206.1329.

2-(3-Chloropropyl)-1-phenyl-2,3-butadien-1-ol (3k): yield 840 mg (93%) from **1d** (1.17 g, 6 mmol) and benzaldehyde (0.42 g, 4 mmol) using procedure B; purified by flash chromatography (hexane–EtOAc (98.2)); **3k:4k** = 97.3; IR (neat) 3390 (br), 3062 (s), 3029 (s), 2956 (s), 2916 (s), 1956 (s), 1494 (s), 1452 (s) cm^{-1}; ^1H NMR δ 7.32 (m, 5 H), 5.13 (br s, 1 H), 5.01 (m, 2 H), 3.48 (m, 2 H), 2.18 (br s, 1 H), 2.05–1.82 (m, 4 H); ^{13}C NMR δ 204.6, 142.0, 128.3, 127.8, 126.5, 106.9, 79.7, 74.4, 44.3, 30.6, 24.9; mass (CI, NH_3) 240 (MNH_4^+, 3), 222 (9), 205 (8), 136 (100); HRMS calcd for $C_{13}H_{15}ClONH_4^+$ 240.1155, found 240.1136.

1-(1-(3-Chloropropyl)-1,2-propadienyl)cyclohexan-1-ol (3l): yield 630 mg (72%) from **1d** (1.17 g, 6 mmol) and cyclohexanone (0.39 g, 4 mmol) using procedure B; purified by flash chromatography (hexane–EtOAc (98:2)); **3l:4l** = 97:3; IR (neat) 3425 (br), 2935 (s), 2856 (s), 1951 (s), 1447 (s) cm^{-1}; ^1H NMR δ 4.88 (m, 2 H), 3.59 (m, 2 H), 2.19 (m, 2 H), 1.93 (m, 2 H), 1.73–1.42 (m, 10 H), 1.36 (s, 1 H); ^{13}C NMR δ 204.5, 110.2, 79.0, 71.8, 44.6, 36.9, 31.1, 25.6, 23.3, 22.4; mass (EI, 70 eV) 214 (M^+, 5), 99 (100), 81 (44); HRMS calcd for $C_{12}H_{19}ClO$ 214.1124, found 214.1120.

1-(Hydroxybenzyl)-5,6-heptadienenitrile (3m): yield, 750 mg (82%) from **1e** (1.12 g, 6 mmol) and benzaldehyde (0.42 g, 4 mmol) using procedure B; purified by flash chromatography (hexane–EtOAc (85:15)); **3m:4m** 96.5:3.5; IR (neat) 3454 (br), 3062 (s), 3029 (s), 2938 (s), 2247 (s), 1956 (s), 1452 (s) cm^{-1}; ^1H NMR δ 7.34 (m, 5 H), 5.16 (s, 1 H), 5.02 (m, 2 H), 2.01 (m, 3 H), 1.98 (m, 2 H), 1.76 (m, 2 H); ^{13}C NMR δ 204.8, 141.9, 128.4, 127.9, 126.4, 119.3, 106.3, 79.8, 74.4, 26.5, 23.5, 16.4; mass (EI, 70 eV) 213 (M^+, 3), 195 (4), 184 (3), 107 (100); HRMS calcd for $C_{14}H_{15}NO$ 213.1154, found 213.1146.

1-[(1-Hydroxycyclohexyl)methyl]-5,6-heptadienenitrile (3n): yield 760 mg (86%) from **1e** (1.12 g, 6 mmol) and cyclohexanecarboxaldehyde (0.45 g, 4 mmol) using procedure B; purified by flash chromatography (hexane–EtOAc (85:15)); **3n:4n** = 94.6; IR (neat) 3446 (br), 2920 (m), 2248 (s), 1955 (s), 1676 (s), 1450 (s) cm^{-1}; ^1H NMR δ 4.88 (m, 2 H), 3.78 (m, 1 H), 2.40 (m, 2 H), 2.11 (m, 2 H), 1.95–0.88 (m, 14 H); ^{13}C NMR δ 204.9, 119.2, 104.4, 78.2, 76.9, 41.6, 29.7, 27.9, 26.3, 26.0, 25.8, 25.6, 23.5, 16.5; mass (CI, NH_3) 237 (MNH_4^+, 100), 219 (46), 202 (63), 136 (61); HRMS calcd for $C_{14}H_{21}NONH_4$ 237.1967, found 237.1975.

1-Phenyl-2-propyl-3-butyn-1-ol (11): yield 340 mg (90%) from benzaldehyde (0.21 g, 2 mmol) and 3-bromo-1-hexyne **10** (0.48 g, 3 mmol) using procedure B; purified by flash chromatography (hexane–EtOAc (98:2)); mixture of diastereoisomers, 60:40; IR (neat) 3412 (br), 3300 (s), 3064 (s), 3031 (s), 2959 (s), 2932 (s), 2113 (s), 1604 (s), 1495 (s), cm^{-1}; ^1H NMR δ 7.44–7.21 (m, 10 H), 4.74 (m, 1 H), 4.57 (m, 1 H), 2.87–2.67 (m, 2 H), 2.56 (br s, 1 H), 2.31 (br s, 1 H), 2.21 (m, 1 H), 2.11 (m, 1 H), 1.70–1.24 (m, 8 H), 0.97–0.79 (m, 6 H); ^{13}C NMR δ 141.7, 128.3, 128.1, 127.9, 127.8, 126.7, 84.7, 84.2, 76.1, 75.8, 72.3, 71.8, 40.9, 39.9, 33.4, 31.8, 20.4, 13.7, 13.6; mass (EI, 70 eV) 188 (M^+, 2), 146 (6), 107 (100), 79 (37); HRMS calcd for $C_{13}H_{16}O$ 188.1201, found 188.1199.

Acknowledgment. We would like to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of Michigan (Office of the Vice President for Research) for support of this research.

