1.5 h the reaction mixture was cooled to room temperature. The reaction mixture was poured into THF (20 mL) and NaOH (10 mL, 10 M). After 1 h, ether (10 mL) was added, and the aqueous layer was acidified to pH 3 with $NaHSO_4$. Aqueous workup (ether, $MgSO_4$) afforded 15.7 mg (81%) of acid **28a**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.40–7.26 (m, 5 H, Ar*H*), 5.48–5.44 (m, 1 H, C=C*H*CH_2), 5.24–5.17 (m, 2 H, CH_2Ph), 4.87–4.80 (m, 1 H, NC*H*CO_2H), 4.04 (d, J = 6.0 Hz, 1 H, NC*H*), 2.74–2.57 (m, 1 H, CH=CHC*H*H), 2.56–2.37 (m, 1 H, CH=CHCH*H*), 2.37–0.53 (m, 8 H, CH_2); IR (CCl_4) 1735, 1715 cm^{-1}; MS (EI, 20 eV) m/z 315 (M^+, 38), 271 (8), 226 (74), 180 (63), 134 (27), 91 (100); HRMS for $C_{18}H_{21}NO_4$ calcd 315.1471, found 315.1475. To a solution of acid **28a** (27.5 mg, 0.09 mmol, prepared in a different run) and ether (2 mL) was added diazomethane (9 mL of a 0.2 M solution, 1.7 mmol). After 30 min, a stream of N_2 was passed through the solution to remove unreacted diazomethane; concentration afforded crude ester **28b**. Flash chromatography (20:1 hexane/ethyl acetate) afforded 19.4 mg (67%) of ester **28b**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.30 (m, 5 H, Ar*H*), 5.38 (d, J = 4.2 Hz, 1 H, ArCH*H*), 5.23 (m, 1 H, *H*C=C), 5.10 (m, 1 H, ArC*H*H), 4.73 (dd, J = 2.9, 5.7 Hz, 1 H, NC*H*CO_2), 3.56 (d, J = 20.5 Hz, 1 H, NC*H*), 3.10 (br s, 3 H, CO_2CH_3), 2.90–0.90 (m, 8 H, CH_2); IR (CCl_4) 1750, 1715 cm^{-1}; MS (EI, 20 eV) m/z 329 (M^+, 11), 270 (10), 226 (50), 194 (39), 136 (28), 91 (100); HRMS for $C_{19}H_{23}NO_4$ calcd 329.1628, found 329.1615.

(1*S,2*S**)-2-Amino-1-ethenyl-1-cyclohexanol (30).** The procedure described for the preparation of **26** was carried out with carbamate **29** (460 mg, 1.70 mmol), MeOH (42.4 mL), H_2O (4.2 mL), and KOH (36.2 g, 0.65 mol) to afford 164.5 mg (68%) of **30** as a yellow oil: ^1H NMR (300 MHz, $CDCl_3$) δ 5.76 (dd, J = 10.6, 17.2 Hz, 1 H, *H*C=CHH), 5.32 (d, J = 17.2 Hz, 1 H, HC=C*H*H), 5.09 (d, J = 10.6 Hz, HC=CH*H*), 2.68 (m, 1 H, C*H*NH_2), 2.00–1.00 (m, 8 H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.8, 113.2, 76.2, 54.0, 35.7, 30.0, 24.6, 20.7; IR (CCl_4) 3610, 3470, 2930, 1020 cm^{-1}; MS (EI, 20 eV) m/z 141 (M^+, 26), 124 (31), 107 (49), 69 (100), 56 (56); HRMS for $C_8H_{15}NO$ calcd 141.1154, found 141.1150.

(4a*S,8a*S**)-4-(Benzyloxycarbonyl)-8a-ethenyl-2-oxo-3,4,4a,5,6,7,8,8a-octahydro-2*H*-1,4-benzoxazine (31).** The same procedure described for the preparation of **27** was carried out with amine **30** (200 mg, 1.4 mmol), triethylamine (0.39 mL, 2.8 mmol), and ethyl α-bromoacetate (0.19 mL, 1.71 mmol) to afford 243.9 mg (77%) of crude amine as a yellow oil. The above amine (243.9 mg, 1.1 mmol) was submitted to the same conditions as used for the synthesis of **27**, saturated $NaHCO_3$ (5 mL), CH_2Cl_2 (5.5 mL), and benzyl chloroformate (0.19 mL, 1.33 mmol) to afford a yellow oil. Flash chromatography (3:1 hexane/ethyl acetate) afforded 295.7 mg (76%) of (1*S**,2*S**)-[*N*-(benzyloxycarbonyl)-*N*-[(ethoxycarbonyl)methyl]amino]-1-ethenyl-1-cyclohexanol as a clear oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.00 (m, 5 H, Ar*H*), 6.50 (m, 1 H, *H*C=CH_2), 5.70 (m, 2 H, HC=CH_2), 4.20 (dd, 1 H, *H*CN), 3.90 (m, 2 H, NCH_2), 2.00–1.00 (m, 8 H, CH_2). A solution of the above carbamate (125 mg, 0.35 mmol), benzene (20 mL), and *p*-toluenesulfonic acid (4.1 mg, 0.022 mmol) was heated to 100 °C for 4 h in a flask equipped with a Dean–Stark trap. During the course of the reaction additional *p*-toluenesulfonic acid (5.0 mg) and benzene were added. After cooling to room temperature the reaction mixture was concentrated and flash chromatographed (6:1 hexane/ethyl acetate) to afford 42.4 mg (39%) of **31** as a clear oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (m, 5 H, Ar*H*), 5.87 (dd, J = 11.0, 17.0 Hz, *H*C=CH_2), 5.45–5.25 (m, 4 H, HC=CH_2, ArCH_2), 4.38–4.18 (m, 3 H, NCH_2, NC*H*), 2.18–1.28 (m, 8 H, CH_2); IR (CCl_4) 1745, 1700 cm^{-1}; MS (EI, 20 eV) m/z 315 (M^+, 8), 152 (18), 91 (100), 65 (11); HRMS for $C_{18}H_{21}NO_4$ calcd 315.1471, found 315.1475.

