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A Convenient Synthetic Method for Preparing 2,5-Disubstituted 1,6-Methano[10]annulenes from 1,6-Diacetylcyclohepta-1,3,5-triene

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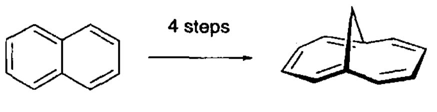
The reaction of 1,6-diacetylcyclohepta-1,3,5-triene with various Grignard reagents gave high yields of addition products **5**, which were treated with a catalytic amount of *p*-toluenesulfonic acid or pyridinium *p*-toluenesulfonate to afford 2,5-disubstituted 2,3-dihydro-1,6-methano[10]annulenes **6** via 1,6-bis(1-substituted vinyl)cyclohepta-1,3,5-trienes **8** and 2,5-disubstituted 3,4-dihydro-1,6-methano[10]annulenes **9**. On the other hand, reactions under more forcing conditions gave the rearrangement products: 4,7-disubstituted 1,2-benzocyclohepta-1,3-dienes **7**. The oxidation of **6** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone gave the 2,5-disubstituted 1,6-methano[10]annulens **4** in moderate-to-good yields. Conversion from **5** into **4** can be achieved by a one-flask procedure, providing a convenient synthetic method for preparing the title annulenes, particularly 2,5-diaryl ones. The reaction mechanism from **8** to **6**, **7**, and **9** is discussed on the basis of semiempirical molecular orbital calculations.

In 1964 Vogel and Roth first synthesized 1,6-methano-[10]annulene (**1**)[1] from naphtalene in 4 steps (Scheme 1).[2,3] The derivatization of **1** by an electrophilic substitution reaction has been extensively studied by Vogel, Effenberger, and Cerfontain et al., and the reactivity is highly advantageous to synthesize 2-substituted derivatives.[4—7] However, further electrophilic substitution of these derivatives usually gave a mixture of 2,5- and 2,7-ones, and limited examples of the selective subsititution leading to 2,5-disubstituted ones are known.[6] Later on, Vogel et al. developed an alternative synthetic route to **1** and its 3- and 3,4-substituted derivatives starting from 1,6-diacetylcyclohepta-1,3,5-triene (**2**), as depicted in Scheme 2.[8] In this method they first transformed **2** into 1,6-diformylcyclohepta-1,3,5-triene (**3**) and by the Wittig reactions those formyl groups were elongated to give halogenated divinylcycloheptatrienes, which were subjected to thermolysis to produce the annulenes via electrocyclization and subsequent dehydrohalogenation. Although this sequence provides an important synthetic route to the 3- and 3,4-substituted annulenes, the method is inefficient from the viewpoint of atom-economy,[9] i.e., it wastes two methyl carbon atoms of the acetyl groups in **2**. During the course of our program to synthesize π-conjugated oligomers and polymers having 2,5-diaryl-1,6-methano[10]annulene as a monomeric unit,[10] an efficient synthetic pathway to those anuulenes was required. We wish to report here on an atom-economical, convenient synthetic method for preparing the title 2,5-disubstituted 1,6-methano[10]annulenes **4** from **2**. We also discuss the mechanism for the formation of intermediates toward **4**.



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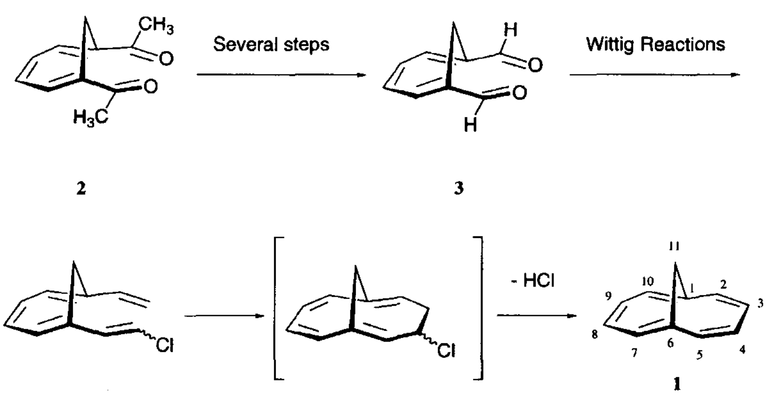
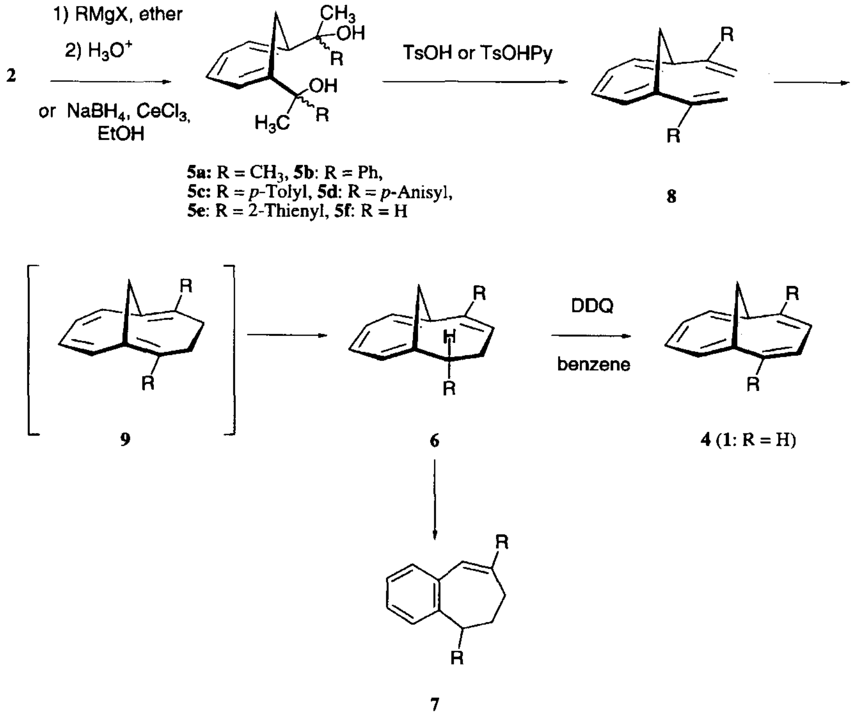
Scheme 1.

Results and Discussion

Synthesis of 2,5-Disubstituted 1,6-Methano[10]annulenes 4. Reactions of **2** with an excess of Grignard reagents, methyl, phenyl, *p*-tolyl, *p*-anisyl, and 2-thienylmagnesium compounds, gave high yields (81—96% yield) of the diols **5a**—**e** (Scheme 3).[11] The treatment of **5b**, **c**, and **e** with a catalytic amount of *p*-toluenesulfonic acid (*p*-TsOH) in refluxing benzene for 0.5—1.5 h gave 2,5-disubstituted 2,3-dihydro-1,6-methano[10]annulenes **6b**, **c**, and **e** in good-to-high yields and **5d** with pyridinium *p*-toluenesulfonate[12] (*p*-TsOHPy) in refluxing benzene for 20 h gave **6d** in high yield (Table 1). It should be pointed out that under more forcing conditions **5b**—**e** gave the rearranged products **7b**—**e** in moderate yields. On the other hand, the diol **5a** under the acidic reaction conditions afforded an unseparable mixture of **6a** and **7a**, accompanied by a substantial amount of unidentified products. It is naturally considered that these reactions are initiated by double dehydration to afford 1,6-bis(1-substituted vinyl)cyclohepta-1,3,5-trienes **8**, which undergo electrocyclization at the termini of their vinyl groups to give 2,5-disubstituted 3,4-dihydro-1,6-methano[10]annulenes **9**, as can be seen in the experiments by Vogel et al. A formal 1,9-hydrogen shift from the 3 to 5 position in **9** produces **6** (vide infra). Indeed, intermediates **8a**—**d** could be isolated



Scheme 2.



Scheme 3.

as a slightly unstable oil under milder acidic conditions,[13] such as with a catalytic amount of *p*-TsOH in benzene at room temperature or *p*-TsOHPy in refluxing benzene for a short reaction period, and be independently converted to **6** under the same acidic conditions. The formation of the rearranged product **7** is thought to be derived from **6** based on the reaction conditions; this was confirmed by an independent conversion of **6** into **7**. It was also found that this conversion dose not proceed without acid. Thus, the importance of the amount and kind of acid and the reaction temperature and period in the acid-catalyzed reaction from **5** to **6** to attain a good yield of **6** should be pointed out. It is worth noting that the dehydration of **5e** under mild acidic conditions afforded an unseparable mixture of **8e** and **9e**, whose structures were fully confirmed by spectral data of the mixture. Typical signals for the latter in the ^{1}H NMR spectrum are two doublets at δ = 2.37 and 3.53 with a coupling constant of 11.5 Hz for the bridge-head methylene protons and two doublet protons at δ = 2.78 and 3.05 with a coupling constant of 9.4 Hz for methylene protons at the 3 and 4 positions. Although the reason why only **5e** afforded a mixture of **8e** and **9e** in contrast to other cases is not yet clear, an observation of **9e** in this reaction strongly suggests that **6a**—**d** are also derived from **9a**—**d**, which were not detected in similar dehydration reactions. The oxidation of **6b**—**e** with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in refluxing benzene for 1 h gave **4b**—**e** in 60 to 97% yields, and a mixture containing **6a** was also oxidized to give **4a**[14] in 37% yield (Table 2).[15,16] We also found that conversion from **5** to **4** can be done by a one-flask procedure. For example, **5c** was dehydrated with 5% molar amounts of *p*-TsOH in refluxing benzene for 30 min. Then, 5% molar amounts of pyridine and an equimolar amount of DDQ were added to this reaction solution; this resulting mixture was refluxed for an additional 1 h. The solvent was evaporated and the residue was chromatographed with hexane as an eluent to give **4c** in 92% yield based on **5c** (Table 3).

