Thermolytic Behavior of 4-Fold Bridged *syn*-Tricyclo[4.2.0.0^{2,5}]octa-3,7-dienes

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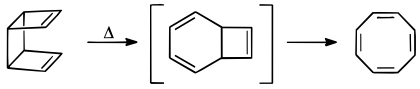
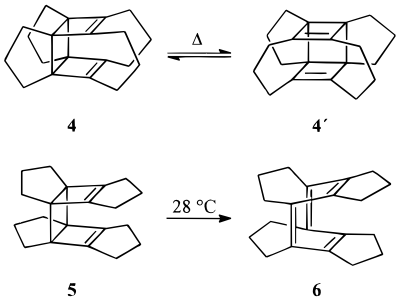
The syntheses of the 4-fold-bridged compounds *syn*-1,2,3,4,5,6,7,8,9,10,11,12-dodecahydro-8b,12b-butanobenzo[3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2-*e*]biphenylene (**7**), *syn*-1,4,5,8,9,12-hexahydro-8b,12b-(but-3-eno)benzo[3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2-*e*]biphenylene (**8**), and 2,3,4,5,6,7,8,-9,10,11,12,13,14,15-tetradecahydro-10b,15b-pentano-1*H*-cyclobuta[1″,2″:2,3;3″,4″:3′,4′]dicyclobuta[1,2:3,4:1′,2′]triscycloheptene (**9**) have been achieved starting from the cyclic diynes **10**−**12**. Heating **7** and **8** at 200 °C without solvent leads to 1,2,3,4,5,6,7,8,9,10,11,12-dodecahydro-8b,12b-butanobenzo[3,4]cyclobuta[1,2-*l*]phenanthrene (**18**) and 1,4,5,8,9,12-hexahydro-8b,12b-(but-3-eno)benzo[3,4]cyclobuta[1,2-*l*]phenanthrene (**19**). Both systems contain a bridged bicyclo[4.2.0]octa-2,4,7-triene skeleton. The thermolysis of **9** yields ($\Delta^{5a,5b;10a,11;11a,16a;17,17a}$)-2,3,4,5,6,7,8,9,10,12,13,14,15,16-tetradecahydro-11,17-pentano-1*H*-triscyclohepta[*a,c,f*]cyclooctene (**20**), a 4-fold-bridged cyclooctatetraene derivative. Treatment of **8** with DDQ leads to the dehydrogenation products **21** and **22**. The different behavior in the thermolysis of **7** and **8** as compared to **9** is ascribed to the different lengths of the bridges.

syn-Tricyclo[4.2.0.0^{2,5}]octa-3,7-diene (**1**) and most of its alkyl derivatives react similarly under thermolytic conditions. The parent system rearranges to cyclooctatetraene (**3**) when heated (Scheme 1). Bicyclo[4.2.0]octa-2,4,7-triene (**2**) has been formulated as an intermediate.[1] A radical-mediated bond reorganization process has been discussed as an alternative to disrotatory ring opening of one cyclobutene unit, because the latter is a thermally "forbidden" process.[2] When heated, the 1,3,5,7- and 1,2,4,7-tetraalkyl-substituted (alkyl = *tert*-butyl, isopropyl, *n*-butyl) derivatives of **1** reacted analogously.[3] An exception to this behavior was reported for the thermolysis of *syn*- and *anti*-octamethyltricyclo[4.2.0.0^{2,5}]octa-3,7-diene.[4] Our interest in this chemistry arose when we investigated the thermolysis of the 4-fold-bridged *syn*-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene derivatives **4** and **5**, obtained from cyclodeca-1,6-diyne by a metal-template synthesis.[5] In the case of **4**, a degenerate Cope rearrangement was observed.[5] The free enthalpy of activation of this process was estimated to be 71−76 kJ/mol. The close proximity of the double bonds in **4**, forced by the bridges, was made responsible for the different behavior of **4** as compared to **1**. The isomer **5** rearranges already at room temperature to the bridged cyclooctatetraene derivative **6** (Scheme 2).[5] In this paper, we report the synthesis and reactivity of the congeners of **4** and **5**: *syn*-1,2,3,4,5,6,7,8,9,10,11,12-dodecahydro-8b,12b-butanobenzo[3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2-*e*]biphenylene (**7**), *syn*-1,4,5,8,9,12-hexahydro-8b,12b-(but-3-eno)benzo[3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2-*e*]biphenylene (**8**), and 2,3,4,5,6,7,8,-9,10,11,12,13,14,15-tetradecahydro-10b,15b-pentano-1*H*-cyclobuta[1″,2″:2,3; 3″,4″:3′,4′]dicyclobuta[1,2:3,4:1′,2′]triscycloheptene (**9**).

