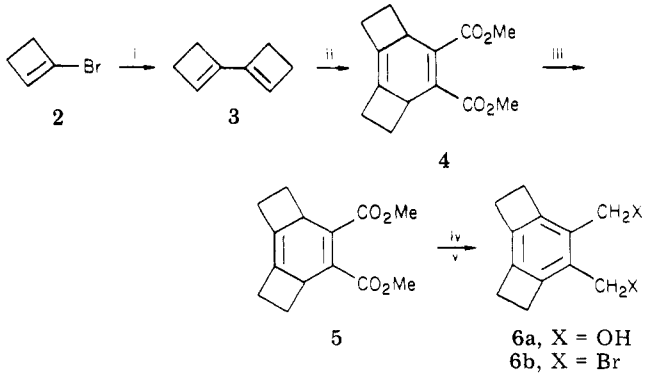
The syntheses of tricyclobuta[1,2:3,4:6,7]naphthalene (**1a**), dicyclobuta[1,2:3,4]cyclopenta[6,7]naphthalene (**1b**), and dicyclobuta[1,2:3,4]cyclohexa[6,7]naphthalene (**1c**) are described via a route involving annelation of the appropriate dilithiated 1,2-diester with 5,6-bis(bromomethyl)dicyclobutabenzene (**6b**). The ^{13}C NMR spectra of this series of annelated naphthalenes indicate a considerable change in hybridization at the C-5(8) atoms. A similar synthetic route to dicyclobuta[1,2:3,4]anthracene (**14**), presently the only known anthracene derivative annelated by two small rings on one phenyl ring, is described, and the ^{13}C NMR spectrum indicates a similar strain as for **1c**. An alternative preparation of tricyclobutabenzene (**21**) by a route involving pyrolysis of the sulfoxide derived from **6b** is outlined.

Benzene, naphthalene, and their higher homologues are more readily susceptible to out-of-plane rather than in-plane distortions.[1] Changes in the aromatic character of benzenoid systems are thus more likely to become manifest in compounds in which the aromatic rings have undergone bond angle and bond length distortion. Such systems might also exhibit the elusive Mills–Nixon effect.[2] We describe the synthesis of a series of dicyclobuta[1,2:3,4]-naphthalenes, which are annelated by a third carbocyclic ring in the 6,7-position, the preparation of dicyclobuta-[1,2:3,4]anthracene, and an alternative route to tricyclobutabenzene and discuss some properties of these compounds.[3]

Results and Discussion

Tricyclobuta[1,2:3,4:6,7]naphthalene (1a), Dicyclobuta[1,2:3,4]cyclopenta[6,7]naphthalene (1b), and Dicyclobuta[1,2:3,4]cyclohexa[6,7]naphthalene (1c). We have recently introduced a method of annelation utilizing the reaction of dilithiated vicinal diesters and carboximides with benzylic α,ω-dihalides,[4] and we have employed this reaction in the synthesis of compounds **1a–c**.

Scheme I[a]



[a] i, Mg, $Cu_2(I)Cl_2$, ii, $MeO_2CC{\equiv}CCO_2Me$, Δ; iii, DDQ; iv, $LiAlH_4$, THF; v, PBr_3.

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(1) See Davalian, D.; Garratt, P. J.; Koller, W.; Mansuri, M. M. *J. Org. Chem.* **1980**, *45*, 4183 and references therein.

0022-3263/84/1949-1412$01.50/0

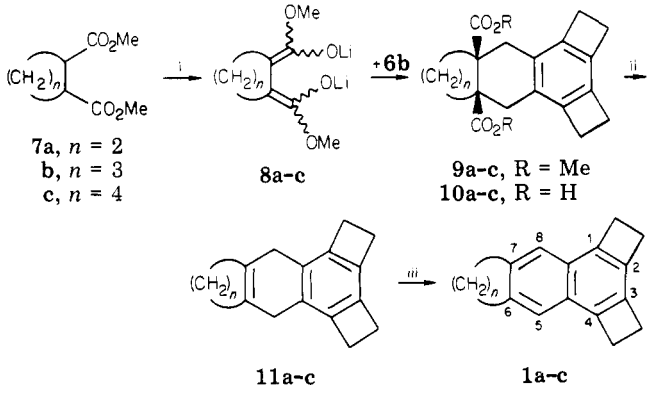
Table I. ^1H and ^{13}C NMR Spectra of 1a-c[a]

compd	H-5,8	H-6α,7α	H-2α,3α	H-1α,4α	H-6β,7β
1a	7.21 (s, 2 H)	3.31 (s, 4 H)	3.31 (m, 4 H)[b]	3.25 (m, 4 H)[b]	
1b	7.54 (s, 2 H)	3.02 (m, 4 H)	3.33 (m, 4 H)[b]	3.19 (m, 4 H)[b]	2.11 (m, 2 H)
1c	7.38 (s, 2 H)	2.92 (m, 4 H)	3.31 (m, 4 H)[b]	3.19 (m, 4 H)[b]	1.82 (m, 4 H)

compd	C-1(4)	C-2(3)	C-9(10)	C-5(8)	C-6(7)	C-1(4)α	C-2(3)α	C-5(6)α	C-5(6)β
1a	141.0[b]	143.6[b]	128.6	115.5	136.5	28.8[b]	29.2[b]		
1b	140.8[b]	142.3[b]	128.1	117.4	137.0	28.7[b]	28.9[b]	32.8	26.2
1c	137.2[b]	140.4[b]	127.6	121.9	135.2	28.7[b]	28.9[b]	30.0	23.5

[a] Chemical shifts in δ from $(CH_3)_4Si$ as internal standard. [b] These values could be interchanged.