(2*S,8a*S**)-1-(Benzyloxycarbonyl)-2-carbomethoxy-1,2,3,5,6,7,8,8a-octahydroquinoline (32b).** The same procedure described for the preparation of **28b** was carried out with lactone **31** (19 mg, 0.06 mmol) to afford 15.7 mg (83%) of acid **32a** as a yellow oil [IR (CCl_4) 1725, 1705 cm^{-1}]. Esterification with CH_2N_2 (6 mL of a 0.2 M solution, 1.1 mmol) afforded crude ester **32b**. Flash chromatography (20:1 hexane/ethyl acetate) afforded 11.4 mg (69%) of ester **32b**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.28 (m, 5 H, Ar*H*), 5.44 (br s, 1 H, C=C*H*), 5.23 (br s, 3 H, ArCH_2, NC*H*CO_2), 4.15 (br s, 1 H, NC*H*), 3.68 (s, 3 H, CO_2CH_3), 2.70–0.80 (m, 10 H, CH_2); IR (CCl_4) 1745, 1705 cm^{-1}; MS (EI, 20 eV) m/z 329 (M^+, 15), 270 (14), 226 (81), 194 (83), 134 (20), 91 (100); HRMS for $C_{19}H_{23}NO_4$ calcd 329.1627, found 329.1617.

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Supplementary Material Available: Summary of NOE and decoupling data and ^1H and ^{13}C NMR spectra of new compounds (49 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Synthesis and Properties of Dihydrocyclobuta[*e*]pyrene and Tetrahydrodicyclobuta[*e*,*l*]pyrene

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Dihydrocyclobuta[*e*]pyrene and tetrahydrodicyclobuta[*e*,*l*]pyrene were prepared by the sequence of photocycloaddition of stryene derivatives, transannulation, and aromatization through lithiation. They reacted with dienophiles at 180 °C to afford Diels–Alder adducts in excellent yields.

Introduction

Since the synthesis of benzocyclobutene (1) and its Diels–Alder reaction were reported by Cava in 1956,[1a] its homologs such as **2–8** have attracted much attention.[1,2] Syntheses of related compounds having substituents and/or multiple cyclobutene rings have been investigated. Their structures were examined thoroughly by spectroscopic and X-ray crystallographic methods.[3] These com-

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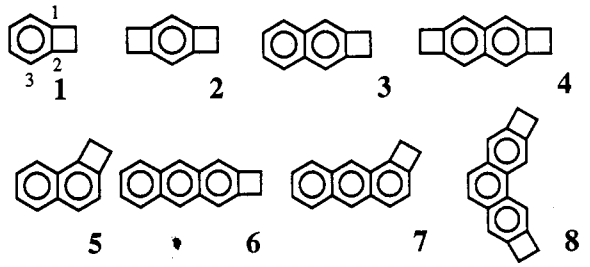
0022-3263/92/1957-5955$03.00/0

Table I. ^{13}C NMR Chemical Shifts of Cycloalkene-Fused Pyrenes

compd	C4	C10a	C3a	C9	C2	C10b	C1	C3	Ccb
9	140.62	131.96	127.71	127.51	125.59	124.55	124.37	119.22	28.27
10	141.06	129.95	(C10a)	(C4)	125.79		(C3)	119.01	28.14
pyrene	127.28	131.03	(C10a)	(C4)	125.74	124.56	(C3)	124.84	
Me_4-pyrene[a]	131.48	129.71	(C10a)	(C4)	125.46		(C3)	120.90	
19	130.87	130.25	128.17	127.07	125.62	123.34	124.69	120.47	
20	130.78	129.61	127.74	127.06	125.53	123.12	124.76	120.16	
21a	130.42	128.24	(C10a)	(C4)	125.78		(C3)	120.42	

[a] 4,5,9,10-Tetramethylpyrene.

