Novel Intramolecular Cyclization of 2-(Buta-1,3-dienyl)benzyl Anions to 6,7(9)-Dihydro-5*H*-benzocycloheptenyl Anions Leading to Successive Formation of 1,2-Dihydrocyclopropa[*a*]naphthalenes

by **Hisashi Saitoh**, **Hisako K. Ijuin**, **Nobuko Watanabe**, and **Masakatsu Matsumoto***

Department of Chemistry, Kanagawa University, Tsuchiya, Hiratsuka, Kanagawa 259-1293, Japan (phone: +81-463-59-4111; fax: +81-463-58-9684; e-mail: matsumo-chem@kanagawa-u.ac.jp)

When treated with LiN^iPr_2 (LDA) at −78°, 1-[(methylsulfanyl)methyl]-2-[(1*Z*,3*E*)-4-phenylbuta-1,3-dien-1-yl]benzene easily cyclized to form benzocycloheptenyl anion, which successively underwent intramolecular nucleophilic substitution to give a cyclopropanaphthalene. Similar LDA-mediated cyclization also occurred for 4-phenyl- or 4-methyl-substituted 1-[2-(methoxymethyl)phenyl]buta-1,3-dienes to furnish the corresponding benzocycloheptenes and cyclopropanaphthalenes. A 4-*tert*-butyl analog also underwent LDA-mediated cyclization to give a benzocycloheptene, but not a cyclopropanaphthalene.

Introduction. – Electrocyclization of hexa-1,3,5-trienes or penta-2,4-dienyl cations, such as an intermediate in the *Nazarov* cyclization, is an important strategy for constructing six- or five-membered ring compounds [1][2]. In addition to such conjugate π-electron systems, a hepta-2,4,6-trienyl anion and its related cation represent a $C_7/8\pi$- or $C_7/6\pi$-electron system, respectively, that can undergo electrocyclization to give seven-membered ring compounds[1])[2]) (*Scheme 1*) [3–5]. Thus, we investigated the facile generation of hepta-2,4,6-trienyl anions **1** (see *Scheme 2*) and their cyclization; though **1** is a benzo analog of a heptatrienyl anion, it is easy to synthesize a precursor for **1**[3]). Formally, the conjugated π-electron system of **1** can be regarded as a $C_{11}/12\pi$-electron system or simply an *ortho*-buta-1,3-dienyl-substituted benzylic anion system, *i.e.*, a $C_7/8\pi$-electron system.

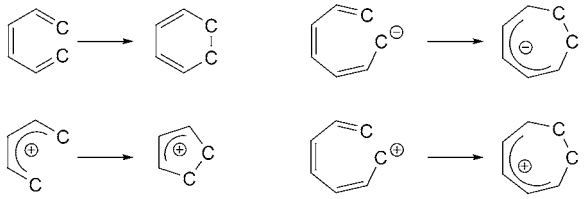
Results and Discussion. – We prepared various precursors for **1**, including 1-[(methylsulfanyl)methyl]-2-[(1*Z*,3*E*)-4-phenylbuta-1,3-dien-1-yl]benzene (**2a**) and 1-

[1]) A preliminary communication reported that heptatrienyl anions undergo rearrangement to cycloheptadienyl anions, though the corresponding seven-membered ring compounds have not yet been satisfactorily isolated [3].

[2]) Recently, we reported that LiN^iPr_2 (LDA) induced the cyclization of 2-(buta-1,3-dienyl)-3-methylpyrazines and 3-(buta-1,3-dienyl)-4-methyl-1,2,5-oxadiazoles to 5*H*-cycloheptapyrazines and 4*H*-cyclohepta-1,2,5-oxadiazoles, respectively [4]. These LDA-mediated intramolecular cyclizations could be considered the electrocyclization of a $C_7/8\pi$-electron system. However, we cannot exclude the possibility of a mechanism that involves an intramolecular conjugate 1,6-addition [5] of a methyl carbanion to a butadienylimine moiety as an activated alkene in the same molecule.

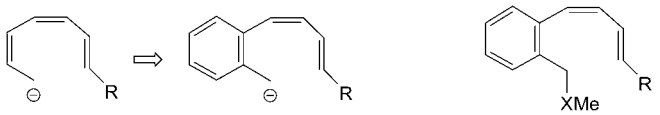
[3]) An MO calculation indicated that heptatrienyl anion **1** would undergo a conrotatory cyclization to a cycloheptadienyl anion.

Scheme 1. *Electrocyclizations of Hexa-1,3,5-triene and Penta-2,4-dienyl Cation Systems, and the Cyclizations of Hepta-2,4,6-trienyl Anion and Hepta-2,4,6-trienyl Cation*



[2-(methoxymethyl)phenyl]buta-1,3-dienes with 4-Ph, 4-Me (**2c**), 4-^{t}Bu, and 4-COOMe substituents, *i.e.*, **2b**–**2d**, in the butadienyl (*Scheme 2*). Compounds **2a**–**2e** were synthesized by the *Wittig* reaction of 2-[(methylsulfanyl)methyl]benzaldehyde or 2-(methoxymethyl)benzaldehyde with the corresponding phosphonium ylides.

Scheme 2. *Benzo Analogs of a Hepta-2,4,6-trienyl Anion as a C_7/8π-Electron System and Its Precursors*



1

	X	R
2a	S	Ph
2b	O	Ph
2c	O	Me
2d	O	*tert*-Bu
2e	O	COOMe

First, we investigated the LDA-mediated reaction of precursor **2a**, since the benzylic CH_2 group would be activated by a MeS group to easily form a carbanion **3a** on treatment with a base [6]. When **2a** was treated with LDA in THF under N_2 at $-78°$, intramolecular cyclization rapidly took place to give the expected 6,9-dihydro-5*H*-benzocycloheptene **4a** (65%) and its 6,7-dihydro-isomer **5a** (10%), together with 1-phenylcyclopropa[*a*]naphthalene **6** (18%)[4]) [7], in a ratio of **4a**/**5a**/**6** 70:11:19 (*Scheme 3* and *Table 1*). When the reaction time was prolonged to 120 min, the percentages of benzocycloheptenes **4a** and **5a** decreased, while that of cyclopropanaphthalene **6** increased threefold (**4a**/**5a**/**6** 40:5:55). This result suggested that anion **3a** initially cyclized to the intermediary benzocycloheptenyl anion **7a**, which successively underwent intramolecular nucleophilic substitution to give cyclopropanaphthalene **6** (*Scheme 3*).