Scheme II[a]



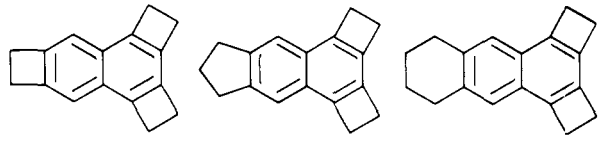
[a] i, LDA; ii, $Pb(OAc)_4$, C_5H_5N; iii, DDQ, C_6H_6.

5,6-Bis(bromomethyl)dicyclobuta[1,2:3,4]benzene (**6b**) was prepared by the route outlined in Scheme I. 1-Bromocyclobutene (**2**)[5] was treated with magnesium and copper(I) chloride to give bicyclobutenyl (**3**).[6] The Diels–Alder reaction between **3** and dimethyl acetylenedicarboxylate gave the diester **4** in ca. 95% yield. The ester was dehydrogenated with dichlorodicyanoquinone (DDQ) to give dimethyl dicyclobutaphthalate (**5**) which was reduced with $LiAlH_4$ to the diol **6a** and this, in turn, was converted to the desired dibromide **6b** with PBr_3.

The dibromide **6b** was now available as an electrophile to annelate the species obtained by lithiation of dimethyl cyclobutane-1,2-dicarboxylate (**7a**), dimethyl cyclopentane-1,2-dicarboxylate (**7b**), and dimethyl cyclohexane-1,2-dicarboxylate (**7c**). Solutions of the dilithiated species **8a–c**, prepared by respective treatment of **7a–c** with lithium diisopropylamide (LDA), were allowed to react with **6b** to give the annelated tetrahydronaphthalenes **9a–c** (Scheme II). Compounds **9a,b** were obtained in good yield but a poorer yield (37%) of the cyclohexyl derivative **9c** was obtained. The reason for the low yield of **9c** is not apparent since the corresponding dilithiated dimethyl cyclohex-4-ene-1,2-dicarboxylate (**15**) gave a good yield of annelation product (vide infra). However, models do suggest that **8c** is more sterically hindered than **15** and this may account for the lower reactivity of the former.

Hydrolysis of the diesters was readily accomplished in high yield in the case of **9a,b**, but the cyclohexyl diester **9c** proved extremely difficult to hydrolyze, presumably because of steric protection of the ester groups (vide infra). This problem was eventually solved by treatment of **9c** with KO-*t*-Bu in $(CH_3)_2SO$ at 100 °C for 4 h when the diacid **10c** was obtained. Oxidative decarboxylation of the diacids **10a–c** with $Pb(OAc)_4$ in pyridine gave a mixture of the dihydronaphthalenes **11a–c** and the corresponding naphthalenes **1a–c**. These mixtures were dehydrogenated with DDQ to give the pure naphthalenes **1a–c**.

Table II. Electronic Spectra of 1a-c



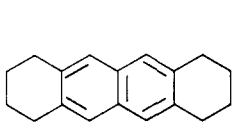
nm	ε	nm	ε	nm	ε
240	48 000	219	27 000	220	19 500
244	48 000	242	49 000	242	43 000
		245	51 000	245	42 000
289	4 400	266	2 200	264	5 900
		279 sh	2 900	271 sh	3 400
301	4 600	288	3 800	282 sh	2 800
		299	4 000	292	3 400
		307 sh	2 700	304	3 400
326	700	326 sh	500	316 sh	2 200
				328 sh	500

The ^1H and ^{13}C NMR spectra of the substituted naphthalenes **1a–c** are collected in Table I. The increasing strain incurred by decreasing the size of the ring annelating the 6,7-position is nicely reflected in the ^{13}C NMR spectra by the chemical shift of the C-5(8) carbons. In compound **1c** this signal appears at δ 121.9, at somewhat higher field than the corresponding signal in 1,4,6,7-tetramethylnaphthalene.[7] There is a further upfield shift of δ 4.5 on decreasing the annelating ring from 6- to 5-membered (**1b**), and a further δ 1.9 upfield shift when all the rings become 4-membered (**1a**). The actual chemical shifts of these carbon atoms are also noteworthy; the chemical shift in the cyclopentane derivative **1b** (δ 117.4) is at higher field than the corresponding carbons in cyclobutanaphthalene (δ 120.3)[8] and the chemical shift in **1a** (δ 115.5) is closer to that of cyclopropanaphthalene (δ 112.3).[9] The greater upfield shifts observed in **1a–c** are presumably due to the changes in bond angle and hybridization being relieved *only* at the nonsubstituted carbons, confined in these cases to C-5,8. A related observation has been made in the series dicyclopropa[*b*,*e*]naphthalene,[10] cyclopropa[*e*]cyclobuta[*b*]naphthalene,[1] and dicyclobuta[*b*,*e*]naphthalene,[8] in which the asymmetrically substituted compound shows a higher field shift for the carbons ortho to the cyclopropane ring and a lower field shift for the carbons ortho to the

