1,9-Dimethyl-2,7-diphenyl-8-azatricyclo[4.3.1.0^{2,7}]dec-8-ene (22). Colorless oil. ^{1}H NMR: δ 1.02 (s, MeC(1)); 1.1–1.7 (m, 4 H); 1.58 (s, MeC(9)); 1.7–2.4 (m, 5 H); 6.7–7.6 (m, 10 H).

Thermal Isomerization of 20. Pure **20** (36 mg, 0.1 mmol), in 1 mL of C_6H_6 was heated to 234 °C for 88 h and gave a 1:1:1 mixture on **20/21/22** together with polymeric materials.

Thermolysis of 28. A 3:2 mixture of **28** and **28′** (692 mg, ca. 2.1 mmol) in 5 mL of C_6H_6 was heated in sealed tube to 120 °C for 24 h. The ^{1}H NMR of the crude mixture (650 mg) showed that only **28** reacted. Column chromatography on silica gel (30 g) yielded a first fraction containing 310 mg of **30** (45%) on elution with petroleum ether/ether (9:2). A second fraction of 240 mg of unreacted **28′** (34%) was obtained with the same eluent.

Characteristics of 30. Oil, ^{1}H NMR: δ 0.4–1.3 (m, 2 H); 1.6–2.5 (m, 4 H); 2.07 (s, 3 H, Me); 4.6–5.1 (m, 2 H); 5.1–5.9 (m, 1 H); 6.8–7.3 (m, 6 H); 7.3–7.6 (m, 2 H); 7.6–7.9 (m, 2 H); 8.5–8.7 (m, 1 H).

Catalyzed Intramolecular Cycloaddition of 8c. **8c** (96 mg, 0.3 mmol) and 155 mg (0.2 mmol) of (4-Br-$C_6H_4)_3NSbCl_6$ in 2 mL of CH_2Cl_2 were heated to 135 °C for 20 h in a sealed Pyrex tube under N_2 atmosphere. After cooling, the tube was opened and the solution filtered through silica gel (petroleum ether/ether). The solvent was evaporated in vacuo and the residue analyzed by ^{1}H NMR (see Table IV).

Catalyzed Intramolecular Cycloaddition of 8d. (a) **8d** (115 mg, 0.4 mmol) and 78 mg (0.1 mmol) of (4-Br-$C_6H_4)_3NSbCl_6$ in 2.5 mL of CH_2Cl_2 were heated to 135 °C for 62 h and analyzed after workup (see above and Table IV). (b) **8d** (68 mg, 0.2 mmol) and 33 mg (0.05 mmol) of Eu(thd)$_3$ in 0.5 mL of C_6H_6 were heated to 180 °C for 43 h. The same workup conditions as above were used (see Table IV). (c) **8d** (166 mg, 0.5 mmol) and 49 mg (0.05 mmol) of Yb(fod)$_3$ in 1 mL of C_6H_6 were heated to 190 °C for 72 h. (d) **8d** (115 mg, 0.4 mmol) and 38 mg (0.04 mmol) of Eu(fod)$_3$ in 0.5 mL of C_6H_6 were heated to 192 °C for 63 h. (e) **8d** (66 mg, 0.2 mmol) and 18 mg (0.06 mmol) of Ni(acac)$_2$ in 0.5 mL of C_6H_6 were heated to 193 °C for 40 h. (f) **8d** (100 mg, 0.3 mmol) and 50 mg (0.2 mmol) of $ZnBr_2$ in 0.8 mL of C_6H_6 were heated to 155 °C for 63 h. After cooling, the tube was opened, and 50 mL of ether was added to the residue. Hydrolysis with 10% NaOH was performed. After drying, the solvent was evaporated in vacuo and the residue analyzed by ^{1}H NMR (see Table IV).

Ab initio MO calculations with the minimal STO-3G basis set were carried out by using the MONSTERGAUSS 81 program[23] on a CYBER 170-855 CDC computer. The geometries were fully optimized with respect to all bond lengths and bond angles by using Davidon's method with standard convergence criteria.[26] Due to the size of the molecules calculated and computer time limitations, we were forced to use the minimal STO-3G basis set. Systematic errors on the total energies should be canceled, in part at least, on comparing rigid isomers as it is done in our model studies.

Acknowledgment. We thank Hoffmann-La Roche and Co. AG, Basel, the Swiss National Science Foundation and the Fonds Herbette, Lausanne, for financial support. We are most grateful to the Ecole Polytechnique Fédérale de Lausanne and its Centre de Calcul (Mr. P. Santschi) for generous computing time. We also thank (NRS/France) for financial support and DGRST (France) for a fellowship (A.E.).