The stereochemical relationship between the hydrogen at

Table 1. Reaction of the Diols **6** with Acids

Entry	Diol	Acid/Condition[a]	Product	Yield/%
1	**5a**	*p*-TsOH (10%)/r.t./5 h	**8a**	88
2	**5a**	*p*-TsOH (10%)/reflux/1 h	**6a**+**7a**[b]	—[b]
3	**5b**	*p*-TsOH (10%)/r.t./3 h	**8b**	76[c]
4	**5b**	*p*-TsOH (10%)/reflux/1 h	**6b**	74[d]
5	**5b**	*p*-TsOH (10%)/reflux/5 h	**7b**	56
6	**5c**	*p*-TsOH (10%)/r.t./0.5 h	**8c**	98
7	**5c**	*p*-TsOH (10%)/reflux/0.5 h	**6c**	94
8	**5c**	*p*-TsOH (10%)/reflux/20 h	**7c**	76
9	**5d**	*p*-TsOH•Py (5%)/reflux/1 h	**8d**	98
10	**5d**	*p*-TsOH•Py (5%)/reflux/20 h	**6d**	96
11	**5d**	*p*-TsOH (5%)/reflux/2 h	**7d**	89
12	**5e**	*p*-TsOH (5%)/r.t./1 h	**8e**+**9e**[e]	83
13	**5e**	*p*-TsOH (5%)/reflux/1 h	**6e**	95
14	**5e**	*p*-TsOH (5%)/reflux/3 h	**7e**	33

a) Benzene was used as solvent for all reactions. b) The ratio of **6a** to **7a** was determined to be 3:1 by ^{1}H NMR analysis which also revealed this mixture contained a substantial amount of unidentified products. c) A 12% yield of **6b** was obtained as a minor component. d) The 10% yield of **8b** was obtained as a minor component. e) The ratio of **8e** to **9e** was found to be 1:2 by ^{1}H NMR analysis.

Table 2. Results of DDQ Oxidation of **6** in Refluxing Benzene Producing **4**

Entry	Substrate	Yield of **4**[a] /%
1	**6a**[b]	37
2	**6b**	83
3	**6c**	92
4	**6d**	97
5	**6e**	60

a) Yields after silica-gel chromatographic purification. b) A mixture containing **6a** and **7a** was used.

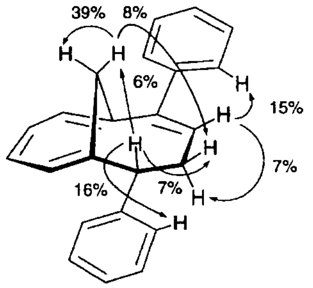


Fig. 1. Observed NOE for the compound **6b**.

the 2-position and the bridging methylene group in **6** was determined to be a syn configuration by NOE experiments, as shown in Fig. 1 as one example.

Attempts to prepare the parent 1,6-methano[10]annulene (**1**) by our method met with little success, as follows. The diol **5f**, prepared from **2** by NaBH$_4$ reduction in the presence of cerium(III) chloride in 91% yield, was dehydrated in the presence of a catalytic amount of *p*-TsOH in refluxing benzene for 1 h to give 1,6-divinylcyclohepta-1,3,5-triene **8f**[17] in 53% yield. Although the prolonged reaction time under the conditions did not show the formation of the desired **6f**, **8f** was further treated with *p*-TsOH in refluxing toluene for 3 h to give an intractable reaction mixture, the ^{1}H NMR spectrum of which showed the formation of **6f** as a minor product.[18] DDQ oxidation of this crude reaction mixture gave only a 4% yield of **1**, accompanied by several unidentified hydrocarbons.

Physical Properties of 2,5-Disubstituted 1,6-Methano-

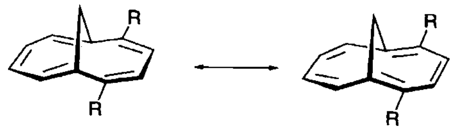
Table 3. Results of the One-Pot Procedure from **5** to **4**

Entry	Diol	Condition[a,b]	Yield of **4**[c] /%
1	**5a**	1) *p*-TsOH (10%)/reflux/3 h 2) Pyridine (10%), DDQ/reflux/1 h	19
2	**5b**	1) *p*-TsOH (10%)/reflux/1 h 2) Pyridine (10%), DDQ/reflux/1 h	84
3	**5c**	1) *p*-TsOH (5%)/reflux/0.5 h 2) Pyridine (5%), DDQ/reflux/1.5 h	92
4	**5d**	1) *p*-TsOH•Py (5%)/reflux/1 h 2) DDQ/reflux/1.5 h	96
5	**5e**	1) *p*-TsOH (10%)/reflux/0.5 h 2) DDQ/reflux/1 h	58

a) Benzene was used as solvent for all reactions. b) One molar amount of DDQ to **5** was used. c) Yields were after chromatographic purification.

[10]annulenes 4. All 2,5-disubstituted 1,6-methano[10]-annulenes **4a**—**e** prepared in this study were isolated as a yellow substance having their longest absorption maxima at 340—420 nm, as seen in previously known derivatives.[3,19] The NMR spectral data of **4a**—**e** and **1** are listed in Table 4. The number of ^{13}C NMR signals clearly shows a plane of symmetry through bridging methylene atoms and the middle between C3–C4 and C8–C9 in the structure of **4a**—**e**. The carbon signal assignment shown in the table was achieved by an analysis of the HMQC and HMBC spectra. Although bridge-carbon signals of **4a**—**e** and **1** were observed in a narrow range of 34.9—35.9 ppm, the proton signals were found to be affected by the substituents at the 2 and 5 positions. Substitution of two methyl groups at the 2 and 5 positions shifts one of the methylene protons oriented to the side of the substituents[20] to a slightly lower magnetic field and the other one to a higher field; the average shift value ($\delta_{av} = -0.45$) is same to that of **1**.[21] On the other hand, the aryl substitution shifts both protons appreciably to a lower field, particularly one oriented to the side of the substituents (to the side of 2 and 5 positions) by 0.67—0.85 ppm (Fig. 2). Although we hardly rationalize the effect of methyl groups on the chemical shift, the lower-field shift by aryl substituents might be attributable to deshielding of their anisotropical ring-current effect and also to a diminution of the diatropicity of the aryl-substituted seven-membered ring part derived from the contribution of the dimethylenecycloheptadiene structure A (Chart 1) because of conjugation between the diene part and the aryl groups.

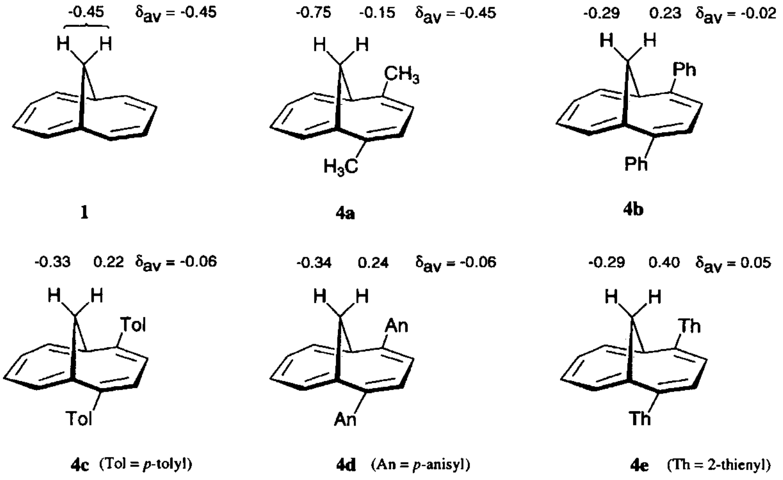
Reaction Mechanism on the Formation of 6, 7, and 9. In this section, we discuss the mechanistic courses of the formation of **6**, **7**, and **9** based on semiempirical molecular orbital calculations by the PM3 method. We chose the phenyl-substituted compounds as a model for calculations, since these reactions gave sufficient results. It is surprising that electrocyclization at the termini of the vinyl groups of **8** provides an efficient synthetic method for preparing the 1,6-methano[10]annulene carbon skeleton, as demonstrated by our and Vogel's works, because the feasibility of facing of the two slightly distant p-orbitals of the vinyl groups at the 1 and 6 positions[22] seems to be quite rare, and cycloheptatriens are known to undergo a relatively facile 1,5-hydrogen shift[23] and a methylene walk rearrangement.[24] For the thermal cyclization step of **8b** to **6b** we first evaluated two possible pathways by direct disrotatory 10π electrocyclization vs. stepwise 6π electrocyclization, a cycloheptatriene (CHT) to a norcaradiene (NCD) form, and a subsequent Cope rearrangement (divinylcyclopropane rearrangenment), as outlined in Scheme 4. The calculation results[25] of the ground states of **8b**, **9b**, and **10b** and the transition states[26,27] along the pathways clearly show that the latter stepwise route is favored over the former direct process (Fig. 3). The heats of reaction ($\Delta\Delta Hf$ = 14.8 kcal mol^{-1}, 1 cal mol^{-1} = 4.18 J mol^{-1}) for the process from **8b** to **10b** seem to be exaggerated compared with previous results by ab initio calculations of unsubstituted CHT and NCD,[28,29] and as a result activation enthalpies from **8b** to **TSa** should be similarly exaggerated. However, the relative difference in the activation enthalpies, obtained by calculations at this level, are valuable enough to evaluate the reaction course. Other possible reactions, such as a 1,5-hydrogen shift and a methylene walk rearrangement (1,5-sigmatropic rearrangement), neither of which was observed in the reaction of **8b**, were calculated to be less favorable than the electrocyclization based on their calculated activation enthalpies.[30]



A **B**

Chart 1.

Secondly, a concerted suprafacial 1,9-hydrogen shift, allowed by the Woodward–Hoffmann rule,[31] in **9b** was examined. For the two pathways in which a hydrogen atom migrates through the top (path a) and bottom (path b) sides[32] of p-orbital array, the transition states **TSd** and **e** were obtained (Fig. 4). Although the heats of formation of opti-



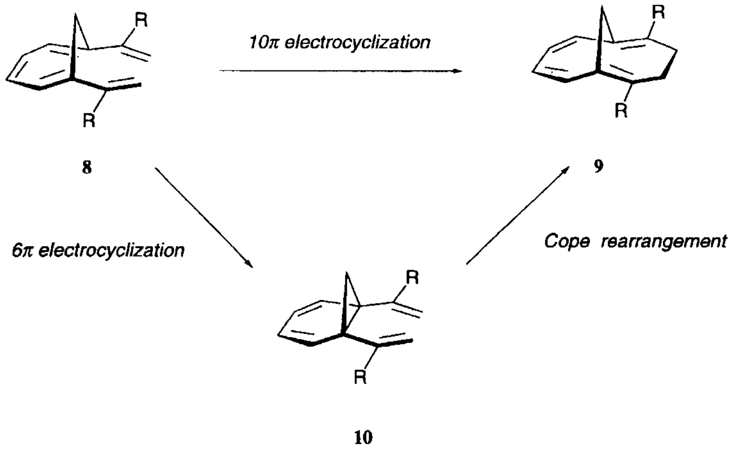
4c (Tol = *p*-tolyl) **4d** (An = *p*-anisyl) **4e** (Th = 2-thienyl)

Fig. 2. Chemical shift values (δ ppm) of the methylene protons of **1** and **4**.