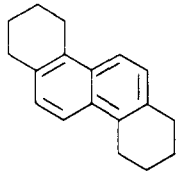
(2) Mills, W. H.; Nixon, I. G. *J. Chem. Soc.* **1930**, 2510.
(3) For preliminary accounts of part of this work, see: Bilyard, K. G.; Garratt, P. J.; Underwood, A. J.; Zahler, R. *Tetrahedron Lett.* **1979**, 1815. Doecke, C. W.; Garratt, P. J. *J. Chem. Soc., Chem. Commun.* **1981**, 873.
(4) See: Bilyard, K. G.; Garratt, P. J.; Hunter, R.; Lete, E. *J. Org. Chem.* **1982**, *47*, 4731 and references therein.
(5) Willstätter, R.; von Schmaedel, W. *Chem. Ber.* **1905**, *38*, 1992.
(6) This route was described by Heinrich, F.; Lüttke, W. *Liebigs Ann. Chem.* **1978**, 1880 after the completion of our initial work.
(7) Dalling, D. K.; Lander, K. H.; Grant, D. M.; Woolfenden, W. R. *J. Am. Chem. Soc.* **1977**, *99*, 7142. For a review of ^{13}C NMR chemical shifts in polycyclic aromatic systems, see: Hensen, P. E. *Org. Magn. Reson.* **1979**, *12*, 109.
(8) Thummel, R. P.; Nutakul, W. *J. Am. Chem.* Soc. **1978**, *100*, 6171.
(9) Adcock, W.; Gupta, B. D.; Khar, T. C.; Doddrell, D.; Kitching, W. *J. Org. Chem.* **1976**, *41*, 751.
(10) Ippen, J.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 736.

cyclobutane ring when compared with the chemical shifts of the corresponding symmetrical system.

The electronic spectra of the three naphthalenes are collected in Table II. The ^1B band[11] has shifted bathochromically compared to the corresponding band in naphthalene (219 nm), a normal feature of alkylated aromatic sytstem.[5] Thus, for example, this band has shifted to 236 nm in both 1,2,3,4,7,8,9,10-octahydrotetracene (**12**)[8] and 1,2,3,4,7,8,9,10-octahydrochrysene (**13**).[12] The ap-



12



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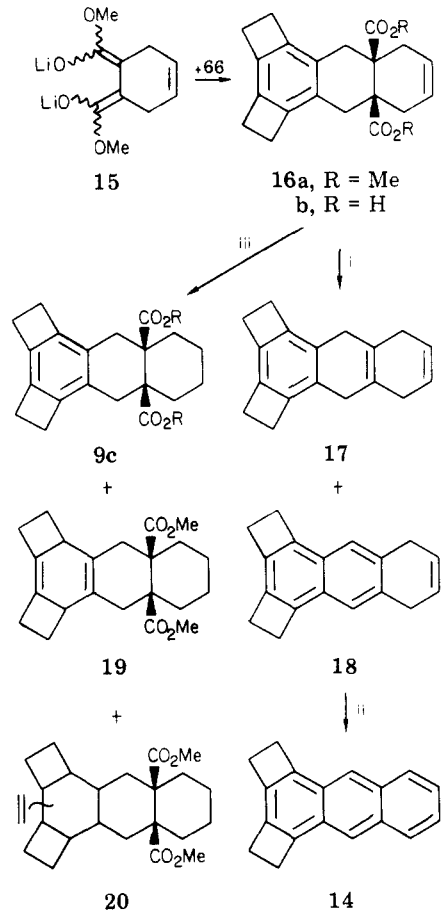
pearance of the spectra also suggests that the ^1L_A and ^1L_B bands[11] have also shifted bathochromically and that these bands have coalesced, the ^1L_B band not showing the increase in intensity exhibited by other strained, annelated naphthalenes. Thus the ^1L_B lowest energy absorption in dicyclopropa[*b,e*]naphthalene (326 nm),[10] cyclopropa[*e*]-cyclobuta[*b*]naphthalene (324 nm),[1] and dicyclobuta[*b,e*]naphthalene (322 nm)[8] are all of considerable intensity (ϵ ca. 6×10^3), whereas these bands in **1a–c** are at similar wavelength but are much less intense (ϵ ca. 5×10^2). That this is not merely a consequence of the geometry of annelation can be seen by comparison of the electronic spectra of **12** and **13** which both have similar long wavelength absorptions with O–O bands of comparable intensity (ca. ϵ 2×10^3).

Dicyclobuta[1,2:3,4]anthracene and Related Systems. Although benzene and naphthalene have been annelated with both two and three small-membered rings, it has proved difficult to annelate the larger polyacenes. The 1,1-difluoro and 1,1-dichlorocyclopropanthracenes have been prepared[13] but the parent system is still unknown, although anthracenes[15] and phenanthrenes[16] annelated with 4-membered rings have been prepared. However, no compound in the polyacene series with more than one 4-membered ring fused to a single constituent phenyl ring had so far been prepared, and dicyclobuta-[1,2:3,4]anthracene (**14**) thus constituted an interesting target molecule. The reaction of **6b** with dilithiated dimethyl cyclohex-4-ene-1,2-dicarboxylate (**15**) should provide a precursor readily converted into **14** and we accordingly investigated this reaction.

Treatment of a solution of **6b** in THF with a solution of **15** gave the desired annelated diester **16a** in 56% yield (Scheme III). Hydrolysis of the diester under base-catalyzed conditions proceeded in quantitative yield to the diacid **16b**, in marked contrast to the difficulty experienced in hydrolyzing the related diester **9c**. Models indicate that the ester groups in the half-chair conformation of **16a** are more accesible than those in the chair form of **9c**, although even in the latter case the axial ester group appears relatively exposed.

Scheme III[a]



[a] i, $Pb(OAc)_4$; ii, DDQ; iii, H_2, $Pd/CaCO_3$.