Registry No. (*E*)-**5a**, 110775-23-0; (*E*)-**5a** (hydrazone), 107112-63-0; (*Z*)-**5a**, 110775-27-4; (*Z*)-**5a** (hydrazone), 107112-62-9; (*E*)-**5c**, 110775-24-1; (*E*)-**5c** (hydrazone), 110775-58-1; (*Z*)-**5c**, 110775-28-5; (*Z*)-**5c** (hydrazone), 110775-55-8; (*E*)-**5e**, 110775-25-2; (*E*)-**5e** (hydrazone), 110775-56-9; (*Z*)-**5e**, 110775-29-6; (*Z*)-**5e** (hydrazone), 110775-59-2; (*E*)-**5g**, 110775-26-3; (*E*)-**5g** (hydrazone), 110775-57-0; (*Z*)-**5g**, 110775-30-9; (*Z*)-**5g** (hydrazone), 110775-60-5; (*E*)-**5j**, 75406-55-2; (*Z*)-**5j**, 75406-54-1; **6a**, 58130-08-8; **6c**, 62901-83-1; **6g**, 110775-31-0; **6i**, 100589-87-5; **6j**, 14491-02-2; **7j**, 22524-25-0; **7k**, 15177-05-6; **8a**, 92898-36-7; **8b**, 92898-34-5; **8c**, 92898-33-4; **8d**, 92898-27-6; **8e**, 110775-32-1; **8f**, 110775-33-2; **8g**, 110775-34-3; **8h**, 110775-35-4; **8i**, 110775-36-5; **8j**, 110775-37-6; **8k**, 110775-39-8; **10a**, 92898-37-8; **10b**, 92898-39-0; **11a**, 92898-38-9; **11b**, 92898-35-6; **12a**, 110775-48-9; **12b**, 92898-30-1; **13a**, 110775-49-0; **14a**, 110775-43-4; **14b**, 92898-32-3; **15a**, 110775-44-5; **15b**, 92898-31-2; **16a**, 110775-45-6; **16b**, 92898-28-7; **17a**, 110775-46-7; **17b**, 92898-29-8; **18**, 110775-50-3; **19**, 110775-51-4; **20**, 110849-70-2; **21**, 110775-52-5; **22**, 110775-53-6; **23**, 110775-47-8; **24**, 110775-40-1; **28**, 110775-41-2; **28′**, 110775-42-3; **30**, 110775-54-7; Eu(thd)$_3$, 15522-71-1; Yb(fod)$_3$, 18323-96-1; Eu(fod)$_3$, 17631-68-4; Ni(acac)$_2$, 3264-82-2; CH_2=$CH(CH_2)_3CH(Ph)NH_2$, 110775-38-7; CH_2=$CH(CH_2)_2CH(Ph)NH_2$, 109925-99-7; (4-Br$C_6H_4)_3NSbCl_3$, 24964-91-8; (*Z*)-EtC(Ph)=$NNMe_2$, 75406-34-7; $Br(CH_2)_3CH$=CH_2, 1119-51-3; (*Z*)-$PhCH_2C(Me)$=$NNMe_2$, 66930-29-8; $Br(CH_2)_2CH$=CH_2, 5162-44-7; ICH_2CH=CH_2, 556-56-9; PhCOEt, 93-55-0; PhCOMe, 98-86-2; PhCN, 100-47-0; $Br(CH_2)_4CH$=CH_2, 2695-47-8; (*E*)-EtC(Ph)=$NNMe_2$, 75406-33-6; (*E*)-$PhCH_2C(Me)$=$NNMe_2$, 66930-19-6; 2,3-dimethyl-2-phenyl-2*H*-azirine, 57573-53-2; α-tetralone, 529-34-0.

Supplementary Material Available: Spectra data and elemental analyses of compounds **8b–e,i–k**, **24**, **28**, **28′**, **10a**, **11a**, **10b**, **11b**, **14a**, **15a**, **16a**, **17a**, **14b**, **15b**, **16b**, **17b**, **12a**, **13a**, **12b**, **18–22** and **30** and ab initio STO-3G-optimized geometries of 1*H*- (**31**), 2*H*- (**32**), and 3*H*-pyrrole (**33**) and 1-azabicyclo[2.2.1]hept-2-ene (**35**) (17 pages). Ordering information is given on any current masthead page.

Doubly Clamped Cope Systems

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Cyclizations of *meso*-**15** and of *d,l*-**15** with phenyllithium lead to the "crossed Cope system" **6B**, the constitution of which is confirmed by 2D NMR and X-ray analysis (*d,l* configuration). Conformationally fixed biallyl skeletons of this type are shown not to undergo the typical rearrangement.

Introduction

The activation parameters of the Cope rearrangement are strongly influenced by substituents and by small rings condensed to the biallyl skeleton.[1] By formal replacement of small rings in the Cope system (cf. homotropilidene, **I**, B = CH_2) by larger, e.g., medium-sized or multimembered rings, we have attempted to examine other influences on the Cope rearrangement. The strain of a medium ring

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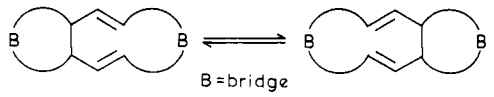
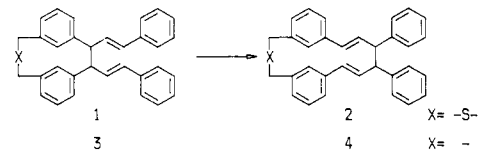
(1) Vogel, E. *Justus Liebigs Ann. Chem.* **1958**, *615*, 1. Doering, W. v. E.; Roth, W. R. *Tetrahedron* **1963**, *19*, 715.

0022-3263/87/1952-5560$01.50/0 © 1987 American Chemical Society

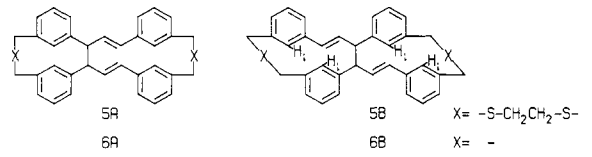
should lower not only the rearrangement barrier but also the conformational fixation of the biallyl skeleton by means of the bridge.