pounds show unusual spectroscopic properties due to the strain introduced by fused cyclobutene ring(s), e.g., unusual chemical shifts[4] and coupling constants[4,5] in NMR spectroscopy, hyperfine splitting constants in ESR spectroscopy,[6] bathochromic shifts in UV spectroscopy,[7] and abnormal bond lengths and angles revealed by X-ray crystallographic analysis. These properties are generally interpreted as reflecting rehybridization of aromatic carbon atoms (Streitwieser's model).[8] Moreover, they generate *o*-quinodimethanes, which are highly reactive diene intermediates[9] and undergo the Diels–Alder reaction with dienophiles.[2c,10] These reactive intermediates have been used to synthesize many natural products,[10] condensed polycyclic aromatic compounds,[11] cyclophanes,[11b] and functional polymers.[12]

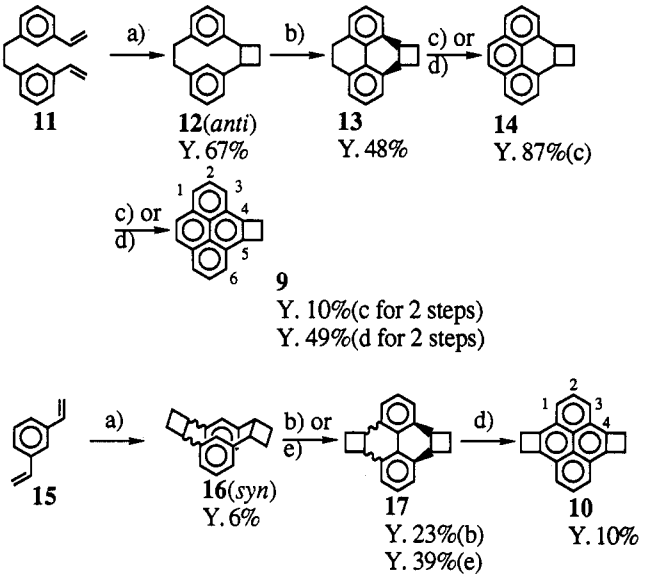


We here report the synthesis of dihydrocyclobuta[*e*]pyrene (**9**)[13] and tetrahydrodicyclobuta[*e,l*]pyrene (**10**)[13] and describe the physical and chemical properties of these new homologs in the benzocyclobutene family.

Results and Discussion

Syntheses of 9 and 10. Several methods for synthesizing benzocyclobutene derivatives have been reported.[2] They are classified into two groups. One is the sequence where the cyclobutene ring is introduced by thermolysis at the final step. The other is the aromatization of compounds with fused cyclobutane or cyclobutene rings. The latter route seems to be better for condensed polycyclic aromatic compounds or multiple cyclobutene fused rings, for example **4**,[7b] **6**,[1b,14] **7**,[1b,14] or **8**.[15] We designed the syntheses of **9** and **10** along this latter strategy using the sequence of photocycloaddition of styrene derivatives to cyclobutane-ring-bridged cyclophanes,[16] transannulation,[17a] and finally aromatization through lithiation[18] (Scheme I).

Scheme I[a]



[a] (a) HP Hg lamp, benzene; (b) Py-HBr_3, CH_2Cl_2, 0 °C; (c) DDQ, benzene, reflux; (d) *n*-BuLi, TMEDA, cyclohexane, reflux; (e) HP Hg lamp, quartz, I_2, K_2CO_3, cyclohexane.

The photocycloaddition of 1,2-bis(*m*-vinylphenyl)ethane (**11**) gave *anti*-metacyclophane **12** in moderate yield.[16b] For the transannulation of **12** to **13**, pyridinium bromide perbromide (Py-HBr_3)[17a] in CH_2Cl_2 was the best among reagents tried (Experimental Section).[17]

The tetrahydropyrene derivative **13** was aromatized to **9** in 49% yield by *n*-BuLi/TMEDA.[18] DDQ oxidized **13** to half-aromatized product **14** in 87% yield, although further reaction gave **9** in only 10% yield. This result may reflect consumption of **9** by DDQ at the high reaction temperature.

Compound **10** was prepared by the same sequence used for **9** (Scheme I). *syn*-Metacyclophane **16** was transannulated to afford tetrahydropyrene derivative **17** in 39% yield, using an iodine-catalyzed photoreaction.[19] Reagent

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(13) IUPAC names of **9** and **10** are 1,2-dihydrocyclobuta[*e*]pyrene and 1,2,6,7-tetrahydrodicyclobuta[*e,l*]pyrene, respectively.
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(16) (a) Nishimura, J.; Doi, H.; Ueda, E.; Ohobayashi, A.; Oku, A. *J. Am. Chem. Soc.* **1987**, *109*, 5293. (b) Nishimura, J.; Ohobayashi, A.; Doi, H.; Nishimura, K.; Oku, A. *Chem. Ber.* **1988**, *121*, 2019. (c) Nishimura, J.; Horikoshi, Y.; Wada, Y.; Takahashi, H.; Sato, M. *J. Am. Chem. Soc.* **1991**, *113*, 3485.
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Table II. Diels–Alder Reaction of 9 and 10

entry	diene precursor	dienophile	molar ratio	conditions	product	yield, %
1	9	maleic anhydride	5.2	180 °C, 1 h	19	93
2	9	diethyl fumarate	5.5	200 °C, 0.5 h	20	100
3	9	diethyl acetylenedicarboxylate	4.9	180 °C, 1 h	22	73
4	10	diethyl maleate	14.2	180 °C, 1 h	21	96
5	9	*p*-quinone	4.9	180 °C, 1 h		0
6	9	anthracene	5.0	180 °C, 1 h	23	50[a]
7	9	none		180 °C, 1 h	23	53

[a] Only dimer 23 was formed.