The structures of **4a**, **5a**, and **6** were determined by ^{1}H- and ^{13}C-NMR, IR, MS, and HR-MS analyses. Furthermore, X-ray single-crystal analysis was successfully performed for **4a** and **6**. The ORTEP views presented in the *Figure* reveal that the MeS and Ph groups on the seven-membered ring of **4a** are *trans*-configurated, and the Ph group on the cyclopropane ring of **6** is *exo*-oriented: crystallographic data of **4a** and **6** are

[4]) Phenylcarbene has been reported to add to naphthalene to give **6** in 9% yield [7].

Scheme 3. *Cyclization of Carbanions* **3a** *and* **3b** *Generated from* **2a** *and* **2b**, *Respectively*

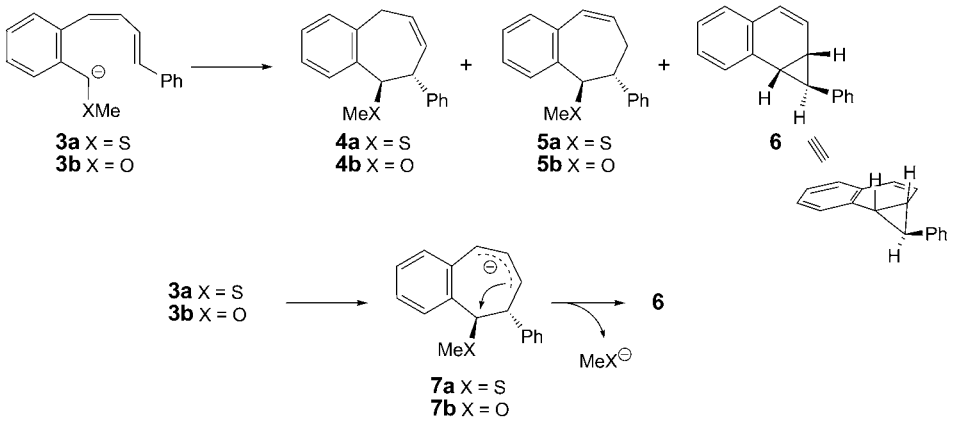


Table 1. *LDA-Mediated Cyclization of 1-[(Methylsulfanyl)methyl]-2-[(1Z,3*E*)-4-phenylbuta-1,3-dien-1-yl]benzene* (**2a**) *and Its 2-(Methoxymethyl)phenyl Analogs* **2b**–**2d**[a])

Substrate	Product distribution [%]			Total Yield [%]
	4	**5**	**6**	
2a	70	11	19	93
2a[b])	40	5	55	90
2b	59	5	36	89
2b[b])	ND[c])	ND	100	84
2c[d])	46[e])	3[e])	51	70
2d[f])	100	ND	ND	54

[a]) Unless otherwise stated, the reaction was carried out at −78° for *ca.* 30 min. [b]) The mixture was allowed to stand to reach room temperature within 120 min. [c]) ND, Not detected. [d]) (*Z*,*E*)-and (*E*,*E*)-isomer mixture (50 : 50) was used. [e]) A mixture **4c**/**5c** was obtained. [f]) (*Z*,*E*)-and (*E*,*E*)-isomer mixture (54 : 46) was used.

compiled in *Table 2*. The isomeric benzocycloheptene **5a** presumably possesses the MeS and the Ph groups also in a *trans*-relationship.

In contrast to the case of an alkyl benzyl thioether, the α-carbanion of an alkyl benzyl ether is generally unstable and often undergoes protophilic cleavage (elimination) or *Wittig* rearrangement even at a low temperature, and thus its use in organic synthesis has been quite limited [8]. However, when **2b** was treated with LDA, as **2a**, at −78°, the expected cyclization effectively took place to give an isomeric mixture of benzocycloheptene **4b** and **5b**, together with **6** (**4b**/**5b**/**6** 59 : 5 : 36; total yield 89%; *Table 1*). When a mixture of **2b** was allowed to stand until it reached room temperature (*ca.* 45 min), **4b** and **5b** disappeared, and only **6** was isolated in 84% yield. These results are compiled, together with those for **2a**, **2c**, and **2d** (*vide infra*), in *Table 1*.

Next, we investigated whether or not base-mediated cyclization also took place in the case of ω-alkyl-substituted buta-1,3-diene analogs of **2b**. Thus, we selected Me