Some time ago we succeeded in fixing a tetraaryl biallyl skeleton by a *single* bridge of the metacyclophane type (cf. **1**, **3**). Such singly bridged Cope systems underwent spontaneous Cope rearrangements (**1** → **2** and **3** → **4**) under mild conditions.[2]



The preparation of *doubly* bridged Cope systems such as **5** or **6** involves an additional difficulty, namely, the possibility of the formation of two constitutional isomers A and B.



Earlier investigations on the synthesis of the biallyl system **5** bearing two rather long and less strained bridges revealed that the choice of the stereochemistry of the open chained starting compound **15** (*meso* or *d,l*) is decisive for the constitution of the cyclization product **5**: *meso*-**15** on cyclization yielded **5B**, whereas the stereoisomeric starting material *d,l*-**15** yielded the isomeric biallyl compound **5A**.[3]

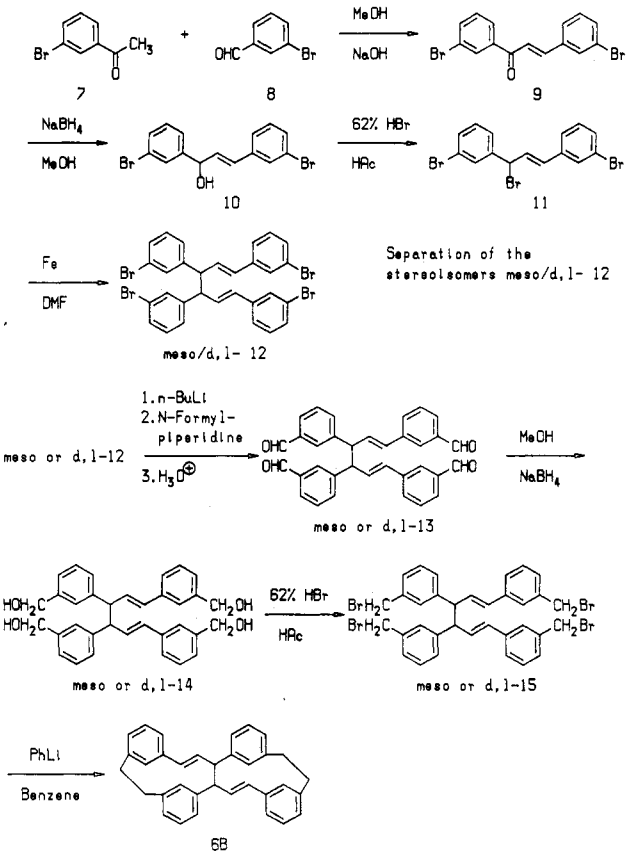
In thermal rearrangement studies, different results were found for the corresponding open chain tetraaryl-1,5-hexadienes of type **12**: the open chain *meso* or *d,l* isomers of **12** after 4 h heating to 140 °C both yield a 1:1 mixture of the *meso*/*d,l* diastereomeric compounds **12**. In contrast to this, in the thermolysis of **5B** after cooling only the constitutional isomer **5A** was detected by means of ^{1}H NMR spectroscopy.[3]

In the present work, the bridges in the Cope system **I** were chosen to be as short as possible, shorter than the bridges in **5**. The structure **6** was chosen in order to obtain more strongly strained doubly bridged Cope skeletons for which a lower barrier of rearrangement could be expected. A structure such as **6A** should be degenerate with respect to a Cope rearrangement if the configuration (*meso* or *d,l*) remains the same in the corresponding starting and end products. A rapid valence isomerization should then be detectable by use of dynamic NMR spectroscopy.

Syntheses

The synthetic approach to the small-bridged biallyl system **6B** is shown in Scheme I. The *meso* intermediates **12–15** were obtained more easily and in larger amounts than the corresponding *d,l* isomers due to solubility, ease of crystallization, purification, and other reasons (cf. ref 4). The cyclizations (C–C coupling with phenyllithium)

Scheme I



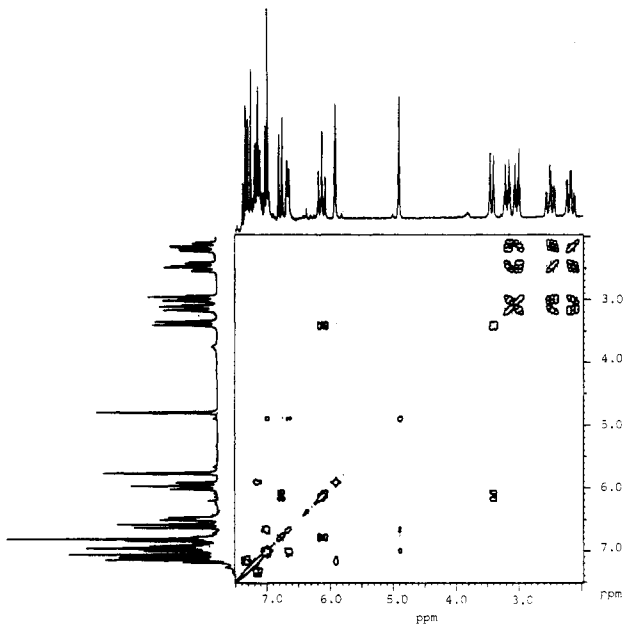


Figure 1. ^{1}H–^{1}H-correlated 2D NMR spectrum of **6B** (COSY 45).

were carried out in boiling solvent (benzene/ether) starting with *meso*-**15** and, separately, with *d,l*-**15**. The cyclization products **6** isolated from the reactions could not be characterized by normal 1 D NMR methods (^{1}H, ^{13}C). The decisive twofold cyclization reaction of both *meso*- and *d,l*-**15** with phenyllithium yielded the doubly bridged biallyl carbon skeleton **6B** in 1.5% yield[5] (Experimental Section).