Table 4. Spectral Data of **4a**—**e** and **1**

Compound	Bp or mp	IR/ν cm^{-1}	UV-vis (MeOH)/ λ/nm (log ε)	^{1}H NMR/δ/ppm (multiplicity, J in Hz)	^{13}C NMR/δ/ppm (J in Hz)
4a	Yellow oil	(film) 3035s, 2940s, 2860s, 1535m, 1447s, 1398w, 1374m, 1361m, 1254m, 1196m, 1126w, 1096w, 1027w, 992m, 904w, 815s, 759w, 723s, 635s, 484m	259 (4.63), 316 (3.70), 370 (2.25), 378(2.29), 388 (2.31), 392 (2.32), 396 (2.32), 402 (2.34), 4.12 (2.23)	−0.75 (11-H, d, J = 9.3 Hz), −0.15(11-H, dt, J = 9.3, 1.2 Hz), 2.55(CH_3,s), 7.19 —7.21(8,9-H, m), 7.37(3,4-H, s), 7.41(6,9-H, m),	18.9 (CH_3), 35.7(11-C), 116.1 (1,6-C), 125.6(7,10-C), 126.4 (8,9-C), 127.4(3,4-C), 136.2 (2,5-C)
4b	Yellow prisms, Mp 102—103 °C	(KBr) 3045m, 3010w, 2955w, 1590w, 1485m, 1445m, 1320w, 1300w, 1260w, 1180w, 1085w, 830m, 760s, 700s, 660m, 595w	219(3.40), 278 (3.60), 347(3.29)	−0.29(11-H, d, J = 9.3 Hz), 0.23 (11-H, dt, J = 9.3, 1.2 Hz), 7.19—7.21(8,9-H, m), 7.37(3,4-H, s), 7.41(6,9-H, m), 7.46—7.50(Ph,m), 7.16—7.38(Ph, m), 7.51—7.54(Ph, m)	35.9(11-C), 116.6(1,6-C), 125.9(3,4-C), 127.6(Ph), 128.3(8,9-C), 128.4(Ph), 128.9(7,10-C), 130.9(Ph), 139.9(Ph), 143.2(2,5-C)
4c	Yellow prisms, Mp 153—154 °C	(KBr) 3020m. 2913m, 1655w, 1560w, 1542w, 1506s, 1442, 1376w, 1181m, 1114m, 807s, 760m, 722m, 711m, 659m, 595w, 571w, 488m	219(3.47), 277 (3.60), 350(3.70)	−0.33(11-H, d, J = 9.3 Hz), 0.22(11-H, dt, J = 9.3, 1.2 Hz), 2.43(CH_3, s), 7.17(8,9-H, m), 7.21 (3,4-H, s), 7.28(tolyl, d, J = 7.8 Hz), 7.51(7,10-H, m),7.69(tolyl, d, J = 7.8 Hz)	21.2 (CH_3), 35.9(11-C), 116.8(1,6-C), 125.6(3,4-C), 128.2(8,9-C), 128.9 (7,10-C), 129.2(Tol), 130.8 (Tol), 137.3(Tol), 137.4 (Tol), 142.9(2,5-C)
4d	Yellow needles, Mp 146—147 °C	(KBr) 3015w, 2990w, 2940w, 2820w, 1600s, 1565w, 1500s, 1460m, 1435m,1280s, 1245vs, 1170s, 1110m, 1025s,840m, 810s, 760s, 710w, 705w, 660m, 505m	220sh(4.49), 292sh (4.52), 274(4.61), 358(4.37)	−0.34(11-H, d, J = 9.3 Hz), 0.24(11-H, d, J = 9.3 Hz), 3.88(OCH_3, s), 7.01(anisyl, dm, J = 8.8 Hz), 7.17(3,4-H, s), 7.18(8,9-H, m), 7.50(7,10-H, m), 7.73(anisyl, dm, J = 8.8 Hz)	35.9(11-C), 55.4 (OCH_3), 113.8(An), 117.1(1,6-C), 125.2(3,4-C), 128.2(8,9-C), 128.8(7,10-C), 132.0(An), 133.0(An), 142.3(2,5-C), 159.3(An).
4e	Yellow microcrystals, Mp 106—108 °C	(KBr) 3035w, 2939w, 1655w, 1500w, 1444m, 1425m, 1387w, 1261w, 1128w, 1065w, 1044w, 997w, 850s, 811s, 756m, 694s, 470m	219(4.35), 280 (4.39), 301sh (4.33), 378(4.31)	−0.29(11-H, d, J = 9.5 Hz), 0.40(11-H, dt, J = 9.3, 1.2 Hz), 7.15(8,9-H, m), 7.24(3,4-H, s), 7.26(8,9-H, m),7.36(thienyl, dd, J = 5.3, 1.1 Hz), 7.54(thienyl, dd, J = 3.5, 1.1 Hz), 7.77(7,10-H, m)	35.7(11-C), 117.9(1,6-C), 125.2(3,4-C), 126.4(Th), 127.2(Th), 127.9(Th), 128.4(8,9-C), 129.1 (7,10-C), 135.9, 143.5 (2,5-C)
1	Colorless crystals, Mp 28—29 °C[a] Bp 68—72 °C /1 Torr[c]	(film) 3040m, 2950m, 2925m, 1592w, 1461m, 1446m, 1247w, 1175w, 1089s, 832w, 756s, 627m, 601m, 474m[b]	254(4.46), 298 (3.60), 353(2.13), 360(2.12), 377sh (2.06), 385sh(1.98) 390sh(1.90),399 (1.81)[b]	−0.45(11-H, s), 7.10(3,4,8,9-H, m), 7.45 (2,5,7,10-H, m)[b]	34.9(11-C), 114.9(1,6-C), 126.2(3,4,8,9-C), 128.8 (2,5,7,10,-C)[b]

a) Taken from Ref. 3. b) Data obtained in this work. c) Taken from Ref. 2.



Scheme 4.

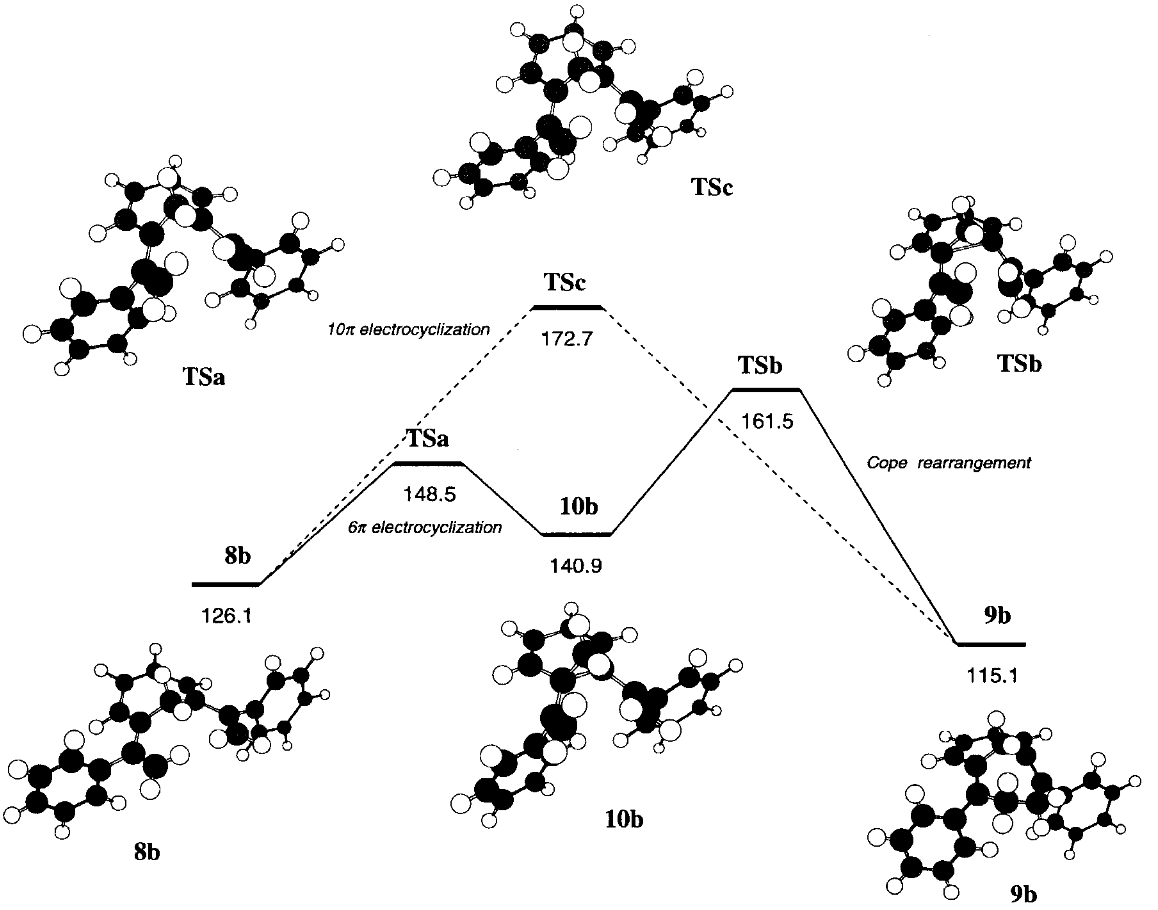


Fig. 3. Calculated energy (ΔH_f in kcal mol^{-1}) diagram for conversion of **8** into **9** and optimized structures (Chem 3D output).

mized **6b** and **6b′**, which has a hydrogen atom at the 5-position with an anti configuration to the methano bridge, by this PM3 method are slightly greater than that of **9b**, density functional theory calculations (BLYP/ 3-21G*) show that **6b** and **6b′** are more stable than **9b**.[33] The calculated enthalpies of activation, $\Delta H^{\ddagger}_{9b\to TSd}$ = 54.2 kcal mol^{-1} and $\Delta H^{\ddagger}_{9b\to TSe}$ = 76.2 kcal mol^{-1}, for both processes are far greater than that of the electrocyclization ($\Delta H^{\ddagger}_{8\to TSa}$ = 22.4 kcal mol^{-1} and $\Delta H^{\ddagger}_{10\to TSb}$ = 20.6 kcal mol^{-1}) and the process leading to **6b′** is more favorable than the former, contrary to the fact that both electrocyclization and hydrogen shift reactions proceed at similar temperatures and the reaction gave **6b**, which has a hydrogen atom at the 5-position with a *syn* configuration to the methano bridge. Thus, it is suggested that the hydogen shift may proceed via an ionic mechanism, depicted in Scheme 5, rather than in a concerted manner. Indeed, the transformation of **8** into **9** dose not proceed without acid (vide supra). Judging from the optimized structure

