Chiral Cyclopentadienes[1]

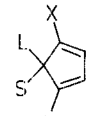
Katerina Matcheva,[a] Marion Beckmann,[a] Dietmar Schomburg,[b] Ekkehard Winterfeldt*[a]

[a] Institut für Organische Chemie der Universität Hannover, Schneiderberg 1 B, D-3000 Hannover 1, Federal Republic of Germany
[b] GBF, Gesellschaft für Biotechnologische Forschung mbH, Mascheroder Weg 1, D-3000 Braunschweig, Federal Republik of Germany

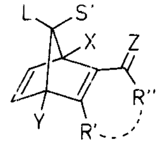
Dedicated to Dr. Günther Ohloff on the occasion of his 65th birthday.

Efficient syntheses of enantiomerically pure cyclopentadienes which undergo stereoselective and regioselective high pressure cycloadditions with nonsymmetric dienophiles are reported. As these compounds show a quite high chemical as well as thermal stability they are useful as templates in the generation of pure enantiomers by diastereoselective adduct transformation and subsequent retro-Diels-Alder reaction.

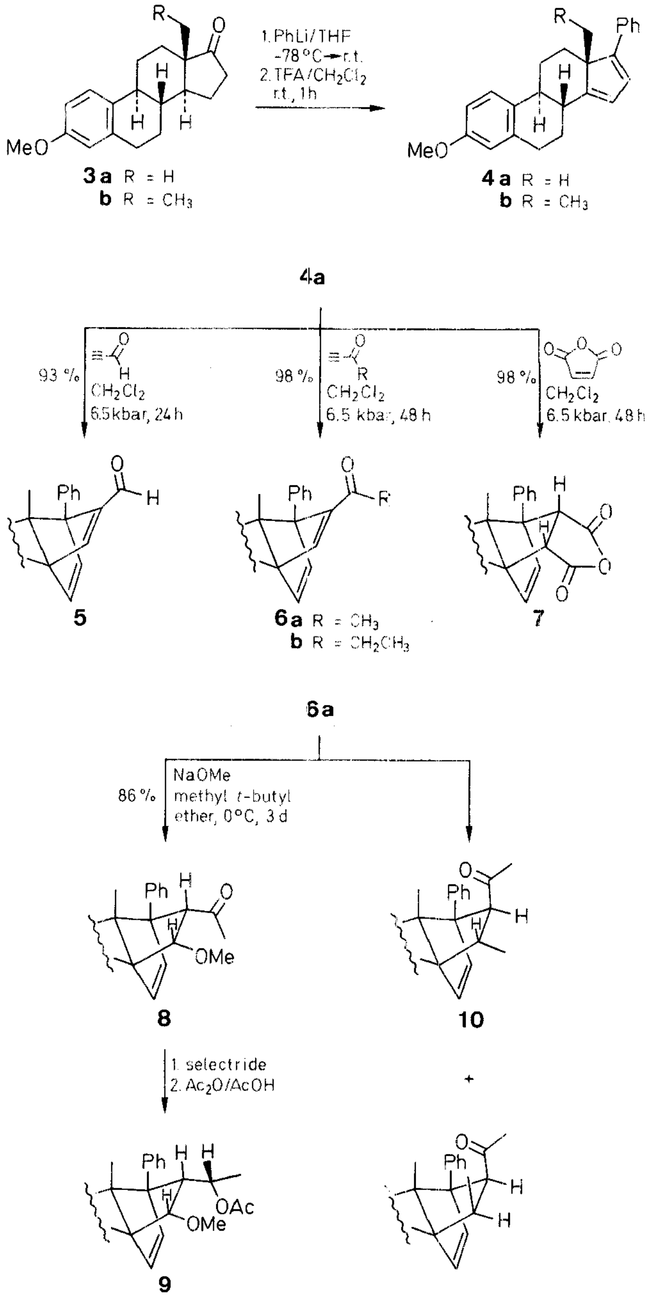
Chiral butadienes can be used as chiral templates in a Diels-Alder/retro-Diels-Alder reaction sequence. Thus butadienes of the general type **1** can undergo $2\pi/4\pi$ cycloaddition to give products **2**, multistep diastereoselective transformation and retro-Diels-Alder reaction could then give pure enantiomers. We have recently investigated the cycloaddtion products of ergosterol.[2,3]