(2) Vögtle, F.; Eisen, N. *Angew. Chem.* **1986**, *98*, 1029; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1026.
(3) Vögtle, F.; Eisen, N.; Mayenfels, P.; Knoch, F. *Tetrahedron Lett.* **1986**, *27*, 695.
(4) Eisen, N. Ph.D. Thesis, Universität Bonn, 1986.

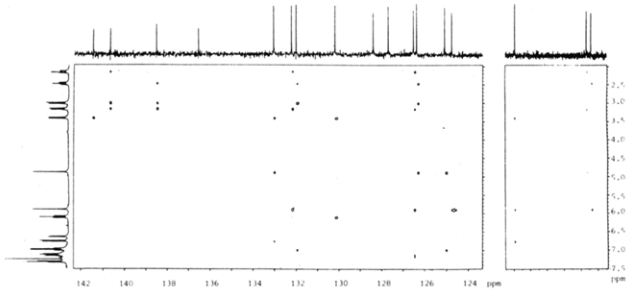


Figure 2. ^1H–^{13}C-COLOC experiment of **6B**.

Table I. Interpretation of 2D-C–H Correlations (400 MHz) for 6B

δ_C	δ_H	$^1J_{CH}$, Hz	δ_{COLOC}
141.42			3.42
140.63			2.17 AB 3.17
			3.01
138.47			2.48 AB 3.01
			3.17
136.50			6.12
133.03	6.78 (C=C, d)	158	3.42; 4.9
132.21	5.9 (H_i)	152	2.17 AB 3.17
131.99	4.9 (H_i)	158	2.48 AB 3.01
			7.0
130.18	6.12 (C=C, t)	152	3.42
128.40	7.31	158	7.17
127.68	7.0	158	2.17 AB 3.17
			5.9; 7.18
126.37	6.98	158	2.48 AB 3.01
			4.9
125.08	6.65	158	4.9; 7.0
124.76	7.15	158	5.9
47.85	3.42	130	3.42
39.26	2.48 AB 3.01	130	2.17 AB 3.17
38.71	2.17 AB 3.17	130	2.48

NMR Studies

In order to determine the constitution of the cyclization products **6** which were obtained by cyclization of *meso*- and *d,l*-**15** with phenyllithium, 2D NMR spectroscopic methods were used. Figures 1 and 2 show the ^1H–^1H correlated 2D NMR spectrum (COSY 45) and ^1H–^{13}C COLOC experiments. The interpretation of these spectra led to the data listed in Table I, which confirmed the constitution of the cyclization products to be **6B** and not **6A**.

In addition to this, the intraanular H_i proton absorptions of **6B** (δ 4.9, cf. formula **6B**) and the strong splitting of the AA′BB′ systems of the protons of the ethano bridges (24-line pattern) reflect the ring strain which is present in this double [4.2]metacyclophane system.

X-ray Structure Analysis

The X-ray structure analysis of the cyclization product of *d,l*-**15** suffered from low quality of the obtained crystals but definitely proved the presence of the isomer *d,l*-**6B** (cf. Figure 3).

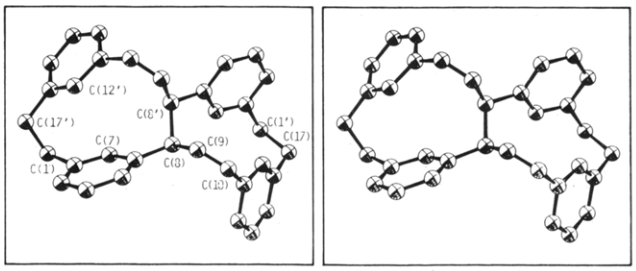


Figure 3. Stereoscopic view of **6B** with indication of the numbering scheme for the atoms.

6B has a twofold axis of symmetry which crosses the central bridging bond C(8)–C(8′). Half of a molecule is situated in the asymmetric unit.

Due to steric strain in the [4.2]metacyclophane ring system of **6B** the C–C bond of the central bridges C(8)–C(8′) is significantly longer (160 pm) than a usual C–C single bond. This also holds true to a lesser extent for the bond C(1)–C(17′) (156 pm). The bond angles at the sp^2-hybridized C atoms C(9) and C(10) are wider (126.9° and 125.8°, respectively) relative to normal sp^3-hybridized centers.

The benzene rings are planar (maximal deviation of a least squares plane 2.9 and 3.5 pm, respectively). The shortest distance between the two atoms (C) within the metacyclophane units [C(7)–C(12′)] amounts to 297.7 pm.

Rearrangement Studies and Conclusions

Experiments to rearrange **6B** thermally gave no hint of the formation of the constitutional isomer **6A**. This is plausible as the steric arrangement of the 1,5-hexadiene system in **6B**, fixed by the short bridges, is not favorable for a Cope rearrangement. It is also plausible from molecular model considerations that the constitution **6A**, which would be valuable for comparison purposes, is sterically unfavorable. As a consequence, in the bridge-forming step of the doubly bridged biallyl system the stereoisomer **6B**—containing two equal large rings with one vinyl group each—should be formed more easily, as is found experimentally. In conclusion, doubly bridged "crossed" biallyl systems of type **6B** do not seem to be appropriate candidates for Cope rearrangements. Cope systems of type **6A** bearing two symmetrical cyclophane-type bridges capable of undergoing (degenerate) Cope rearrangements are not known hitherto and therefore remain a challenge for synthesis. To obtain these, new synthetic strategies will have to be developed.