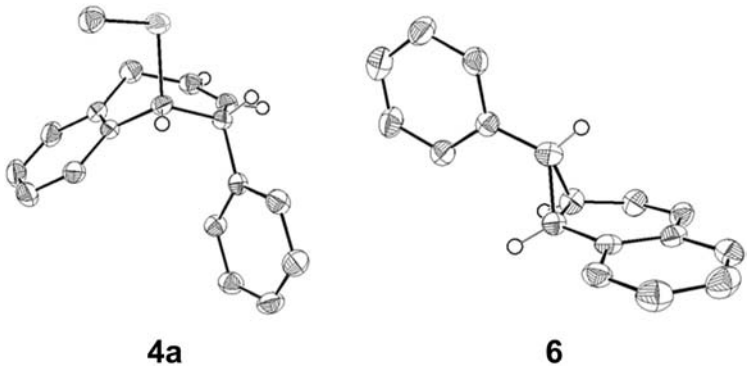


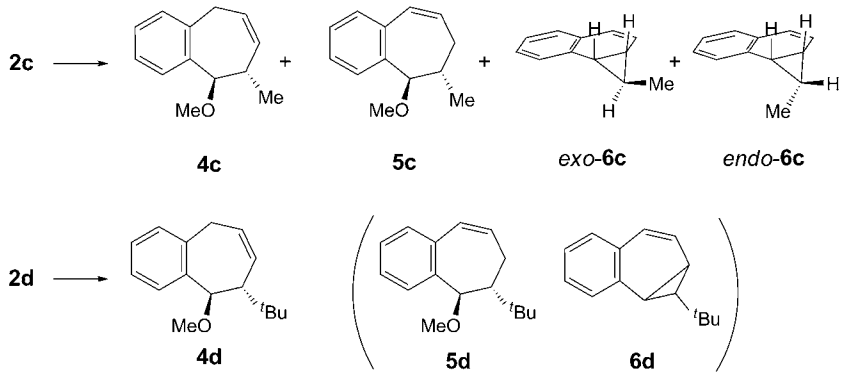
Figure. *ORTEP Representations of benzocycloheptene* **4a** *and cyclopropa[*a*]naphthalene* **6**

Table 2. *Crystallographic Data and Structure Refinement of* **4a** *and* **6**

	4a	**6**
Empirical formula	$C_{18}H_{18}S$	$C_{17}H_{14}$
M_r	266.40	218.30
Crystal color, habit	colorless; prism	colorless; platelet
Crystal dimensions [mm]	$0.20 \times 0.20 \times 0.20$	$0.30 \times 0.25 \times 0.08$
Radiation type, λ [Å]	MoK_α, 0.71070	MoK_α, 0.71070
Temp. [K]	150.1	150.1
Crystal system	tetragonal	monoclinic
Space group	$P4_1$	$P2_1$
Z	4	2
Unit cell parameters:		
a [Å]	11.530 (4)	8.42 (3)
b [Å]	11.530 (4)	5.718 (10)
c [Å]	18.844 (4)	12.43 (2)
β [°]	90	101.626 (12)
V [Å^3]	1441.7 (9)	586.5 (22)
D_x (calc.) [g cm^{-3}]	1.227	1.236
μ [mm^{-1}]	0.208	0.070
F(000)	568	232
Scan type	Multi-scan	Multi-scan
θ Range [°]	3.1 – 27.45	3.2 – 27.48
Index range	$-14 \le h \le 12$	$-10 \le h \le 9$
	$-11 \le k \le 14$	$-6 \le k \le 7$
	$-14 \le l \le 14$	$-15 \le l \le 16$
Measured reflections	15277	5783
Independent reflections	3005	1614
Reflections with $I > 2\sigma(I)$	3255	2380
R_{int}	0.029	0.040
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data, parameters	3255/190	2380/169
R ($F_o^2 > 2\sigma(F_o^2)$)	$R^1 = 0.033$	$R^1 = 0.086$
R (all data)	$R^1 = 0.036$, $wR^2 = 0.088$	$R^1 = 0.099$, $wR^2 = 0.239$
Goodness-of-fit on F^2	1.021	1.006
$\Delta\rho$ (max; min) [e Å^{-3}]	0.43; −0.43	0.57; −0.61

analog **2c** and ^{t}Bu analog **2d** as representatives, though we used (*Z*,*E*)/(*E*,*E*)-isomer mixtures: 50:50 for **2c** and 54:46 for **2d**. When the stereoisomer mixture of **2c** was treated with LDA, as in the case of **2a** and **2b**, the expected cyclization occured to give a mixture of isomeric benzocycloheptenes **4c**/**5c** (94:6) in 34% yield, and methylcyclopropanaphthalene **6c** in 36% yield. The thus obtained methylcyclopropanaphthalene **6c** was a 76:24 mixture of *exo*-**6c** and *endo*-**6c** (*Scheme 4*). The structures of these stereoisomers were assigned based on a comparison of their ^{1}H-NMR spectra with those reported in the literature: coupling constants between a H-atom at the C-atom neighboring a Me group and the cyclopropa bridgehead H-atoms were 4.6 and 4.6 Hz for *exo*-**6c**, and 8.7 and 8.7 Hz for *endo*-**6c** [9][10].

Scheme 4



The ^{t}Bu-analog **2d** also underwent LDA-mediated cyclization to give *(tert*-butyl)-benzocycloheptene **4d** in 54% yield. The results for **2c** and **2d** indicated that the (*E*,*E*)-isomers of **2c** and **2d** apparently underwent the cyclization after isomerization to the corresponding (*Z*,*E*)-isomers or their anionic forms[5]). Notably, the LDA-mediated cyclization of **2d** gave neither detectable amount of cyclopropanaphthalene **6d**, nor 6,7-dihydro isomer **5d** of **4d**.

We described above that benzo-fused hepta-2,4,6-trienyl anions generated from **2** effectively underwent cyclization to give the corresponding benzocycloheptenes **4** and **5**, and that intermediary benzocycloheptenyl anions **7** further underwent intramolecular nucleophilic substitution to give the corresponding cyclopropanaphthalenes **6**. On the other hand, the conjugate addition of a carbanion to a buta-1,3-diene system with an electron-withdrawing group in the ω-position, such as penta-2,4-dien-1-one and penta-2,4-dienoate, has been reported [5]. Thus, we finally investigated whether or not a benzylic anion **3e**, generated from ω-MeOCO analog **2e**, underwent cyclization to give seven-membered ring products **4e** and **5e** as in the case of **2a**–**2d**, or an attack to a conjugate dienecarboxylate system in the same molecule occurs to give the six-membered ring product **8** (*Scheme 5*). However, when treated with LDA, **2e** did not

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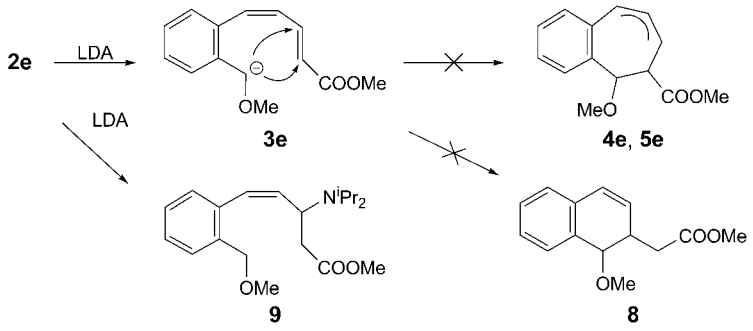
[5]) It has been suggested that hepta-2,4,6-trienyl anion readily undergoes (*E*)/(*Z*) isomerization [3].