1



2



Although even nonsymmetric dienophiles (e.g. propargylic aldehyde) underwent highly regioselective and stereoselective cycloadditions, the corresponding cycloaddition products underwent a remarkably fast retro Diels-Alder process to give aromatic seco-steroids. As a consequence we looked at stable cyclopentadienes which, after cycloaddition, cannot decompose in a similar way. Various chiral and optical active butadienes have, of course, been described before[4] but there were very few reports of substituted cyclopentadienes with a rigid conformation, which could potentially offer high regioselectivity and thermal stability.[5,6] Solo et al. had already prepared ring-D derived steroidal cyclopentadienes, and this as well as the work of Bull et al.[7] demonstrated the stereoselectivity and regioselectivity of the Diels-Alder processes. Additionally Hofmeister et al.[8] has reported the high thermal stability of the corresponding alkyl cyclopentadiene derivatives. On this basis we decided to prepare and study the phenyl derivatives of type **4**.

Starting from dehydrooestrone,[10] the diene **4a** was generated by treatment with phenyllithium and subsequent acidic workup with an overall yield of 85-87%. NMR, IR and UV spectral data are all consistant with the phenylcyclopentadiene moiety of **4a**. The compound **4a** exhibited high thermal stability and could be purified by distillation at approximately 300°C/12 mm (Kugelrohr). Reaction of **4a** with propargylic aldehyde, 3-butyn-2-one and succinic anhydride gave the cycloaddition products **5**, **6** and **7** which are formed with excellent stereoselectivity and regioselectivity. The cycloadditions are performed at room temperature under high pressure conditions (6-7 kbar), under these conditions yields are quantitative. Solo et al.[6] has already shown that in an analogous case attack occurs on the β-face of the steroid diene, he also reported that this process was regioselective. Additionally evidence for the diastereoselectivity of the cycloaddition was obtained by X-ray structure determination of the methoxyacetate **9** (figure). Compound **9** is obtained from **6** as a single diastereoisomer by the following sequence; thermodynamically controlled base catalyzed methanol addition, selectride reduction, and acetylation. The structural data (see plot) confirms not only β-attack in the cycloaddition process but also α-attack for the *trans*-addition of methanol and additionally indicates a Felkin–Ahn approach in the selectride reduction of the methyl ketone. Similar additions were also exhibited by the aldehyde **5**.

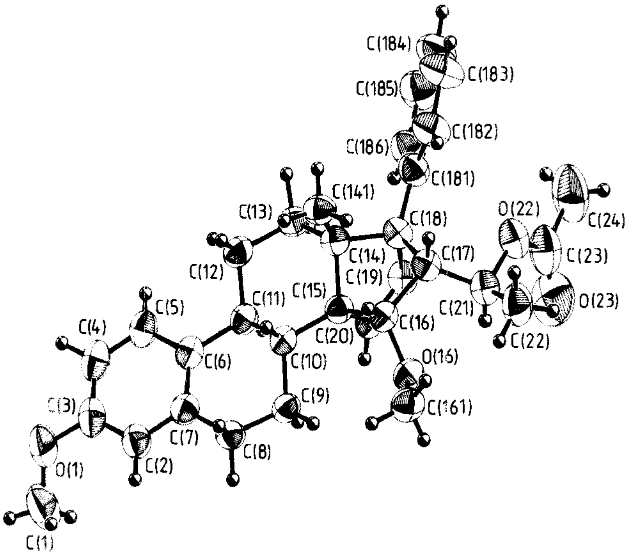
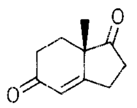


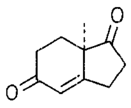
Figure. X-Ray structure determination of methoxyacetate **9**.