Scheme 1



Scheme 2



Preparation of 7−9. To prepare **7**−**9**, we made use

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1997.

(1) (a) Frey, H. M.; Martin, H.-D.; Hekman, M. *J. Chem. Soc., Chem. Commun.* **1975**, 204−205. (b) Case, R. S.; Dewar, M. J. S.; Kirschner, S.; Pettit, R.; Slegeir, W. *J. Am. Chem. Soc.* **1974**, *96*, 7581−7582. Hassenrück, K.; Martin, H.-D.; Walsh, R. *Chem. Rev.* **1989**, *89*, 1125−1146.

(2) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1970.

(3) Boussie, T. R.; Streitwieser, A. *J. Org. Chem.* **1993**, *58*, 2377−2380.

(4) The thermolysis of *syn*- and *anti*-octamethyltricyclo[4.2.0.0^{2,5}]octa-3,7-diene gave rise to products with the bicyclo[3.3.0]octadiene skeleton: Criegee, R.; Louis, G. *Chem. Ber.* **1957**, *90*, 417−424. Criegee, R.; Wirth, W.-D.; Engel, W.; Brune, H. A. *Chem. Ber.* **1963**, *96*, 2230−2237. Bollinger, J. M.; Olah, G. A. *J. Am. Chem. Soc.* **1969**, *91*, 3380−3382. Askani, R.; Wieduwilt, M. *Chem. Ber.* **1976**, *109*, 1887−1897. Criegee, R.; Schröder, G. *Liebigs Ann. Chem.* **1959**, *623*, 1−8. Criegee, R.; Schröder, G.; Maier, G.; Fischer, H.-G. *Chem. Ber.* **1960**, *93*, 1553−1559. Criegee, R.; Askani, R. *Angew. Chem.* **1968**, *80*, 531−532; *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 537−538.

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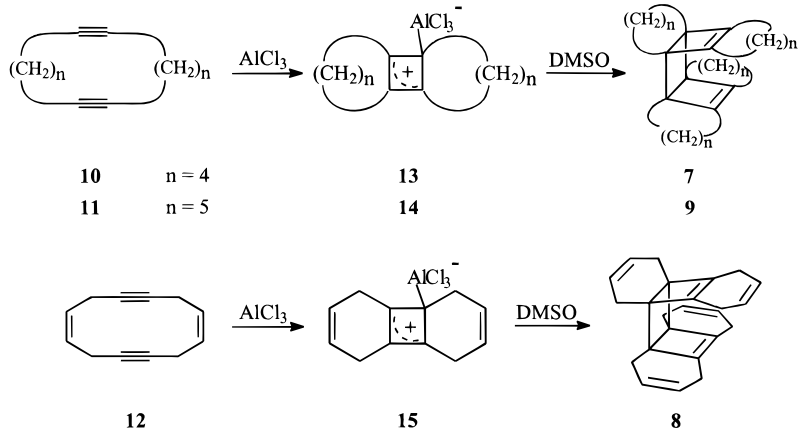
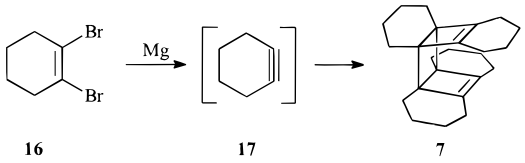
S0022-3263(96)02393-6 CCC: $14.00