Registry No. **1a**, 100859-51-6; **1b**, 18495-26-6; **1c**, 63857-37-4; **1d**, 61863-12-5; **1e**, 53574-62-2; **3a**, 35281-62-0; **3b**, 141375-85-1; **3c**, 141375-86-2; **3d**, 141375-87-3; **3e**, 141375-88-4; **3f**, 141375-89-5; **3g**, 141375-90-8; **3h**, 141375-91-9; **3i**, 141375-92-0; **3j**, 141375-93-1; **3k**, 141375-94-2; **3l**, 141375-95-3; **3m**, 141375-96-4; **3n**, 141375-97-5; **4a**, 1002-36-4; **4c**, 34506-51-9; **4d**, 1002-37-5; **4e**, 69285-47-8; **5**, 14420-47-4; **6**, 34506-50-8; **8**, 1002-37-5; **9**, 69285-47-8; **10**, 49769-87-1; **10** tosylate, 141375-98-6; (*R**,*R**)-**11**, 57185-94-1; (*R**,*S**)-**11**, 57185-95-2; *i*-PrCHO, 78-84-2; PhCHO, 100-52-7; c-HexCHO, 2043-61-0; *n*-PentCHO, 66-25-1; $PhCOCH_3$, 98-86-2; $CrCl_3$, 10025-73-7; 3-carbethoxypropylzinc iodide, 104089-17-0; 1-hexyn-3-ol, 105-31-7.

Supplementary Material Available: ^{13}C NMR spectra of all compounds (22 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Orthocyclophanes. 1. Synthesis and Characterization of [1_4]- and [1_5]Orthocyclophanes and Bicyclic Biscyclophanes

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Received February 10, 1992

[1_4]- and [1_5]orthocyclophanes have been designed, synthesized and characterized. Dimetalation of bis(2-bromophenyl)methane (**14**) to the corresponding dilithio reagent **21**, followed by reaction with aromatic dialdehydes bis(2-formylphenyl)methane (**20**) and 1,2-bis(2-formylbenzyl)benzene (**27**), gave cyclic diols **22** and **28**, respectively. Oxidation of the diols with PCC to the corresponding cyclic diketones **23** and **29**, followed by palladium-catalyzed reduction, afforded [1_4]- and [1_5]orthocyclophanes, **4** and **5**. Bicyclic biscyclophanes were also prepared from the cyclic diketones giving rise to a new family of cyclophanes. Treatment of **23** and **29**, respectively, with McMurry or Clemmensen reagents gave rise to intramolecular olefination to provide bicyclic biscyclophanes **24** and **30**. Pd-catalyzed hydrogenation of **24** and **30** also gave **4** and **5**. The benzylic positions of the cycloheptatriene moieties in **24** and **30** were very susceptible to oxidation to give ketones **26** and **32**.

Introduction

Since the first report on the synthesis and properties of [2.2]paracyclophane,[1,2] there has been tremendous interest in the synthesis[3-5] and inclusion behavior[6-8] of cyclophanes. In spite of the extensive studies on cyclophanes, only a few [1_n]orthocyclophanes that contain more than three aromatic rings have been reported. In 1915, Robinson[9] first prepared an orthocyclophane, **1**, cyclotriveratrylene (CTV), by the acid-catalyzed condensation of veratrol and formaldehyde to produce a crystalline solid (mp 227 °C), and the structure was assigned later as a rigid crown confor-

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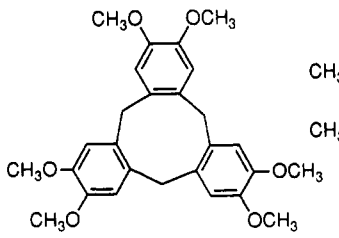
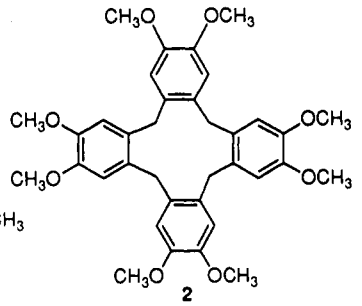
0022-3263/92/1957-4074$03.00/0

mation.[10-12] In this reaction, the formation of 1 is always accompanied by the tetrameric homolog 2, cyclotetraveratrylene (CTTV, mp 319–321 °C), which was separated and characterized by White and Gesner.[13] However, [1.1.1]orthocyclophane (3), the parent hydrocarbon of 1, was synthesized by Sato et al.[14] by the acid-catalyzed reaction of bis[2-(hydroxymethyl)phenyl]methane (19) with benzene. However, [1₄]orthocyclophane 4, the parent hydrocarbon of 2, has not been reported to date.

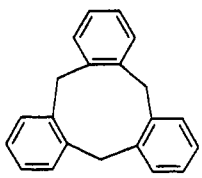


1



2

Following the work of Robinson, derivatives of 3 and 4 have been extensively investigated by Collet and others.[15,16] In spite of extensive work on orthocyclophanes, investigations focused on the parent hydrocarbons of [1ₙ]orthocyclophanes have thus far been overlooked. It is of interest to synthesize the higher homologs, such as [1₄]-, [1₅]-, and [1₆]orthocyclophanes, in which more than four aromatic rings are incorporated in the macroring. Since the benzylic methylenes between the aromatic rings are expected to be prone to oxidation, these higher homologs are of interest for the preparation of novel ketonic cyclophanes as a new family of host molecules. The present paper reports the synthesis of [1₄]orthocyclophane 4 and [1₅]orthocyclophane 5. Dimetalation of bis(2-bromophenyl)methane (14) with butyllithium, followed by condensation with aromatic dialdehydes bis(2-formylphenyl)methane (20) and 1,2-bis(2-formylbenzyl)benzene (27), gave rise to cyclic diols 22 and 28, respectively. Oxidation of the diols to the corresponding cyclic diketones 23 and 29, followed by palladium-catalyzed hydrogenation, furnished 4 and 5. Herein we also report a novel intramolecular reductive coupling of cyclophanyl diketones, such as 23 and 29, which yielded bicyclic cyclophanes 24 and 30, respectively.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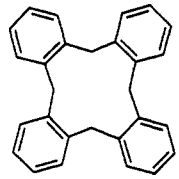
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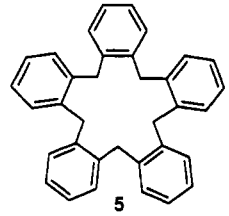
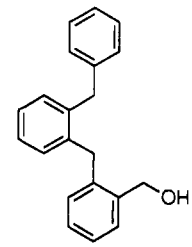
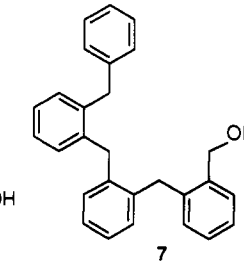

5

Results and Discussion

Recently, we reported[17] a new synthesis of [1.1.1]-orthocyclophane (3) by treatment of 2-(2-benzylbenzyl)-benzyl alcohol (6) with sulfuric acid to give an intramolecular Friedel–Crafts cycloalkylation product. However, it was known that treatment of 2-[2-(2-benzylbenzyl)-benzyl]benzyl alcohol (7) with sulfuric acid did not effect conversion to [1₄]orthocyclophane (4), but gave a cyclic product [1.1.1.1](1,2)(1,2)(1,2)(1,3)cyclophane 8.[18] Thus, we were unable to prepare 4 by use of the acid-catalyzed cyclization reaction of a benzylic alcohol.