To investigate the stereoselectivity of carbon–carbon bond formation, we studied cuprate additions to the ketone **6a**. The best chemical yields were obtained with the Lipshutz reagent,[10] generated from thienyllithium. However, even in this case ketone **10** was not formed exclusively, but as mixture of **10** and its epimer in an 87/13 ratio. Therefore we decided to prepare the corresponding 13-ethyl compound **4b**, in order to gain some information on the influence of the angular substituent on the stereoselectivity of the cycloaddition step and also on subsequent transformations of the Diels–Alder adducts.

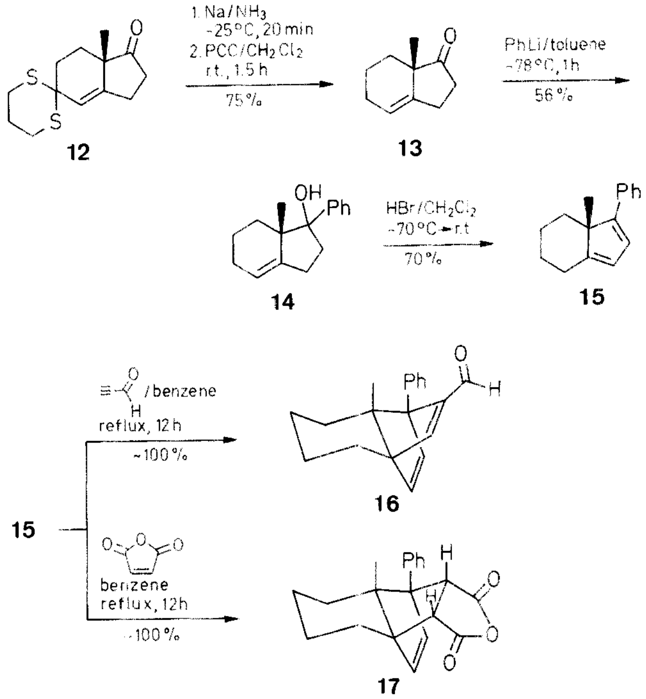
Compound **3b** was prepared by elimination of HBr from the 16-bromoketone.[11,12] While this preparation is very efficient in the oestrone series, the corresponding ethyl compound was always accompanied by substantial amounts of Δ 14/15 olefin which could not be transformed to the diene **4b**. Cycloaddition of **4b** to 3-butyn-2-one at pressures > 13 kbar and with an excess of dienophile yielded a mixture of three products, including a 2:1 addition product, which were not investigated further.

The difficulties in preparation and the very discouraging results with subsequent cycloadditions led to the decision not to investigate the ethyl series further. However, as compound **4a** had exhibited highly selective cycloadditions and excellent diastereoselectivities for cycloadduct transformations with **5**, **6**, and **7**, we decided to persue this approach further with a simplified system particularly as retro-Diels–Alder processes could be run with high chemical yields.


(*S*)-**11**


(*R*)-**11**

In order to simplify the diene molecule and to gain configurational flexibility over the fixed absolute configuration of the steroid system, we next investigated the Hajos–Wiechert ketone **11**[13] which can be obtained in both absolute configurations thus presenting a route to both configurational series.



The ketone (*S*)-**11** was converted to the thioacetal (*S*)-**12** by known methods. Birch reduction of (*S*)-**12** yielded a crude mixture of ketone (*S*)-**13** and the corresponding reduction product the epimeric 1-alcohols. Reoxidation of the crude mixture with pyridinium chlorochromate gave the ketone (*S*)-**13** as the sole product. Treatment of (*S*)-**13** with phenyllithium and subsequent acid-catalyzed elimination–isomerization yielded the phenyl substituted diene (*S*)-**15** in moderate yield. Cycloaddition of propynal or succinic anhydride to (*S*)-**15** gave **16** and **17** respectively with excellent stereo- and regioselectivity.

^{1}H-NMR spectra were obtained using a Bruker AM 300 and a WP 200 spectrometer with TMS as internal standard. IR spectra were obtained using a Perkin-Elmer 457 spectrometer. UV spectra were obtained using a Beckman 3600 spectrometer. Mass spectra were obtained using a Finnigan MAT 312 spectrometer at 70 eV. Optical rotations were obtained with a Perkin-Elmer 241 spectrometer. Melting points were taken using a Leitz 350 and are uncorrected.