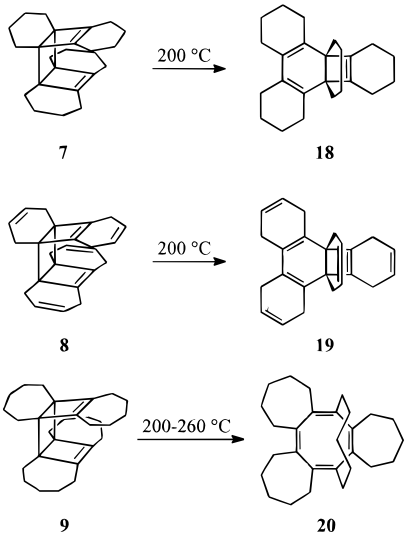
Scheme 3



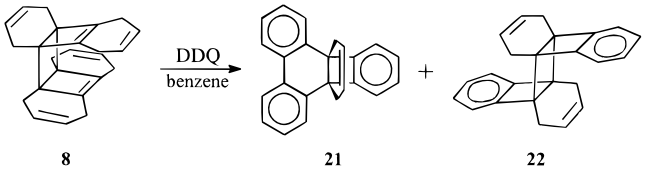
Scheme 4



Scheme 5



Scheme 6



of the observation that cyclic diynes[6] react with $AlCl_3$ to form a cyclobutadiene−$AlCl_3$ complex, which provides the free cyclobutadiene upon treatment with DMSO.[7] So far, the cyclobutadiene intermediate has been trapped with electrophilic double or triple bond systems to form the bicyclo[2.2.0]hexane skeleton.[7,8] We figured that without a dienophile an intermolecular dimerization of two cyclobutadienes should be within the reach. Therefore, our synthesis of **7**−**9** commenced with a cyclic diyne of proper ring size. The starting materials for **7** and **9** were cyclododeca-1,7-diyne (**10**) and cyclotetradeca-1,8-diyne (**11**), respectively (Scheme 3). When we started with (*Z*,*Z*)-4,10-cyclododecadiene-1,7-diyne (**12**)[9] we aimed at **8**. Treatment of **10**−**12** with $AlCl_3$ in methylene chloride between −40 °C and room temperature afforded a red-colored solution. The addition of DMSO to this mixture at −78 °C led to the tricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene derivatives **7**−**9** in about 40−60% yield. An alternative route to **7** was reported by Wittig and Mayer[10] by treatment of 1,2-dibromocyclohexene (**16**) with metals, such as magnesium (Scheme 4). It can be looked at as the tetramer of intermediately formed cyclohexyne (**17**). The assignment of the structures of **7**−**9** is based mainly on their NMR spectroscopic data, which indicate C_s symmetry with two pairs of nonequivalent quarternary carbon signals (**7**: δ 144.0, 137.7, 49.2, 48.0; **8**: δ 141.2, 135.8, 50.1, 44.2; **9**: δ 145.0, 143.9, 54.1, 50.3). We also succeeded in isolating single crystals of **7** and **9**. The results of the X-ray investigations were hampered by disorder but good enough to confirm the configuration of the carbon skeleton of both compounds.[11]

Thermolysis of 7−9. The thermolysis of **7** was first studied by Wittig and Mayer.[10] By heating **7** in xylene under reflux or at 200 °C, they obtained 1,2,3,4,5,6,-7,8,9,10,11,12-dodecahydro-8b,12b-butanobenzo[3,4]-cyclobuta[1,2-*l*]phenanthrene (**18**) in high yields (Scheme 5). By heating **7** for 15 min without solvent under argon atmosphere, we could confirm their result. After chromatographic purification of the raw material we isolated **18** in 71% yield. The thermolysis of **8** under the same conditions afforded the anticipated 1,4,5,8,9,12-hexahydro-8b,12b-(but-3-eno)benzo[3,4]cyclobuta[1,2-*l*]phenanthrene (**19**, 88% yield). The assignment of the structures of both compounds is mainly based on their NMR spectroscopic data. The characteristic signals in the case of **18** are at δ 145.2, 131.4, and 124.3 from the sp^2-carbon centers and at δ 52.1 from the quarternary carbon atoms. The main difference in the ^{13}C NMR spectra of **18** and **19** is due to the double bonds in the bridges (δ = 126.2−

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(7) Hogeveen, H.; Kok, D. M., In *The Chemistry of Triple-Bonded Functional groups*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983; Suppl. C, Part 2, pp 981−1013.

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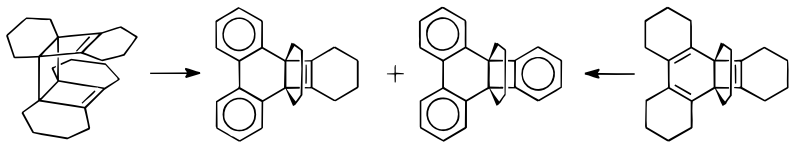
(9) Gleiter, R.; Merger, R.; Nuber, B. *J. Am. Chem. Soc.* **1992**, *114*, 8921−8927.