6



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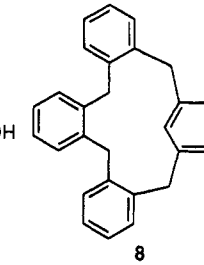
8

The synthesis of [1₄]orthocyclophane (4) has been carried out by a series of procedures as illustrated in Schemes I–III. One of the starting materials, bis(2-bromophenyl)methane (14), was prepared by modifying literature procedures,[19] as shown in Scheme I. Treatment of 2-bromobenzaldehyde (9) with potassium cyanide in dimethylformamide (DMF) gave rise to a benzoin condensation product, dibromobenzoin 10. Treatment of 10 with potassium bromate ($KBrO_3$) by refluxing in aqueous potassium hydroxide solution afforded dibromobenzhydrol 12 and subsequent oxidation of 12 with PCC gave the corresponding ketone, dibromobenzophenone 13. Clemmensen reduction of 13 was not a clean reaction. The best method for the reduction was treatment of the ketone 13 with I_2/P in refluxing hydriodic acid (HI), which afforded bis(2-bromophenyl)methane (14) as an oil.

The other starting material, bis(2-formylphenyl)methane (20), was prepared as illustrated in Scheme II. 1,2-Bis(hydroxymethyl)benzene (15), which was prepared by the $LiAlH_4$ reduction of phthalic anhydride,[20] was monochlorinated with 1 molar equiv of thionyl chloride, and the resulting 2-(chloromethyl)benzyl alcohol (16) was protected with dihydropyran to give THP ether 17. The reaction of 17 with Grignard reagent 18 in the presence of CuI, followed by removal of the THP protecting group of the coupling product by treatment with TsOH in methanol, gave the benzylic diol 19.[14] Oxidation of 19 with PDC in DMF furnished aromatic dialdehyde 20.

Finally, completion of the synthesis of 4 involved the synthetic procedure illustrated in Scheme III. The dibromide 14 was lithiated with 2 molar equiv of *n*-butyllithium (*n*-BuLi) first at −30 °C and then at room temperature for 60 min. During the lithiation, the reaction mixture became a dark red-brown color, which gradually lightened as the base was added to give a clear, brown-yellow solution, indicating the formation of dilithio reagent 21. Coupling of 21 with the dialdehyde 20 gave the cyclic diol 22, which was oxidized with pyridinium dichromate (PDC) to afford the corresponding diketone 23 as a col-

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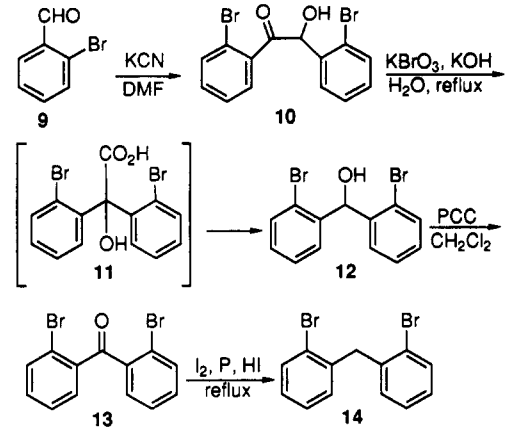
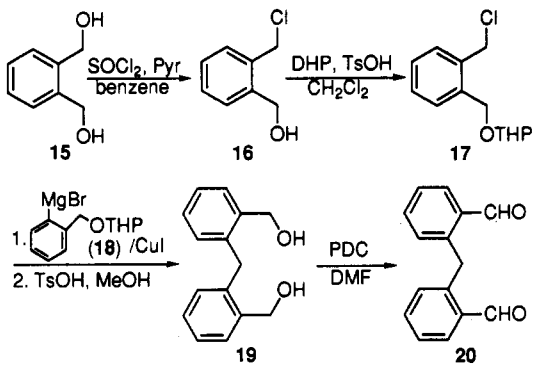
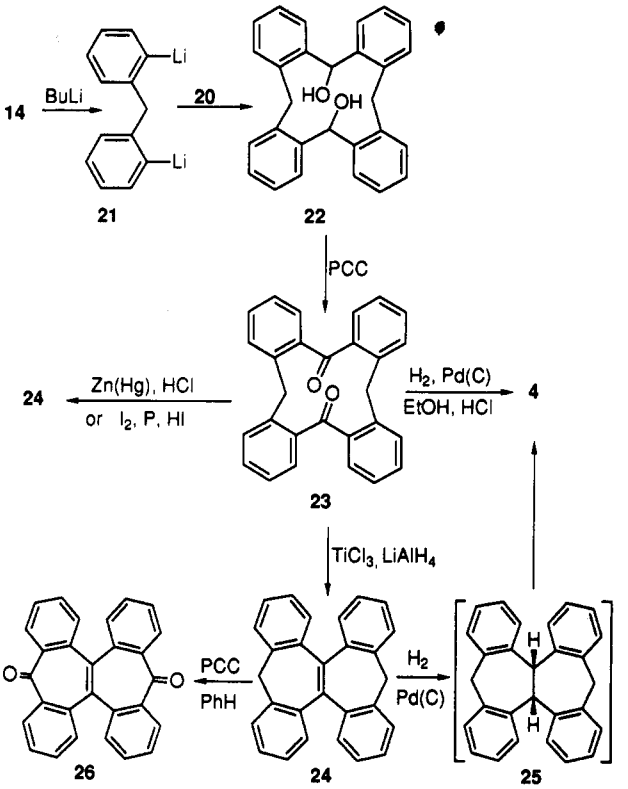
Scheme I



Scheme II



Scheme III



orless crystalline solid, mp 349–351 °C dec. The ^{1}H NMR spectrum of **23** disclosed an AB quartet for the resonances of the benzylic protons at δ 4.11 and δ 3.76 (J_{AB} = 17 Hz), indicating a rigid conformation of the cyclic diketone **23** on the NMR time scale.