Experimental Section

Melting points were taken on a Kofler Mikroskopheiztisch and are uncorrected. NMR spectra were recorded on Bruker WH-90 (90 MHz) and WH-400 (400 MHz) spectrometers. For mass spectra, spectrometers MS-30 and MS-50, A.E.I., Manchester, England, were used; in all bromo compounds the isotope ^{79}Br is given.

1,3-Bis(3-bromophenyl)-2-propen-1-one (9) through Aldol Condensation of *m*-Bromobenzaldehyde (8) with *m*-Bromoacetophenone (7). Freshly distilled *m*-bromoacetophenone (**7**; 10.0 g, 50.0 mmol) and freshly distilled *m*-bromobenzaldehyde (**8**; 9.30 g, 50.0 mmol) were added to 200 mL of methanol in a three-necked flask fitted with reflux condenser, magnetic stirrer, and dropping funnel. To this solution a solution of NaOH (0.80 g, 20.0 mmol) in 40 mL of ethanol was dropped at room temperature. After the mixture was stirred overnight, a yellow material precipitated, which was filtered and washed successively with water and methanol. The precipitate was dried and recrystallized from ethanol: 11–16.5 g (60–90% yield) of **9** (yellow crystals of mp 84–86 °C); R_f 0.63 (SiO_2, $CHCl_3$); ^1H NMR

(5) From molecular models it becomes clear that with the longer bridges in compounds **5A,B** the cisoid configuration **5A** here is well possible and not much more strained than the transoid isomer **5B**. In contrast to **5**, in the compound series **6** the isomer **6A** seems to be less stable than **6B** because of the two shorter bridges, which makes it plausible that **6A** is not formed under these conditions. *meso*-**15** yields the same result as *d,l*-**15**: both products **6B** give the same NMR spectra, and they have the same constitution. As an X-ray analysis could not be obtained for the product formed from *meso*-**15**, the configuration of this product is not sure; in any case **6A** is not formed.

($CDCl_3/TMS_{int}$) δ 7.22–8.16 (2 × 4 aryl H and 2=CH); MS, *m/z* 364 (M^+), 285 (M^+–Br), 102 (C_6H_6 CH=CH, 100%); high-resolution MS, $C_{15}H_{10}Br_2O$, 363.9104. Calcd: C, 49.22; H, 2.75. Found: C, 49.06; H, 2.71.

1,3-Bis(bromophenyl)-1-hydroxy-2-propene (10) through Reduction of 1,3-Bis(3-bromophenyl)-2-propen-1-one (9) with Sodium Borohydride in Methanol.[6,7] 1,3-Bis(3-bromophenyl)-2-propen-1-one (**9**; 30.0 g, 82.5 mmol) was suspended in 1 L of methanol in a 2-L three-necked flask fitted with reflux condenser, bubble counter, and magnetic stirrer. Sodium borohydride was added portionwise in excess. The suspension became clear under H_2 development, and at the end of the reaction a clear solution resulted. Stirring was continued for 1 h. The solution was evaporated to dryness. The residue was dissolved in a chloroform/water mixture and the organic phase separated. It was washed twice with distilled water and dried over $MgSO_4$. Evaporation yielded a viscous oil in 90–98% yield. This substance was ^1H NMR spectroscopically pure and was used for the following synthetic step: R_f 0.3 (SiO_2, $CHCl_3$); ^1H NMR ($CDCl_3/TMS_{int}$) δ 2.57 (m, br, 1 OH), 5.27 (d, J = 6 Hz, 1 CH), 6.25 (dd, J_{AB} = 6 and 16 Hz, 1 =CH), 6.58 (d, J_{AB} = 16 Hz, 1 =CH); MS, *m/z* 366 (M^+), 287 (M^+ – Br), 183 (BrC_6H_4C=O, 100%); high-resolution MS, $C_{15}H_{12}Br_2O$, 365.9255. Calcd: C, 48.95; H, 3.29. Found: C, 49.17; H, 3.45.

1-Bromo-1,3-bis(3-bromophenyl)-2-propene (11). 1,3-Bis(3-bromophenyl)-1-hydroxy-2-propene (**10**; 44.0 g, 0.12 mmol) was dissolved in 200 mL of hot acetic acid. After cooling to room temperature this solution was dropped to a solution of 63% HBr (18.0 mL, d = 1.73) in 10 mL of acetic acid, which was cooled in an ice bath. After the mixture was stirred for 12 h, the heavy phase was separated and freed from the rest of the solvent in vacuo. The resulting brown oil (75–90% yield) was used for the following reaction without further purification. The product should not be brought in contact with metals because this will decompose it: ^1H NMR ($CDCl_3/TMS_{int}$) δ 5.69 (d, J = 7 Hz, 1 CH), 6.34–6.78 (m, 2 =CH), 7.04–7.63 (m, 8 aryl H); MS, *m/z* 428 (not registered), 349 (M^+ – Br), 270 (M^+ – 2Br, 100%), 191 (M^+ – 3Br); high-resolution MS, M^+ – Br, 348.9227 (because of low stability of this substance the M^+ – Br peak is taken as a reference). Calcd: C, 41.80; H, 2.58. Found: C, 39.19; H, 2.67.