(10) Wittig, G.; Mayer, U. *Chem. Ber.* **1963**, *96*, 342−348.

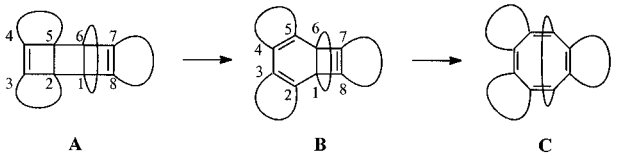
(11) Brand, S. Dissertation, Heidelberg University 1997. Brand, S.; Irngartinger, H. Unpublished results.

Scheme 7



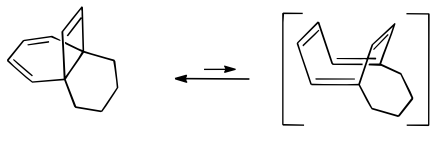
7 **24** **25** **18**

Scheme 8

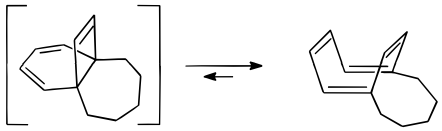


A **B** **C**

Scheme 9

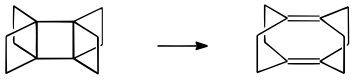


26 **27**

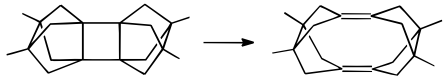


28 **29**

Scheme 10

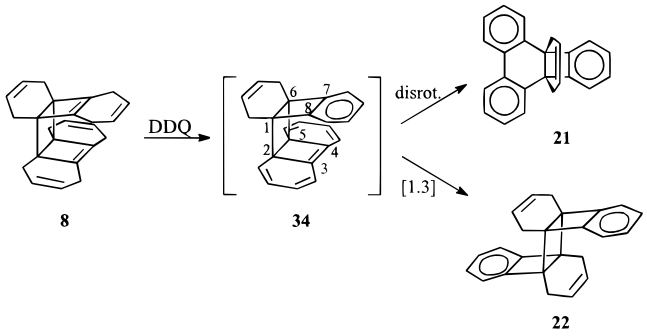


30 **31**



32 **33**

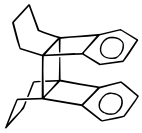
Scheme 11



8 **34** **21** **22**

123.4). The sp^2-carbon atoms of the bicyclo[4.2.0]octa-2,4,7-triene skeleton of **19** manifest themselves in the signals at δ 139.7, 129.0, and 122.1. The resonance for the quarternary carbon atoms was found at δ 52.2. The thermolysis of **9** yields ($\Delta^{5a,5b;10a,11;11a,16a;17,17a}$)-2,3,4,5,6,7,-8,9,10,12,13,14,15,16-tetradecahydro-11,17-pentano-1*H*-triscyclohepta[*a*,*c*,*f*]cyclooctene (**20**) in 53% yield. The structural assignment of **20** is mainly based on NMR spectroscopic data. In contrast to the ^{13}C NMR spectra of **18** and **19**, the signal for a quarternary carbon atom in the ^{13}C NMR spectrum of **20** is missing. Instead, four signals in the region of quarternary sp^2-carbon atoms can be found (δ = 140.4−137.2). The spectral data resemble very closely those of **6**.

Oxidation Reactions. The cyclohexene rings in **8** prompted us to try dehydrogenation experiments. Heating **8** in benzene under reflux in the presence of DDQ yielded 8b,12b-(but-3-eno)benzo[3,4]cyclobuta[1,2-*l*]phenanthrene (**21**, 37%) and *anti*-4b,8c:4c,8b-di(but-3-eno)cyclobuta[1″,2″:3,4;3″,4″:3′,4′]dicyclobuta[1,2:1′,2′]dibenzene (**22**, 10%). As anticipated, the dehydrogenation was only possible in those rings where a benzene structure could be established. To prevent **19** from being formed first and then dehydrogenated, we carried out the reaction shown in Scheme 6 at room temperature. After 23 h, we could detect **21** and **22** in yields of 24% and 4%, respectively. Compound **8** was found to be stable at room temperature. Our assumption of the *anti*-configuration of **22** is based on comparison of its spectral data with that of **23**[12] and on mechanistic considerations. Wittig



23

and Mayer presumably obtained **24** and **25**[10] from both **7** and **18** in boiling xylene (144 °C) in the presence of chloranil (Scheme 7).