3-Methoxy-17-phenyl-1,3,5(10),14(15),16(17)-estrapentaene (4a); Typical Procedure:

15(16)-Didehydrooestron methyl ether **3a** 12.63 g (44.7 mmol) is dissolved in anhydrous THF (300 mL) and cooled to −78 °C. A mixture of 2 M solution of phenyllithium in benzene (36 mL, 72 mmol) and anhydrous THF (150 mL) is added slowly, the reaction mixture is kept at −78 °C for 15 min and then the cooling bath is removed and the reaction mixture kept at ambient temperature for 30 min. The yellow solution is poured into sat. aq. NH_4Cl and extracted with methyl-*tert*-butyl ether. The combined extracts are washed with brine (50 mL) and dried ($MgSO_4$). The solvent is removed in vacuo and the residue is dissolved in anhydrous CH_2Cl_2 (60 mL). Trifluoroacetic acid (3.5 mL, 45 mmol) is added and the solution stirred at r.t. for 1 h. The solution is evaporated and the residue redissolved in CH_2Cl_2 and washed with aq. $NaHCO_3$ (50 mL) and brine (50 mL), and dried ($MgSO_4$). The solvent was removed *in vacuo* and the crude residue crystallized from $EtOAc/Et_2O$ (1:1) to give **4a**; yield 11.2 g; $[\alpha]_D^{22}$ +454.8° (c = 0.5, $CHCl_3$).

Table. Compounds **4a**, **4b**, **5**, **6a**, **6b**, **7**, **8**, **9** and **10** Prepared.

