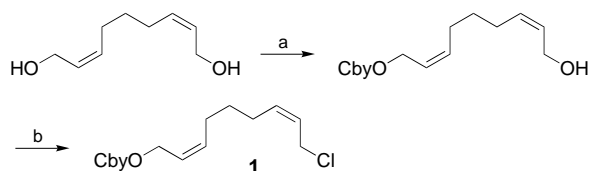


# Enantioselective Synthesis of Functionalized 1,5-Cyclononadienes by Intramolecular Cycloalkylation under $\alpha,\alpha'$ -Diallyl Coupling\*\*

Alexander Deiters, Roland Fröhlich, and Dieter Hoppe\*

In spite of the biological importance of medium-size carbocycles, only a few ring-closing reactions are known for the synthesis of nine-membered monocarbocyclic rings.<sup>[1]</sup> Classic examples are the acyloin condensation of nonanedioic acid dimethyl esters<sup>[2a]</sup> and the McMurry reaction<sup>[2b]</sup>; however, for reasonable yields, a high dilution of the substrate and a long reaction time are always necessary.<sup>[2c]</sup>

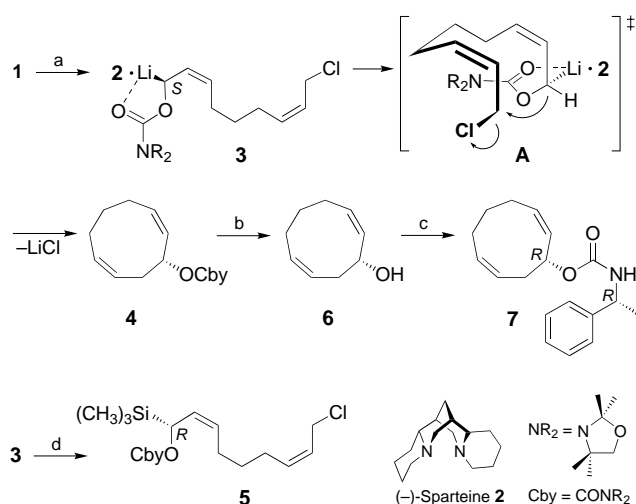
When we applied our protocol for an intramolecular lithium-ene reaction<sup>[3]</sup> on the (2*Z*,7*Z*)-9-chloro-2,7-nona-dienyl carbamate **1**, we found a suprisingly efficient synthesis of a nine-membered carbocycle. The reaction proceeds to completion without any by-products within 2 h, even in 0.15 M solution. On the other hand, the (2*E*,7*E*)-isomer furnishes the expected *cis*-1,2-dialkenylcyclopentane **14**, as we recently reported (see Scheme 5).<sup>[3]</sup> Compound **1** was synthesized from the known compound *cis,cis*-nona-2,7-diene-1,9-diol (Scheme 1).<sup>[4]</sup>



Scheme 1. Synthesis of the dieny carbamate **1**. a) 0.3 equiv NaH, 0.3 equiv CbyCl, THF,  $\Delta$ , 85 %; b) 1.0 equiv *n*BuLi, 1.3 equiv MsCl, 1.0 equiv LiCl, THF,  $-78^\circ\text{C} \rightarrow \text{RT}$ , 73 %.<sup>[23]</sup> Cby = 2,2,4,4-tetramethyl-1,3-oxazolidin-3-ylcarbonyl, Ms = methanesulfonyl.