Discussion

The thermolysis of **7**−**9** can be rationalized analogously to that of **1** and the tetraalkyl congeners by assuming a stepwise ring-opening process. In a first step, the 2,5-bond of the tricyclo[4.2.0.0^{2,5}]octa-3,7-diene unit of *A* opens to yield a 4-fold-bridged bicyclo[4.2.0]octa-2,4,7-triene derivative *B* (Scheme 8). The opening of the 1,6-bond in *B* depends on the chain length of the transannular bridge. In the case of a pentamethylene chain, a ring opening is possible (**9**); this is not likely for a four-carbon bridge (**7**, **8**). This interpretation is supported by the observation that **26** shows no tendency to isomerize to the corresponding cyclooctatetraene derivative **27** between 40 and 165 °C, whereas **28** rearranges smoothly to **29** at room temperature (Scheme 9).[13]

The low-temperature cycloreversion reaction of **5** is in accord with its high strain energy. The way the centers are bridged in **5** provides two [3.2.2]propellane units[14] or a [3.3.2.2]buttaflane system.[12] Both views suggest a thermally labile system that reverts to the olefinic system

(12) Kimura, K.; Ohno, H.; Morikawa, K.; Hiramatsu, Y.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2169−2173.

(13) (a) Paquette, L. A. *Acc. Chem. Res.* **1993**, *26*, 57−62. (b) Paquette, L. A.; Philips, J. C.; Wingard, R. E., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 4516−4522.

(14) Wiberg, K. B. *Chem. Rev.* **1989**, *89*, 975−983.

6 at low temperature.[15] An example for a system with two [2.2.2]propellane units is provided by **30**[16] and by **32**[17] for a system with two [3.3.2]propellane units (Scheme 10). Both revert at ambient temperature to the corresponding cyclophanes **31** and **33**, respectively. Further examples that should be mentioned in this context are the thermal reversion of the dimer of cubene,[18] of [*n*.2.2]propellanes,[15] and of dibenzo[4.4.2.2]buttaflanes.[19]

Most surprising in our studies are the relatively low temperatures at which the oxidation reactions take place and the occurrence of **22** during the reaction between DDQ and **8** in benzene.

To rationalize our experimental data we assume **34** as an intermediate (Scheme 11). Ring-opening of the 2,5-bond in the cyclobutene ring will create two new 6π systems, and thus, the activation energy for such a process should be lowered considerably. The occurrence of **22** can be rationalized by a suprafacial 1,3-shift. The usually high activation energy for this process will be lowered due to the formation of a new 6π system in the transition state.

Experimental Section

General Methods. All reactions were carried out under an argon atmosphere. CH_2Cl_2 was freshly distilled from sicapent and benzene from Na−benzophenone. The ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz if not otherwise noted. $AlCl_3$ was obtained from Aldrich (99.99%). Elemental analyses were performed at the Mikroanalytisches Laboratorium der Universität Heidelberg, Germany.

General Procedure for the Preparation of the 4-Fold-Bridged *syn*-Tricyclo[4.2.0.0^{2,5}]octa-3,7-dienes 7−9. A magnetically stirred slurry of $AlCl_3$ in CH_2Cl_2 was cooled to −40 °C in a Schlenk flask, and a solution of the cycloalkadiyne in CH_2Cl_2 was added slowly. Upon warming to room temperature, the color of the mixture turned to orange or red and the $AlCl_3$ disappeared. DMSO was added quickly at −78 °C. Upon warming to room temperature, a colorless suspension was observed and the mixture poured into ice/methylene chloride and separated. The aqueous layer was extracted with CH_2Cl_2 and the organic layer dried with $MgSO_4$. The solvent was removed in vacuo, and the crude products were purified by column chromatography.