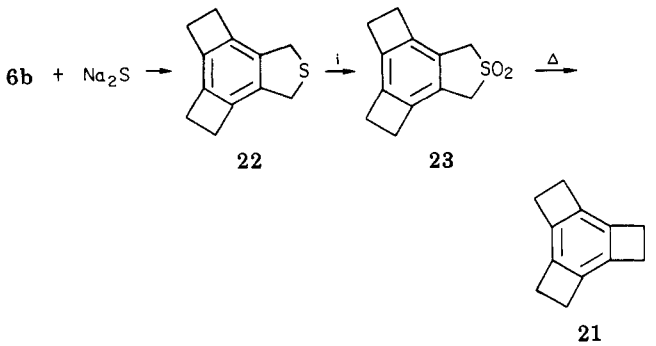
Decarboxylation of the diacid **16b** with $Pb(OAc)_4$ gave a mixture of **17** and the dehydrogenated compound **18**. The components of this mixture were not separated and it was dehydrogenated with DDQ to the desired dicyclobuta[1,2:3,4]anthracene (**14**) in 32% yield.

The ^1H NMR spectrum of **14** had signals at δ 8.27 (s, H-9,10), 7.93–8.0 (m, H-5,8), 7.35–7.45 (m, H-6,7), 3.44–3.49 (m, 4 H), and 3.27–3.32 (m, 4 H) and is similar to that of cyclobuta[*b*]anthracene.[8] The ^{13}C NMR spectra shows signals at δ 141.3, 138.6 (C-1,2,3,4), 132.9, 127.8, 125.0, 121.4 (C-9,10), 29.3, and 29.1. We attribute the high-field signal at δ 121.4 to C-9,10 and the system thus appears to have a comparable strain to that observed for its tetrahydro derivative **1c**. The electronic spectrum of **14** shows absorption maxima (hexane) at 228 nm (ϵ 22 000), 238 (21 000), 249 (29 000), 255 (59 000), 261 (129 000), 281 (2800), 337 (1800), 355 (3400), 374 (5200), 390 (3300), and 395 (5000). The spectrum is similar to but bathochromically shifted from that of anthracene.

The low yield of **9c** obtained from treatment of **6b** with **7c** (vide supra) caused us to explore compound **16a** as a possible precursor of **9c**. However, hydrogenation of **16a** over $Pd/CaCO_3$ led to a complex mixture which, from the ^1H NMR and mass spectra appeared to consist of **9c**, **19**, and **20**. Partial hydrogenation of the benzene ring has occurred under these very mild conditions and no modification of conditions could be found to prevent this occurrence. Presumably the strain engendered by annelating three rings to benzene, including two 4-membered rings, has increased the ground state energy of the benzene ring and rendered it susceptible to hydrogenation. The dicyclobutaphenanthrenes prepared by Perkins and Vollhardt[16] showed a similar ease of hydrogenation, giving a

(11) Klevens, H. B.; Platt, J. R. *J. Chem. Phys.* **1949**, *17*, 470. Platt, J. R. *Ibid.* **1949**, *17*, 484.
(12) "U.V. Atlas of Organic Compounds"; Perkampus, H. H., Sandeman, I., Timmons, C. J., Eds.; Butterworths-Verlag Chemie: London 1967; Vol. 3.
(13) Müller, P.; Rey, M. *Helv. Chim. Acta* **1981**, *64*, 354.
(14) For an attempted preparation see ref 1 and Billups, W. E. *Acc. Chem. Res.* **1978**, *11*, 245.
(15) Thummel, R. P.; Cravey, W. E.; Nutakul, W. *J. Org. Chem.* **1978**, *43*, 2473.
(16) Perkins, P.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 615.

Scheme IV[a]



[a] i, m-$ClC_6H_4CO_3H$.

mixture of substituted naphthalene and tetrasubstituted benzene derivatives.

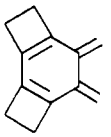
Dicyclobuta[1,2:3,4]anthracene (**14**) was also obtained when the dihydronaphthalene **11c** was treated with DDQ in benzene for a prolonged time, which further suggests a rather similar energy is required for the introduction or loss of successive double bonds in these strained molecules.

Tricyclobutabenzene. One of our initial reasons for seeking routes to bicyclobutylidene (**3**) was as a Diels–Alder diene precursor to tricyclobutabenzene (**21**). We carried out the Diels–Alder reaction of **3** with dimethyl cyclobutene-1,2-dicarboxylate, which proceeded in good yield, but then found that oxidative decarboxylation of the hydrolyzed adduct proceeded in variable, but invariably dismal yield and were unable to adequately characterize the product.[17] These findings are substantiated by the synthesis of tricyclobutabenzene through this route by Thummel and co-workers[18] who were elegantly successful in characterizing **21** and developing the oxidative decarboxylation to give a maximum yield of 3.6% in this step. We, meanwhile, had sought other routes to **21** and for these the dibromide **6b** appeared an excellent candidate for a precursor. The sulfoxide route to cyclobutanes, pioneered by Cava and his co-workers,[19] seemed the most appropriate for our purpose.

The dibromide **6b** reacts smoothly with Na_2S in ethanol to give the sulfide **22** in 81% yield after purification by sublimation (Scheme IV). Oxidation of **22** with m-chloroperoxybenzoic acid in CH_2Cl_2 gave the sulfone **23** in 83% yield. We were encouraged to observe that the most intense peak in the mass spectrum of **23** was at m/e 156, which corresponds to the desired **21** or an isomer. After considerable experimentation, pyrolysis conditions were found to convert the sulfone **23** into **21**. The sulfone was sublimed at 90–100 °C from a preoven through the main horizontal furnace at 320 °C at a pressure of 0.005 mmHg. The product was contaminated by small amounts of polymer and the sulfone, from which it was separated to give **21** in 53% yield based on recovered sulfone. The spectral properties were identical with those reported by Thummel and co-workers[18] except for some small differences in the electronic spectrum.