Product	Yield (%)	mp (°C)	Molecular Formula[a]	IR (KBr) ν(cm^{-1})	^{1}H-NMR (CDCl$_3$/TMS) δ, J(H$_2$)	MS (70 eV) m/z (%)
4a	73	146	$C_{25}H_{26}O$ (342.5)	3057, 2946, 2857, 2833, 1600, 1500, 1284, 1257	1.22 (s, 3H); 1.37 (dt, 1H, *H* = 4, 13); 1.57–2.00 (m, 2H); 2.16–2.46 (m, 4H, *J* = 3, 13); 2.95–3.08 (m, 2H); 3.79 (s, 3H); 6.07 (t, 1H, *J* = 2); 6.66–6.81 (m, 3H); 7.15–7.40 (m, 4H); 7.50–7.60 (m, 2H)	342 (97); 327 (24); 186 (100); 174 (78); 169 (59)
4b	20	208	$C_{26}H_{28}O$ (356.5)	3060, 2980, 1610, 1540, 1510, 1265, 1245	0.35 (t, 3H, *J* = 7); 1.15–3.10 (m, 12H); 3.80 (s, 3H); 6.10 (m, 1H); 6.65–6.80 (m, 3H); 7.20–7.43 (m, 4H); 7.50–7.60 (m, 2H)	356 (100); 327 (55); 186 (85); 174 (84)
5	93	125–135	$C_{28}H_{28}O_2$[b] (396.5)	2926, 2715, 1674, 1610, 1543, 1500, 1257, 1047	0.86–0.99 (m, 1H); 1.05 (s, 3H); 1.20–1.74 (m, 1H); 1.76–1.97 (m, 2H); 2.06–2.32 (m, 2H); 2.38–2.70 (m, 2H); 2.91–3.03 (m, 2H); 3.97 (s, 3H); 6.64–6.76 (m, 2H); 6.82 (d, 1H, *J* = 5.5); 7.06 (d, 1H, *J* = 5.5); 7.15–7.40 (m, 6H); 7.95 (s, 1H); 9.80 (s, 1H)	396 (5); 339 (2); 174 (100); 159 (16); 147 (18); 115 (11); 91 (10)
6a	98	103	$C_{29}H_{30}O_2$ (410.5)	2930, 1670, 1610, 1540. 1500, 1260	1.04 (s, 3H); 2.25 (s, 3H); 1.00–2.70 (m, 7H); 2.8–3.0 (m, 4H); 3.79 (s, 3H); 6.60–6.80 (m, 3H); 7.0–7.4 (m, 7H); 7.59 (s, 1H)	410 (20); 223 (17); 222 (22); 221 (21); 174 (100)
6b	98	166	$C_{30}H_{32}O_2$ (424.6)	3059, 2863, 1666, 1610, 1500, 1258	1.05 (s, 3H); 1.10 (t, 3H, *J* = 7); 1.10–1.50 (m, 2H); 1.74–1.93 (m, 2H); 2.58 (dq, 2H, *J* = 7); 2.06–2.64 (m, 4H); 2.90–3.03 (m, 2H); 3.79 (s, 3H); 6.64–6.76 (m, 2H); 6.78 (d, 1H, *J* = 5.5); 7.02–7.12 (m, 3H); 7.21 (d, 1H, *J* = 8); 7.20–7.37 (m, 3H); 7.54 (s, 1H)	424 (10); 273 (8); 221 (10); 174 (100); 159 (15); 147 (18); 115 (10); 91 (10)
7	98	233	$C_{29}H_{28}O_4$ (440.5)	2950, 1850, 1780, 1610, 1580, 1500, 1240	0.82 (s, 3H); 0.9 (m, 1H); 1.10–1.40 (m, 1H); 1.6–1.85 (m, 2H); 2.05–2.30 (m, 2H); 2.5–3.0 (m, 4H); 3.65 (d, 1H, *J* = 8); 3.79 (s, 3H); 4.42 (d, 1H, *J* = 8); 6.32 (d, 1H, *J* = 5); 6.48 (d, 1H, *J* = 5); 6.69 (m, 2H); 7.18 (d, 1H, *J* = 8); 7.4 (m, 5H)	440 (30); 342 (100); 185 (78); 174 (86)
8	86	220	$C_{30}H_{34}O_3$ (442.6)	2930, 1705, 1690, 1610, 1580, 1500, 1100	0.78 (s, 3H); 1.10–3.30 (m, 10H); 2.10 (s, 3H); 3.38 (s, 3H); 3.78 (s, 3H); 4.21 (ABq, 2H, *J* = 8); 5.00–5.30 (m, 3H); 6.29 (d, 1H, *J* = 6); 7.25 (m, 6H)	442 (1); 409 (5); 342 (100); 181 (60); 174 (50)
9	97	183	$C_{32}H_{38}O_4$ (486.7)	2930, 1730, 1610, 1580, 1500, 1250	0.80 (s, 3H); 1.11 (s, 3H); 1.25 (d, 3H, *J* = 6); 1.30–3.0 (m, 14H); 3.40 (m, 1H); 3.41 (s, 3H); 3.76 (s, 3H); 4.01 (d, 1H, *J* = 7.5); 4.88 (m, 1H); 6.25 (s, 2H); 6.70 (m, 2H); 7.25 (m, 6H)	
10	80	162	$C_{30}H_{34}O_2$ (426.0)	–	0.95–3.05 (m, 8H); 1.00 (s, 3H); 1.08 (s, 3H); 1.34 (d, 3H, *J* = 7); 1.92 (s, 3H); 3.60 (d, 1H, *J* = 5); 3.78 (s, 3H); 6.05 (d, 1H, *J* = 6); 6.32 (d, 1H, *J* = 6); 6.69 (m, 2H); 7.1–7.4 (m, 6H)	426 (15); 342 (100); 326 (31); 185 (86)

[a] Satisfactory microanalysis obtained: C $\pm$0.37, H $\pm$0.11. Exception; **6b**, C −0.69, H −0.16.

[b] Characterized by MS determination of the accurate molecular mass: **5:** $C_{28}H_{28}O_2$ requires: 396.2089; found: 396.2087 (−0.2 ppm).

13α-Ethyl-3-methoxy-17-phenyl-1,3,5(10),14(15),16(17)-gonapentaene (4b):

Starting from 13α-ethyl-3-methoxy-17-oxo-1,3,5(10),15(16)-gona (**3b**). $[\alpha]_D^{20}$ + 439.3° (c = 0.7, $CHCl_3$).