Treatment of **1** with *n*-butyllithium/(–)-sparteine (**2**)<sup>[5]</sup> in toluene at  $-88^\circ\text{C}$  provided the (1*R*,2*Z*,7*Z*)-2,7-cyclononadienyl carbamate **4** in 73 % yield and with an *ee* value of 88 % (e.r. = 94:6; Scheme 2).<sup>[6,7]</sup> The *S* configuration of the intermediate lithium complex **3** was confirmed by conversion into the silane (*R*)-**5** (87 % *ee*).<sup>[8,9]</sup> Thus, the  $\alpha,\alpha'$ -coupling<sup>[10]</sup> of the allyl moieties in **3** proceeds under inversion of configuration at the metal-bearing carbon atom and, therefore, presumably passes through the transition state **A**.<sup>[11]</sup>

The cleavage<sup>[12]</sup> of the carbamate group led to the (*R*)-cyclononadienol **6** and addition of this to (*R*)-1-phenylethyl



Scheme 2. Cycloalkylation of the dieny carbamate **1** and synthesis of the silane **5**. a) 2.0 equiv *n*BuLi, 2.0 equiv **2**, toluene,  $-88^\circ\text{C}$ , 73 %, e.r. = 94:6 (88 % *ee*.); b) 1.) 2.0 equiv  $\text{CH}_3\text{SO}_3\text{H}$ ,  $\text{CH}_3\text{OH}$ ,  $\Delta$ ; 2.) 4.0 equiv KOH,  $\text{CH}_3\text{OH}$ ,  $\Delta$ , 96 %; c) 3.0 equiv (*R*)-(+)-1-phenylethyl isocyanate,  $\text{CH}_2\text{Cl}_2$ ,  $\Delta$ , 63 %; d) 1.5 equiv *n*BuLi, 1.5 equiv (–)-sparteine, 2.7 equiv  $(\text{CH}_3)_3\text{SiCl}$ , toluene,  $-78^\circ\text{C}$ , 61 %, 87 % *ee*.<sup>[23]</sup>

isocyanate furnished the carbamate **7**. The X-ray analysis<sup>[13]</sup> of **7** (Figure 1) clearly shows the relative configuration *l* and hence the *R* configuration for (+)-**6** and (+)-**4**.

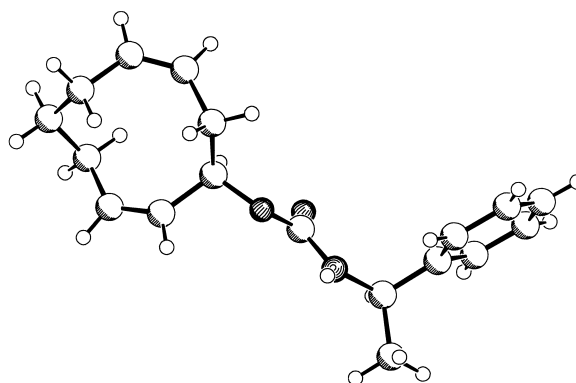


Figure 1. X-ray crystal structure analysis of **7**.<sup>[13]</sup>

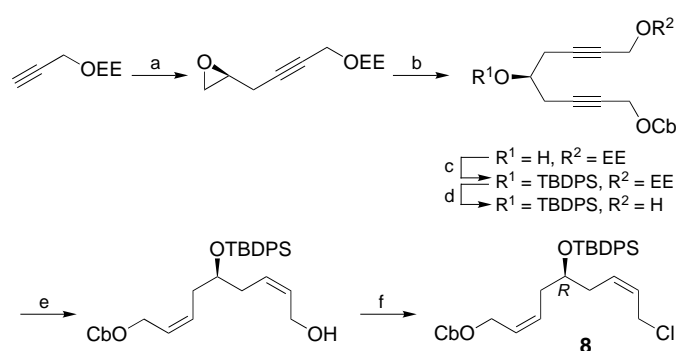
The analogous TBDPS-oxidiényl carbamate (*R*)-**8** has been synthesized starting from (*S*)-epichlorohydrin (Scheme 3). Cyclization of (*R*)-**8** (100 % *ee*) by means of *n*BuLi/**2** furnished the enantiomerically pure cyclononadiendiol derivatives (1*R*,5*S*)-**9** and (1*S*,5*S*)-**9**, in a diastereomeric ratio of 94:6, which are easily separated by chromatography.<sup>[15]</sup> The stereogenic center at C-5 affects neither the deprotonation nor the cyclization step; by use of the achiral base *n*BuLi/TMEDA, (1*R*,5*S*)-**9** and (1*S*,5*S*)-**9** were obtained in the ratio 53:47. Corresponding to this, *rac*-**8** furnished, after treatment with *n*BuLi/**2**, the epimers (1*R*,5*S*)-**9** and (1*R*,5*R*)-**9** in 74 % yield with a diastereomeric ratio of 55:45 and each with an *ee* value of 92 % (Scheme 4). After deprotection to the alcohol (1*R*,5*R*)-**10** and X-ray analysis, the relative configuration *l* was confirmed (Figure 2).<sup>[16]</sup>