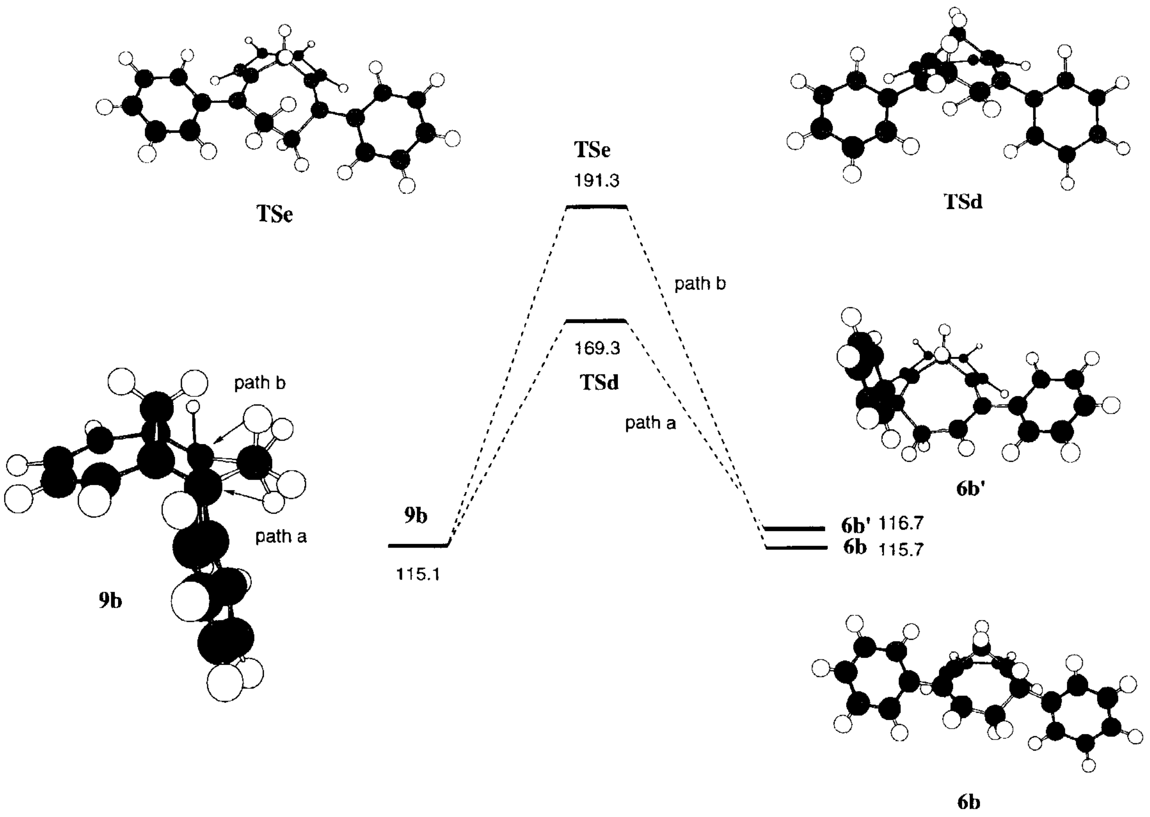
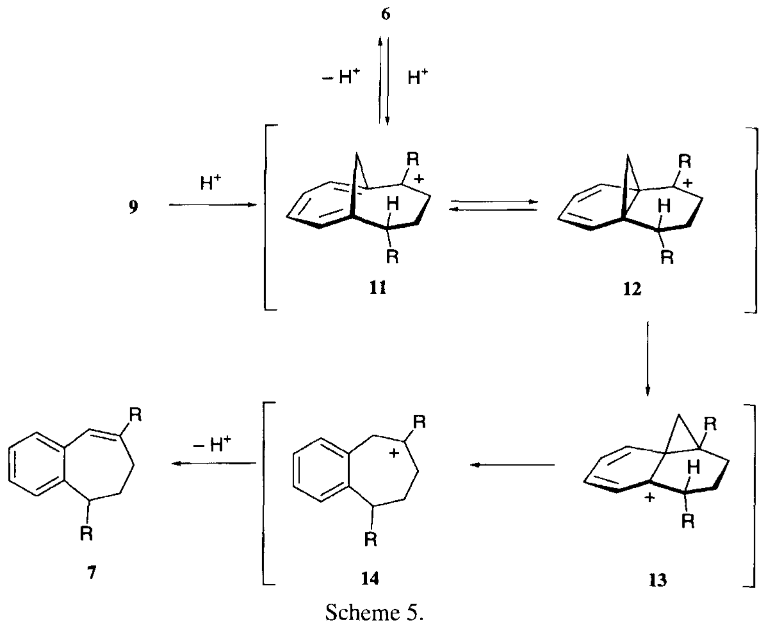


Fig. 4. Calculated energy (ΔH_f in kcal mol^{-1}) diagram for conversion of **9** into **6** and optimized structures (Chem 3D output).



Scheme 5.

of **9b**, the syn face of **9b** is sterically less crowded for an electrophilic attack (Fig. 5). Therefore, the stereoselective addition of proton at the first step in the formation of **6** may be due to the steric hindrance between the proton and an ortho hydrogen atom of the phenyl group.

The formation of **7** from either **6** or **9** can be rationalized by a sequence involving protonation, 6π-electrocyclization to the norcadiene form, 1,2-shift of the cyclopropane ring leading to a phenonium ion-type intermediate, cyclopropane ring-opening, and deprotonation, as shown in Scheme 5. Some examples of a similar rearrangement of a cyclopropane ring were observed in the bicyclo[4.4.1]undecane system.[34] The calculated heats of formation of cations **11b**, **12b**, **13b**, and **14b** show that the process from **11b** to **12b** is endothermic and that the others from **13b** to **14b** and from **12b** to **13b** are exothermic (Table 5). The driving force from **6b** to **7b** seems to be both a release of the strain in the congested ring systems in **11b**, **12b**, and **13b** based on their heats of for-

Table 5. Calculated Heats of Formation (kcal mol^{-1}) of Cationic Spieces **11b**—**14b** and Transition States, Heats of Reaction, Enthalpies of Activation by the PM3 Method

Cation	Heats of formation	Transition state	Heats of formation	Reaction	Heats of reaction	Process	Activation enthalpy
11b	279.1						
		$\mathbf{TSf}_{\mathbf{11b}\to\mathbf{12b}}$	293.7			**11b**→**TSf**	14.6
12b	286.4			**11b** → **12b**	7.3		
		$\mathbf{TSg}_{\mathbf{12b}\to\mathbf{13b}}$	307.6			**12b**→**TSg**	21.2
13b	272.0			**12b** → **13b**	−14.4		
		$\mathbf{TSh}_{\mathbf{13b}\to\mathbf{14b}}$	N.O.[a]				
14b	252.6			**13b** → **14b**	−19.4		

a) N. O. means not obtained.

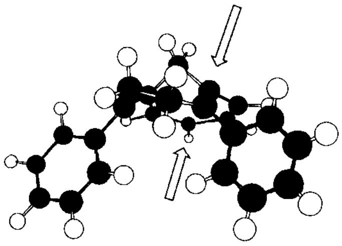


Fig. 5. Optimized structure of **9b** for electrophilic attack.

mation and aromatization forming a benzene ring. Although a transition state from **13b** to **14b** was not obtained by the calculations, the other calculated transition states from **11b** to **12b** and from **12b** to **13b** suggest that the latter step is rate-determining for the conversion of **6b** and **9b** to **7b**.

Summary

We have demonstrated an atom-economical, convenient synthetic method for preparing 2,5-disubstituted 1,6-methano[10]annulenes **4** from 1,6-diacetylcyclohepta-1,3,5-triene **2**. Although the presented method indicates a limitation for the preparation of the parent **1**, 2,5-diaryl-1,6-methano[10]annulenes were obtained in good yields by a two-flask procedure from **2**. Semiempirical molecular orbital calculations suggest that the transformation of **8** into **9** is mediated by a norcadiene form, and that the hydrogen shift from **9** leading to **6** proceeds by an ionic mechanism in which the proton addition occurs stereoselectively due to steric reasons.

Experimental

The melting points were measured on a Yanaco MP-3 and are uncorrected. IR spectra were recorded on JASCO-810 and Perkin-Elmer Spectrum RX I spectrometers. UV-vis spectra were measured on a Shimadzu UV-256FS spectrometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded in a $CDCl_3$ solution with tetramethylsilane as an internal standard on a JEOL α400. Mass spectra were measured on JEOL JMS-D-300 and GC-Mate mass spectrometers at an ionization energy of either 20 or 70 eV. Column chromatography was performed with Merck Kieselgel 60 Art 7734. 1,6-Diacetylcyclohepta-1,3,5-triene (**2**) was synthesized in two steps from cyclohepta-1,3,5-triene by the reported method.[35,36] Ethyl ether was purified just before use by distillation from calcium hydride. Semiempirical molecular orbital and density functional theory calculations were performed on an IBM RS/6000-397 computer by using the MOPAC program in the CAChe system (4.1.1 ver., CAChe Scientific, Inc.) and the DGauss program (Oxford Molecular Ltd.).

The Grignard Reaction of 2; A General Procedure: A solution of **2** (1.88 g, 10.0 mmol) in ethyl ether (15 ml) was added dropwise to a solution of Grignard reagent (40.0 mmol) in ethyl ether (50 ml), prepared from the corresponding halide compound and magnesium by a standard method, at 0 °C under a nitrogen atmosphere. After the addition, the resulting mixture was stirred at room temp for 2 h, and then poured into water (100 ml) and extracted with ethyl ether (3×50 ml). The combined organic layer was washed with brine and dried with $MgSO_4$. After evaporation of the solvent, the residual pale yellow oil was purified by chromatography (SiO_2, ethyl acetate/hexane) to give **5** as a pale yellow oil. This oil was used in the next reaction without further purification. Crystallization and subsequent recrystallization of **5b**—**e** from ethyl acetate–hexane gave pure *meso*-**5** in a 20—50% recovery yield.

1,6-Bis(1-hydroxy-1-methylethyl)cyclohepta-1,3,5-triene (5a): Colorless needles; mp 108—109 °C. IR (KBr) 3270s, 3220s, 3020w, 2990m, 2960s, 2860w, 2825w, 1480m, 1430m, 1380m, 1320w, 1240m, 1220w, 1160s, 1140s, 1095m, 955m, 930w, 910w, 870w, 845m, 740s, 660w cm^{-1}; ^{1}H NMR δ = 1.48 (12H, s, $-CH_3$), 2.66 (2H, s), 3.50 (2H, brs, -OH), 6.09 (2H, m), 6.50 (2H, m); ^{13}C NMR δ = 27.3, 30.2, 72.7, 119.8, 129.8, 144.0. UV/vis (MeOH) λ_{max} 211 (log ε = 3.69) nm, 278 (3.14); EIMS (70 eV) *m*/*z* (rel intensity) 208 (M$^+$; 12), 190 (73), 175 (28), 172 (63), 157 (38), 147 (32), 144 (22), 129 (22), 117 (22), 105 (100), 91 (15). HRMS: Found: *m*/*z* 208.1463. Calcd for $C_{13}H_{20}O_2$: M, 208.1463. Found: C, 74.76; H, 9.83%. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68%.