***syn*-1,2,3,4,5,6,7,8,9,10,11,12-Dodecahydro-8b,12b-butanobenzo[3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2-*e*]biphenylene (7).** Starting materials: 202 mg (1.5 mmol) of $AlCl_3$ in 15 mL of CH_2Cl_2, 242 mg (1.5 mmol) of cyclododeca-1,7-diyne **(10)** in 6 mL of CH_2Cl_2, 0.15 mL (2.1 mmol) of DMSO. Purification by column chromatography (neutral Al_2O_3; petroleum ether) afforded 104 mg (43%) of **7** as colorless crystals: mp 129 °C (lit.[10] mp 132−133 °C); ^1H NMR (C_6D_6) δ 2.35−0.95 (m, 32H); ^{13}C NMR (C_6D_6) δ 144.0, 137.7, 49.2, 48.0, 27.1, 24.7, 24.2, 23.7, 23.6, 23.5, 22.3, 21.6; IR (KBr) 2918, 2840, 1441 cm^{-1}; MS (EI) *m*/*z* 320.

***syn*-1,4,5,8,9,12-Hexahydro-8b,12b-(but-3-eno)benzo[3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2-*e*]biphenylene (8).** Starting materials: 825 mg (6.2 mmol) of $AlCl_3$ in 40 mL of CH_2Cl_2, 966 mg (6.2 mmol) of (*Z*,*Z*)-4,10-cyclododecadiene-1,7-diyne **(12)**[9] in 6 mL of CH_2Cl_2, 0.7 mL (9.9 mmol) of DMSO. Purification by column chromatography (silica gel; petroleum ether) afforded 558 mg (58%) of **8** as colorless crystals: mp 83 °C; ^1H NMR (C_6D_6) δ 5.90−5.88 (m, 2H), 5.75−5.66 (m, 4H), 5.65−5.58 (m, 2H), 2.65−2.35 (m, 8H), 2.18 (s, 4H), 2.04−2.05 (m, 4H); ^{13}C NMR (C_6D_6) δ 141.2, 135.8, 128.3, 126.8, 125.62, 125.56, 50.1, 44.2, 24.94, 24.88, 24.4, 22.5; IR (KBr) 3019, 2917, 2876, 2859, 2829, 2816, 1425, 657 cm^{-1}. Anal. Calcd for $C_{24}H_{24}$: C, 92.26; H, 7.74. Found C, 92.06; H, 7.80.

2,3,4,5,6,7,8,9,10,11,12,13,14,15-Tetradecahydro-10b,15b-pentano-1*H*-cyclobuta[1″,2″:2,3;3″,4″:3′,4′]dicyclobuta[1,2:3,4:1′,2′]triscycloheptene (9). Starting materials: 170 mg (1.3 mmol) of $AlCl_3$ in 25 mL of CH_2Cl_2, 240 mg (1.3 mmol) of cyclotetradeca-1,8-diyne **(11)** in 6 mL of CH_2Cl_2, 0.3 mL (4.2 mmol) of DMSO. Purification by column chromatography (neutral Al_2O_3; petroleum ether) afforded 130 mg (54%) of **9** as colorless crystals: mp 143 °C; ^1H NMR (C_6D_6) δ 2.25−1.0 (m, 40H); ^{13}C NMR (C_6D_6) δ 145.0, 143.9, 54.1, 50.3, 34.2, 31.2, 30.2, 30.1, 29.9, 28.8, 28.6, 28.5, 28.16, 28.13, 28.07; IR (KBr) 2917, 2844, 1446 cm^{-1}. Anal. Calcd for $C_{28}H_{40}$: C, 89.30; H 10.70. Found C, 89.13; H, 10.60.

Thermolysis of 7. Sixty-two mg (0.19 mmol) of **7** was heated without solvent in a Schlenk tube for 15 min to 200 °C (oil bath). Chromatographic purification (silica gel; petroleum ether) of the raw material furnished 44 mg (71%) of **18** as colorless crystals: mp 145 °C (lit.[10] mp 148−149 °C); ^1H NMR ($CDCl_3$) δ 2.25−1.32 (m, 32H); ^{13}C NMR ($CDCl_3$) δ 145.2, 131.4, 124.3, 52.1, 27.4, 25.9, 25.1, 23.6, 23.3, 23.2, 22.7, 17.1; MS (EI) *m*/*z* 320.