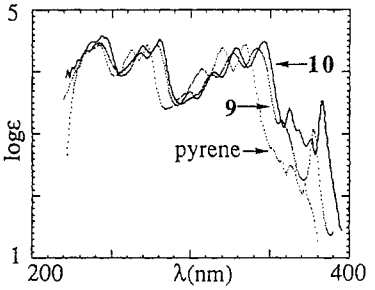


Figure 1. Electronic spectra of 9, 10, and pyrene.

$Py{\cdot}HBr_3$ was not suitable in this case, probably because of its low reactivity with rather rigid cyclophane 16.[16c] The structures of 9 and 10 were determined by ^1H, ^{13}C, ^1H–^1H COSY, and ^1H–^{13}C HETCOSY NMR experiments.

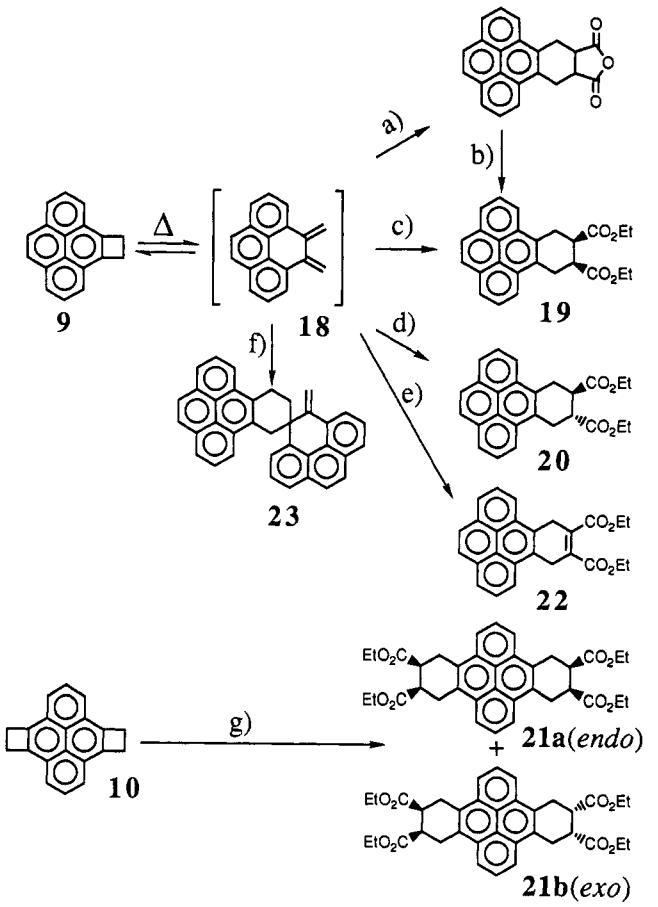
Spectroscopic Properties of 9 and 10. The ^1H NMR chemical shifts of cyclobutene methylene protons shift more to downfield, as the containing aromatic nuclei become larger, i.e., 1 (δ 3.17),[20] 3 (δ 3.28),[14] and 6 (δ 3.38).[14] Compounds 9 (δ 3.60) and 10 (δ 3.57) record the highest downfielded shifts among the homologs ever reported.[21]

Streitwieser presented a model on the orbital hybridization of aromatic carbons around cyclobutene-fused positions,[8] by which many unusual reactivities and properties were interpreted reasonably. That is, by the fused small rings, the carbon at position 1 gains more p-character and the carbon at position 3 does more s-character (see structure 1 for numbering). As shown in Table I, ^{13}C NMR spectra of 9 and 10 show a large downfielded shift at C4 (corresponding to C1 for 1) due to the increase of p-character of this carbon, and a small but apparent high-fielded shift at C3a (corresponding to C3 for 1) due to the increase of its s-character. Thus, their ^{13}C NMR chemical shift tendency is also reasonably interpreted by Streitwieser's model.[8]

The electronic spectra of 9 and 10 in cyclohexane exhibit bathochromic shifts as the strain increases, compared with pyrene (Figure 1). Similar bathochromic shifts of benzene and naphthalene analogs have been reported.[7]

Diels–Alder Reaction of 9 and 10 with Dienophiles. Benzocyclobutene derivatives react easily with dienophiles through electrocyclic ring opening followed by Diels–Alder cycloaddition. The temperature required for the electrocyclic ring-opening reaction depends on substituents at the cyclobutene moiety. Generally, when benzocyclobutene is substituted by electron-donating groups or π-conjugating groups, it cleaves at lower temperatures.[2c] Actually, 7,8-diphenylbenzocyclobutene undergoes reaction at 25 °C,[1d] whereas benzocyclobutene requires a temperature >200 °C.