Diels–Alder Cycloaddition to 4a; General Procedure:

Phenyl diene **4a** (10 mmol) is dissolved in anhydrous CH_2Cl_2 (50 mL) and dienophile (15 mmol) is added. This mixture is left at 6.5 kbar for 24 h at r.t.. The crude reaction mixture is filtered through silica gel (eluting with Et_2O/hexane 1 : 3) and the solvent removed *in vacuo*. The formation of **6b** and **7** require 48 h.

Diels–Alder Cycloaddition to 4b:

The above procedure was executed at 13 and 15 kbar to yield a mixture of 6 main products after filtration.

16α-Acetyl-3,15α-dimethoxy-17β-phenyl-14α,17α-ethenoestra-1,3,5(10)-triene (8):

Ketone **6a** (300 mg, 0,73 mmol) is dissolved in methyl *tert*-butyl ether and cooled to 0 °C. A solution of Na (40 mg) in MeOH (8 mL) is added and the mixture left at 0 °C for 3 d. The reaction mixure is poured into ice cold 20% aq. citric acid (30 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined CH_2Cl_2 extracts are washed with sat. aq. $NaHCO_3$ (30 mL), brine (20 mL) and dried ($MgSO_4$). The solvent is removed *in vacuo* and the residue triturated with MeOH to give **8** as a crystalline solid; yield: 280 mg.

(1′*S*)-16α(1′-Acetoxyethyl)-3,15α-dimethoxy-17β-phenyl-14α,17α-ethenoestra-1,3,5(10)triene (9):

Ketone **8** (75 mg, 0.17 mmol) is dissolved in anhydrous THF (5 mL), 1 M selectride solution (0.28 mL, 1.5 mmol) is added slowly at 0 °C. After 4 h at r.t. the reaction mixture is poured into ice cold 20% aq. citric acid (10 mL) and extracted with CH_2Cl_2 (3 × 5 mL) the combined CH_2Cl_2 extracts are washed with sat. aq. $NaHCO_3$ (10 mL), brine (10 mL) and dried ($MgSO_4$). The solvent is removed in vacuo and the remaining residue immediately redissolved in Ac_2O (10 ml) and left over night at r.t. The Ac_2O is removed in vacuo and the residue crystallized from Et_2O to give acetate **9**; yield: 80 mg.

16β-Acetyl-3-methoxy-15α-methyl-17β-phenyl-14α,17α-ethenoestra-1,3,5(10)-triene (10):

Ketone **6a** (205 mg, 0.5 mmol) is dissolved in anhydrous THF (5 mL) and at − 78 °C slowly added to a solution prepared from Lipshutz reagent[10] (5.4 mL, 2 mmol) and methyllithium (1.6 mmol). The mixture is left at − 78 °C for 10 min and then for 1 h at r.t. The reaction mixture is then treated with sat. aq. NH_4Cl (20 mL) and then extracted with CH_2Cl_2 (3 × 5 mL). The solvent is removed in vacuo and the main reaction product crystallized from hexane to give ketone **10**; yield: 170 mg.

(9*R*)-9-Methylbicyclo[4.3.0]nona-4(5)ene-1,6-dione 6-Trimethylene Dithioacetal (12):

Ketone **11** (23.7 g, 0.144 mol) is dissolved in MeOH (120 mL) and 1,3-

propane dithiol (18 mL) is added. At 0°C this mixture is treated with $BF_3 \cdot Et_2O$ (17.9 mL, 0.146 mol) and left at 0°C for 15 h. The precipitate is filtered and combined with a second precipitate which is formed on concentration of the mother liquor to give thioketal **12**; yield: 36.6 g (100%); mp 139°C.

$C_{13}H_{18}OS_2$ calc. 254.0799
(254) found 254.0799

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.17 (s, 3H); 1.64–1.78 (m, 2H); 1.86–2.40 (m, 4H); 2.47–3.11 (m, 8H); 5.71 (m, 1H).