Attempted reduction of **23** using a variety of methods gave rise to two different products depending on the reducing agent used: Pd(C)-catalyzed reduction of **23** in EtOH–HCl[21] furnished a normal deoxygenated product **4**, mp 345–346 °C dec, in 80% yield. The new cyclophane **4** was barely soluble in organic solvents. The benzylic protons of **4** give rise to a broadened singlet at δ 3.72, whereas the corresponding protons in **3** appear as an AB quartet at δ 3.45 and 4.70.[14] The NMR pattern of **4** is similar to that of the octamethoxy derivative **2**, wherein the benzylic protons appear as a broadened singlet at δ 3.59.[13] It should be noted that Luz et al. observed four AB quartets corresponding to the benzylic protons of dodecamethoxy[1$_4$]orthocyclophane (DCP), which indicated the existence of sofa and boat conformations in solution.[16] Thus, the room-temperature NMR spectrum shows that **4** has a greater degree of flexibility with the possibility of fast sofa–sofa pseudorotation and sofa–boat interconversion. The mass spectrum of **4** reveals a molecular ion at m/z 360 and, as noted by Erdman,[11] progressive degradation to trimer, dimer, and monomer units (m/z 270, 180, and 90).

Oddly enough, however, the Clemmensen reduction of **23** did not afford **4**, but rather gave a reductive coupling product **24**, exclusively, mp 337–338 °C dec, in 91% yield. To explain these results, we need to recognize that similar behavior has already been observed by previous workers in the Clemmensen reduction of ketones, especially aryl ketones, which gave intermolecular dimeric olefins as side products.[22] In the Clemmensen reduction of **23**, the bicyclic biscyclophane **24** was not a side product, but rather the only product. This result can probably be interpreted as arising from the structural advantage of the cyclic diketone **23**, in which two carbonyl groups are close to each other, forcing the intramolecular reductive olefination to give the relatively stable **24** as the main product. The formation of **24** could also be accomplished by treating **23** with McMurry's reagent,[23] $TiCl_3/LiAlH_4$, to give the intramolecular olefination product **24** in 81% yield. Reduction of **23** with I_2/P/HI also gave the identical reduction product **24**. The benzylic proton resonances of **24** appear as an AB quartet at δ 4.07 and δ 3.90 (J_{AB} = 12 Hz), indicating that **24** exists in solution in a rgid conformation in which the methylene protons are symmetry nonequivalent. Pd(C)-catalyzed hydrogenation of **24** did not give the anticipated bicyclic biscyclophane **25** of cis conformation, but rather the orthocyclophane **4**, exclusively. This may be interpreted by cleavage of the olefinic double bond during the formation of the unstable cis form, **25**. A molecular model of **25** shows severe steric strain due to syn addition of hydrogen to the olefinic double bond of **24** followed by simultaneous sp^2-to-sp^3 rehybridization. Furthermore, in spite of many attempts, reduction of **24** to an anti addition product, the trans isomer of **25**, could not be achieved; reduction of **24** with Na/t-BuOH in HMPA[24] or with $LiAlH_4$–$CoCl_2$ in THF[25] failed to give the trans isomer of **25** and gave only the starting material. On the other hand, the fused biscyclophane **24** was found to be very susceptible to oxidation, and the benzylic methylenes were converted to carbonyls by treatment with pyridinium chlorochromate (PCC), yielding the correspond-

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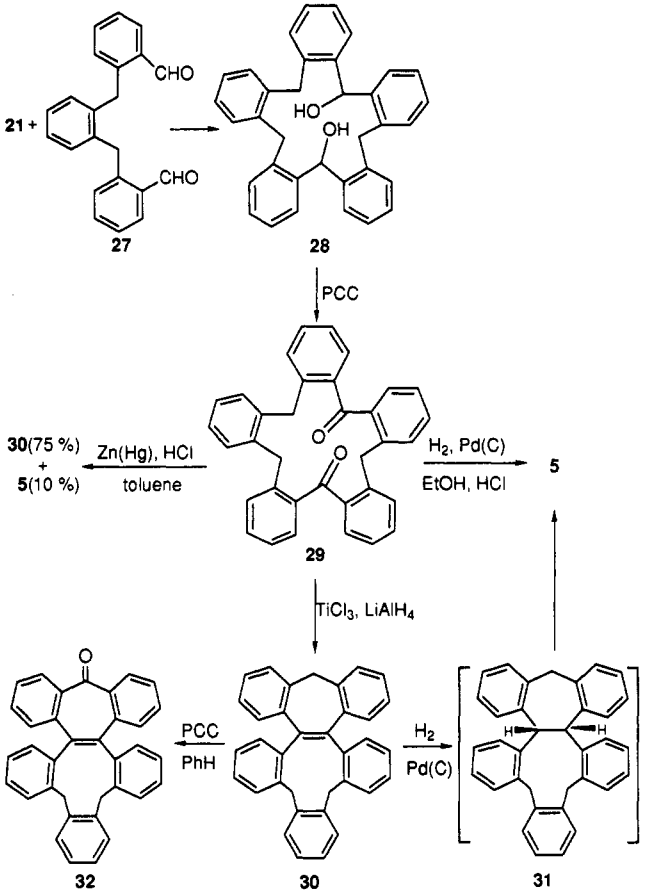
(25) Ashby, E. C.; Lin, J. J. *Tetrahedron Lett.* **1977**, 4481.

Scheme IV



ing diketone **26** of cycloheptatrienone structure.

The first synthesis of [1₅]orthocyclophane (**5**) was achieved by a synthetic procedure outlined in Scheme IV. Treatment of 1,2-bis(2-formylbenzyl)benzene (**27**), prepared by the literature procedure,[26] with 1 molar equiv of dilithio reagent **21** gave rise to a condensation product, cyclic diol **28**. Oxidation of **28**, without purification, with PCC afforded the corresponding diketone **29** in 30% overall yield as a colorless crystalline solid, mp 224–237 °C dec. The benzylic protons of **29** appear as two singlets, at δ 3.85 (2 H) and δ 3.64 (4 H), which reveal a more flexible structure this cycle than that of the lower homolog **23**, which shows an AB quartet for its benzylic protons.

Reduction of **29**, as was observed in the reduction of the cyclic diketone **23**, gave different products depending on the reducing agent used: Pd-catalyzed hydrogenation of **29** in EtOH–HCl gave the normal deoxygenated product, [1₅]orthocyclophane (**5**), in 93% yield as a colorless crystalline solid, mp 257–258 °C. In contrast with the insolubility of the lower homolog **4**, the orthocyclophane **5**, despite its higher molecular weight, showed a modest solubility in organic solvents, such as dichloromethane and chloroform. The benzylic protons of **5** give a sharp singlet at δ 3.75, which reveals the much more flexible structure of the cycle than the lower homolog **4** in which the corresponding protons give a broadened singlet. The Clemmensen reduction of **29**, unlike that of the lower homolog **23**, effected both reductive olefination[22] and normal reduction to give a mixture of a fused biscyclophane **30** (ca. 75%) and orthocyclophane **5** (ca. 10%). This may be interpreted to mean that in the rather flexible conformation of **29** the two carbonyl groups are further apart from each other, making this reductive coupling less effective. McMurry's reagent,[23] however, converted **29** completely into **30**.