***meso*-/*d,l*-1,3,4,6-Tetrakis(3-bromophenyl)-1,5-hexadiene (12).**[8] 1-Bromo-1,3-bis(3-bromophenyl)-2-propene (**11**; 50.0 mmol) in 250 mL of *N,N*-dimethylformamide was put into a three-necked flask fitted with inner thermometer, reflux condenser, and magnetic stirrer. Iron powder (25.0 mmol) was added in portions, whereupon a dark color and heat development was observed. After the addition the solution was stirred overnight at 60 °C. The solvent was removed and the residue dissolved in a chloroform/water mixture and acidified with an HCl solution. The organic phase was separated and washed several times with water until the phase was pH neutral. The chloroform solution was dried over $MgSO_4$. Evaporation yielded a yellow-orange residue, which was dissolved in acetone. Crystallization of the *meso* isomer took place, which was separated through suction from the dissolved *d,l* isomer. Whereas the *meso* isomer was isolated as a colorless powder, the *d,l* isomer remained even after removal of acetone as an impure oil, which had to be purified by column chromatography (SiO_2; ethyl acetate/cyclohexane, 1:10). The purified *d/l* isomer which appeared first as a yellow oil crystallized extremely slowly to yield a colorless powder. The total yields for the *meso* and *d,l* isomers were between 55% and 65%. *meso*-**12**: mp 172–175 °C; ^1H NMR ($CDCl_3/TMS_{int}$) δ 3.78 (m, 2 CH), 6.13 (m, 4 =CH), 7.01–7.37 (m, 16 aryl H). *d,l*-**12**: mp 135–137 °C; ^1H NMR ($CDCl_3/TMS_{int}$) δ 3.77 (m, 2 CH), 6.31 (m, 4 =CH), 6.83–7.53 (m, 16 aryl H). MS (*meso*/*d,l* form), *m/z* 698 (M^+), 619 (M^+ – Br), 349 ($M^+/2$, 100%), 270 ($M^+/2$ – Br), 191 ($M^+/2$ – 2Br), 115 (C_6H_4CHCH=CH); high-resolution MS (because of instability in the mass spectrometer $M^+/2$ was taken as a reference); 348.9220. Calcd: C, 51.32; H, 3.16. Found: C, 51.48; H, 3.13.

***meso*-1,3,4,6-Tetrakis(3-formylphenyl)-1,5-hexadiene (13).** *meso*-1,3,4,6-Tetrakis(3-bromophenyl)-1,5-hexadiene (**12**; 5.00 g, 7.10 mmol) was suspended in a 250-mL, three-necked flask fitted with a bubble counter, gas inlet tube, and septum cap. The flask had been heated before and filled with argon. The following reaction because of the heterogeneous conditions took place in a supersonic bath filled with ice–water. Over a period of 3 h a 1.5 M solution of *n*-butyllithium (in *n*-hexane, 20.0 mL, 32.05 mmol) was slowly added. Stirring was continued for 2 h, whereupon a color change from colorless to reddish and brown was observed. By means of a syringe *N*-formylpiperidine (3.60 mL, 32.0 mmol) was then added. After 2 h of being stirred the mixture was acidified with 3 N HCl. The remaining brown solid was sucked off, dried, and then purified chromatographically on a column (SiO_2; ethyl acetate/cyclohexane, 1:2): 1.8 g (51%) of pure product.

***d,l*-1,3,4,6-Tetrakis(3-formylphenyl)-1,5-hexadiene (13).** The apparatus used and the procedure were the same as in the experiment described above. As the *d/l* isomer of **12** was soluble in ether, the use of a supersonic bath was not necessary and instead a magnetic stirrer could be applied. The complete reaction could be carried out at room temperature. After hydrolysis and phase separation using usual workup procedures (washing of the organic phase with water, saturated $NaHCO_3$ solution, saturated NaCl solution, and again water) a yellow oil was obtained, which was purified by column chromatography (SiO_2; ethyl acetate/cyclohexane, 1:2). The yields (around 25%) were significantly lower than those obtained for the *meso* isomer. *meso*-**13**: mp 172–175 °C. *d,l*-**13**: mp 52–54 °C. ^1H NMR (*meso* form, $CDCl_3/TMS_{int}$) δ 4.09 (m, 2 CH), 6.30 (m, 4 =CH), 7.27–7.98 (m, 16 aryl H), 9.95, 10.04 (2 s, 2 × 2 CHO); ^1H NMR (*d,l* form, $CDCl_3/TMS_{int}$) δ 4.11 (m, 2 CH), 6.61 (m, 4 =CH), 7.24–7.93 (m, 16 aryl H), 9.91, 9.97 (2 s, 2 × 2 CHO); MS, *m/z* 498 (M^+), 249 ($M^+/2$, 100%), 211 ($M^+/2$ – CO), 193 ($M^+/2$ – 2CO), 115 (C_9H_7), 91; high-resolution MS, $C_{34}H_{26}O_4$, 498.1804. Calcd: C, 81.91; H, 5.26. Found: C, 81.46; H, 5.22.