Scheme II[a]



[a] (a) Maleic anhydride; (b) esterification, yield 75% (for two steps); (c) diethyl maleate, yield 93%; (d) diethyl fumarate, yield 100%; (e) diethyl acetylenedicarboxylate, yield 73%; (f) in the absence of dienophile, yield 53%; (g) diethyl maleate, total yield 96%.

Compound 9 reacts with dienophiles such as maleic anhydride, diethyl maleate, diethyl fumarate, and diethyl acetylenedicarboxylate in diethyl phthalate under a N_2 atmosphere at 180 °C for 1 h and affords Diels–Alder adducts in 75%,[22] 93%, quantitative, and 73% yields, respectively (Scheme II and Table II). The *o*-quinodimethane intermediate 18 is presumed to be involved. Compared with the reaction of other unsubstituted benzocyclobutene homologs like 1, 3,[23] and 5,[23] this reaction temperature at 180 °C is quite low and the yields of adducts are remarkably high. This result seems to reflect the stability of intermediate 18.

This cycloaddition reaction proceeds stereospecifically; i.e., 9 gives a cis product from the cis dienophile and a trans product from the trans dienophile. This conclusion was

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(21) The same tendency is recognized in chemical shifts of methyl groups attached to aromatic nuclei, i.e., toluene (δ 2.35), 2-methylnaphthalene (δ 2.46), 2-methylanthracene (δ 2.53), 9-methylphenanthrene (δ 2.60), and 4-methylpyrene (δ 2.80).
(22) Structural analysis of this adduct was carried out after esterification with ethanol.
(23) Cava, M. P.; Shirley, R. L.; Erickson, B. W. *J. Org. Chem.* **1962**, *27*, 755.

reached by ^1H NMR spectroscopy. The spectrum of *cis*-**19** shows two kinds of ethyl groups, while that of *trans*-**20** shows only one.

In the absence of dienophiles, **9** dimerized to afford **23** (53%), which was unstable at high temperature and polymerized to give chloroform-insoluble material.[1c,24] Although a [4 + 4] cycloaddition reaction between anthracene and a biradical species generated from **1** is known,[25] **9** and anthracene did not give any product of this sort. This result seems to indicate a concerted process for its ring opening, which has been suggested by a molecular orbital calculation.[26]

Compound **10** also reacted with diethyl maleate to afford an adduct as a mixture of two diastereomers (**20a**/**20b** = 1/1) in 96% yield.

Experimental Section

General. Elemental analyses were carried out at the Microanalytical Center for Gunma University. Melting points are not corrected. NMR spectra were recorded on a Varian Gemini-200 FT NMR spectrometer. IR spectra were taken by a Hitachi 270-50 infrared spectrophotometer. UV spectra were taken by a Shimadzu UV-160A spectrophotometer. Reversed-phase HPLC was carried out with a Shimadzu LC-6A HPLC apparatus.

Materials. Dienophiles and diethyl phthalate were highest grade commercially available reagents and were used without further purification. Styrene derivatives and cyclophanes were prepared as described elsewhere.[16c]

4,5-Ethano-4,5,9,10-tetrahydropyrene (13). Cyclophane **12**[16b] (50.0 mg, 0.213 mmol) was dissolved in 8.4 mL of CH_2Cl_2 and cooled to 0 °C. Into the solution pyridinium bromide perbromide (Py·HBr_3,[17a] 68.6 mg, 0.214 mmol) was added quickly with vigorous stirring. The reaction was monitored by TLC. After 21 h the reaction mixture was poured into aqueous $NaHSO_3$ and extracted with benzene (3 × 50 mL). The combined organic layer was washed with water, neutralized with aqueous $NaHCO_3$, washed with water again, dried over Na_2SO_4, and evaporated in vacuo.

The product **13** was isolated by column chromatography (SiO_2, hexane) and obtained in 48% yield (24.0 mg) as white crystals: mp 49.3–50.2 °C; ^1H NMR δ 7.14 (2 H, t, J = 7.3 Hz), 7.03 (2 H, dd, J = 8.8 and 1.6 Hz), 6.99 (2 H, dd, J = 7.2 and 1.6 Hz), 3.71 (2 H, m), 2.92 (4 H, s), 2.51 (2 H, m), 2.16 (2 H, m); ^{13}C NMR δ 137.2, 135.6, 129.4, 127.6, 126.4, 126.2, 36.7, 30.7, 28.6; IR (KBr) 2932, 1452, 1164, 810, 786, 735, 630 cm^{-1}; UV (λ_{max}, nm (log ε)), 218.0 (4.63), 285.0 (4.19).