Pd-catalyzed hydrogenation of **30** did not give the anticipated bicycle **31** of cis conformation, but rather the orthocyclophane **5** as the sole product. This result can also be rationalized by the instability of **31**, due to steric strain, which hastens bond cleavage. The attempted anti reduction of **30** failed, and the trans isomer of **31** could not be obtained. As was observed in **24**, it was found that the fused biscyclophane **30** was very susceptible to oxidation, and thus the methylene function of the cycloheptatriene unit was easily converted to a carbonyl by the action of PCC in benzene to give the corresponding ketone **32**, containing a cycloheptatrienone moiety.

In summary, the first total syntheses of [1₄]- and [1₅]-orthocyclophane have been achieved, confirming the assigned structures. Their relatively flexible conformations, compared with the rigid [1₃]orthocyclophane (**3**), were revealed by ^{1}H NMR spectra. Whereas the benzylic proton resonances of **3** exhibit a sharp AB quartet, those of **4** display a broadened singlet, and as was expected, **5** shows a sharp singlet, indicating a high degree of flexibility. The [1$_n$]orthocyclophanes synthesized thus far are found to possess very low solubility in organic solvents. However, whereas [1₃]- and [1₅]orthocyclophane are slightly soluble in organic solvents such as dichloromethane and chloroform, [1₄]orthocyclophane is so insoluble that the ^{13}C NMR spectrum could not be obtained. The conformation of the cycle is likely to be responsible for its degree of solubility, depending on the number, odd or even, of n in [1$_n$]-orthocyclophanes. Thus, it might be suggested that [1₆]orthocyclophane will be much more insoluble in organic solvents than [1₄]orthocyclophane (**4**), since [1₆]orthocyclophane has an even number of benzene rings and a higher molecular weight than **4**. It is also noted that Clemmensen reduction of rigid cyclophanyl diketones, such as **23** and **29**, always gave rise to reductive coupling to give McMurry-type intramolecular olefination products. The actions of the newly synthesized cyclophanes **4**, **5**, **24**, **26**, **30**, and **32** as hosts toward organic molecules have not yet been examined. Further investigations with [1₆]orthocyclophane are currently underway and will be reported in the near future.

Experimental Section

General. All anhydrous reactions were conducted with precautions for rigorous exclusion of air and moisture. Diethyl ether and THF were purified by refluxing with sodium benzophenone ketyl under nitrogen, followed by distilling prior to use. CH_2Cl_2 was dried by distilling over CaH_2. Flash chromatography was carried out on silica gel 60 (E. M. Merck, particle size 0.040–0.063 mm, 230–400 mesh ASTM). Melting points are uncorrected. Chemicals were purified, when necessary, according to the reported procedures.[27]

Bis(2-bromophenyl) Ketone (13). A solution of 2-bromobenzaldehyde (**9**) (25 g, 135 mmol) and KCN (4 g, 60 mmol) in DMF (120 mL) was stirred at rt for 2 days. The reaction mixture was diluted with water, extracted with CH_2Cl_2, washed with water, and dried ($MgSO_4$). Evaporation of the solvent gave a crude benzoin condensation product **10**, which was used for the next reaction without purification. To a solution of NaOH (13 g, 325 mmol) and $KBrO_3$ (3.5 g, 20 mmol) in water (50 mL) was added the crude benzoin **10**, and the mixture was refluxed for 20 h. The reaction mixture was acidified with 4 N aqueous H_2SO_4, extracted with CH_2Cl_2, washed with brine, and dried ($MgSO_4$), and the solvent was removed in vacuo to give crude benzhydrol **12** as a dark red solid. A mixture of the crude **12**, PCC (20 g), and Celite

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(27) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R., *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: New York, 1980.

(15 g) in dry CH_2Cl_2 was stirred at rt for 6 h. The reaction mixture was filtered through silica gel, and the filtrate was evaporated under reduced pressure to give an oxidation product. The crude product was purified by chromatography on silica gel eluting with *n*-hexane/CH_2Cl_2 (2:1) and then recrystallized from ether/*n*-hexane to give 9.3 g (40.4% overall) of **13** as a crystalline solid: mp 87–88 °C; IR (KBr) 3080, 3050, 1665, 1580, 1460, 770, 750, 630 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 7.71–7.55 (m, 2 H, Ar*H*), 7.49–7.28 (m, 6 H, Ar*H*); ^{13}C NMR ($CDCl_3$, 50.29 MHz) δ 195.08 (*C*=O), 139.21, 133.96, 132.39, 131.18, 127.19, 121.04; EIMS *m/z* (relative intensity) 342 (M^+, 49.6), 340 (M^+, 99.8), 338 (M^+, 50.6), 259 (9.2), 185 (98.3), 183 (100), 155 (25.4).

Bis(2-bromophenyl)methane (14). A mixture of red phosphorus (15 g, 480 mmol), iodine (3 g, 12 mmol), and **13** (6.8 g, 20 mmol) in 47% HI (80 mL) was heated with stirring at 140 °C for 24 h. The reaction mixture was cooled to rt, poured into ice–water, extracted with CH_2Cl_2, washed successively with aqueous $NaHCO_3$ and water, dried ($MgSO_4$), and concentrated. The crude product was chromatographed on silica gel eluting with *n*-hexane to give 6.0 g (92%) of **14** as an oil: IR (KBr) 3050, 3020, 1585, 1565, 1465, 1440, 1025, 745 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 7.62–7.01 (m, 8 H, Ar*H*), 4.49 (s, 2 H, ArCH_2Ar); ^{13}C NMR ($CDCl_3$, 20.15 MHz) δ 138.83, 132.78, 130.64, 128.01, 127.44, 125.03, 42.01; EIMS (*m/z*) 328 (M^+, 6.5), 326 (M^+, 12.6), 324 (M^+, 6.5), 248 (31), 246 (31), 167 (100), 166 (57), 165 (69), 152 (17).