***meso*-1,6-Bis(α-hydroxy-α-methylbenzyl)cyclohepta-1,3,5-triene (5b):** Colorless needles, mp 156—158 °C. IR (KBr) 3271s, 3022s, 2978s, 2932m, 1599w, 1490s, 1445s, 1406m, 1367s, 1328m, 1211s, 1178m, 1123s, 1070s, 1027m, 936m, 910m, 855m, 763s,740s, 699s, 584m cm^{-1}; ^{1}H NMR δ = 1.51 (1H, d, *J* = 13.7 Hz), 1.68 (6H, s, $-CH_3$), 2.46 (1H, d, *J* = 13.7 Hz), 5.01 (2H, brs, -**OH**), 6.37 (2H, m), 6.59 (2H, m), 7.16 (2H, m, Ar-**H**), 7.25 (4H, m, Ar-**H**), 7.42 (4H, m, Ar-**H**); ^{13}C NMR δ = 29.9, 30.3, 77.4, 121.3, 125.1, 126.9, 128.1, 130.1, 143.0, 146.9. UV (MeOH) λ_{max} 280 (log ε = 3.07) nm; EIMS (70 eV) *m*/*z* (rel intensity) 332 (M$^+$; 3), 315 (15), 314 (52), 296 (51), 281 (30), 271 (68), 268 (36), 205 (61), 193 (95), 179 (54), 178 (73), 165 (36), 115 (98), 105 (100), 103 (83), 91 (86), 77 (71). Found: C, 83.36; H, 7.42%. Calcd for $C_{23}H_{24}O_2$: C, 83.10; H, 7.28%.

***meso*-1,6-Bis(α-hydroxy-α,1-dimethylbenzyl)cyclohepta-1,3,5-triene (5c):** Colorless needles; mp 149—152 °C. IR (KBr) 3309s, 3009m, 2978m, 2927m, 2364m, 2344m, 1509m, 1446m, 1405m, 1365m, 1328m, 1207m, 1179m, 1104s, 1081m, 1021m, 980m, 934m, 912m, 855m, 817s, 743s, 583m, 560m cm^{-1}; ^{1}H NMR δ = 1.53 (1H, d, *J* = 14.0 Hz), 1.66 (6H, s, $-CH_3$), 2.29 (6H, s, Ar-CH_3), 2.52 (1H, d, *J* = 14.0 Hz), 4.43 (2H, brs, -**OH**), 6.35 (2H, m), 6.57 (2H, m), 7.06 (4H, d, *J* = 8.3 Hz, Ar-**H**), 7.30

(4H, d, J = 8.3 Hz, Ar-**H**); ^{13}C NMR δ = 21.0, 29.8, 30.5, 77.3, 121.3, 125.1, 128.8, 130.0, 136.1, 143.2, 143.9. UV (MeOH) λ_{max} 261sh (log ε = 3.67) nm, 266sh, (3.74), 273 (3.78), 285sh (3.75); EIMS (20 eV) *m*/*z* (rel intensity) 360 (M$^+$; 0.4), 342 (25), 324 (72), 309 (31), 299 (26), 296 (41), 219 (61), 217 (30), 207 (66), 192 (36), 178 (20), 165 (18), 129 (21), 119 (65), 117 (100), 115 (86), 105 (50), 91 (61), 77 (13), 65 (15). Found: C, 83.35; H, 8.06%. Calcd for $C_{25}H_{28}O_2$: C, 83.29; H, 7.83%.

***meso*-1,6-Bis(α-hydroxy-4-methoxy-α-methylbenzyl)cyclohepta-1,3,5-triene (5d):** Colorless needles; mp 129—131 °C. IR (KBr) 3317s, 3036w, 3015w, 2980m, 2932m, 2835m, 2049w, 1891w, 1608s, 1581w, 1508s, 1442s, 1399m, 1369m, 1333m, 1298s, 1245s, 1173s, 1121m, 1102s, 1072m, 1060m, 1030s, 982w, 933w, 907s, 876w, 858m, 830s, 799m, 757s, 587m, 570m, 522m cm^{-1}; ^{1}H NMR δ = 1.32 (1H, d, J = 13.2 Hz), 1.57 (6H, s, –C**H**$_3$), 2.40 (1H, d, J = 13.2 Hz), 3.73 (6H, s, –OC**H**$_3$), 4.82 (2H, brs, –O**H**), 6.34 (2H, m), 6.56 (2H, m), 6.82 (4H, d, J = 8.8 Hz, Ar-**H**), 7.29 (4H, d, J = 8.8 Hz, Ar-**H**); ^{13}C NMR δ = 30.5, 30.8, 55.8, 77.4, 114.2, 121.9, 127.3, 130.8, 140.6, 144.5, 159.3. UV (MeOH) λ_{max} 223 (log ε = 3.32) nm, 276 (2.97), 283 (2.94); EIMS (20 eV) *m*/*z* (rel intensity) 393 (M$^+$+1; 0.1), 356 (56), 341 (12), 331 (15), 328 (31), 248 (15), 235 (31), 223 (28), 178 (14), 165 (12), 151 (6), 135 (32), 133 (100), 121 (45), 115 (27), 91 (13), 77 (17). Found: C, 76.60; H, 7.15%. Calcd for $C_{25}H_{28}O_4$: C, 76.50; H, 7.19%.

***meso*-1,6-Bis{1-hydroxy-1-(2-thienyl)ethyl)}cyclohepta-1,3,5-triene (5e):** Pale yellow needles; mp 149—152 °C. IR (KBr) 3275s, 3014m, 2976m, 1793w, 1719w, 1654w, 1623w, 1526w, 1431m, 1370s, 1323m, 1286m, 1230s, 1170m, 1116s, 1071m, 1055m, 1026m, 984m, 937m, 908m, 875m, 855m, 828m, 803w, 750s, 703s, 611m, 520m cm^{-1}; ^{1}H NMR δ = 1.81 (6H, s, –C**H**$_3$), 1.89 (1H, d, J = 13.4 Hz), 2.93 (1H, dm, J = 13.4 Hz), 4.82 (2H, brs, –O**H**), 6.28 (2H, m), 6.56 (2H, m), 6.88 (4H, m, Ar-**H**), 7.15 (2H, dd, J = 4.4, 2.0 Hz, Ar-**H**); ^{13}C NMR δ = 28.8, 30.9, 76.0, 121.6, 123.1, 124.1, 126.7, 130.2, 142.2, 152.9. UV (MeOH) λ_{max} 235 (log ε = 4.24) nm, 280 (3.79); EIMS (70 eV) *m*/*z* (rel intensity) 344 (M$^+$; 0.2), 356 (56), 226 (14), 293 (27), 283 (29), 280 (39), 260 (15), 259 (16), 224 (21), 224 (21), 223 (23), 211 (55), 199 (35), 198 (21), 197 (23), 184 (30), 178 (18), 165 (33), 152 (14), 139 (13), 127 (14), 115 (42), 109 (100), 97 (36), 77 (17), 65 (29). Found: C, 66.27; H, 5.80%. Calcd for $C_{19}H_{20}O_2S_2$: C, 66.25; H, 5.85%.

The Sodium Borohydride-Cerium Chloride Reduction of 2: A *meso*- and *dl*-Mixture of 1,6-Bis(1-hydroxyethyl)cyclohepta-1,3,5-triene (5f): To a solution of sodium borohydride (378 mg, 10.0 mmol) at 0 °C was added 4.93g (20.0 mmol) of cerium chloride, followed by the dropwise addition of a solution **2** (1.88 g, 10.0 mmol) in ethanol (20 ml). After being stirred at room temp for 30 min, the resulting mixture was poured into water (100 ml) and extracted with ethyl ether (3×50 ml). The combined organic layer was washed with brine and dried with $MgSO_4$. After evaporation of the solvent, the residual pale yellow oil was purified by chromatography (SiO_2, ethyl acetate/hexane = 1/1) to give **5f** as a colorless oil: IR (film) 3338s, 3013w, 2973s, 2930w, 2879w, 1632w, 1451m, 1368s, 1306s, 1174m, 1138m, 1066s, 1004m, 892s, 740s cm^{-1}; ^{1}H NMR δ = 1.40 (6H×0.55, d, J = 6.5 Hz, –C**H**$_3$), 1.42 (6H×0.45, d, J = 6.5 Hz, –C**H**$_3$), 2.19 (1H×0.45, d, J = 12.7 Hz), 2.50 (s, 2H×0.55), 2.79 (1H×0.45, d, J = 12.7 Hz), 4.39 (2H, brs, –O**H**), 4.450 (2H×0.45, q, J = 6.5 Hz, –C**H**–OH), 4.454 (2H×0.55, q, J = 6.5 Hz, –C**H**–OH), 6.10 (2H, m), 6.48 (2H, m); ^{13}C NMR δ = 22.2, 22.5, 26.8, 29.1, 70.8, 71.3, 120.9, 121.4, 128.3, 129.7, 140.2, 140.4. UV/vis (MeOH) λ_{max} 275 (log ε = 3.58) nm; EIMS (70 eV) *m*/*z* (rel intensity) 180 (M$^+$; 6), 162 (14), 119 (51), 91 (100), 77 (13).

1,6-Bis{1-(3,5-dinitrobenzoyloxy)ethyl}cyclohepta-1,3,5-triene: Yellow leaflets; mp 142—144 °C. Found: C, 52.82; H, 3.52; N, 9.83%. Calcd for $C_{25}H_{20}N_4O_{12}$: C, 52.82; H, 3.55; N, 9.86%.

2,5-Disubstituted 2,3-Dihydro-1,6-methano[10]annulenes (6b—e): A General Procedure: A solution of **5b—e** (20.0 mmol) and *p*-TsOH monohydrate (180 mg, 1.00 mmol) or *p*-TsOHPy (253 mg, 1.00 mmol) in benzene (10 ml) was refluxed for an appropriate time. The reaction mixture was washed with water (2×50 ml) and brine. After drying with anhydrous magnesium sulfate, evaporation gave a slightly brown crude oil, which was chromatographed (SiO_2, benzene/hexane) to give **5b—e**. In a similar manner **6** was obtained by the reaction of **8**.