Scheme 5



afford any of the expected products, and instead gave only a small amount of **9**, the conjugate-addition product of LDA.

Conclusions. – LDA-Mediated deprotonation from 1-[(methylsulfanyl)methyl]-2-[(1*Z*,3*E*)-4-phenylbuta-1,3-dien-1-yl]benzene (**2a**) and its 2-(methoxymethyl)phenyl analogs **2b**–**2d** afforded hepta-2,4,6-trienyl anions **1** fused with a benzene ring, which underwent effectively intramolecular cyclization to give the corresponding benzocycloheptenyl anions **7**, the quenching of which gave benzocycloheptenes **4** and **5**. On the other hand, anions **7** underwent an intramolecular nucleophilic reaction to furnish the corresponding cyclopropanaphthalenes **6**.

Experimental Part

General. Column chromatography (CC): with silica gel (SiO_2; *Wako*). M.p.: uncorrected. IR Spectra: *JASCO FT/IR-300* spectrometer. ^{1}H- and ^{13}C-NMR spectra: *JEOL JNM-Ex 400* and *JNM-ECP-500* FT-NMR spectrometer; at 400 and 500 MHz (^{1}H) and 100 and 125 MHz (^{13}C). MS: double-focusing mass spectrometers *JEOL JMS 700* and *JEOL AH-505H* and an ESI/APCI-TOF mass spectrometer *JEOL JMS-T100LC*.

Crystal data were collected with an *Rigaku Mercury CCD* diffractometer fitted with a *Rigaku AFC8* detector (graphite monochromated MoK_α (λ 0.71070 Å) radiation). Data collection, cell refinement, data reduction, and analysis were carried out with the CrystalClear software (*Rigaku Corp.*) [11]. The structures were solved by direct methods using SIR-92 [12] for compound **4a** and SHELXS-97 for compound **6**, and refined by full-matrix least-squares on F^2 for all data using SHELXL-97 [13]. All H-atoms were added at calculated positions and refined using a riding model. All calculations were performed using the CrystalStructure [14] crystallographic software package. CCDC-882724 and 882725 contain the supplementary crystallographic data for compound **4a** and compound **6**, resp. These data can be obtained free of charge from the *Cambridge Crystallographic Data Center via* http://www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of 1-[(Methylsulfanyl)methyl]-2-[4-phenylbuta-1,3-dien-1-yl]benzene (**2a**). *Representative Procedure.* BuLi (1.60M in hexane, 7.80 ml, 12.5 mmol) was added to a suspension of (cinnamyl)(triphenyl)phosphonium chloride (5.24 g, 12.6 mmol) in dry THF (40 ml) under N_2 at $-78°$, and the mixture was stirred at r.t. for 30 min. Then, 2-[(methylsulfanyl)methyl]benzaldehyde (2.00 g, 12.0 mmol) in dry THF (10 ml) was added dropwise for 30 min at $-78°$, and the mixture was stirred at r.t. for 1 h. The mixture was poured into sat. aq. NH_4Cl, and extracted with AcOEt. The org. layer was washed with sat. aq. NaCl (3×), dried (anh. $MgSO_4$), and concentrated *in vacuo*. The residue was chromatographed over

SiO_2 (AcOEt/hexane 1:40) to give (*Z,E*)-**2a** (1.66 g, 52%) as a pale yellow oil, and (*E,E*)-**2a** (1.26 g, 39%) as a pale yellow solid.

*Data of (*Z,E*)-***2a***.* Pale-yellow oil. IR (film): 3025, 2913, 1597, 1492. ^{1}H-NMR (400 MHz, $CDCl_3$): 2.03 (*s*, 3 H); 3.71 (*s*, 2 H); 6.51 (*dd* with fine coupling, *J* = 11.5, 11.2, 1 H); 6.70 (*d*, *J* = 15.6, 1 H); 6.75 (*d*, *J* = 11.5, 1 H); 7.05 (*dd* with fine coupling, *J* = 15.6, 11.2, 1 H); 7.18–7.36 (*m*, 9 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 15.2; 36.1; 125.2; 126.5 (2 C); 126.9; 127.3; 127.7; 128.5 (2 C); 128.7; 129.8; 130.4; 131.3; 134.6; 136.1; 136.6; 137.2. MS: 266 (86, M^+), 219 (26), 218 (35), 204 (19), 203 (21), 202 (19), 150 (25), 141 (14), 115 (18), 91 (100). HR-MS (APCI): 267.1206 ($[M+H]^+$, $C_{18}H_{19}S^+$; calc. 267.1208).

*Data of (*E,E*)-***2a***:* Pale-yellow needles. M.p. 72.0–72.5° (hexane/AcOEt). IR (KBr): 3024, 2911, 1481, 1449, 1244, 986. ^{1}H-NMR (400 MHz, $CDCl_3$): 2.06 (*s*, 3 H); 3.79 (*s*, 2 H); 6.69 (*d*, *J* = 15.6, 1 H); 6.91 (*dd*, *J* = 14.6, 10.9, 1 H); 7.03 (*dd*, *J* = 15.6, 10.9, 1 H); 7.04 (*d*, *J* = 14.6, 1 H); 7.17–7.29 (*m*, 4 H); 7.34 (*t*, *J* = 7.6, 2 H); 7.46 (*d*, *J* = 7.6, 2 H); 7.61 (*d*, *J* = 7.6, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 15.2; 36.0; 125.8; 126.4 (2 C); 127.2; 127.5; 127.6; 128.6 (2 C); 129.4; 129.5; 130.4; 131.0; 133.1; 135.0; 136.3; 137.3. MS: 266 (100, M^+), 218 (37), 204 (22), 203 (23), 150 (25), 141 (14). HR-MS (APCI): 267.1200 ($[M+H]^+$, $C_{18}H_{19}S^+$; calc. 267.1208).