Although this route to **21** involves more steps than that described by Thummel and co-workers,[18] the overall yield from **6b** is 36% and the reactions involved could be further optimized. We are currently exploring the chemistry of **21**.

The bromide **6b** is also a potential precursor to a second $C_{12}H_{12}$ isomer, dicyclobuta[1,2:3,4]dimethylene[5,6]cyclohexadiene (**24**). Some preliminary experiments involving debromination of **6b** with zinc indicated that **24** was formed in low yield.



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Experimental Section

^1H NMR spectra were obtained on either a Varian T-60, a Jeol PMX-60, or a Varian XL-200 spectrometer in $CDCl_3$ as solvent (unless stated otherwise) and are reported in δ units with Me_4Si an internal standard. ^{13}C NMR spectra were obtained on either a Varian CFT-20 or XL-200 spectrometer in $CDCl_3$ as solvent and are reported in δ units with Me_4Si as internal standard. Mass spectra were obtained on a VE-7070F spectrometer. IR spectra were recorded on a Perkin-Elmer 177 spectrometer and only strong and medium bands are reported. Melting points were recorded on a Kofler hot-stage melting-point apparatus and are uncorrected. Solvents were purified by standard methods.

Preparation of Bicyclobutenyl (3). 1-Bromocyclobutene (31.0 g, 0.23 mol) in THF (100 mL) was added to dry magnesium (9 g) in THF (200 mL) under N_2. The reaction was allowed to stand for 30 min, during which time in some cases reaction occurred. After 30 min copper(I) chloride (30 g) was added and, if no reaction had occurred, it was initiated by the addition of 1,2-dibromoethane. The reaction vessel was cooled in a water bath to moderate the reaction and, after it had subsided, the mixture was heated to reflux for 1 h and then stirred at room temperature for 16 h. The mixture was filtered through Celite and the filtrate distilled under reduced pressure (10–20 mmHg). To prepare pure **3** the distillate was fractionally distilled under reduced pressure, but for most preparations the amount of **3** in the distillate was estimated by ^1H NMR spectroscopy and the THF solution used for subsequent experiments. In a typical experiment the isolated yield of **3** was 5.8 g (0.0055 mol, 48%) and the estimated yield by ^1H NMR in the solution was ca, 55–60%.

Treatment of 3 with Dimethyl Acetylenedicarboxylate. Dimethyl acetylenedicarboxylate (30 mL, 95%) and quinol (1.8 g) were added to the THF solution of the diene **3** obtained as described in the previous experiment. The solvent was then removed by distillation until the temperature in the vessel rose to 80–85 °C and the residue was then heated under reflux for 1 h. The remaining solvent was removed under vacuo and the residue was distilled under reduced pressure to remove excess dimethyl acetylenedicarboxylate. The residue, which consisted of the desired product and quinol, was separated by chromatography on florisil, eluting with petroleum ether (40–60 °C)–ether to give the diene **4** (13.6 g, 0.059 mol): mass spectrum, m/e 248.1049 (calcd for $C_{14}H_{16}O_4$, m/e 248.1049), 248, 217 ($M^+ - 31$), 189 ($M^+ - 59$); ^1H NMR, 3.80 (s, 6 H), 3.70 (m, 2 H), 2.88–1.79 (m, 8 H).

Dehydrogenation of 4. The diene **4** (2.80 g, 11 mmol) and DDQ (2.72 g, 12 mmol) were added to benzene (125 mL) and the mixture heated to reflux for 16 h. The mixture was filtered and the filtrate distilled under vacuo to remove the solvent. The residue was chromatographed on florisil, eluting with petroleum ether (40–60 °C)–ether, to give **5**, recrystallized from petroleum ether (60–80 °C) as white needles: 2.35 g (9.6 mmol, 85%); mp 104–105 °C; mass spectrum, m/e 246.0886 (calcd for $C_{14}H_{14}O_4$, m/e 246.0892) 246, 231, 217, 216, 215; ^1H NMR (CCl_4) 3.78 (s, 6 H), 3.17 (m, 8 H); electronic spectrum λ_{max} (EtOH) 2.4 (log ϵ 4.15), 248 (4.05), and 297 nm (3.71). Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.36; H, 5.64.

Reduction of 5. The diester **5** (700 mg, 2.8 mmol) was dissolved in dry ether (20 mL) and $LiAlH_4$ (350 mg) was added to the cooled solution (ice bath) under N_2. The mixture was stirred

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and allowed to come to room temperature and stirring continued for 48 h. The mixture was cooled and water (0.4 mL), aqueous NaOH (16%, 0.4 mL), and water (1 mL) were successively added. The mixture was filtered, the residue washed with ether (2 × 5 mL), and the combined filtrates evaporated under reduced pressure. The resulting solid was recrystallized from ethanol to give **6a**: 435 mg (2.3 mmol, 82%); mp 122–124 °C; mass spectrum, *m/e* 190.0990 (calcd for $C_{12}H_{14}O_2$, *m/e* 190.0094), 190 (M^+), 172 ($M^+ - H_2O$); ^1H NMR, 4.62 (s, 4 H), 3.15 (br s, 8 H), 2.48 (br s, 2 H); electronic spectrum, λ_{max} (EtOH) 222 (sh) (log ϵ 4.06), 232 (3.70), 273 (3.38), 278 (3.42), and 282 nm (3.40). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.32; H, 7.21.