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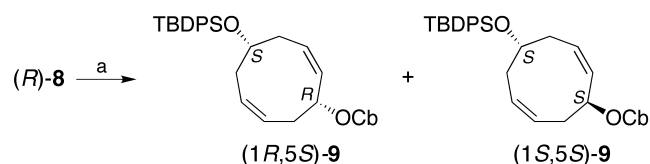
[+] X-ray analysis

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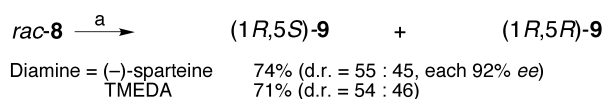
Supporting information for this article is available on the WWW under <http://www.wiley-vch.de/home/angewandte/> or from the author.



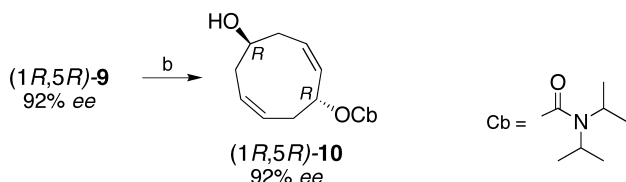
Scheme 3. Synthesis of the enantiomerically pure dienyl carbamate **8**. a) 1.) 1.0 equiv *n*BuLi, 0.5 equiv (*S*)-(+)-epichlorohydrin, 1.0 equiv BF<sub>3</sub>·OEt<sub>2</sub>, THF, -78 °C → RT; 2.) 1.0 equiv NaH, THF, -10 °C, 89 %; b) 2.0 equiv HCCCH<sub>2</sub>OCb,<sup>[14a]</sup> 2.0 equiv *n*BuLi, 2.0 equiv BF<sub>3</sub>·OEt<sub>2</sub>, THF, -78 °C → RT, 98 %;<sup>[14b]</sup> c) 1.2 equiv TBDPSCl, 2.5 equiv imidazole, DMF, 83 %; d) 0.07 mass % amberlyst 15, MeOH, 40 °C, 95 %; e) H<sub>2</sub>, 5.0 mass % Lindlar catalyst, 0.15 equiv quinoline, MeOH, 96 %; f) 1.0 equiv *Cb*=diisopropylaminocarbonyl, 1.2 equiv MsCl, 1.0 equiv LiCl, THF, -78 °C → RT, 76 %.<sup>[23]</sup> *Cb*=diisopropylaminocarbonyl, EE=ethoxyethyl, TBDPS = *tert*-butyldiphenylsilyl.



Diamine = (-)-sparteine	79% (d.r. = 94 : 6, each 100% ee)
TMEDA	70% (d.r. = 53 : 47, each 100% ee)



Diamine = (-)-sparteine	74% (d.r. = 55 : 45, each 92% <i>ee</i> )
TMEDA	71% (d.r. = 54 : 46)



Scheme 4. Cycloalkylation of the dienyl carbamate **8** and deprotection of the product **9**. a) 2.0 equiv *n*BuLi, 2.0 equiv diamine, toluene,  $-88^{\circ}\text{C}$ , 2 h; b) 3.0 equiv tetrabutylammonium fluoride, THF, 74%.<sup>[23]</sup> TMEDA = *N,N,N',N'*-tetramethylethylenediamine.