According to the procedure described above, *1-(methoxymethyl)-2-[4-phenylbuta-1,3-dien-1-yl]benzene* (**2b**), *1-(methoxymethyl)-2-[penta-1,3-dien-1-yl]benzene* (**2c**), *1-[5,5-dimethylhexa-1,3-dien-1-yl]-2-(methoxymethyl)benzene* (**2d**), and *methyl 5-[2-(methoxymethyl)phenyl]penta-2,4-dienoate* (**2e**) were synthesized by using the corresponding phosphonium salt instead of (cinnamyl)(triphenyl)phosphonium chloride used for the synthesis of **2a**.

1-(Methoxymethyl)-2-[4-phenylbuta-1,3-dien-1-yl]benzene (**2b**). Yield: 91%. As a 60:40 mixture (*Z,E*)-**2b**/(*E,E*)-**2b**.

*Data of (*Z,E*)-***2b***.* Pale-yellow oil. IR (film): 3026, 2924, 2866, 2819, 1090. ^{1}H-NMR (400 MHz, $CDCl_3$): 3.40 (*s*, 3 H); 4.47 (*s*, 2 H); 6.50 (*t*, *J* = 11.2, 1 H); 6.65 (*d*, *J* = 11.2, 1 H); 6.68 (*d*, *J* = 15.6, 1 H); 7.07 (*dd*, *J* = 15.6, 11.2, 1 H); 7.18–7.38 (*m*, 8 H); 7.42–7.45 (*m*, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 58.1; 72.5; 125.1; 126.4 (2 C); 127.2; 127.3; 127.5; 128.3; 128.4 (2 C); 128.4; 129.8; 131.1; 134.5; 136.1; 136.1; 137.1. MS: 250 (100, M^+), 218 (64), 217 (64), 215 (27), 205 (41), 203 (47), 159 (63), 146 (22), 144 (26), 134 (84), 128 (22), 121 (21), 116 (27), 115 (30). HR-MS (ESI): 273.1288, ($[M+Na]^+$, $C_{18}H_{18}NaO^+$; calc. 273.1255).

*Data of (*E,E*)-***2b***.* Colorless granules. M.p. 72.0° (hexane/AcOEt). IR (KBr): 3019, 2924, 2819, 1645, 1450, 1379, 1192, 1095. ^{1}H-NMR (400 MHz, $CDCl_3$): 3.41 (*s*, 3 H); 4.55 (*s*, 2 H); 6.68 (*d*, *J* = 15.5, 1 H); 6.86–7.04 (*m*, 3 H); 7.20–7.36 (*m*, 6 H); 7.43–7.46 (*m*, 2 H); 7.60–7.63 (*m*, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 58.0; 72.9; 125.4; 126.4 (2 C); 127.3; 127.6; 128.2; 128.6 (2 C); 129.4; 129.5; 129.5; 131.0; 133.0; 134.9; 136.5; 137.3. MS: 250 (100, M^+), 218 (46), 205 (30), 159 (47), 134 (68), 128 (12), 121 (16), 116 (19).

1-(Methoxymethyl)-2-[penta-1,3-dien-1-yl]benzene (**2c**). Yield: 85%. As a 50:50 mixture of (*Z,E*)-**2c**/(*E,E*)-**2c**.

*Data of (*Z,E*)-***2c***.* Pale-yellow oil. IR (film): 3018, 2922, 2819, 1645, 1446, 1375, 1194, 1097. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.74 (*d*, *J* = 6.9, 3 H); 3.38 (*s*, 3 H); 4.43 (*s*, 2 H); 5.85 (*dq*, *J* = 13.7, 6.9, 1 H); 6.23–6.37 (*m*, 2 H); 6.40 (*d*, *J* = 10.5, 1 H); 7.23–7.31 (*m*, 3 H); 7.38–7.41 (*m*, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 18.3; 58.2; 72.6; 125.3; 126.9; 127.1; 127.8; 128.1; 129.7; 131.2; 132.0; 135.9; 136.4. MS: 188 (37, M^+), 159 (45), 150 (45), 149 (73), 143 (40), 141 (85), 137 (23), 129 (84), 115 (74), 109 (22), 95 (33), 69 (100).

*Data of (*E,E*)-***2c***.* Colorless oil. IR (film): 3020, 2924, 2866, 2819, 1645, 1450, 1379, 1192, 1095. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.82 (*d* with fine coupling, *J* = 6.8, 3 H); 3.39 (*s*, 3 H); 4.50 (*s*, 2 H); 5.84 (*dq*, *J* = 13.7, 6.8, 1 H); 6.23–6.31 (*m*, 1 H); 6.64–6.74 (*m*, 2 H); 7.18 (*t* with fine coupling, *J* = 7.6, 1 H); 7.18 (*t* with fine coupling, *J* = 7.6, 1 H); 7.30 (*d* with fine coupling, *J* = 7.6, 1 H); 7.52 (*d* with fine coupling, *J* = 7.6, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 18.4; 58.0; 72.9; 125.2; 126.3; 126.8; 128.0; 129.2; 130.5; 131.2; 132.1; 134.6; 136.7. MS: 188 (57, M^+), 159 (52), 156 (60), 143 (47), 141 (100), 129 (95), 128 (88), 115 (74).

1-[5,5-Dimethylhexa-1,3-dien-1-yl]-2-(methoxymethyl)benzene (**2d**). Yield: 99%. As a 54:46 mixture (*Z,E*)-**2d**/(*E,E*)-**2d**.