Treatment of 6a with PBr_3. The diol **6a** (430 mg, 2.3 mmol) was dissolved in benzene (3 mL) and PBr_3 (1.1 g, 4.0 mmol) and pyridine (0.3 mL) were added, cooling the flask in an ice bath. The mixture was stirred and allowed to come to room temperature and stirring was continued for 16 h. The mixture was the heated under reflux for 30 min, cooled, poured into H_2O, and extracted (CH_2Cl_2). The solvents were removed under reduced pressure to give **6b** as a white solid, 471 mg (1.5 mmol, 65%). Recrystallization from petroleum ether 60–80 °C gave samples with variable melting points. Mass spectrum, *m/e* 313.9304 (calcd for $C_{12}H_{12}{}^{79}Br_2$, *m/e* 313.9304), 318, 316, 314; ^1H NMR, 4.53 (s, 4 H), 3.13 (br s, 8 H).

Preparation of Dilithiated Diester 8a–c, 15. The diester (1.0 mmol) was dissolved in dry THF (5 mL) and added to a stirred solution of *i*-Pr_2NLi (1.1 mmol, prepared from *i*-Pr_2NH and *n*-BuLi) in dry THF (5 mL) containing HMPA (0.5 mL) at −75 °C under N_2. The mixture was stirred for 30 min at −75 °C and then, except for **8a**, allowed to warm to 20 °C.

Treatment of the Dibromide 6b with the Dilithiated Diesters 8a–c. The dibromide (253 mg, 0.6 mmol) in dry THF (2 mL) was added by syringe to a stirred solution of the lithiated diester (0.9 mmol) in THF (7 mL) containing HMPA (0.4 mL, 2.4 mmol) at −75 °C under N_2. The mixture was stirred for 2 h, allowed to come to room temperature and stirred for a further 18 h (except with **8a**, when the mixture was kept at −75 °C). The mixture was cooled to −30 °C and aqueous acetic acid added (3 mL). NaCl was added until the aqueous phase was saturated and the mixture was extracted with CH_2Cl_2 (4 × 25 mL). The combined extracts were washed with a saturated solution of $NaHCO_3$ (3 × 25 mL) and brine (25 mL) and dried (Mg SO_4). The solvent was removed under reduced pressure and the resulting solid purified by column or preparative TL chromatography.

Compound 9a: 209 mg (0.64 mmol, 80%); mass spectrum, *m/e* 326.1509 (calcd for $C_{20}H_{22}O_4$, *m/e* 326.1518); ^1H NMR 3.69 (s, 6 H), 3.07 (m, 10 H), 2.70 (br d, 2 H), 2.36 (m, 2 H), 1.35 (m, 2 H).

Compound 9b: 149 mg (0.44 mmol, 55%); mass spectrum, *m/e* 340.1826 (calcd for $C_{21}H_{24}O_4$, *m/e* 340.1831); ^1H NMR 3.67 (s, 6 H), 3.07 (br s, 8 H), 2.92, 2.71 (ABq, J = 15.3 Hz, 4 H), 2.30–2.22 (m, 2 H), 1.78–1.26 (m, 4 H).

Compound 9c: 104.5 mg (0.30 mmol, 37%); mass spectrum, *m/e* 354.1780 (calcd for $C_{22}H_{26}O_4$, *m/e* 354.1831); ^1H NMR 3.68 (s, 6 H), 3.04 (br s, 8 H), 3.12–2.78 (m, 4 H), 2.05–1.26 (m, 8 H).

Hydrolysis of the Diesters 9a,b. The diester (0.45 mmol) was suspended in absolute methanol (5 mL) to which was added water (0.7 mL) and KOH (pellets, 940 mg, 16.7 mmol) and the mixture was stirred and heated under reflux for 48 h. Methanol (5 mL), water (0.7 mL) and KOH (pellets, 940 mg, 16.7 mmol) were added and the mixture heated to reflux for a further 20 h. The mixture was cooled, diluted with water (60 mL), and extracted with CH_2Cl_2 (2 × 20 mL). The aqueous solution was acidified with HCl (concentrated) and then saturated with NaCl, and the mixture was extracted with MeOAc (3 × 25 mL). The combined extracts were washed with brine (30 mL) and dried ($MgSO_4$). The solvent was removed to give a white solid, triturated with boiling pentane to give the diacid.

Compound 10a: 134 mg (0.45 mmol, 100%)

Compound 10b: 129 mg (0.41 mmol, 92%); mp 180–82 °C; mass spectrum, *m/e* 312.1357 (calcd for $C_{19}H_{20}O_4$, *m/e* 312.1360); ^1H NMR 9.52 (br s, 2 H), 3.09 (s, 6 H), 2.99, 2.81 (AB q, J = 15.8 Hz, 4 H), 2.41–2.23 (m, 2 H), 1.87–1.41 (m, 4 H).

Hydrolysis of Diester 9c. KO-t-Bu (2.5 g, 22.3 mmol) was added to a stirred solution of **9c** (240 mg, 0.67 mmol) in dry $(CH_3)_2SO$ (10 mL) and the mixture was heated at 100 °C for 4 h. The mixture was cooled, diluted with ice water (25 mL) and washed with ether (3 × 25 mL) The aqueous layer was acidified with concentrated HCl, saturated with NaCl and extracted with CH_2Cl_2 (5 × 25 mL). The combined extracts were dried (Na_2SO_4) and the solvent removed under reduced pressure to give a yellow oil, shown by ^1H NMR to be the diacid contaminated with $(CH_3)_2SO$. This product was decarboxylated without further purification: ^1H NMR, 9.71 (br s, 2 H), 3.07 (br s, 8 H), 3.19–1.50 (m, 12 H).