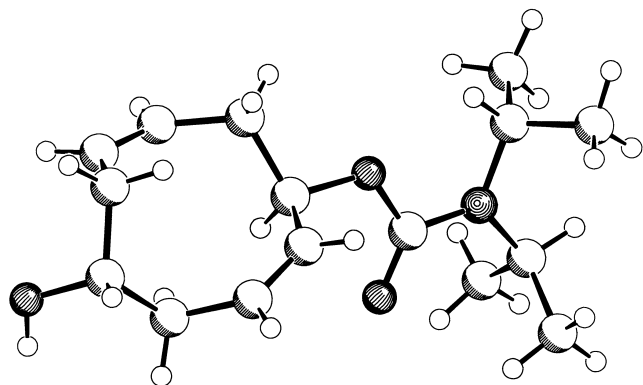
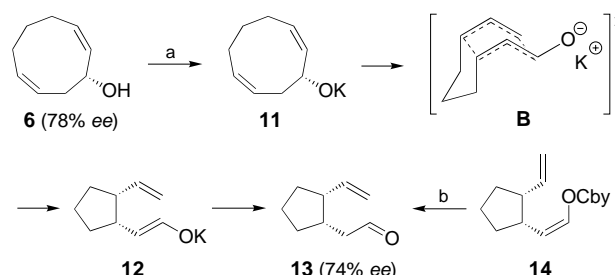


Figure 2. X-ray crystal structure analysis of (1*R*,5*R*)-**10**.<sup>[16]</sup>

The (Z,Z)-cyclonona-1,5-diene structure is destined for Cope rearrangements which pass through boatlike transition states:<sup>[17]</sup> After conversion of **6** into the potassium alcoholate **11** an anionic oxy-Cope rearrangement<sup>[18a]</sup> takes place at room temperature. The aldehyde (+)-**13**, obtained after protonation of the potassium enolate **12**, shows 95 % stereoselectivity for the rearrangement.<sup>[18b]</sup> This seems to be the highest grade of chiral transmission in anionic oxy-Cope rearrangements of dienols which only contain a stereogenic center at the oxygen-bearing carbon atom.<sup>[19]</sup> The absolute configuration of **13** was determined by its synthesis from **14**<sup>[3]</sup> through deprotection of the enol.<sup>[20]</sup> Together with the *R* configuration of **6**, a reaction pathway via the transition state **B** with an equatorial oxido group<sup>[19c]</sup> takes place (Scheme 5).



Scheme 5. Enantioselective anionic oxy-Cope rearrangement. a) 1.3 equiv KN(Si(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>, THF, RT, 75 %; b) 15 equiv Al*i*Bu<sub>3</sub>H, toluene, RT, 65 %.

The method reported herein provides simple, flexible, and also enantioselective access to highly functionalized nine-membered carbocycles. The application of the homoenolate chemistry<sup>[5a, 21]</sup> on the configuratively stable secondary lithium species generated by deprotonation of **4** bears additional possibilities in the synthesis of nine-membered ring compounds.<sup>[22]</sup>

## Experimental Section

Under argon, compounds **1** (500 mg, 1.52 mmol) and **2** (713 mg, 3.04 mmol) were dissolved in toluene (10 mL). After cooling to  $-88^{\circ}\text{C}$ , a 1.6M solution of *n*-butyllithium in hexane (1.90 mL, 3.04 mmol) was slowly injected and the solution was stirred at this temperature for 2 h. Subsequently,  $\text{CH}_3\text{OH}$  (1 mL) and saturated aqueous  $\text{NH}_4\text{Cl}$  (1 mL) were added and the reaction mixture was allowed to warm to room temperature. Standard work up and purification by flash column chromatography over silica gel ( $\text{Et}_2\text{O}$ :pentane = 2:5) furnished **4** (324 mg, 73 %, 88 % *ee*) as a colorless solid (m.p.  $72^{\circ}\text{C}$ ).