2-(Chloromethyl)benzyl Alcohol (16). To a solution of phthalyl alcohol **15**[20] (6.20 g, 44.9 mmol) and pyridine (5.40 g, 45.4 mmol) in benzene (50 mL) was added dropwise with stirring a solution of $SOCl_2$ (5.40 g, 45.5 mmol) in benzene (5 mL) at 10–15 °C. The mixture was stirred overnight at rt and then poured into ice–water (100 mL), extracted with ether, washed successively with aqueous $NaHCO_3$ and water, dried ($MgSO_4$), and concentrated. The crude product was chromatographed on a silica gel column eluting with CH_2Cl_2 to give 4.18 g (59.5%) of **16** as colorless crystals: mp 51–51.5 °C; IR (KBr) 3320 (broad), 3060, 3020, 2960, 2870, 1600, 1450, 1180, 1095, 1040, 1005, 765 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 7.36–7.28 (m, 4 H, Ar*H*), 4.78 (s, 2 H, ArCH_2O), 4.68 (s, 2 H, ArCH_2Cl), 2.07 (s, 1 H, O*H*); ^{13}C NMR ($CDCl_3$, 20.15 MHz) δ 138.94, 135.08, 130.03, 128.86, 128.44 and 127.98, 61.96 (CH_2Cl), 43.51 (CH_2OH); EIMS (*m/z*) 156 (M^+, 4.3), 140 (34), 138 (100), 120 (10), 119 (14), 91 (28); HRMS calcd for C_8H_9ClO 156.0341, found 156.0353.

Bis[2-(hydroxymethyl)phenyl]methane (19). The benzylic alcohol **16** was protected in the routine way by reaction with dihydropyran and *p*-toluenesulfonic acid (TsOH) in CH_2Cl_2 to give the corresponding THP ether **17** in 93% yield. To a solution of **17** (6.37 g, 26.5 mmol) containing a catalytic amount of CuI (0.5 g) in THF (40 mL) was added at 0 °C, by cannulation under nitrogen, the Grignard reagent **18** that was prepared from 2-bromobenzyl THP ether (9.0 g, 33 mmol). The mixture was stirred overnight at 50 °C and then treated with aqueous NH_4Cl solution, extracted with CH_2Cl_2, dried ($MgSO_4$), and concentrated to give the coupling product, a di-THP ether. The THP protecting groups were removed from the crude product by heating with TsOH in methanol. Usual workup and purification by chromatography (silica gel/CH_2Cl_2) afforded 3.95 g (66.6%) of an aromatic diol **19** as a colorless crystalline solid: mp 160.9–161.5 °C (lit.[14] mp 157.5–158.5 °C); IR (KBr) 3250 (broad), 2900, 1600, 1480, 1450, 1100, 740 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 7.46–6.84 (m, 8 H, Ar*H*), 5.08 (m, 2 H, O*H*), 4.48 (d, 4 H, ArCH_2O), 3.99 (s, 2 H, ArCH_2Ar); ^{13}C NMR ($CDCl_3$, 50.29 MHz) δ 140.24, 137.34, 128.92, 126.99, 126.80, 126.00, 60.83 (CH_2OH), 33.59 (ArCH_2Ar); EIMS (*m/z*) 210 ($M^+ - H_2O$, 100), 192 (19), 179 (80), 165 (47), 152 (12), 141 (3.0).

Bis(2-formylphenyl)methane (20). A solution of **19** (4.02 g, 17.6 mmol) and PDC (20 g) in DMF (40 mL) was stirred for 6 h at rt. This reaction mixture was diluted with water (200 mL), extracted with CH_2Cl_2, washed with water, dried ($MgSO_4$), and concentrated. The crude product was chromatographed on a silica gel column eluting with dichloromethane/*n*-hexane (1:1, v/v) to give 3.1 g (78.7%) of **20** as a colorless crystalline solid: mp 38–39 °C; IR (KBr) 3060, 2840, 2740, 1690, 1600, 1570, 1480, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 10.14 (s, 2 H, C*H*O), 7.87–6.93 (m, 8 H, Ar*H*), 4.86 (s, 2 H, ArCH_2Ar); ^{13}C NMR ($CDCl_3$, 50.29 MHz) δ 192.33 (*C*=O), 141.89, 133.74, 133.66, 132.78, 130.84, 126.82, 34.56 (ArCH_2Ar); EIMS (*m/z*) 224 (M^+, 5.7), 209 (5.9), 196 (33), 195 (100), 179 (34), 178 (68), 165 (41), 152 (13); HRMS calcd for $C_{15}H_{12}O_2$ 224.0837, found 224.0828.

Pentacyclo[22.4.0.0^{3,8}.0^{10,15}.0^{17,22}]octacosa-1(24),3(8),4,6,10-(15),11,13,17(22),18,20,25,27-dodecaene-2,16-dione (23). The dilithio reagent **21** was prepared by dropwise addition of *n*-BuLi (2.5 M, 4 mL, 10 mmol) to a solution of **14** (1.63 g, 5 mmol) in THF (300 mL) at −30 °C. After completion of the addition, the yellow solution was allowed to warm to rt and then stirred for 2 h. To this dilithio reagent **21** was added a solution of dialdehyde **20** (1.12 g, 5 mmol) in THF (100 mL). The mixture was stirred at rt for 2 h, heated under reflux for 20 h, and treated with aqueous NH_4Cl. After evaporation of the solvent in vacuo, the reaction mixture was extracted with CH_2Cl_2, dried ($MgSO_4$), and concentrated to give the coupling product, a cyclic diol **22**. The crude **22** was so difficult to purify that is was oxidized directly, without purification, by stirring with PCC (4 g) and Celite (3 g) in CH_2Cl_2 (70 mL) for 4 h. The reaction mixture was filtered, and the solvent was removed from the filtrate at reduced pressure to give the corresponding diketone **23**. Column chromatography of the crude **23** on silica gel eluting with CH_2Cl_2 followed by recrystallization from *n*-hexane/CH_2Cl_2 gave 452 mg (23%) of **23** as colorless crystalline solid: mp 349–351 °C dec; IR (KBr) 3050, 3020, 2900, 1655, 1595, 1440, 930, 730 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.58–6.73 (m, 16 H, Ar*H*), 4.11 (d, J_{AB} = 17 Hz, 2 H, ArCH_2Ar, quasi equatorial), 3.76 (d, J_{AB} = 17 Hz, 2 H, ArCH_2Ar, quasi axial); EIMS (*m/z*) 388 (M^+, 100), 370 (16), 352 (4.9), 296 (11), 252 (6.7), 194 (31), 178 (5.6); HRMS calcd for $C_{28}H_{20}O_2$ 388.1458, found 388.1433. The compound **23** was so insoluble in organic solvents that the ^{13}C NMR spectrum could not be obtained.