Oxidative Decarboxylation of 10a–c. $Pb(OAc)_4$ (488 mg, 1.1 mmol) was added to a stirred mixture of the diacid (0.5 mmol) in dry $(CH_3)_2SO$ (5 mL) and pyridine (5 mL),[20] maintaining the temperature at 15 °C. The mixture was then heated to 60 °C for 15 min, poured onto crushed ice (ca. 20 mL), and acidified with 2 M HNO_3. The aqueous solution was saturated with NaCl and the mixture extracted with CH_2Cl_2 (5 × 20 mL). The combined extracts were washed with saturated $NaHCO_3$ solution and dried ($MgSO_4$). the solvent was removed under reduced pressure and the resulting semisolid purified by chromatography on silica gel, eluting with pentane (**10a,b**) or CH_2Cl_2–pentane (5:95) (**10c**). In each case a mixture of the dihydronaphthalene and naphthalene was obtained.

Compound 11a and 1a: 18 mg (0.09 mmol, 17%); mass and ^1H NMR indicate a 1:1 mixture of **11a** and **1a**.

Compound 11b and 1b: 12 mg (0.05 mmol, 10%); mass and ^1H NMR spectroscopy indicated a 1:1 mixture of **11b** and **1b**.

Compound 11c and 1b: 33 mg (0.14 mmol, 28%); mass and ^1H NMR spectroscopy indicated a 4:1 mixture of **11c** and **1c**.

Dehydrogenation of 11a–c. The mixture of dihydronaphthalene and naphthalene derivatives obtained in the previous experiment was dissolved in dry benzene (3 mL per mmol of mixture) and DDQ (1 mmol per mmol of mixture) was added. The mixture was stirred at 15 °C for 1 h, diluted with pentane (15 mL), filtered through silica gel, and the filtrate concentrated under reduced pressure. The concentrated residue was chromatographed on silica gel, eluting with CH_2Cl_2:pentane to give the desired product.

Compound 1a: 13 mg (0.06 mmol); mp 171–173 °C; mass spectrum, *m/e* 206.1095 (calcd for $C_{16}H_{14}$, *m/e* 206.1095), 206, 191, 178; ^1H NMR ^{13}C NMR spectra, see Table I; electronic spectrum, see Table II.

Compound 1b: 10 mg (0.046 mmol); mp 177–180 °C dec; mass spectrum, *m/e* 220.1254 (calcd for $C_{17}H_{16}$, *m/e* 220.1252), 221, 220, 205, 203, 191, 189; ^1H and ^{13}C NMR spectra, see Table I; electronic spectrum, see Table II.

Compound 1c: 19 mg (0.08 mmol); mp 153–55 °C dec; mass spectrum, *m/e* 234.1406 (calcd for $C_{18}H_{18}$, *m/e* 234.1408); ^1H and ^{13}C NMR spectra, see Table I; electronic spectra, see Table II.

Treatment of the Dibromide 6b with the Dilithiated Diester 15. The red solution of **15** (0.9 mmol) in THF/hexane (5 mL) was added dropwise to a stirred solution of **6b** (265 mg, 0.84 mmol) in THF (3 mL) under N_2 at room temperature and the stirring was continued for 84 h. The mixture was cooled to −78 °C, and water–HOAc (2:1, 3 mL) was added followed by water (50 mL). The mixture was allowed to come to room temperature and extracted with CH_2Cl_2 (3 × 20 mL). The combined extracts were washed with water (25 mL), saturated $NaHCO_3$ solution (25 mL), and brine (25 mL) and dried ($MgSO_4$). The solvent was removed under vacuo to give an orange oil which on preparative TLC on silica gel, eluting with ether–petroleum ether 40–60 °C (1:4), gave **16a**: 178 mg (0.51 mmol, 56%); mp 140–143 °C; mass spectrum, *m/e* 352.1674 (calcd for $C_{22}H_{24}O_4$, *m/e* 352.1675); ^1H NMR 5.60 (br s, 2 H), 3.67 (s, 6 H), 3.03 (br s, 8 H), 3.22–2.19 (m 8 H).

Hydrolysis of 16a. Carried out as for **9a,b** (vide supra). Compound **16b**, 120 mg (85%), was obtained as a white solid.

Oxidative Decarboxylation of 16b. Carried out as for **10a–c**. A mixture of **17** and **18**, 61 mg (0.26 mmol, 52%), was obtained, largely composed of **17**: mass spectrum, *m/e* 234.1301 (calcd for $C_{18}H_{18}$, *m/e* 234.1408); ^1H NMR, 5.63 (br s, 2 H), 3.5–2.30 (m, 8 H), 2.93 (br s, 8 H).

Dehydrogenation of 17. The above mixture was suspended in CCl_4 (1.5 mL) and DDQ (140 mg, 0.62 mmol) was added and the mixture stirred under N_2 at room temperature for 20 h and then at 50 °C for 2 h. The mixture was cooled and filtered and the filtrate concentrated under reduced pressure. Chromatog-

raphy on silica gel, eluting with pentane, gave essentially pure **14** (19 mg, 32%). Further purification could be afforded by preparative TLC with petroleum ether 40–60 °C. Compound **14**: mp 176–180 °C; mass spectrum, *m/e* 230.1095 (calcd for $C_{18}H_{14}$, 230.1096); ^1H and ^{13}C NMR spectra, see discussion; electronic spectrum, see discussion.