(9*R*)-9-Methylbicyclo[4.3.0]nona-4(5)ene-1-one (13):
Thioacetal **12** (12.7 g, 50 mmol) is dissolved in anhydrous THF (100 mL) and then added slowly to a solution of Na (7.9 g) in ammonia (800 mL) which is kept at −25°C. After 20 min at this temperature the mixture is treated with MeOH (25 mL) and the ammonia is evaporated. The residue is dissolved in Et_2O (100 mL), washed with sat. aq. $NaHCO_3$ (30 mL) and the solvent is evaporated. The residue, which is a roughly 1:1 mixture of **13** and the epimeric 1-alcohols is redissolved in CH_2Cl_2 (100 mL) and added to a solution of PCC (6.9 g) in CH_2Cl_2 (200 mL) and this is left at r.t. for 1.5 h. The solution is then decanted and filtered through silica gel eluting with Et_2O. The solvent is removed by careful distillation and then distilled (Kugelrohr) to give **13** as a colorless oil; yield: 5.6 g (75%); bp 100°C; $[\alpha]_D^{20}$ + 379.1 (c = 0.7, CH_2Cl_2).

$C_{10}H_{14}O$ calc. 150.1044
(150.1) found 150.1044

MS (EI): m/z (%) = 150 (5); 145 (44); 134 (28); 108 (35); 107 (32); 93 (100); 91 (39); 79 (23); 77 (28).

IR ($CHCl_3$): ν = 2940, 1730, 1680, 1450 cm^{-1}

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.13 (s, 3H); 1.20–2.81 (m, 10H); 5.58 (m, 1H).

(9*R*)-1-Hydroxy-9-methyl-1-phenylbicyclo [4.3.0]nona-4(5)-ene (14):
Ketone **13** (4.5 g, 0.03 mol) is dissolved in anhydrous toluene (150 mL) and cooled to −78°C. A 2M solution of phenyllithium (75 mL, 0.15 mol) in benzene/ether (75:25) is added and the reaction mixture maintained at −78°C for 1 h. Sat. aq. NH_4Cl (30 mL) is added and the mixture is extracted with Et_2O (3 × 20 mL). The combined extracts are dried ($MgSO_4$), and distilled. The fractions between 100°C and 140°C are collected and purified by chromatography on a silica gel column eluting with cyclohexane/Et_2O (20:1) to give **14** as a colourless oil; yield: 3.80 g (56%).

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.61 (m, 1H); 1.25 (s, 3H); 1.30–1.90 (m, 6H); 2.30 (m, 3H); 2.79 (m, 1H); 5.40 (m, 1H); 7.26 (m, 5H).

(9*R*)-9-Methylbicyclo[4.3.0]nona-1(2),3(4)-diene (15):
The hydroxy compound **14** (200 mg, 0.88 mmol) is dissolved in anhydrous CH_2Cl_2 (8 mL) and the solution cooled to −70°C. Sat. HBr in anhydrous CH_2Cl_2 (15 mL) cooled to 0°C is added and the mixture left at r.t. for 12 h. The solvent is evaporated and the residue is dissolved in Et_2O (10 mL). The ethereal solution is washed with sat. aq. $NaHCO_3$ (3 mL) and brine (3 mL). The Et_2O is evaporated and the residue distilled (Kugelrohr) to give the diene **14**; yield: 128 mg (70%); $[\alpha]_D^{20}$ + 82.25° (c = 0.7, $CHCl_3$).

$C_{16}H_{18}$ calc. 210.1409
(210) found 210.1408

MS (EI): m/z (%) = 210 (100); 195 (53); 182 (26); 181 (49); 180 (40); 179 (34); 178 (36); 167 (75); 165 (74); 152 (31).

IR ($CHCl_3$): ν = 3060, 2940, 2860, 1595, 1530, 1490 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.02–2.70 (m, 8H); 1.19 (s, 3H); 6.02 (m, 1H); 6.73 (d, 1H, J = 2 Hz); 7.12–7.56 (m, 5H).

Diels-Alder Cycloaddition 15:
See typical procedure for cycloadditions t **4a**.

16:
$C_{19}H_{20}O$ calc. 264.1514
(264) found 264.1514

MS (EI): m/z (%) = 265 (4); 264 (15); 263 (8); 249 (18); 235 (12); 221 (25); 220 (100); 193 (15); 178 (29); 177 (33); 166 (19); 164 (42); 152 (23). 122 (12); 115 (26); 91 (27).