Pentacyclo[22.4.0.0^{3,8}.0^{10,15}.0^{17,22}]octacosa-1(24),3(8),4,6,10-(15),11,13,17(22),18,20,25,27-dodecaene (4) ([1$_4$]Orthocyclophane). Pd-Catalyzed Reduction of 23. In a reaction bottle diketone **23** (50 mg, 0.13 mmol) was dissolved in ethanol (50 mL), and concd HCl (2 mL), water (5 mL), and 10% Pd/C (20 mg) were added. The reaction bottle was connected to a hydrogen reservior at an initial pressure of 35 psi. After vigorous stirring at rt for 3 days, the reaction mixture was diluted with water and extracted with CH_2Cl_2. The extract was washed with water, dried ($MgSO_4$), and concentrated. The crude product was purified on a silica gel column eluting with CH_2Cl_2 and then recrystallized from CH_2Cl_2/ether to give 37 mg (80%) of **4** as colorless crystals: mp 345–346 °C dec; IR (KBr) 3055, 3020, 2960, 1595, 1485, 1450, 800, 750, 740, 625 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.17 (m, 16 H, Ar*H*), 3.72 (broad s, 8 H, ArCH_2Ar); EIMS (*m/z*) 360 (M^+, 100), 270 (11), 269 (52), 255 (20), 192 (34), 180 (23), 179 (97), 178 (47), 91 (19); HRMS calcd for $C_{28}H_{24}$ 360.1878, found 360.1883. Anal. Calcd for $C_{28}H_{24}$: C, 93.28; H, 6.72. Found: C, 93.21; H, 6.69. The compound **4** was so insoluble in organic solvents that the ^{13}C NMR spectrum could not be obtained.

Hexacyclo[22.4.0.0^{2,16}.0^{3,8}.0^{10,15}.0^{17,22}]octacosa-1(24),2(16),3-(8),4,6,10(15),11,13,17(22),18,20,25,27-tridecaene (24). Clemmensen Reduction of 23. A mixture of zinc (9 g) and $HgCl_2$ (0.9 g) was treated with a solution of concd HCl (3 mL) in water (10 mL) for 60 min. To the resulting amalgamated zinc was added a solution of the cyclic diketone **23** (76 mg, 0.2 mmol) in toluene (10 mL), followed by addition of concd HCl (20 mL) that was diluted with water (10 mL). The mixture was refluxed for 1–2 days, during which time additional HCl was added in small portions, 3 mL every 4 h. After being cooled, the organic layer was separated, washed with water, dried ($MgSO_4$), and concentrated. The crude product was chromatographed on a silica gel column eluting with CH_2Cl_2/*n*-hexane (1:1, v/v) to give 65 mg (91%) of **24** as a colorless crystalline solid: mp 337–338 °C dec; IR (KBr) 3050, 2950, 2830, 1580, 1440, 765, 745 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.37–6.88 (m, 16 H, Ar*H*), 4.07 (d, J_{AB} = 12 Hz, 2 H, ArCH_2Ar, quasi equatorial), 3.90 (d, J_{AB} = 12 Hz, 2 H, ArCH_2Ar, quasi axial); ^{13}C NMR (CD_2Cl_2, 75.47 MHz) δ 131.61, 131.27, 130.10, 129.44, 128.64, 126.60, 125.55, 36.09 (ArCH_2Ar); EIMS (*m/z*) 356 (M^+, 100), 340 (4.2), 339 (9.0), 314 (2.1), 313 (4.4), 278 (1.0), 265 (8.0), 179 (25), 178 (48); HRMS calcd for $C_{28}H_{20}$ 356.1565, found 356.1570.

McMurry Olefination of 23. A mixture of $LiAlH_4$ (40 mg, 1 mmol) and $TiCl_3$ (460 mg, 3 mmol) in dry THF (100 mL) was refluxed under nitrogen for 20 min. Following the addition of **23** (150 mg, 0.39 mmol), the resultant mixture was refluxed for 3 days. After the solvent was evaporated in vacuo, the reaction

mixture was diluted with water and taken up with CH_2Cl_2. The organic layer was washed successively with aqueous $NaHCO_3$ and water, dried ($MgSO_4$), and concentrated. The crude product was purified by chromatography (silica gel/CH_2Cl_2) and then recrystallized from ether/CH_2Cl_2 to give 112 mg (81%) of a bicyclic compound **24**. **Reduction of 23 with P/I_2 in HI** also afforded the fused cycloheptatriene **24** in 85% yield.

Hexacyclo[22.4.0.0^{2,16}.0^{3,8}.0^{10,15}.0^{17,22}]octacosa-1(24),2(16),3-(8),4,6,10(15),11,13,17(22),18,20,25,27-tridecaene-9,23-dione (26). A suspension of **24** (90 mg, 0.253 mmol), PCC (1 g), and Celite (1 g) in benzene (50 mL) was refluxed for 16 h. The reaction mixture was filtered off to remove the solid materials, followed by washing the precipitate several times with CH_2Cl_2 and concentration in vacuo. The crude product was crystallized from CH_2Cl_2/ether to give 75 mg (77%) of **26** as colorless crystals: mp >350 °C; IR (KBr) 3060, 1685, 1590, 1310, 1260, 935, 775, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$, 80 MHz) δ 7.61–6.86 (m, 16 H, Ar*H*); EIMS (*m*/*z*) 384 (M$^+$, 100), 355 (25), 329 (13), 326 (40), 300 (6.0), 192 (4.8), 162 (18); HRMS calcd for $C_{28}H_{16}O_2$, 384.1150, found 384.1152. The compound **26** was so insoluble in organic solvents that the ^{13}C NMR spectrum could not be obtained.