Reagent Py·HBr_3 in CH_2Cl_2 was the most favorable for this transannulation among the following ones (yields of **13** are in parentheses): Py·HBr_3 (48%),[17a] ICl/CH_3CO_2H/6 M HNO_3(aq) (28%),[17b] $I_2/h\nu$ (27%),[17c] $I_2/AgClO_4$ (17%),[17c] and Br_2/Fe (10%).[17b]

Dihydrocyclobuta[*e*]pyrene (9). *n*-BuLi (1.29 mmol, 0.87 mL of 1.6 M of hexane solution) was added to a mixture of **13** (53.1 mg, 0.23 mmol) and TMEDA (1.03 mL) in cyclohexane (1.37 mL) with stirring under a N_2 atmosphere. The reaction mixture was heated gradually. It changed color to brownish violet, and an exothermic reaction ceased within 15 min. Then the mixture was heated to reflux. The reaction was monitored by TLC. After 1 h the starting material disappeared. The mixture was cooled, poured into water, and extracted with benzene (3 × 50 mL). The combined organic layer was washed with 10% HCl to remove TMEDA, neutralized with aqueous $NaHCO_3$, washed with water, dried over Na_2SO_4, and evaporated in vacuo. Column chromatography (SiO_2, hexane) and then HPLC (Shim-pack C_{18}, MeOH) gave **9** in 49% yield (25.6 mg) as white crystals: mp 171.0–171.8 °C; ^1H NMR δ 8.15 (2 H, dd, J = 7.1 and 1.8 Hz), 8.07 (2 H, dd, J = 7.4 and 1.8 Hz), 8.06 (2 H, s), 8.03 (2 H, t, J = 7.0 Hz), 3.60 (4 H, s); ^{13}C NMR δ 140.6 (2 C, C4), 132.0 (2 C, C10a), 127.7 (2 C, C3a), 127.5 (2 C, C9), 125.6 (2 C, C2), 124.6 (2 C, C10b), 124.4 (2 C, C1), 119.2 (2 C, C3), 28.3 (2 C, C_{CB}); IR (KBr) 2914, 1602, 1179, 828, 756, 714 cm^{-1}; UV (λ_{max}, nm (log ε)), 243.9 (4.45), 267.9 (4.31), 278.4 (4.43), 327.6 (4.30), 343.2 (4.38); MS ($M^{\cdot+}$) m/z 228. Anal. Calcd for $C_{18}H_{12}$: C, 94.70; H, 5.30. Found: C, 94.29; H, 5.71.

4,5-Ethano-4,5-dihydropyrene (14). A mixture of **13** (97.5 mg, 0.42 mmol) and DDQ (227 mg, 1.00 mmol) in benzene (42.3 mL) was refluxed under a N_2 atmosphere for 3 h. After the mixture was cooled to room temperature and evaporated, **14** was isolated in 87% yield (84.5 mg) by column chromatography (SiO_2, hexane): mp 97.8–98.3 °C; ^1H NMR δ 7.64 (2 H, dd, J = 6.4 and 1.5 Hz), 7.67 (2 H, s), 7.54 (2 H, t, J = 7.5 Hz), 7.31 (2 H, dd, J = 5.6 and 1.4 Hz), 4.07 (2 H, m), 2.67 (2 H, m), 2.25 (2 H, m); ^{13}C NMR δ 137.8, 134.2, 131.3, 127.0, 126.9, 126.0, 36.8, 31.7; IR (KBr) 2932, 1446, 1173, 831, 765, 729 cm^{-1}; UV (λ_{max}, nm (log ε)), 224.2 (4.72), 267.6 (4.56), 301.2 (4.10). Anal. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 93.60; H, 6.40.

Tetrahydrodicyclobuta[*e*,*l*]pyrene (10). Cyclophane **16**[10c] (32.8 mg, 0.13 mmol) and I_2 (34.5 mg, 0.14 mmol) in cyclohexane (15 mL) were irradiated with a 400-W high-pressure mercury lamp with stirring under a N_2 atmosphere for 1.8 h. Then the reaction mixture was poured into aqueous $NaHSO_3$ and extracted with benzene (3 × 50 mL). The combined organic layer was washed with water, neutralized with aqueous $NaHCO_3$, washed again with water, dried over Na_2SO_4, and evaporated in vacuo. Compound **17** was isolated by column chromatography (SiO_2, hexane) in 39% yield (13.2 mg) as white crystals. Product **17** consisted of two stereoisomers (endo/exo = 1/1) and was used for further reaction without separation. Some starting material **17** was recovered (6.6 mg).

n-BuLi (0.93 mmol, 0.59 mL of 1.6 M of hexane solution) was added to a mixture of **17** (30.0 mg, 0.12 mmol) and TMEDA (0.70 mL) in cyclohexane (0.70 mL) with stirring under a N_2 atmosphere. Workup was the same as used for **9**. Compound **10** was isolated by column chromatography (SiO_2, hexane) and HPLC (Shim-pack C_{18}, MeOH) in 10% yield (2.9 mg) as white crystals. The mp could not be determined because of gradual decomposition at high temperature: ^1H NMR δ 8.00 (6 H, m), 3.57 (8 H, s); ^{13}C NMR δ 141.1 (4 C, C4), 129.0 (4 C, C3a), 125.8 (4 C, C2, C10b), 119.0 (4 C, C1), 28.1 (4 C, C_{CB}); IR (KBr) 2914, 1602, 1311, 1212, 1158, 810, 768, 717 cm^{-1}; UV (λ_{max}, nm (log ε)), 243.6 (4.59), 267.4 (4.41), 280.0 (4.52), 328.4 (4.40), 346.3 (4.49); MS ($M^{\cdot+}$) m/z 254.