IR ($CHCl_3$): ν = 3019, 2932, 2860, 1668, 1540, 1498 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.67–2.36 (m, 8H); 1.03 (s, 3H); 6.64 (d, 1H, J = 5 Hz); 6.98 (d, 1H, J = 5 Hz); 7.12–7.40 (m, 5H); 7.72 (s, 1H); 9.77 (s, 1H).

17:

mp 195°C

$C_{20}H_{20}O_3$ calc. 77.89 H 6.54
(308) found 77.72 6.57

MS (EI): m/z (%) = 308 (3); 307 (13); 281 (11); 280 (46); 237 (14); 236 (72); 235 (18); 222 (19); 221 (100); 210 (23); 207 (22); 194 (42); 179 (39); 178 (43); 168 (34); 167 (68); 165 (58).

IR ($CHCl_3$): ν = 1885, 1775 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.69–2.38 (m, 8H); 0.80 (s, 3H); 3.43 (d, 1H, J = 8 Hz); 4.34 (d, 1H, J = 8 Hz); 6.28 (ABq, 2H, J = 6 Hz); 7.22–7.47 (m, 5H).

Financial support by the Deutsche Forschungsgemeinschaft (Wi 206/39-1) and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank R. Wiechert and H. Laurent of the Schering Company Berlin, for providing valuable starting materials and the VW Foundation in Hannover for financial support.

Received: 7 July 1989

(1) Part 2 of a series on dienes as chiral templates.
For Part 1 see: Schomburg, D., Thielmann, M., Winterfeldt, E. *Tetrahedron Lett.* **1986**, *27*, 5833.
(2) Chowdhury, P.K., Prelle, A., Schomburg, D., Winterfeldt, E. *Liebigs Ann. Chem.* **1987**, 1059.
(3) Prelle, A., Winterfeldt, E. *Heterocycles* **1989**, *28*, 333.
(4) Paquette, L.A. *Asymmetric Synthesis, Vol. 3.* Academic Press, New York, 1984.
(5) Solo, A.J., Singh, B., Shefter, E., Cooper, A. *Steroids* **1968**, *11*, 637.
Solo, A.J., Singh, B., Kapoor, J.N. *Tetrahedron* **1969**, *25*, 4579.
Solo, A.J., Eng, S., Singh, B. *J. Org. Chem.* **1972**, *37*, 3542.
(6) Haltermann, R.L., Vollhardt, K.P.C. *Organometallics* **1988**, *7*, 883.
McLaughlin, M.L., McKinney, J.A., Paquette, L.A. *Tetrahedron Lett.* **1986**, *27*, 5595.
Paquette, L.A., Gugelchuk, M., McLaughlin, M.L. *J. Org. Chem.* **1987**, *52*, 4732.
(7) Bull, J.R., Thomson, R.I. *J. Chem. Soc., Chem. Commun.* **1986**, 451.
(8) Dr. H. Hofmeister, Schering Company, Berlin. Personal communication.
(9) Phillips, D.K., Wickham, P.P., Potts, G.O., Arnold, A. *J. Med. Chem.* **1968**, *11*, 924.
(10) Lipshutz, B.H., Koerner, M., Parker, D.A. *Tetrahedron Lett.* **1987**, *28*, 945.
(11) Smith, H., Hughes, G.A., Douglas, G.H., Wendt, G.R., Buzby, G.C., Jr., Edgren, R.A., Fischer, J., Foell, T., Gadsby, B., Hartley, D., Herbst, D., Jansen, A.B.A., Ledig, K.M., Laughlin, B.J., McMenamin, J., Pattison, T.W., Phillips, P.C., Rees, R., Siddall, J., Siuda, J., Smith, L.L., Tokolics, J., Watson, D.H.P. *J. Chem. Soc.* **1964**, 4472.
(12) Johnson, W.S., Johns, W.F. *J. Am. Chem. Soc.* **1957**, *79*, 2005.
(13) Eder, U., Sauer, G., Wiechert, R. *Angew. Chem.* **1971**, *83*, 492. *Angew. Chem. Int. Ed. Engl.* **1971**, *10*, 496.