*Data of (*Z,E*)-***2d***.* IR (film): 3026, 2958, 2866, 2820, 1457, 1362, 1194, 1099. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.01 (*s*, 9 H); 3.39 (*s*, 3 H); 4.44 (*s*, 2 H); 5.84–5.91 (*m*, 1 H); 6.25–6.32 (*m*, 2 H); 6.40–6.46 (*m*, 1 H); 7.23–7.35 (*m*, 3 H); 7.39–7.42 (*m*, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 29.4 (3 C); 33.3; 58.1; 72.5;

121.3; 125.6; 126.9; 127.1; 128.2; 129.5; 131.7; 135.9; 136.4, 148.3. MS: 230 (76, M^+), 198 (18), 183 (99), 173 (23), 168 (27), 159 (48), 155 (81), 146 (14), 143 (37), 141 (84), 128 (100), 116 (43), 115 (64), 99 (46).

*Data of (*E,E*)*-**2d**. Colorless oil. IR (film): 3024, 2957, 2866, 2819, 1640, 1457, 1362, 1194, 1099. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.08 (*s*, 9 H); 3.40 (*s*, 3 H); 4.52 (*s*, 2 H); 5.87 (*d*, *J* = 15.4, 1 H); 6.20 (*dd*, *J* = 15.4, 9.5, 1 H); 6.69 (*dd*, *J* = 15.4, 9.5, 1 H); 6.76 (*d*, *J* = 15.4, 1 H); 7.19 (*dd* with fine coupling, *J* = 7.6, 7.3, 1 H); 7.27 (*t* with fine coupling, *J* = 7.6, 1 H); 7.31 (*d* with fine coupling, *J* = 7.3, 1 H); 7.54 (*d*, *J* = 7.6, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 29.5 (3 C); 33.4; 58.0; 72.8; 125.3; 125.7; 126.8; 126.8; 128.0; 129.3; 131.8; 134.7; 136.9; 147.0. MS: 230 (6, M^+), 229 (24), 197 (45), 171 (21), 159 (16), 141 (62), 101 (100).

Methyl 5-[2-(Methoxymethyl)phenyl]penta-2,4-dienoate (**2e**): Yield: 67%. As a 17:83 mixture (*Z*,*E*)-**2e**/(*E*,*E*)-**2e**.

*Data of the 17:83 mixture of (*Z,E*)-***2e****/(*E,E*)-***2e***. Colorless oil. IR (film): 2988, 2948, 2822, 1714, 1627, 1623, 1436, 1311, 1268, 1243, 1163, 1140. ^{1}H-NMR (400 MHz, $CDCl_3$): 3.37 (*s*, 3 H × 0.17); 3.41 (*s*, 3 H × 0.83); 3.72 (*s*, 3 H × 0.17); 3.78 (*s*, 3 H × 0.83); 4.31 (*s*, 2 H × 0.17); 4.52 (*s*, 2 H × 0.83); 6.01 (*d*, *J* = 15.4, 1 H × 0.83); 6.03 (*d*, *J* = 15.4, 1 H × 0.17); 6.44 (*dd*, *J* = 11.5, 11.2, 1 H × 0.17); 6.84 (*dd*, *J* = 18.8, 11.2, 1 H × 0.83); 7.01 (*d*, *J* = 11.2, 1 H × 0.17); 7.22 – 7.42 (*m*, 4 H + 1 H × 0.17); 7.50 (*dd* with fine coupling, *J* = 15.4, 11.2, 1 H × 0.83); 7.61 – 7.63(*m*, 1 H × 0.83). ^{13}C-NMR (125 MHz, $CDCl_3$): 51.3; 58.0; 72.5 (0.17 C); 72.6 (0.83 C); 120.8 (0.83 C); 122.9 (0.17 C); 125.8 (0.83 C); 127.6 (0.17 C); 127.7 (0.83 C); 128.1 (0.17 C); 128.2 (0.83 C); 128.2 (0.17 C); 128.6; 129.6 (0.83 C); 129.9 (0.17 C); 135.0 (0.17 C); 135.1 (0.83 C); 135.8 (0.83 C); 136.1 (0.17 C); 136.2 (0.17 C); 037.3 (0.83 C); 140.4 (0.17 C); 144.9 (0.83 C); 167.2. MS: 232 (26, M^+), 200 (45), 185 (18), 168 (75), 158 (31), 141 (100), 129 (27), 115 (25).

*Base-Mediated Cyclization of (*Z,E*)-***2a***. Representative Procedure.* BuLi (1.60M in hexane, 1.71 ml, 2.74 mmol, 2.09 equiv.) was added to a soln. of ^{i}Pr$_2$NH (0.40 ml, 2.85 mmol, 2.20 equiv.) in dry THF (3 ml) under N_2 at r.t., and then the mixture was stirred for 30 min. Then, (*Z,E*)-**2a** (348 mg, 1.31 mmol) in dry THF (4 ml) was added dropwise at −78° for 20 min and stirred for 15 min. The mixture was poured into H_2O and extracted with AcOEt. The org. layer was washed with sat. aq. NaCl (3 ×), dried (anh. $MgSO_4$), and concentrated *in vacuo*. The residue was chromatographed over SiO_2 (*NH-DM1020*, *Fuji Silicia*; hexane) to give *(5*R*,6*R*)-6,9-dihydro-5-(methylsulfanyl)-6-phenyl-5*H*-benzo[7]annulene* (**4a**; 227 mg, 65%), *(5*R*,6*R*)-6,7-dihydro-5-(methylsulfanyl)-6-phenyl-5*H*-benzo[7]annulene* (**5a**; 36 mg, 10%), and *(1*R*,1a*R*,7b*R*)-1a,7b-dihydro-1-phenyl-1*H*-cyclopropa[*a*]naphthalene* (**6**; 51.2 mg, 18%).

Data of **4a**. Colorless granules. M.p. 70.0° (hexane). IR (KBr): 3013, 2913, 2857, 1450, 1488, 1450, 1179. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.96 (*s*, 3 H); 3.32 (*dd*, *J* = 17.9, 7.6, 1 H); 3.94 (*d*, *J* = 3.9 Hz, 1 H); 4.02 (*d* with fine coupling *J* = 3.9, 1 H); 4.40 (*d* with fine coupling, *J* = 17.9, 1 H); 5.55 – 5.60 (*m*, 1 H); 5.93 – 5.99 (*m*, 1 H); 6.55 (*d*, *J* = 7.3, 1 H); 6.87 – 6.93 (*m*, 3 H); 7.07 – 7.14 (*m*, 5 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 15.7; 35.0; 50.6; 59.2; 125.6; 126.5; 126.8; 127.0; 127.9 (2 C); 128.5 (2 C); 128.7; 129.8; 130.8; 136.7; 140.9; 142.3. MS: 266 (3, M^+), 219 (23), 218 (100), 217 (45), 215 (11), 203 (17), 202 (13), 91 (24). HR-MS (EI): 266.1087 (M^+, $C_{18}H_{18}S^+$; calc. 266.1129).