2,5-Diphenyl-2,3-dihydro-1,6-methano[10]annulene (6b): A yellow oil; IR (film) 3025s, 2927m, 2360m, 1600w, 1493s, 1444m, 1075w, 755s, 699s cm^{-1}; ^{1}H NMR δ = 0.76 (1H, d, J = 9.3 Hz, H-11), 2.50 (1H, m, H-4), 3.16 (1H, m, H-4), 3.71 (1H, d, J = 9.3 Hz, H-11), 4.23 (1H, m, H-5), 5.56 (1H, dd, J = 7.1, 4.4 Hz, H-3), 5.66 (1H, d, J = 4.2 Hz, H-10), 6.17 (1H, d, J = 4.9 Hz, H-7), 6.63 (2H, m, H-8, 9), 6.85 (2H, m, Ar-**H**), 7.16—7.38 (6H, m, Ar-**H**), 7.49—7.52 (2H, m, Ar-**H**); ^{13}C NMR δ = 35.9, 37.4, 47.0, 108.6, 117.7, 120.8, 121.1, 121.6, 126.4, 126.5, 127.3, 128.0, 128.1, 128.2, 128.3, 128.8, 140.8, 144.2, 144.5. UV/vis (MeOH) λ_{max} 236 (log ε = 4.49) nm, 321 (3.83); EIMS (70 eV) *m*/*z* (rel intensity) 296 (M$^+$; 29), 268 (19), 205 (37), 193 (25), 192 (13), 191 (14), 178 (22), 115 (25), 105 (100), 103 (34), 91 (26), 77 (69). HRMS: Found: *m*/*z* 296.1590. Calcd for $C_{23}H_{20}$: M, 296.1565.

2,5-Di-*p*-tolyl-2,3-dihydro-1,6-methano[10]annulene (6c): Yellow needles; mp 95—96 °C. IR (KBr) 3010m, 2927m, 1655w, 1638w, 1616w, 1542w, 1510s, 1438m, 1319w, 1201w, 1112m, 1018w, 899w, 871w, 842m, 808s, 782m, 758s, 742s, 718m, 606w, 501m cm^{-1}; ^{1}H NMR δ = 0.75 (1H, d, J = 9.0 Hz, H-11), 2.29 (3H, s, –C**H**$_3$), 2.38 (3H, s, –C**H**$_3$), 2.46 (1H, ddd, J = 16.4, 6.8, 5.0 Hz, H-4), 3.11 (1H, ddd, J = 16.4, 7.0, 4.6 Hz, H-4), 3.69 (1H, d, J = 9.0 Hz, H-11), 4.18 (1H, t-like, J = 4.4 Hz, H-5), 5.54 (1H, dd, J = 7.0, 4.6 Hz, H-3), 5.67 (1H, d-like, J = 4.2 Hz, H-7), 6.16 (1H, d, J = 5.1 Hz, H-10), 6.63 (2H, m, H-8, 9), 6.75 (2H, d, J = 8.1 Hz, Ar-**H**), 7.02 (2H, d, J = 8.3 Hz, Ar-**H**), 7.17 (2H, d, J = 8.3 Hz, Ar-**H**), 7.40 (2H, d, J = 8.3 Hz, Ar-**H**); ^{13}C NMR δ = 21.0, 21.2, 36.1, 37.7, 46.6, 109.2, 118.4, 120.2, 120.9, 121.3, 126.5, 127.8, 127.9, 128.7, 128.8, 128.9, 135.8, 137.0, 137.9, 141.2, 144.3. UV/vis (MeOH) λ_{max} 248 (log ε = 4.31) nm, 300sh (3.63); EIMS (70 eV) *m*/*z* (rel intensity) 324 (M$^+$; 53), 220 (29), 219 (100), 217 (23), 204 (24), 105 (37). Found: C, 92.61; H, 7.46%. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.79%.

2,5-Di-*p*-anisyl-2,3-dihydro-1,6-methano[10]annulene (6d): Yellow needles; mp 106—107 °C. IR (KBr) 3000m, 2950w, 2900w, 1605m, 1501m, 1452m, 1238s, 1168s, 1030s, 816s, 743m cm^{-1}; ^{1}H NMR δ = 0.74 (1H, d, J = 9.1 Hz, H-11), 2.44 (1H, ddd, J = 16.6, 6.8, 5.2 Hz, H-4), 3.11 (1H, ddd, J = 16.6, 5.2, 4.6 Hz, H-4), 3.69 (1H, d, J = 9.1 Hz, H-11), 3.76 (3H, s, –OC**H**$_3$), 3.84 (3H, s, –OC**H**$_3$), 4.18 (1H, t, J = 5.2 Hz, H-5), 5.50 (1H, dd, J = 6.8, 4.6 Hz, H-3), 5.67 (1H, m, H-7), 6.17 (1H, m, H-10), 6.65 (2H, m, H-8,9), 6.75 (4H, m, Ar-**H**), 6.90 (2H, d, J = 8.8 Hz, Ar-**H**), 7.36 (2H, d, J = 8.8 Hz, Ar-**H**); ^{13}C NMR δ = 36.2, 37.9, 46.3, 55.2, 55.3, 110.3, 113.5, 113.6, 119.5, 119.6, 120.8, 121.2, 126.6, 128.91, 128.93, 129.0, 133.3, 136.4, 143.9, 158.0, 159.0. UV/vis (MeOH) λ_{max} 226sh (log ε = 4.42) nm, 259 (4.35), 286sh (3.95); EIMS (70 eV) *m*/*z* (rel intensity) 356 (M$^+$; 71), 341(12), 248 (15), 235 (84), 222 (20), 220 (17), 203 (13), 185 (21), 178 (14), 165 (12), 133 (100), 91 (13), 77 (9). Found: C, 83.96; H, 6.94%. Calcd for $C_{25}H_{24}O_2$: C, 84.24; H, 6.79%.

2,5-Di(2-thieny)-2,3-dihydro-1,6-methano[10]annulene (6e): A yellow oil; IR (film) 3103m, 3069m, 3016s, 2927s, 1575w, 1545w, 1481m, 1435s, 1375w, 1320m, 1223s, 1093w, 1076m, 1042m, 902w, 879w, 840s, 743s, 694s, 648m, 605w cm^{-1}; ^{1}H NMR δ = 1.05 (1H, d, J = 9.5 Hz, H-11), 2.34 (1H, ddd, J = 15.7, 8.8, 5.1 Hz, H-4), 2.87 (1H, ddd, J = 15.7, 5.9, 5.2 Hz, H-4), 3.46 (1H, d, J = 9.5 Hz, H-11), 4.29 (1H, dd, J = 8.8, 5.2 Hz, H-5), 5.87 (1H, d, J = 5.1 Hz, H-7), 5.88 (1H, dd, J = 5.9, 5.1 Hz, H-5), 6.26 (1H, d, J = 5.9 Hz, H-10), 6.67 (1H, m, H-8), 6.67 (1H, m, H-9), 6.81 (1H, dd, J = 3.4, 1.1 Hz, Ar-**H**), 6.93 (1H, dd, J = 5.1, 3.4 Hz, Ar-**H**), 7.03 (1H, dd, J = 5.1, 3.4 Hz, Ar-**H**), 7.14 (1H, dd, J = 5.1, 1.1 Hz, Ar-**H**), 7.21 (1H, dd, J = 5.1, 1.1 Hz, Ar-**H**), 7.29 (1H, dd, J = 3.4, 1.1 Hz, Ar-**H**); ^{13}C NMR δ = 37.2, 40.4, 43.3, 112.5, 119.1, 120.1 (2C), 122.8, 123.6, 124.4, 125.1, 126.3, 127.3, 127.8, 129.1, 139.5, 143.7, 145.9. UV/vis (MeOH) $\lambda_{\max}$ 226 (log ε = 3.87) nm, 270 (3.87), 299sh (3.65), 317sh (3.42); EIMS (70 eV) m/z (rel intensity) 308 (M$^+$; 100), 293 (14), 280 (13), 260 (10), 259 (10), 224 (22), 223 (17), 211 (92), 198 (24), 197 (22), 178 (31), 165 (24), 161 (14), 152 (15), 115 (17), 111 (10), 109 (12), 97 (43), 77 (10). HRMS: Found: m/z 308.0694. Calcd for $C_{19}H_{16}S_2$: M, 308.0683.

3,4-Disubstituted 1,2-Benzocyclohepta-1,3-diene 7 from 5: A solution of **5** (1.00 mmol) and p-TsOH monohydrate (0.05 or 0.10 mmol) in 15 ml of benzene was refluxed for 1—2.5 h. The reaction mixture was cooled to room temp and diluted with 20 ml of benzene, which was washed with a saturated $NaHCO_3$ solution (30 ml) and brine, and then dried with $MgSO_4$. The solvent was removed under reduced pressure and the residual oil was purified by chromatograpy to give **7b**—**e**. In a similar manner, **7** was obtained by the reaction of **8**.

1,5-Diphenyl-3,4-benzocyclohepta-1,3-diene (7b): A colorless prisms; mp 108—110 °C. IR (KBr) 3027m, 2951m, 2854m, 1594m, 1491s, 1447s, 1159w, 1025w, 857w, 755s, 738s, 700s cm^{-1}; ^{1}H NMR δ = 2.42—2.52 (3H, m), 2.69 (1H, m), 4.39 (1H, dm, J = 8.1 Hz), 6.82 (1H, s), 6.94 (1H, dm, J = 7.6 Hz), 7.08 (1H, tm, J = 7.6 Hz), 7.14 (2H, dm, J = 8.4 Hz), 7.16—7.38 (8H, m), 7.43 (2H, dm, J = 8.4 Hz); ^{13}C NMR δ = 30.9, 33.8, 49.6, 126.1 (2C), 126.3, 126.6, 127.1, 128.27, 128.32, 128.5, 129.4, 129.5, 131.8, 136.6, 142.8, 143.0, 143.6, 144.5. UV/vis (MeOH) $\lambda_{\max}$ 285 (log ε = 4.43) nm; EIMS (70 eV) m/z (rel intensity) 296 (M$^+$; 74), 281(14), 268 (50), 205 (100), 192 (16), 178 (20), 115 (15), 91 (31), 77 (13). Found: C, 93.16; H, 6.88%. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80%.