Hexacyclo[29.4.0.0^{3,8}.0^{10,15}.0^{17,22}.0^{24,29}]pentatriaconta-1-(31),3(8),4,6,10(15),11,13,17(22),18,20,24(29),25,27,32,34-pentadecaene-2,16-dione (29). The dilithio reagent **21**, which was prepared from the dibromide **14** (1.63 g, 5 mmol) and *n*-BuLi (2.5 M, 4 mL, 10 mmol) in THF, was treated with a solution of 1,2-bis(2-formylbenzyl)benzene (**27**)[26] (1.63 g, 5 mmol) in THF (100 mL) by the same procedure as that used for **23**. Hydrolytic workup gave a cyclic diol **28**, which was oxidized by stirring with PCC (4 g) and Celite (3 g) in CH_2Cl_2 (100 mL) to give the corresponding diketone. The crude product was chromatographed on silica gel eluting with *n*-hexane/CH_2Cl_2 (2:1, v/v) and then recrystallized from *n*-hexane/CH_2Cl_2 to give 752 mg (31%) of **29** as a colorless crystalline solid: mp 224–237 °C dec; IR (KBr) 3060, 2920, 1660, 1590, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.42–6.71 (m, 20 H, Ar*H*), 3.85 (s, 2 H, ArCH_2Ar), 3.64 (s, 4 H, ArCH_2Ar); ^{13}C NMR ($CDCl_3$, 50.29 MHz) δ 201.32 (*C*=O), 140.53, 139.17, 138.53, 137.81, 136.85, 131.28, 131.22, 130.91, 130.69, 129.9, 129.77, 128.98, 126.88, 126.57, 126.14, 37.10, 36.55; EIMS (*m*/*z*) 478 (M$^+$, 100), 460 (11), 284 (13), 281 (24), 265 (18), 252 (14); HRMS calcd for $C_{35}H_{26}O_2$ 478.1926, found 478.1931.

Hexacyclo[29.4.0.0^{3,8}.0^{10,15}.0^{17,22}.0^{24,29}]pentatriaconta-1-(31),3(8),4,6,10(15),11,13,17(22),18,20,24(29),25,27,32,34-pentadecaene (5) ([1_5]Orthocyclophane). Pd-Catalyzed Reduction of 29. The cyclic diketone **29** (96 mg, 0.2 mmol) was hydrogenated by stirring with 10% Pd/C (20 mg) in a mixture of EtOH (10 mL), concd HCl (0.4 mL), and water (1 mL) for 2 days under hydrogen (35 psi). The crude product was purified by chromatography (silica gel, CH_2Cl_2) and then recrystallized from ether/CH_2Cl_2 to give 84 mg (93%) of **5** as colorless crystals: mp 257–258 °C; IR (KBr) 3050, 2900, 1600, 1480, 1450, 1425, 750, 740, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.99 (m, 20 H, Ar*H*), 3.75 (s, 10 H, ArCH_2Ar); ^{13}C NMR ($CDCl_3$, 50.29 MHz) δ 138.27, 130.24, 126.26, 37.70 (ArCH_2Ar); EIMS (*m*/*z*) 450 (M$^+$, 62), 359 (12), 345 (6.9), 270 (22), 269 (90), 255 (30), 180 (19), 179 (100), 91 (20); HRMS calcd for $C_{35}H_{30}$ 450.2348, found 450.2334. Anal. Calcd for $C_{35}H_{30}$: C, 93.28; H, 6.72. Found: C, 93.01; H, 6.95.

Heptacyclo[29.4.0.0^{2,16}.0^{3,8}.0^{10,15}.0^{17,22}.0^{24,29}]pentatriaconta-1(31),2(16),3(8),4,6,10(15),11,13,17(22),18,20,24(29),25,27,32,34-hexadecaene (30). McMurry Olefination of 29. The reduction was carried out by the same procedure as described in the olefination of **23**. A mixture of $LiAlH_4$ (77 mg, 2 mmol), $TiCl_3$ (770 mg, 5 mmol), and **29** (480 mg, 1 mmol) in THF (100 mL) was refluxed for 2 days under nitrogen. After aqueous workup, the crude product was purified by column chromatography (silica gel/CH_2Cl_2) and then recrystallized from CH_2Cl_2/hexane to afford 421 mg (94%) of **30** as colorless crystals: mp 318 °C dec; IR (KBr) 3050, 2950, 2880, 1475, 1445, 805, 765, 755, 740, 630 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) 7.44–6.85 (m, 20 H, Ar*H*), 4.75–3.44 (m, 6 H, ArCH_2Ar); EIMS (*m*/*z*) 446 (M$^+$, 100), 342 (26), 282 (9.1), 268 (18), 266 (9.2), 252 (9.2), 179 (60), 178 (24). HRMS calcd for $C_{35}H_{26}$ 446.2028, found 446.2007. The compound **30** was so insoluble in organic solvents that the ^{13}C NMR spectrum could not be obtained.

Clemmensen reduction of 29 gave a mixture of **5** (10%) and **30** (75%) which could be separated by column chromatography.

Heptacyclo[29.4.0.0^{2,16}.0^{3,8}.0^{10,15}.0^{17,22}.0^{24,29}]pentatriaconta-1(31),2(16),3(8),4,6,10(15),11,13,17(22),18,20,24(29),25,27,32,34-hexadecaen-9-one (32). A suspension of **30** (110 mg, 0.25 mmol), PCC (1 g), and Celite (1 g) in benzene (50 mL) was refluxed for 16 h. The solid materials were filtered off from the reaction mixture, the precipitate was washed several times with dichloromethane, and the filtrate was concentrated in vacuo. The crude product was chromatographed on silica gel eluting with CH_2Cl_2/*n*-hexane (2:1, v/v) and then recrystallized from CH_2Cl_2/*n*-hexane to give 83 mg (73%) of **32** as colorless crystals: mp 292–293 °C; IR (KBr) 3055, 3020, 2900, 1670, 1595, 1485, 1310, 945, 745, 630 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.97–6.859 (m, 20 H, Ar*H*), 4.28 (d, J_{AB} = 14 Hz, 2 H, ArCH_2Ar, quasi equatorial), 3.62 (d, J_{AB} = 14 Hz, 2 H, ArCH_2Ar, quasi axial); ^{13}C NMR ($CDCl_3$, 50.29 MHz) δ 197.23 (*C*=O), 140.97, 140.23, 139.66, 136.43, 136.41, 135.44, 131.22, 130.99, 130.59, 130.01, 128.99, 128.52, 127.76, 126.78, 126.74, 125.29, 37.26; EIMS (*m*/*z*) 460 (M$^+$, 100), 442 (2.5), 369 (5.3), 356 (14), 281 (20), 265 (16), 252 (6.8), 179 (5.7); HRMS calcd for $C_{35}H_{24}O$ 460.1827, found 460.1829.

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Supplementary Material Available: ^{1}H NMR spectra of **13**, **14**, **16**, **20**, **23**, **24**, **26**, **29**, **30**, and **32** (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.