Data of **5a**. Pale-yellow oil. IR (film): 3059, 3022, 2909, 1601, 1492, 1447, 1182, 1032. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.95 (*s*, 3 H); 2.67 (*d* with fine coupling, *J* = 18.4, 1 H); 2.95 (*d* with fine coupling, *J* = 18.4, 1 H); 3.65 – 3.70 (*m*, 1 H); 4.11 (*d*, *J* = 6.0, 1 H); 6.12 (*d* with fine coupling, *J* = 11.9, 1 H); 6.58 (*d*, *J* = 11.9, 1 H); 6.92 (*d*, *J* = 7.6, 1 H); 6.97 – 7.10 (*m*, 2 H); 7.11 – 7.20 (*m*, 6 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 15.6; 32.6; 49.3; 58.0; 126.2; 126.3; 126.9; 127.0 (2 C); 128.1 (2 C); 130.4; 130.6; 131.1; 131.3; 136.2; 138.5; 144.4. MS: 266 (100, M^+), 219 (28), 218 (37), 215 (15), 205 (13), 204 (22), 203 (23), 202 (21), 150 (25), 115 (18), 91 (94). HR-MS (APCI): 267.1190 ($[M+H]^+$, $C_{18}H_{19}S^+$; calc. 267.1208).

Data of **6**. Colorless granules. M.p. 75.5° (hexane/AcOEt). IR (KBr): 3024, 1599, 1492, 1452. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.25 (*dd*, *J* = 4.4, 4.0, 1 H); 2.36 (*ddd*, *J* = 7.9, 4.6, 4.0, 1 H); 2.77 (*dd*, *J* = 7.9, 4.4, 1 H); 6.33 (*d*, *J* = 9.6, 1 H); 6.37 (*dd*, *J* = 9.6, 4.6, 1 H); 7.03 (*d* with fine coupling, *J* = 7.1, 2 H); 7.12 – 7.22 (*m*, 4 H); 7.28 – 7.37 (*m*, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 26.8; 29.2; 32.4; 124.2; 125.2(2 C); 125.6; 126.1; 127.3; 127.7; 127.8; 128.2; 128.4 (2 C); 130.6; 134.4; 142.7. MS: 218 (100, M^+), 202 (42), 156 (15), 141 (37), 128 (21), 115 (24) 97 (18). HR-EI-MS: 218.1085 (M^+, $C_{17}H_{14}^+$; calc. $C_{17}H_{14}$ 218.1096).

*Base-Mediated Cyclization of (*Z,E*)-***2b***.* According to the procedure for (*Z,E*)-**2a**, (*Z,E*)-**2b** was treated with LDA to give **6** (32%) and a 93:7 mixture **4b**/**5b** (57%), from which only **4b** was isolated by the further chromatographic purification.

Data of a 93:7 Mixture **4b**/**5b**. HR-EI-MS: 250.1324 (M^+, $C_{18}H_{18}O^+$; calc. 250.1358).

*Data of (5*R*,6*R*)-6,9-Dihydro-5-methoxy-6-phenyl-5*H*-benzo[7]annulene* (**4b**). Colorless oil. IR (film): 3021, 2929, 2877, 2821, 1088. ^{1}H-NMR (400 MHz, $CDCl_3$): 3.23 (*s*, 3 H); 3.40 (*dd*, *J* = 16.5, 6.3, 1 H); 3.77 (*dd* with fine coupling, *J* = 16.5, 4.8, 1 H); 3.82–3.89 (*m*, 1 H); 4.51 (*d*, *J* = 6.8, 1 H); 5.49 (*d* with fine coupling, *J* = 11.7, 1 H); 5.97 (*dddd*, *J* = 11.7, 6.3, 4.8, 2.0, 1 H); 6.89 (*d*, *J* = 7.4, 1 H); 7.03–7.23 (*m*, 8 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 33.6; 51.7; 57.2; 87.1; 125.8; 126.2; 126.4; 127.3; 127.9 (2 C); 128.4; 128.5; 128.9 (2 C); 129.9; 137.3; 140.9; 141.4. MS: 250 (14, M^+), 234 (11), 219 (14), 218 (57), 217 (42), 215 (18), 205 (21), 204 (15), 203 (26), 202 (24), 159 (16), 146 (15), 144 (10), 135 (13), 134 (100), 131 (11), 128 (11), 117 (10), 116 (15), 115 (17), 91 (32).

*Base-Mediated Cyclization of the Mixture (*Z,E*)-***2c***/(*E,E*)-***2c***.* According to the procedure for (*Z*,*E*)-**2c**, a 50:50 mixture (*Z*,*E*)-**2c**/(*E*,*E*)-**2c** was treated with LDA to give **4c**/**5c** (94:6; 170 mg, 34%) and **6c** (76:24 mixture *exo*-**6c**/*endo*-**6c**; 148 mg, 36%). These yields were based on (*Z*,*E*)-**2c**.