Diels–Alder Reaction of 9 with Diethyl Maleate. Compound **9** (19.2 mg, 0.084 mmol), diethyl maleate (72.3 mg, 0.42 mmol), and diethyl phthalate (0.14 mL) were put in a 2-mL ampule with a small stirring bar. The ampule was sealed under a N_2 atmosphere and heated at 180 °C for 1 h with stirring. The reaction mixture was cooled and evaporated under reduced pressure to expel the solvent. Adduct **19** was isolated in 93% yield by column chromatography (SiO_2, benzene/hexane) and was recrystallized from hexane: mp 140.7–141.5 °C; ^1H NMR δ 8.34 (2 H, d, J = 7.0 Hz), 8.16 (2 H, d, J = 6.9 Hz), 8.05 (2 H, s), 8.02 (2 H, t, J = 7.7 Hz), 4.18 (4 H, q, J = 7.1 Hz), 3.88 (2 H, m), 3.53 (2 H, m), 3.50 (2 H, s), 1.25 (6 H, t, J = 7.1 Hz); ^{13}C NMR δ 172.8, 130.9, 130.3, 128.2, 127.1, 125.6, 124.7, 123.3, 120.5, 60.6, 39.8, 26.9, 14.1; IR (KBr) 1728 cm^{-1}. Anal. Calcd for $C_{26}H_{24}O_4$: C, 77.97; H, 6.04. Found: C, 78.29; H, 6.12.

Diels–Alder Reaction of 9 with Diethyl Fumarate. Compound **9** (100.4 mg, 0.44 mmol), diethyl fumarate (416.3 mg, 2.42 mmol), and diethyl phthalate (0.68 mL) were treated by the same procedure as above at 200 °C for 30 min. By column chromatography (SiO_2, hexane/benzene) and recrystallization, **20** was obtained in quantitative yield: mp 151.8–152.7 °C; ^1H NMR δ 7.96 (4 H, s), 7.87 (2 H, s), 7.82 (2 H, t, J = 7.6 Hz), 4.29 (4 H, q, J = 7.1 Hz), 3.47 (2 H, m), 2.98 (4 H, t, J = 4.4 Hz), 1.37 (6H, t, J = 7.1 Hz); ^{13}C NMR δ 174.7, 130.8, 129.6, 127.7, 127.1, 125.5, 124.8, 123.1, 120.2, 60.8, 41.7, 29.3, 14.3; IR (KBr) 1728 cm^{-1}. Anal. Calcd for $C_{26}H_{24}O_4$: C, 77.97; H, 6.04. Found: C, 77.28; H, 6.10.

Diels–Alder Reaction of 9 with Diethyl Acetylenedicarboxylate. Compound **9** (101.6 mg, 0.45 mmol), diethyl acetylenedicarboxylate (374.0 mg, 2.20 mmol), and diethyl phthalate (0.68 mL) were treated by the same procedure as above at 180 °C for 1 h. By column chromatography (SiO_2, hexane/benzene) and recrystallization, **22** was obtained in 73% yield (127.9 mg): mp 203.8–204.6 °C; ^1H NMR δ 8.22 (4 H, m), 8.08 (2 H, s),

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8.03 (2 H, t, J = 7.3 Hz), 4.41 (4 H, a, J = 7.1 Hz), 4.25 (4 H, s), 1.44 (6 H, t, J = 7.1 Hz); ^{13}C NMR δ 168.0, 131.9, 131.1, 129.3, 127.4, 126.0, 125.3, 123.8, 120.8, 61.5, 29.5, 14.2; IR (KBr) 1737, 1719 cm^{-1}. Anal. Calcd for $C_{26}H_{22}O_4$: C, 78.37; H, 5.57. Found: C, 78.79; H, 5.83.

Diels–Alder Reaction of 10 with Diethyl Maleate. Compound **10** (10.0 mg, 0.039 mmol) and diethyl maleate (96.6 mg, 0.56 mmol) in diethyl phthalate (0.60 mL) were treated by the same procedure as above at 180 °C for 1 h. Compound **21** was obtained in 96% yield (22.5 mg) as a mixture of endo and exo stereoisomers (1:1): ^{1}H NMR δ 8.34 (4 H, d, J = 7.9 Hz), 8.30 (4 H, d, J = 7.9 Hz), 8.03 (4 H, t, J = 7.9 Hz), 4.17 (16 H, m), 3.91 (4 H, m), 3.82 (4 H, m), 3.58 (4 H, m), 3.46 (12 H, m), 1.25 (12 H, t, J = 7.1 Hz), 1.24 (12 H, t, J = 7.1 Hz); ^{13}C NMR δ 173.0, 130.4, 128.2, 125.8, 120.4, 60.8, 40.1, 27.3, 14.1; IR (KBr), 1731 cm^{-1}. Anal. Calcd for $C_{36}H_{38}O_8$. C, 72.22; H, 6.40. Found: C, 71.92; H, 6.23.