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- [7] Compound **4**: Mp  $72^{\circ}\text{C}$ ;  $[\alpha]_{\text{D}}^{20} = +14.8$  ( $c = 0.59$ , CHCl<sub>3</sub>; 88% ee); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 1.34\text{--}1.56$  (m, 14H, CH<sub>2</sub>, CH<sub>3</sub>(Cby)), 1.85–2.03 (m, 4H, CH<sub>2</sub>), 2.22 and 2.43 (both m, each with 1H, CH<sub>2</sub>), 3.70 and 3.71 (s, 2H, CH<sub>2</sub>(Cby)), 5.10 (dd, 1H, CH, <sup>3</sup>J = 7.8, 7.8 Hz), 5.38 (dt, 1H, CH, <sup>3</sup>J = 9.6, 9.6 Hz), 5.47 (dt, 1H, CH, <sup>3</sup>J = 5.8, 10.1 Hz), 5.62 (m, 1H, CH), 5.79 (dt, 1H, CH, <sup>3</sup>J = 10.1, 8.5 Hz). The enantiomeric ratio of **4** was determined by gas chromatography on a chiral stationary phase (Beta-Dex 120, Supelco, USA).
- [8] Compound **5**:  $[\alpha]_{\text{D}}^{20} = +10.3$  ( $c = 1.27$ , CHCl<sub>3</sub>; 87% ee); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 0.05$  (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 1.30–1.51 (m, 14H, CH<sub>2</sub>, CH<sub>3</sub>(Cby)), 1.96–2.30 (m, 4H, CH<sub>2</sub>), 3.69 (s, 2H, CH<sub>2</sub>(Cby)), 4.07 (dd, 2H, CH<sub>2</sub>Cl, <sup>4</sup>J = 1.8, <sup>3</sup>J = 5.1 Hz), 5.35–5.42 (m, 3H, CH, CHSi), 5.58–5.62 (m, 2H, CH). The enantiomeric ratio of the silane **5** was determined by <sup>1</sup>H NMR shift experiments in the presence of [Eu(hfc)<sub>3</sub>] (hfc = 3-(heptafluoropropylhydroxymethylene)-D-camphorate). After hydrogenation of the double bonds and hydrogenolytic cleavage of the chlorine atom, the corresponding 1-trimethylsilylnonyl carbamate was obtained.<sup>[5]</sup> Its enantiomer was synthesized by the *s*BuLi/(–)-sparteine method.<sup>[5a]</sup> A correlation of the optical rotations assigned the R configuration for (+)-**5**.
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- [13] X-ray crystal structure analysis of **7**: C<sub>18</sub>H<sub>23</sub>NO<sub>2</sub>,  $M_r = 285.37$ , light yellow crystal,  $0.20 \times 0.10 \times 0.05$  mm,  $a = 23.258(1)$ ,  $c = 5.106(1)$  Å,  $\gamma = 120^{\circ}$ ,  $V = 2392.0(5)$  Å<sup>3</sup>,  $\rho_{\text{calcd}} = 1.189$  g cm<sup>–3</sup>,  $\mu = 0.77$  cm<sup>–1</sup>, absorption correction with SORTAV ( $0.985 \leq T \leq 0.996$ ),  $Z = 6$ , trigonal, space group *P*3<sub>1</sub> (No. 144),  $\lambda = 0.71073$  Å,  $T = 198$  K,  $\omega$  and  $\varphi$  scans, 20958 reflections collected ( $\pm h$ ,  $\pm k$ ,  $\pm l$ ),  $[(\sin\theta)/\lambda] = 0.65$  Å<sup>–1</sup>, 7097 independent ( $R_{\text{int}} = 0.056$ ) and 4457 observed reflections [ $I \geq 2\sigma(I)$ ], 387 refined parameters,  $R = 0.066$ ,  $wR^2 = 0.131$ , max./min. residual electron density  $0.42/ -0.25$  e Å<sup>–3</sup>, Flack parameter  $-0.1(14)$ , the asymmetric unit contains two independent, nearly identical molecules, hydrogens were calculated and refined as riding atoms.<sup>[10b]</sup>