*Data of a Mixture (5*R*,6*S*)-6,9-Dihydro-5-methoxy-6-methyl-5*H*-benzo[7]annulene* (**4c**)*/(5*R*,6*S*)-6,7-dihydro-5-methoxy-6-methyl-5*H*-benzo[7]annulene* (**5c**) (94:6). Colorless oil. IR (film): 3014, 2960, 2928, 2913, 2872, 2821, 1489, 1453, 1371, 1141, 1271. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.89 (*d*, *J* = 7.1, 3 H, **5c**); 0.98 (*d*, *J* = 7.1, 3 H, **4c**); 2.01–2.08 (*m*, 1 H, **5c**); 2.59–2.68 (*m*, 1 H, **4c**); 3.24 (*dd*, *J* = 16.6, 6.3, 1 H, **4c**); 3.26 (*s*, 3 H, **5c**); 3.32 (*s*, 3 H, **4c**); 3.37–3.41 (*m*, 2 H, **5c**); 3.65 (*dd* with fine coupling, *J* = 16.6, 4.4, 1 H, **4c**); 4.01 (*d*, *J* = 7.2, 1 H, **5c**); 4.24 (*d*, *J* = 6.6, 1 H, **4c**); 5.35–5.42 (*m*, 1 H, **4c**); 5.73 (*ddd* with fine coupling, *J* = 11.7, 6.3, 4.4, 1 H, **4c**); 5.93–6.00 (*m*, 1 H, **5c**); 6.46 (*d* with fine coupling, *J* = 11.7, 1 H, **5c**); 7.06–7.09 (*m*, 1 H); 7.15–7.34 (*m*, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 17.4 (0.06 C); 18.7 (0.94 C); 32.4 (0.06 C); 33.5 (0.94 C); 38.7 (0.06 C); 39.2 (0.94 C); 57.1 (0.94 C); 57.2 (0.06 C); 87.2 (0.94 C); 87.6 (0.06 C); 124.4 (0.94 C); 125.9 (0.94 C); 126.1 (0.06 C); 127.2 (0.94 C); 128.1 (0.94 C); 128.6 (0.94 C); 129.0 (0.06 C); 129.6 (0.06 C); 130.3 (0.06 C); 131.0 (0.06 C); 132.9 (0.94 C); 128.0 (0.94 C); 141.3 (0.94 C). MS: 188 (4, M^+), 157 (20), 156 (77), 141 (100), 129 (46), 128 (57), 116 (37), 115 (42), 91 (15), 77 (12).

*Data of a Mixture of (1*R*)- and (1*S*)-1a,7b-Dihydro-1-methyl-1*H*-cyclopropa[*a*]naphthalene* (*exo*-**6c**/*endo*-**6c** 76:24): Colorless oil. IR (film): 3016, 2952, 2924, 2865, 1487, 1455, 1381, 1119, 1038. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.09 (*qt*, *J* = 6.0, 4.6, 1 H, *exo*-**6c**); 0.52 (*d*, *J* = 6.4, 3 H, *endo*-**6c**); 1.24 (*d*, *J* = 6.0, 3 H, *exo*-**6c**); 1.48 (*tq*, *J* = 8.7, 6.4, 1 H, *endo*-**6c**); 1.67 (*ddd*, *J* = 7.3, 5.0, 4.6, 1 H, *exo*-**6c**); 2.04 (*td*, *J* = 8.7, 5.0, 1 H, *endo*-**6c**); 2.11 (*dd*, *J* = 7.3, 4.6, 1 H, *exo*-**6c**); 2.45 (*t*, *J* = 8.7, 1 H, *endo*-**6c**); 5.96 (*dd*, *J* = 9.6, 5.0, 1 H, *endo*-**6c**); 6.18 (*d*, *J* = 9.6, 1 H, *exo*-**6c**); 6.24 (*dd*, *J* = 9.6, 5.0, 1 H, *exo*-**6c**); 6.43 (*d*, *J* = 9.6, 1 H, *endo*-**6c**); 7.03–7.18 (*m*, 3 H); 7.25 (*d*, *J* = 6.9, 1 H, *endo*-**6c**); 7.31 (*d*, *J* = 7.3, 1 H, *exo*-**6c**). ^{13}C-NMR (125 MHz, $CDCl_3$): 4.7 (0.24 C); 6.6 (0.24 C); 17.6 (0.76 C); 18.0 (0.76 C); 22.3 (0.24 C); 24.8 (0.24 C); 26.1 (0.76 C); 29.2 (0.76 C); 123.2 (0.76 C); 124.4 (0.24 C); 125.4 (0.76 C); 125.6 (0.24 C); 126.3 (0.24 C); 126.9 (0.76 C); 126.9 (0.24 C); 127.0 (0.24 C); 127.4 (0.76 C); 127.8 (0.76 C); 128.3 (0.76 C); 129.1 (0.24 C); 130.6 (0.76 C); 132.3(0.24 C); 132.7 (0.24 C); 135.0 (0.76 C). MS: 156 (M^+, 44), 155 (19), 153 (10), 142 (19), 141 (100), 129 (18), 128 (23), 115 (20).

*Base-Mediated Cyclization of the Mixture (*Z,E*)-***2d***/(*E,E*)-***2d***.* According to the procedure for (*Z*,*E*)-**2a**, a 54:46 mixture (*Z*,*E*)-**2d**/(*E*,*E*)-**2d** was treated with LDA to give **4d** in 54% yield.

*Data of (5*R*,6*R*)-6-(*tert*-Butyl)-6,9-dihydro-5-methoxy-5*H*-benzo[7]annulene* (**4d**). Colorless oil. IR (film): 3020, 2958, 2817, 1455, 1364, 1193, 1087, 1099. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.77 (*s*, 9 H); 2.56–2.60 (*m*, 1 H); 3.07 (*dd*, *J* = 17.7, 7.7, 1 H); 3.21 (*s*, 3 H); 3.95 (*dd* with fine coupling, *J* = 17.7, 6.2, 1 H); 4.40 (*d* with fine coupling, *J* = 4.2, 1 H); 5.58–5.65 (*m*, 1 H); 5.84–5.90 (*m*, 1 H); 7.04–7.21 (*m*, 4 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 28.5 (3 C); 33.1; 35.1; 54.0; 56.0; 85.4; 125.5; 126.4; 127.6; 127.7; 129.7; 130.6; 137.8; 141.4. MS: 199 (25, $[M-31]^+$), 188 (35), 187 (70), 169 (100), 159 (23), 156 (46), 155 (64), 141 (69), 131 (54), 129 (50), 128 (49), 116 (38), 115 (63).

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