1,5-Di-*p*-tolyl-3,4-benzocyclohepta-1,3-diene (7c): A pale yellow oil; IR (film) 3020s, 2919s, 2859s, 1901w, 1794w, 1731w, 1596w, 1567w, 1512s, 1490m, 1443s, 1378m, 1312w, 1286w, 1212w, 1187m, 1114m, 1039m, 1020m, 945m, 894m, 808s, 781m, 754s, 627w, 583w, 544m, 522m cm^{-1}; ^{1}H NMR δ = 2.31 (3H, s), 2.34 (3H, s), 2.35—2.52 (3H, m), 2.68 (1H, m), 4.33 (1H, dm, J = 7.8 Hz), 6.81 (1H, s), 6.92 (1H, dm, J = 7.7 Hz), 7.04—7.11 (5H, m), 7.14 (2H, dm, J = 8.3 Hz), 7.19 (1H, tm, J = 7.7 Hz), 7.29 (1H, d, J = 7.7 Hz), 7.35 (2H, dm, J = 8.3 Hz); ^{13}C NMR δ = 21.0, 21.1, 30.8, 34.1, 49.2, 126.0, 126.1, 126.5, 128.5, 128.6, 128.9, 129.0, 129.4, 131.6, 135.6, 136.7, 136.8, 140.6, 141.5, 142.8, 143.0. UV/vis (MeOH) $\lambda_{\max}$ 214 (log ε = 3.40) nm, 222sh (3.35), 287 (3.29), 400 (1.97); EIMS (70 eV) m/z (rel intensity) 324 (M$^+$; 73), 309 (18), 296 (65), 232 (15), 219 (100), 218 (30), 217 (28), 204 (26), 192 (14), 178 (15), 119 (14), 117 (20), 105 (44), 91 (21), 77 (11). HRMS: Found: m/z 324.1888. Calcd for $C_{25}H_{24}$: M, 324.1878.

1,5-Di-*p*-anisyl-3,4-benzocyclohepta-1,3-diene (7d): A pale yellow oil. IR (film) 2999w, 2953m, 2930m, 2834m, 2059w, 1886w, 1735w, 1658w, 1607s, 1582w, 1510s, 1463m, 1442m, 1397w, 1354w, 1281m, 1247s, 1179s, 1112m, 1035s, 949w, 894w, 828s, 783w, 758m, 585w, 567w, 548w, 530w cm^{-1}; ^{1}H NMR δ = 2.45 (3H, m), 2.68 (1H, m), 3.79 (3H, s), 3.82 (3H, s), 4.31 (1H, m), 6.78 (1H, m), 6.83 (2H, dm, J = 8.8 Hz), 6.88 (2H, dm, J = 8.8 Hz), 6.93 (1H, dm, J = 7.5 Hz), 7.07 (2H, dm, J = 8.8 Hz), 7.08 (1H, td, J = 7.6, 1.3 Hz), 7.18 (1H, td, J = 7.6, 1.3 Hz), 7.29 (1H, dm, J = 7.6 Hz), 7.40 (2H, dm, J = 8.8 Hz); ^{13}C NMR δ = 30.8, 34.2, 48.7, 55.2, 55.3, 113.6, 113.7, 126.1, 126.4, 127.2, 128.0, 129.4, 129.5, 131.5, 135.8, 136.8, 136.9, 142.3, 143.1, 157.9, 158.9. UV/vis (MeOH) $\lambda_{\max}$ 225sh (log ε = 4.37) nm, 287 (4.33); EIMS (70 eV) m/z (rel intensity) 356 (M$^+$; 100), 342 (16), 328 (76), 248 (31), 235 (79), 203 (16), 178 (7), 165 (11), 133 (27), 121 (59), 91 (11),77 (10). HRMS: Found: m/z 356.1781. Calcd for $C_{25}H_{24}O_2$: M, 356.1776.

1,5-Di(2-thienyl)-3,4-benzocyclohepta-1,3-diene (7e): A greenish-yellow oil; IR (film) 3104w, 3068m, 3016w, 2923m, 1490m, 1442m, 1237m, 1043w, 908m, 844m, 822m, 733s, 696s, 517w cm^{-1}; ^{1}H NMR δ = 2.55 (3H, m), 2.81 (1H, m), 4.59 (1H, t, J = 6.9 Hz), 6.67 (1H, dm, J = 3.4 Hz), 6.91 (1H, dd, J = 5.0, 3.4 Hz), 6.98 (1H, dd, J = 7.5, 1.2 Hz), 7.03 (1H, s), 7.04 (1H, dm, J = 7.5 Hz), 7.09 (1H, dd, J = 3.7, 1.0 Hz), 7.12 (1H, dd, J = 7.5, 1.2 Hz), 7.16 (1H, dd, J = 5.0, 1.0 Hz), 7.17 (1H, dd, J = 5.0, 1.0 Hz), 7.23 (1H, dt, J = 7.5, 1.2 Hz), 7.29 (1H, dd, J = 7.5, 1.2 Hz); ^{13}C NMR δ = 30.1, 35.0, 44.7, 123.1, 123.7, 124.1, 125.1, 126.6, 126.8, 126.9, 127.0, 127.6, 129.2, 131.6, 135.7, 135.8, 142.5, 146.7, 147.5. UV/vis (MeOH) $\lambda_{\max}$ 234 (log ε = 4.32) nm, 305sh (4.35), 316 (4.42), 321sh (4.39); EIMS (70 eV) m/z (rel intensity): 308 (M$^+$; 100), 280 (54), 224 (29), 220 (21), 211 (86), 198 (18), 197 (16), 184 (16), 178 (26), 165 (21), 115 (16), 109 (18), 97 (33). HRMS: Found: m/z 308.0694. Calcd for $C_{19}H_{16}S_2$: M, 308.0683.

Oxidative Transformation of 6 into 2,5-Disubstituted 1,6-Methano[10]annulenes 4: General Procedure: A solution of **6** (1.00 mmol) and DDQ (1.00 mmol) in 15 mL of benzene was refluxed for 1 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by chromatograpy to give **4**. The yields of **4** are shown in Table 2, and some physical properties are listed in Table 4.

2,5-Diphenyl-1,6-methano[10]annulene (4b): EIMS (70 eV) m/z (rel intensity) 294 (M$^+$; 25), 293(100), 292 (43), 278 (41), 277 (29), 264 (21), 262 (17), 252 (19), 238 (16), 216 (48), 215 (29), 214 (77), 202 (23), 201 (78), 188 (26), 165 (20), 148 (23), 139 (20), 138 (23), 121 (19), 115 (17), 91 (63), 77 (20). Found: C, 94.05; H, 6.29%. Calcd for $C_{23}H_{18}$: C, 93.84; H, 6.16%.

2,5-Di-*p*-tolyl-1,6-methano[10]annulene (4c): EIMS (70 eV) m/z (rel intensity) 322 (M$^+$; 100), 306 (51), 292 (28), 291 (17), 288 (17), 230 (23), 228 (32), 216 (27), 214 (66), 149 (20), 105 (30), 91 (9). Found: C, 92.99; H, 6.97%. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88%.

2,5-Di-*p*-anisyl-1,6-methano[10]annulene (4d): EIMS (70 eV) m/z (rel intensity) 354 (M$^+$; 100), 339 (13), 323 (12), 247 (6), 245 (8), 215 (6), 149 (2), 121 (8). Found: C, 85.04; H, 6.34%. Calcd for $C_{25}H_{22}O_2$: C, 85.75; H, 6.22%.

2,5-Di(2-thienyl)-1,6-methano[10]annulene (4e): EIMS (70 eV) m/z (rel intensity) 306 (M$^+$; 100), 273 (27), 272 (142), 271 (19), 258 (15), 247 (11), 245 (10), 221 (26), 189 (10), 97 (22). Found: C, 74.51; H, 4.73%. Calcd for $C_{19}H_{14}S_2$: C, 74.47; H, 4.60%.

1,6-Bis(1-substituted vinyl)cyclo-1,3,5-triene 8 from the Diol 5 with *p*-Toluenesulfonic Acid; A General Procedure: A solution of **5** (1.00 mmol) and p-TsOH monohydrate (0.05 mmol) in 15 ml of benzene was stirred at room temp for 30 min. The reaction mixture was then diluted with benzene (25 ml) and washed with an aqueous saturated solution of $NaHCO_3$ and brine and dried with

$MgSO_4$. After evaporation of the solvent under reduced pressure, the residual oil was purified by chromatography to give **8a**, **b**, **c** and a mixture of **8e** and **9e**.

1,6-Di(1-methylvinyl)cyclohepta-1,3,5-triene (8a): A pale yellow oil; IR (film) 3090w, 3010m, 2960m, 1613m, 1590m, 1440m, 1370m, 1285w, 1120w, 880m, 740s cm^{-1}; ^{1}H NMR δ = 1.98 (6H, s), 2.66 (2H, s), 5.10 (2H,brs), 5.43 (2H, brs), 6.37 (2H, m), 6.66 (2H, m); ^{13}C NMR δ = 21.8, 29.7, 113.7, 122.8, 130.5, 134.1, 142.1. UV/vis (MeOH) $\lambda_{\max}$ 240 ($\log \varepsilon$ = 4.50) nm, 246 (4.56), 320 (3.66); EIMS (70 eV) m/z (rel intensity) 172 (M$^+$; 88), 157 (65), 142 (72), 129 (100). HRMS: Found: m/z 172.1243. Calcd for $C_{13}H_{16}$: M, 172.1252.

1,6-Bis(1-phenylvinyl)cyclohepta-1,3,5-triene (8b): A pale yellow oil; IR (film) 3023m, 2900w, 1599w, 1574w, 1492m, 1445m, 1300w, 1072w, 1027w, 895m, 776s, 700s cm^{-1}; ^{1}H NMR δ = 2.76 (2H, s), 5.22 (2H, d, J = 1.0 Hz), 5.39 (2H, d, J = 1.0 Hz), 6.16 (2H, m), 6.56 (2H, m), 7.23—7.33 (10H, m); ^{13}C NMR δ = 32.9, 115.3, 125.9, 127.4, 127.9, 128.2, 128.9, 130.4, 133.9, 149.9. UV/vis (MeOH) $\lambda_{\max}$ 229 ($\log \varepsilon$ = 4.99) nm, 236 (5.00), 323 (4.35); EIMS (70 eV) m/z (rel intensity) 296 (M$^+$; 47), 268 (11), 205 (100), 192 (26), 178 (21), 115 (24), 105 (21), 103 (16), 91 (36), 77 (19). HRMS: Found: m/z 296.1565. Calcd for $C_{23}H_{20}$: M, 296.1531.