Hydrogenation of 16a. The diester **16a** (226 mg, 0.64 mmol) was dissolved in EtOAc (8 mL) and 10% $Pd/CaCO_3$ (100 mg) was added. The mixture was stirred under a H_2 atmosphere and the uptake of H_2 was followed. After the uptake of 56 mL of H_2 had occurred the reaction was stopped, the mixture filtered through Celite, and the filtrate concentrated under vacuo. The resulting oil (230 mg) was subjected to ^1H NMR and mass spectral analysis. Mass spectrum, *m/e* 354.1829 (calcd for $C_{22}H_{26}O_4$, *m/e* 354.1831), *m/e* 356.2006 (calcd for $C_{22}H_{28}O_4$, *m/e* 356.2024), *m/e* 358.2153 (calcd for $C_{22}H_{30}O_4$, *m/e* 358.2162).

Treatment of 6b with Sodium Sulfide. The dibromide **6b** (325 mg, 1.03 mmol) and $Na_2S{\cdot}9H_2O$ (990 mg, 4.1 mmol) were suspended in 95% EtOH (6 mL) and the mixture was stirred and heated under reflux for 6 h. The mixture was cooled, water (15 mL) was added, and the resultant mixture was allowed to stand overnight in a refrigerator. The precipitated solid was removed by filtration, washed with water, and air dried. CH_2Cl_2 (5 mL) was added and the resulting solution, containing some undissolved material, was filtered through a short column of neutral alumina. The filtrate was evaporated under reduced pressure to give a pale orange solid (179 mg, 92%). Sublimation at 90–100 °C (0.2 mmHg) gave **22**: 158 mg (0.84 mmol, 81%); mp 150–157 °C dec; mass spectrum, *m/e* 188.0645 (calcd for $C_{12}H_{12}S$, *m/e* 188.0659), 189 (14), 188 (100), 187 (50), 173 (43), 172 (18), 171, (17), 128 (18), 115 (18); ^1H NMR 4.07 (br s, 4 H), 3.13 (br s, 8 H).

Oxidation of 22. The sulfide **22** (150 mg, 0.8 mmol) was dissolved in dry CH_2Cl_2 (10 mL), *m*-chloroperoxybenzoic acid (660 mg, 3.2 mmol) was added, and the mixture was stirred at room temperature for 43 h. The resulting solution was washed with $NaHCO_3$ solution (10 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the resulting white solid chromatographed by preparative TLC, eluting with CH_2Cl_2 to give **23**: 145 mg (0.66 mmol, 83%); mp 198–200 °C dec: mass spectrum, *m/e* 220.0496 (calcd for $C_{12}H_{12}SO_2$, *m/e* 220.0558), 220 (10), 157 (14), 156 (100), 155 (11), 141 (21), 139 (14), 128 (13), 115 (17); ^1H NMR 4.17 (br s, 4 H), 3.15 (br s, 8 H).

Pyrolysis of 23. The sulfone **23** (50 mg, 0.23 mmol) was dissolved in CH_2Cl_2 (2 mL) in a 10-mL round-bottomed flask and the solvent removed by a stream of N_2. The flask was then attached to the pyrolysis apparatus and the system evacuated to 0.005 mmHg. The furnace was heated to 320 °C and maintained at this temperature for 2 h. The flask in the preoven was then heated to 90–100 °C when **23** slowly sublimed into the furnace over ca. 3 h. The product was collected in a cold trap at −190 °C. The product was dissolved in CH_2Cl_2 and chromatographed on alumina, eluting with pentane–CH_2Cl_2 (7:3) to give 16.5 mg of **23**, and **21**: 12.6 mg (0.08 mmol, 35%, 53% based on recovered **23**); mp 143–144 °C (lit.[18] 141–142 °C); mass spectrum, *m/e* 156 (100), 155 (20), 153 (10), 141 (36), 128 (15), 115 (22), 105 (23), 91 (36); ^1H NMR 3.12 (s); electronic spectra λ_{max} (cyclohexane) 208, 222 (ε6000), 252 (225), 265 sh (200), 274 sh (170), 290 nm sh (100).

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Calyculones, New Cubitane Diterpenoids from the Caribbean Gorgonian Octocoral *Eunicea calyculata*

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Three new representatives of the rare cubitane class of rearranged diterpenoid molecules have been isolated as minor metabolites from *Eunicea calyculata*, a sea whip collected in the Caribbean Sea. The structure of the crystalline metabolite, calyculone A (**3**) was solved by single-crystal X-ray diffraction analysis. Structures could then be proposed for calyculones B and C (**4** and **5**) by comprehensive ^1H NMR analyses involving difference decoupling and nuclear Overhauser enhancement difference spectrometric methods.

In connection with our investigations of biologically active and structurally novel secondary metabolites from Caribbean gorgonian octocorals (Cnidaria, Gorgonacea), we have examined the sea whip *Eunicea calyculata* (Ellis and Solander) (Plexauridae).[1] While a number of shallow-water *Eunicea* species have been chemically investigated,[2] *E. calyculata* is found in abundance only below 20 meters and had not been previously studied. Recently, we described the structures of two new bicarbocyclic diterpenoid derivatives, **1** and **2** (Chart I), as the major secondary metabolites of *E. calyculata*.[3] In this paper we report the structures of three new monocarbocyclic diterpenoids, calyculones A–C (**3–5**), which were isolated as minor constituents of *E. calyculata*. These compounds are new examples of the rearranged cubitane class of diterpenoids. Cubitene (**6**) was reported as a component of the defensive secretion of the East African termite, *Cubitermes umbratus*.[4] Since then, no compounds of this

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