Dimer 23. Compound **9** (49.7 mg, 0.22 mmol) in diethyl phthalate (0.34 mL) was treated by the same procedure as above at 180 °C for 1 h. Product **11** was obtained in 53% yield (26.3 mg): ^{1}H NMR δ 8.65 (1 H, dd, J = 7.8 and 1.1 Hz), 8.17 (4 H, m), 8.11 (2 H, s), 7.98 (1 H, t, J = 7.7 Hz), 7.88 (1 H, dd, J = 7.9 and 1.2 Hz), 7.79 (1 H, dd, J = 7.8 and 1.3 Hz), 7.79 (2 H, s), 7.75 (2 H, t, J = 7.6 Hz), 7.61 (1 H, t, J = 7.6 Hz), 7.47 (1 H, t, J = 7.7 Hz), 5.38 (1 H, s), 5.23 (1 H, s), 4.35 (1 H, d, J = 16.9 Hz), 4.18 (1 H, d, J = 16.9 Hz), 3.11 (2 H, m), 2.13 (2 H, m); ^{13}C NMR δ 149.2, 142.7, 134.7, 131.8, 131.4, 131.2, 130.7, 130.6, 130.5, 130.0, 129.9, 127.4, 127.1, 126.9, 126.7, 126.5, 126.5, 126.2, 125.9, 125.8, 124.9, 124.6, 123.9, 123.5, 123.2, 121.6, 120.9, 120.4, 113.5, 112.0, 43.2, 34.9, 32.6, 25.1; IR (KBr) 3046, 2920, 1626, 1602, 1587, 1425, 1299, 1179, 897, 825, 756, 732, 678 cm^{-1}; MS (M$^{\cdot+}$) m/z 456.

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Synthesis and Chemistry of Some Tricyclic Cyclopropenes. 3. Tricyclo[3.2.1.0^{2,4}]oct-2(4)-ene[1,2]

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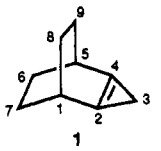
The title compound cyclopropene **2** has been synthesized in situ from dibromide **8** and diiodide **9** via dehalogenation of *tert*-butyllithium in THF at −78 °C. The dihalides were formed in six steps starting with cyclopentadiene and (chloromethyl)maleic anhydride. In the presence of diphenylisobenzofuran (DPIBF) **2** forms a Diels–Alder adduct, most probably **10**. Cyclopropene **2** and a previously synthesized cyclopropene **1** were decomposed under these same conditions, only without DPIBF present, to give complex mixtures of products, some of which were characterized as *tert*-butyl adducts and dimers via the ene reaction of the cyclopropenes.

Due to their unique structure and high reactivity, cyclopropenes continue to present a synthetic challenge to organic chemists. Incorporation of a cyclopropene ring into a bicyclic or tricyclic framework further increases the ring strain of a cyclopropene and makes for more challenging syntheses and trapping experiments. Most of the literature has been reviewed.[3]

We have undertaken the study of several different tricyclic systems in order to determine the effects of ring strain on the stability and ease of synthesis/trapping of these unusual compounds. Our previously published synthesis of tricyclo[3.2.2.0^{2,4}]non-2(4)-ene (**1**) and its Diels–Alder adduct with diphenylisobenzofuran (DPIBF) presented a pathway which has been used as a framework for the synthesis of similar tricyclic cyclopropenes. We report here the synthesis and trapping of tricyclo[3.2.1.0^{2,4}]oct-2(4)-ene (**2**) as well as further studies performed on cyclopropene **1**. Recently Mühlebach and Neuenschwander have synthesized a dehydro analog of **2**, tricyclo[3.2.1.0^{2,4}]octa-2(4),6-diene, and have trapped it in a Diels–Alder reaction with DPIBF.[4]



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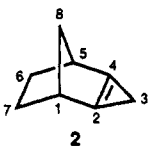

2

Results and Discussion

Synthesis of the Precursor. To assess the effects of ring strain on the synthesis of **2** vs the previously reported **1**, differences between the pathway leading to the two compounds have been explored. Chloro anhydride **3** (Scheme I) can be easily synthesized by a room temperature reaction of (chloromethyl)maleic anhydride with cyclopentadiene. This is much more facile than the homologous reaction with cyclohexadiene, which took 26 h at 110 °C.[5] Ring opening of **4** to produce chloro diester **5** was achieved by a 48-h reflux in HCl-saturated ethanol. The subsequent addition of thionyl chloride and ethanol produced chloro diester **5** in about 35% yield. The product contained a large percentage of starting material. Ring closure by elimination of HCl was attempted by refluxing

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(5) Preliminary experiments with cycloheptadiene and (chloromethyl)maleic anhydride show that a 48-h reflux in toluene in a sealed vessel at 200 °C is necessary for a reasonable yield of the adduct. We thank D. A. Southard, Jr., University of Wisconsin—Eau Claire, for this study. Cyclooctadiene does not react with (chloromethyl)maleic anhydride even after 3 days at 200 °C.

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