***meso*- and *d,l*-1,3,4,6-Tetrakis[3-(hydroxymethyl)phenyl]-1,5-hexadiene (14).** *meso*- or *d,l*-1,3,4,6-tetrakis(3-formylphenyl)-1,5-hexadiene (**13**; 2.00 g, 4.00 mmol) was dissolved or suspended in 200 mL of methanol and put into a 500-mL, three-necked flask fitted with reflux condenser, bubble counter, and magnetic stirrer. Under continuous stirring, sodium borohydride was added portionwise in excess to the suspension or solution at room temperature. Stirring was continued overnight. Then the mixture was evaporated to dryness. Water was added to the residue, and stirring was continued for 12 h. After filtration the solid isolated was dried over P_4O_{10} in vacuo. The solid obtained was pure enough for the following reaction. The yields were around 75–85%: ^1H NMR (*meso* form, CD_3OD/TMS_{int}) δ 3.98 (m, 2 CH), 4.51, 4.60 (2s, 2 × 4 CH_2OH), 6.25 (m, 4 =CH), 7.10–7.39 (m, 16 aryl H); ^1H NMR (*d,l* form, CD_3OD/TMS_{int}) δ 4.0 (m, 2 CH), 4.52, 4.55 (2 s, 2 × 4 CH_2OH), 6.53 (m, 4 =CH), 6.93–7.44 (m, 16 aryl H). *meso* form: mp 68–70 °C. *d,l* form: mp 135–138 °C. MS, *m/z* 506 (M^+), 488 (M^+ – H_2O), 470 (M^+ – 2 H_2O), 253 ($M^+/2$), 205, 115 (C_9H_7), 91; high-resolution MS, $C_{34}H_{34}O_4$, 506.2460. Calcd: C, 80.61; H, 6.76. Found: C, 80.02; H, 6.65.

***meso*- and *d,l*-1,3,4,6-Tetrakis[3-(bromomethyl)phenyl]-1,5-hexadiene (15).** *meso*- or *d,l*-1,3,4,6-tetrakis[3-(hydroxymethyl)phenyl]-1,5-hexadiene (**14**; 1.00 g, 1.98 mmol) was suspended in 150 mL of dry toluene/50 mL of diethyl ether in a 250-mL flask fitted with dropping funnel and magnetic stirrer. From the dropping funnel, slowly a solution of 3.00 mL of phosphorous tribromide in 25 mL of dry toluene was added under stirring at room temperature. Stirring was continued overnight, whereupon a clear pale brown solution was obtained. After evaporation to dryness, the residue was dissolved in chloroform and washed shortly with water. The organic phase was separated, dried over $MgSO_4$, and evaporated to dryness. The residue then was purified by column chromatography (SiO_2; chloroform/toluene, 20:1). The yields were between 75% and 85%: ^1H NMR (*meso* form, $CDCl_3/TMS_{int}$) δ 3.87 (m, 2 CH), 4.44, 4.47 (2 s, 2 × 4 CH_2Br), 6.27 (m, 4 =CH), 7.12–7.34 (m, 16 aryl H); ^1H NMR (*d,l* form, $CDCl_3/TMS_{int}$) δ 3.88 (m, 2 CH), 4.43, 4.48 (2 s, 2 × 4 CH_2Br), 6.48 (m, 4 =CH), 6.95–7.44 (m, 16 aryl H); MS, *m/z* 754 (M^+), 675 (M^+ – Br), 596/594 (M^+ – 2Br), 377 ($M^+/2$, 100%), 298/297 ($M^+/2$ – Br), 219 ($M^+/2$ – 2Br), 79 (Br). Calcd: C, 53.86; H, 3.99. Found: C, 53.41; H, 3.81.

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11,14,32,35-Tetrathia[3.6.3.6.0^{1,22}](1,3)benzenophane-2,23-diene (5A) and 11,14,32,35-Tetrathia[3.6.3.6.0^{1,24}](1,3)-benzenophane-2,22-diene (5B). Benzene (1.7 L) and 0.8 L of ethanol were refluxed in a 4-L 2C-VP apparatus. The solutions of 1.50 g (1.97 mmol) of freshly purified *meso*- or *d,l*-1,3,4,6-tetrakis[3-(bromomethyl)phenyl]-1,5-hexadiene (**15**), respectively, in 250 mL of benzene and 0.46 g (5.00 mmol) of 1,2-ethanedithiol or 1.12 g (0.02 mol) of potassium hydroxide in 250 mL of ethanol were added dropwise simultaneously during 8 h. After complete addition the mixture was heated under reflux for additional 2 h. The mixture was evaporated to dryness, the residue taken up in chloroform, and the solution filtered from the insoluble residue. The solvent was removed and the raw product purified by column chromatography (SiO_2; chloroform/cyclohexane, 1:1): yield, 15–20% of **5A** or **5B**, respectively; ^{1}H NMR (*meso*-**5**, $CDCl_3$/TMS_{int}) δ 2.46, 2.48 (2 s, 2 × 4 H, SCH_2CH_2S), 3.60–3.68 (2 s, 2 × 4 H, SCH_2–aryl), 3.72 (m, 2 CH), 6.04 (m, 4 =CH), 6.8–7.48 (m, 16 aryl H); ^{1}H NMR (*d,l*-**5**, $CDCl_3$/TMS_{int}) δ 2.24, 2.63 (2 s, 2 × 4 H, SCH_2CH_2S), 3.57, 3.62 (2 s, 2 × 4 H, SCH_2–aryl), 3.74 (m, 2 CH), 6.44 (m, 4 =CH), 6.93–7.55 (m, 16 aryl H); MS, *m/z* 622 (M^+) (*meso*-**5** and *d,l*-**5**); high-resolution MS, $C_{38}H_{34}S_4$, 622.1859 (*d,l*-**5**), $C_{38}H_{34}S_4$, 622.1648 (*meso*-**5**).