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- [15] Compound (1*R*,5*S*)-**9**:  $[\alpha]_{\text{D}}^{20} = -37.7$  ( $c = 0.43$ , CHCl<sub>3</sub>, 100% ee); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.07$  (s, 9H, *t*Bu), 1.22 (d, 12H, CH<sub>3</sub>(Cb)), <sup>3</sup>J = 6.9 Hz), 1.93–2.00 (m, 1H, CH<sub>2</sub>), 2.11 (dd, 2H, CH<sub>2</sub>, <sup>3</sup>J = 6.9, 3.6 Hz), 2.19–2.38 (m, 2H, CH<sub>2</sub>, CH<sub>2</sub>), 2.53 (ddd, 1H, CH<sub>2</sub>, <sup>3</sup>J = 8.7, 9.0, <sup>2</sup>J = 12.9 Hz), 3.80–4.03 (m, 3H, CH(Cb), CHOSi), 5.03 (dd, 1H, CHOCb, <sup>3</sup>J = 6.0, 6.9 Hz), 5.35 (dt, 1H, CH, <sup>3</sup>J = 10.6, 5.7 Hz), 5.67–5.81 (m, 3H, CH, CH, CH), 7.32–7.70 (m, 10H, CH(phenyl)). After cleavage of the TBDPS group, the enantiomeric ratio of (1*R*,5*S*)-**10** was determined as described in reference [7].
- [16] a) X-ray crystal structure analysis of (1*R*,5*R*)-**10**: C<sub>16</sub>H<sub>27</sub>NO<sub>3</sub>,  $M_r = 281.39$ , colorless crystal,  $0.40 \times 0.25 \times 0.15$  mm,  $a = 26.159(5)$ ,  $b = 10.884(2)$ ,  $c = 12.918(3)$  Å,  $\beta = 113.71(2)^{\circ}$ ,  $V = 3367.5(12)$  Å<sup>3</sup>,  $\rho_{\text{calcd}} = 1.110$  g cm<sup>–3</sup>,  $\mu = 6.04$  cm<sup>–1</sup>, absorption correction with  $\psi$ -scan data ( $0.794 \leq T \leq 0.915$ ),  $Z = 8$ , monoclinic, space group *C*2 (No. 5),  $\lambda = 1.54178$  Å,  $T = 223$  K,  $\omega/2\theta$  scans, 3697 reflections collected ( $\pm h$ ,  $\pm k$ ,  $\pm l$ ),  $[(\sin\theta)/\lambda] = 0.62$  Å<sup>–1</sup>, 3611 independent ( $R_{\text{int}} = 0.077$ ) and 3159 observed reflections [ $I \geq 2\sigma(I)$ ], 372 refined parameters,  $R = 0.044$ ,  $wR^2 = 0.119$ , max./min. residual electron density  $0.24/ -0.17$  e Å<sup>–3</sup>, Flack Parameter 0.3(2), the asymmetric unit contains two independent, nearly identical molecules, hydrogens were calculated and refined as riding atoms; b) The data sets were collected with Nonius CAD4 and Nonius KappaCCD diffractometers equipped with a Nonius FR590 sealed tube generator or a Nonius FR591 rotating anode generator. The following programs were used: For data collection, EXPRESS (Nonius B.V., **1994**) and COLLECT (Nonius B.V., **1998**); for data reduction, MolEN (K. Fair, Enraf–Nonius B.V., **1990**) and Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307–326); for absorption corrections for CCD data, SORTAV (R. H. Blessing, *Acta Crystallogr. Sect. A* **1995**, *51*, 33–37; R. H. Blessing, *J. Appl. Crystallogr.* **1997**, *30*, 421–426); for structure solution, SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467–473); for structure refinement, SHELXL-97 (G. M. Sheldrick, University of Göttingen, **1997**); for graphics, SCHAKAL (E. Keller, University of Freiburg, **1997**). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-139019 and -139020. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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- [23] All new compounds were analytically pure (error in C,H,N elemental analyses  $\pm 0.4$ ).