Thermolysis of 8. Fifty mg (0.16 mmol) of **8** was heated without solvent in a Schlenk tube for 15 min to 200 °C (oil bath). Chromatographic purification (silica gel; petroleum ether/ether 20:1) of the raw material yielded 44 mg (88%) of **19** as colorless crystals: mp 182 °C; ^1H NMR ($CDCl_3$) δ 5.95−5.65 (m, 8H), 3.05−2.71 (m, 6H), 2.70−2.48 (m, 6H), 2.42 (dm, 2H, ^2J = 14.7 Hz), 1.93 (d, 2H, ^2J = 14.7 Hz); ^{13}C NMR ($CDCl_3$) δ 139.7, 129.0, 122.1, 126.2, 125.6, 124.4, 123.4, 52.2, 28.4, 27.8, 27.3, 22.6; IR (KBr) 3029, 2876, 2816, 1426, 664 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ϵ) 234 (3.93), 284 (3.74), 292 (3.70) nm. Anal. Calcd for $C_{24}H_{24}$: C, 92.26; H, 7.74. Found: C, 92.19; H, 7.32.

Thermolysis of 9. Sixty mg (0.16 mmol) of **9** was heated without solvent in a Schlenk tube for 100 min to 200−260 °C (oil bath). Chromatographic purification (silica gel; petroleum ether) of the yellow, viscous oil gave 32 mg (53%) of **20** as colorless crystals: mp 92 °C; ^1H NMR ($CDCl_3$) δ 2.4−0.98 (m, 40H); ^{13}C NMR ($CDCl_3$) δ 140.4, 137.7, 137.26, 137.20, 33.2, 31.9, 31.2, 31.1, 30.7, 27.80, 27.72, 26.98, 26.96, 25.9, 21.9; IR (KBr) 2925, 2849, 1451 cm^{-1}; UV/vis (*n*-pentane) λ_{max} (log ϵ) 216 (4.04) nm; HRMS (EI) *m*/*z* calcd 376.3224, found 376.3177.

Dehydrogenation of 8 with DDQ. DDQ was added (310 mg, 1.36 mmol) to a solution of 50 mg (0.16 mmol) of **8** in 5 mL of benzene in a two-necked flask with a reflux condenser. The mixture was heated at reflux for 75 min. After dilution with ether, the red solids were removed by filtration. After removal of the solvent in vacuo, the residue was purified by column chromatography (silica gel; petroleum ether/ether 10:1) to yield 18 mg (36.6%) of **21** as colorless crystals and 5 mg (10%) of **22** as pale yellow crystals. **21:** mp 229 °C; ^1H NMR ($CDCl_3$) δ 7.95 (dd, 2H, ^3J = 7.9 Hz, ^4J = 1.3 Hz), 7.67 (dd, 2H, ^3J = 7.5 Hz, ^4J = 1.5 Hz), 7.35 (ddd, 2H, ^3J = 7.4 Hz, ^4J = 1.5 Hz), 7.28 (ddd, 2H, ^3J = 7.8 Hz, ^4J = 1.3 Hz), 7.17 (dd, 2H, ^3J = 5.4 Hz, ^4J = 3.0 Hz), 7.04 (dd, 2H, ^3J = 5.4 Hz, ^4J = 3.0 Hz), 5.87 (dd, 2H, ^3J = ^4J = 3.5 Hz), 3.14 (dm, 2H, ^2J = 14.8 Hz), 2.48 (d, 2H, ^2J = 14.8 Hz); ^{13}C NMR ($CDCl_3$) δ 148.6, 140.1, 130.1, 128.28, 128.27, 127.4, 126.85, 126.76, 123.1, 119.7, 51.5, 35.6; IR (KBr) 3040, 2360, 1454, 1439, 754, 741, 730 cm^{-1}; UV/vis (CH_2Cl_2) λ_{max} (log ϵ) 232 (4.85), 276 (4.24) nm; HRMS (EI) *m*/*z* calcd 306.1408, obsd 306.1373. **22:** mp 217 °C dec; ^1H NMR (200 MHz, $CDCl_3$) δ 7.3−7.15 (m, 8H),

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5.34 (s, 4H), 2.53 (d, 4H, ^2J = 15.9 Hz), 2.34 (d, 4H, ^2J = 15.9 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.5, 127.8, 123.7, 122.7, 53.6, 27.3; IR (KBr) 3059, 3020, 2896, 2828, 1716, 1454, 738, 666 cm^{-1}; UV/vis (CH_3CN) λ_{max} (log ϵ) 272 (4.06), 278 (4.10) nm; HRMS (EI) *m*/*z* calcd 308.1565, found 308.1551.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **20**−**22** (4 pages). This material is contained in 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.

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