1,6-Bis{1-(*p*-tolyl)vinyl}cyclohepta-1,3,5-triene (8c): A pale yellow oil; IR (film) 3087m, 3022s, 2920s, 1906w, 1797w, 1654w, 1608m, 1584m, 1510s, 1446m, 1299m, 1228w, 1182m, 1078m, 1038w, 1020m, 892s, 825s, 749s, 678m, 630w, 602m, 584w cm^{-1}; ^{1}H NMR δ = 2.35 (6H, s), 2.74 (2H, s), 5.19 (2H, d, J = 1.2 Hz), 5.35 (2H, d, J = 1.2 Hz), 6.16 (2H, m), 6.57 (2H, m), 7.12 (4H, d, J = 8.2 Hz), 7.17 (4H, d, J = 8.2 Hz); ^{13}C NMR δ = 21.1, 33.1, 114.9, 125.7, 128.5, 128.7, 130.3, 134.0, 137.1, 138.6, 149.8. UV/vis (MeOH) $\lambda_{\max}$ 212sh ($\log \varepsilon$ = 4.23) nm, 236 (4.18), 320 (3.81); EIMS (70 eV) m/z (rel intensity) 324 (M$^+$; 84), 309 (25), 296 (50), 219 (75), 217 (34), 207 (51), 192 (31), 178 (19), 165 (19), 139 (14), 129 (20), 119 (56), 117 (100), 115 (87), 105 (49), 91 (59), 78 (18), 65 (17). HRMS: Found: m/z 324.1906. Calcd for $C_{25}H_{24}$: M, 324.1878.

A 1:2 Mixture of 1,6-Bis{1-(2-thienyl)vinyl}cyclohepta-1,3,5-triene (8e) and 2,5-Bis(2-thienyl)-3,4-dihydro-1,6-methano[10]annulene (9e): A yellow microcrystals; mp 82—85 °C. IR (KBr) 3088m, 3005w, 2927w, 1486w, 1424w, 1360w, 1248w, 1224w, 1204w, 1051w, 985w, 831m, 696s, 649m cm^{-1}; ^{1}H NMR δ = 2.37 (1H$\times$0.33, d, J = 11.5 Hz), 2.78 (2H$\times$0.33, d, J = 9.4 Hz), 2.84 (2H$\times$0.67, s), 3.05 (2H$\times$0.33, d, J = 9.4 Hz), 3.53 (1H$\times$0.33, d, J = 11.5 Hz), 5.27 (1H$\times$0.67, d, J = 0.8 Hz), 5.39 (1H$\times$0.67, d, J = 0.8 Hz), 6.07 (2H$\times$0.33, m), 6.17 (2H$\times$0.67, dd, J = 3.9, 2.5 Hz), 6.40 (2H$\times$0.67, m), 6.65 (2H$\times$0.67, m), 6.93—6.97 (6H$\times$0.33 and 4H$\times$0.67, m), 7.16 (2H$\times$0.33, dd, J = 5.1, 1.2 Hz), 7.22 (2H$\times$0.67, dd, J = 5.0, 1.3 Hz); ^{13}C NMR δ = 30.0, 34.4, 36.0, 115.4, 119.7, 123.5, 124.6, 124.9, 125.5, 125.8, 126.3, 126.6, 127.1, 130.6, 130.7, 133.3, 135.4, 142.9, 143.7, 145.9. UV/vis (MeOH) $\lambda_{\max}$ 226 ($\log \varepsilon$ = 4.13) nm, 241sh (4.06), 289 (3.99), 416 (3.59); EIMS (70 eV) m/z (rel intensity) 308 (M$^+$; 37), 293 (9), 280 (38), 260 (15), 259 (11), 224 (19), 223 (21), 211 (51), 199 (19), 198 (17), 197 (18), 184 (18), 179 (9), 165 (29), 152 (10), 139 (9), 115 (39), 111 (18), 109 (100), 97 (29), 77 (11), 65 (33). Found: C, 73.76; H, 5.35%. Calcd for $C_{19}H_{16}S_2$: C, 73.98; H, 5.23%.

1,6-Bis{1-(*p*-anisyl)vinyl}cyclohepta-1,3,5-triene (8d): A solution of **5e** (393 mg, 1.00 mmol) and *p*-TsOHPy (13 mg, 0.05 mmol) in 15 ml of benzene was refluxed for 1 h. The reaction mixture was diluted with 15 ml of benzene and washed with water and brine. After drying with $MgSO_4$, evaporation under reduced pressure gave a brown oil, which was purified by SiO_2 chromatography (ethyl acetate/hexane = 1/9) to give **8e** as an yellow oil (345 mg, 97%). IR (film) 3090w, 3003w, 2954w, 2932w, 2835w, 2055w, 1891w, 1733w, 1608s, 1509s, 1462w, 1441w, 1287m, 1247s, 1176s, 1110w, 1034s, 893w, 836s, 783w, 750m, 661m, 626w, 602w, 585w, 524w cm^{-1}; ^{1}H NMR δ = 2.74 (2H, s), 3.81 (6H, s), 5.17 (2H, d, J = 1.2 Hz), 5.32 (2H, d, J = 1.2 Hz), 6.18 (2H, m), 6.59 (2H, m), 6.85 (4H, d, J = 8.8 Hz), 7.20 (4H, d, J = 8.8 Hz); ^{13}C NMR δ = 33.3, 55.3, 113.4, 114.5, 125.6, 129.7, 130.3, 133.9, 134.2, 149.5, 159.0. UV/vis (MeOH) $\lambda_{\max}$ 226 ($\log \varepsilon$ = 4.39) nm, 248sh (4.38), 2.42 (4.42), 255sh (4.30), 260sh (4.25), 321 (3.71); EIMS (70 eV) m/z (rel intensity): 356 (M$^+$; 62), 342 (11), 328 (36), 248 (17), 235 (37), 248 (17), 235 (37), 178 (13), 165 (11), 133 (100), 121 (35), 115 (27), 91 (11), 77 (14). HRMS: Found: m/z 356.1773. Calcd for $C_{25}H_{24}O_2$: M, 356.1776.

1,6-Divinylcyclohepta-1,3,5-triene (8f):[17] A solution of **5f** (720 mg, 4.00 mmol) and *p*-TsOH monohydrate (38 mg, 0.20 mmol) in 15 ml of benzene was refluxed for 1 h. The reaction mixture was diluted with 15 ml of benzene and washed with an aqueous saturated solution of $NaHCO_3$ and brine and dried with $MgSO_4$. After evaporation of the solvent under reduced pressure, the residual oil was purified by SiO_2 chromatography (hexane) to give **8f** as an air-sensitive pale yellow oil (305 mg, 53%). IR (film) 3091w, 3007m, 1618m, 1588m, 1446m, 1413w, 1306w, 1062w, 988s, 895s, 858m, 741s cm^{-1}; ^{1}H NMR δ = 2.59 (2H, s), 5.14 (2H, d, J = 10.7 Hz), 5.53 (2H, d, J = 17.6 Hz), 6.25 (2H, m), 6.54 (2H, dd, J = 17.6, 10.7 Hz), 6.61 (2H, m); ^{13}C NMR δ = 25.2, 113.2, 127.2, 130.3, 132.0, 137.8. UV/vis (hexane) $\lambda_{\max}$ 238 ($\log \varepsilon$ = 4.55) nm, 245 (4.65), 329 (3.71); EIMS (70 eV) m/z (rel intensity) 144 (M$^+$; 13), 143 (11), 129 (39), 111 (20), 110 (11), 109 (11), 101 (11), 99 (12), 98 (23), 97 (34), 87 (17), 81 (30), 79 (10), 73 (85), 71 (51), 69 (68), 57 (100), 56 (38), 55 (99). HRMS: Found: m/z 144.0965. Calcd for $C_{11}H_{12}$: M, 144.0939.

2,5-Dimethyl-1,6-methano[10]annulene (4a):[5] A solution of **8a** (172 mg, 1.00 mmol) and *p*-TsOH (19 mg, 0.10 mmol) in 10 ml of benzene was refluxed for 3 h. Then, DDQ (227 mg, 1.00 mmol) was added to the reaction mixture, which was refluxed for an additional 1 h. The resulting mixture was concentrated under reduced pressure and the residual oil, partly solids, was purified by SiO_2 chromatography to give **4a** (63 mg, 37%) as a pale yellow oil. EIMS (70 eV) m/z (rel intensity) 170 (M$^+$; 38), 155 (100), 154 (14), 153 (24), 152 (16), 141 (9), 129 (13), 128 (19), 127 (10), 115 (20). HRMS: Found: m/z 170.1103. Calcd for $C_{13}H_{14}$: M, 170.1095.

1,6-Methano[10]annulene 1 from 8f:[1] A solution of **8f** (1.00 mmol) and *p*-TsOH monohydrate (18 mg, 0.10 mmol) in 15 ml of toluene was refluxed for 4 h. Then, DDQ (227 mg, 1.00 mmol) was added to the reaction mixture, which was refluxed for an additional 2 h. The resulting mixture was concentrated under reduced pressure and the residual oil, partly solids, was purified by SiO_2 chromatography (hexane) to give **1** (5.7 mg, 4%) as a pale yellow oil.

A One-Flask Procedure of Preparation of 2,5-Disubstituted 1,6-Methano[10]annulenes (4b, c, d, and e) from the Diol (5b, c, d, and e): A solution of **5** (1.00 mmol) and *p*-TsOH monohydrate in 8 ml of benzene was refluxed for an appropriate time, shown in Table 3. Then, pyridine (a molar equivalent to *p*-TsOH) and DDQ (227 mg, 1.00 mmol) was added to the reaction mixture, which was refluxed for 1 h. The resulting mixture was concentrated under reduced pressure and the residual oil, partly solids, was purified by SiO_2 chromatography (hexane) to give **4b**, **c**, **d**, and **e**.

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11 All of the diols having asymmetric carbons were obtained as a mixture of *meso*- and *dl*-compounds. Repeated crystallization of the crude products of **5b**—**e** gave the pure *meso*-diols, but the *dl*-diols were not obtained in pure form in any case so far.

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13 M. Oda et al. reported that reactions of 1-(cyclohepta-1,3,5-trien-1-yl)-1-phenylalkanols with acids, such as trifluoroacetic acid or zinc chloride, gave the cyclization products, dihydrobenz[*a*]-azulenes, as a major product. In the case of 1-(cyclohepta-1,3,5-trien-1-yl)-1-phenylpentanol, brief acid treatment gave the dehydration product in addition to cyclized dihydrobenz[*a*]azulenes. See: K. Mizumoto, K. Okada, and M. Oda, *Tetrahedron Lett.*, **28**, 2999 (1984).

14 By Effenberger et al. **4a** had been synthesized as a mixture of **4a** and 2,7-dimethyl derivative which has not been separated in pure form yet; see Ref. 5.

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16 Although no change was observed on heating **8** in benzene without acid, reaction of **8** with DDQ in the absence of acid also gave **4**, suggesting that **9** can also be dehydrogenated to produce **4**. However, the yields of **4** by this method were found to be less than those under the conditions from **5** with acid except a case of a mixture of **8e** and **9e**, probably because of formation of byproducts which are assumed to be Diels–Alder type adducts between **8** and DDQ.

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BLYP/3-21G* calculations are as follows: −883.853010 for **9b**, −883.863364 for **6b**, and −883.861240 for **6b′**.

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