***d,l*-[3.2.3.2.0^{1,18}](1,3)Benzeneophane-2,19-diene (6B) through Cyclization of *d,l*-1,3,4,6-Tetrakis[3-(bromomethyl)phenyl]-1,5-hexadiene (15) with Phenyllithium.**[5] In a 500-mL, three-necked flask previously heated and filled with argon, fitted with a septum cap, gas inlet tube, reflux condenser with bubble counter, and magnetic stirrer, *d,l*-1,3,4,6-tetrakis-[3-(bromomethyl)phenyl]-1,5-hexadiene (**15**; 1.30 g, 1.715 mmol) was heated to boiling in benzene and phenyllithium (1.8 M in benzene/ether, 70:30, 2.30 mL, 4.28 mmol) was added slowly by means of a syringe, whereupon a color change from yellow to orange and dark red was observed. Stirring under reflux was continued for 2 h. The solvent was removed and the residue taken up in chloroform. The solution was washed with water and the organic phase separated and dried over $MgSO_4$. The chloroform was evaporated to dryness. The byproduct biphenyl was distilled off in sufficient high vacuo. The remaining red residue was purified by column chromatography (SiO_2; chloroform/cyclohexane, 1:5): 12.4 mg (1.7%), yield of pure substance with mp 210 °C; R_f 0.55 (SiO_2; chloroform/cyclohexane, 1:5); ^{1}H NMR ($CDCl_3$/TMS_{int}, 200 MHz) δ 2.17 (d of t, J = 12.6 and 3.6 Hz, 2 H), 2.48 (d of t, J = 12.6 and 3.6 Hz, 2 H), 3.01 (t of d, J = 12.6 and 3.6 Hz, 2 H), 3.17 (t of d, J = 11 Hz) [AA'BB' system], 3.42 (d, 2 CH, J = 11 Hz), 4.9 (s, 2 H_i), 5.9 (s, 2 H_i), 6.12 (t, 2 =CH, J = 11 Hz), 6.65 (m, 2 aryl H), 6.78 (d, 2 =CH, J = 11 Hz), 6.93–7.4 (m, 14 aryl H); MS, *m/z* 438 (M^+); high-resolution MS, $C_{34}H_{30}$, 438.2351. Calcd: C, 93.11; H, 6.89. Found: C, 93.24; H, 7.04.

X-ray Structure Analysis of 6B. Colorless flat needles were obtained by crystallization from chloroform/methanol. Crystal data: $C_{34}H_{30}$; M_r 438.6; crystal dimensions, 0.3 × 0.3 × 1.25 mm^3 orthorhombic, space group $P2_12_12$ (No. 18); a = 1450.2 (2) pm, b = 1403.7 (2) pm, c = 594.4 (6) pm; α = 90.15 (8)°, β = 89.98 (5)°, γ = 89.97 (2)°; U = 1.209 nm^3; Z = 2; d = 1.21 g cm^{-3}; μ = 0.34 cm^{-1}. Final R = 0.101 for 1762 unique reflexions [θ < 28°, $\sigma(I)$ < 0.67(I)], using unit weights. Due to low crystal quality a smaller R value could not be obtained. Intensity data were obtained at 293 K on a four-circle diffractometer CAD4 (Enraf-Nonius) using Mo Kα radiation with graphite monochromator. The structure was solved by direct methods (MULTAN 80[9]). All H atoms could be localized in a difference Fourier map. The refinement was carried out by least-squares methods (170 parameters, SHELX 76[10]) with anisotropic temperature factors for all carbon atoms. H atoms were included with constraints (C–H, 108 ppm) and a common isotropic temperature factor.

Registry No. **5A**, 110044-16-1; **5B**, 103953-96-4; **6A**, 109997-27-5; **6B**, 109997-26-4; **7**, 2142-63-4; **8**, 3132-99-8; **9**, 103953-98-6; (±)-**10**, 109997-24-2; (±)-**11**, 109997-25-3; *meso*-**12**, 103958-69-6; *d,l*-**12**, 103954-01-4; *meso*-**13**, 103954-02-5; *d,l*-**13**, 103954-03-6; *meso*-**14**, 103954-04-7; *d,l*-**14**, 103954-05-8; *meso*-**15**, 103972-41-4; *d,l*-**15**, 103954-06-9.

Supplementary Material Available: Figure of unit cell of **6B** (1 page). Ordering information is given on any current masthead page.

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Reaction of Potassium Triphenylborohydride with Selected Organic Compounds Containing Representative Functional Groups

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Potassium triphenylborohydride (KTPBH) is a very mild reducing agent. With the exception of aldehyde, ketone, quinone, phenyl isocyanate, *n*-alkyl iodide, and aromatic disulfide, most functional groups studied react slowly or are inert toward KTPBH. KTPBH exhibits a remarkable stereoselectivity in the reduction of cyclic ketones. The reductions of epoxides are very slow, but the presence of the Lewis acid Ph_3B dramatically accelerates the rates and changes the regioselectivity in the case of trisubstituted epoxides.

Among the common alkali-metal hydrides LiH, NaH, and KH, potassium hydride has been established as possessing an exceptional ability to transfer hydride to trialkylboranes, producing the corresponding trialkylborohydrides,[1] which are powerful reducing agents,[2] to trialkoxyboranes,[3] which form the corresponding trialkoxyborohydrides,[4] and to dialkylalkoxyborane, producing the corresponding dialkylalkoxyborohydrides,[5] which are very mild but highly selective reducing agents.

Although the preparation of alkali-metal triarylborohydride from the reaction of common alkali-metal hydride and triarylboranes has been reported,[6] application of these

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