[1] G. Bach, S. Breiding-Mack, S. Grabley, P. Hamman, K. Hütter, R. Thiericke, H. Uhr, J. Wink, A. Zeeck, *Liebigs Ann. Chem.* **1993**, 241–250.

[2] a) B. Bethe, Ph.D. thesis, University of Göttingen (Germany), **1994** (ISBN 3-89588-103-1); b) J. Fuchser, A. Zeeck, *Liebigs Ann.Chem.* **1997**, 87–95; c) H.-J. Schiewe, *J. Antibiot.* **1999**, *52*, 635–642.

[3] S. Grabley, R. Thiericke, A. Zeeck in *Drug Discovery from Nature* (Eds.: S. Grabley, R. Thiericke), Springer, Heidelberg, **1999**, pp. 124–148.

[4] H. Bode, M. Walker, A. Zeeck, *Eur. J. Org. Chem.* **2000**, 1451–1456.

[5] D. A. Hopwood, *Microbiology* **1999**, *145*, 2183–2202.

[6] R. Höfs, Ph.D. thesis, University of Göttingen (Germany), **1999** (ISBN 3-932325-74-5).

[7] T. Lindel, J. Junker, M. Köck, *Eur. J. Org. Chem.* **1999**, 573–577.

[8] Crystal structure analysis of **3**: Stoe-Siemens-Huber four-circle diffractometer coupled to a Bruker CCD area detector, graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), ϕ and ω scans, empirical absorption correction with SADABS, structure solved with direct methods, refinement against F^2 by full-matrix least-squares methods with SHELXL-97, a riding model with idealized hydrogen geometry was employed, $C_{26}H_{34}O_9$, 0.5 × 0.4 × 0.1 mm, orthorhombic, space group $P2_12_12_1$, $a = 12.371(3)$, $b = 13.559(3)$, $c = 30.004(6)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 5032.8(17)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.319$ g cm^{-3}, $\mu = 0.100$ mm^{-1}, $2\theta_{max} = 41.84$, $T = 133(2)$ K, 50542 reflections measured, 6207 unique, 5322 used for calculation, 674 refined parameters, $R1 = 0.0390$, $wR2 = 0.0751$, min./max. residual electron density 1.69/–1.79 e Å^3. 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-141597. 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).

[9] I. Ohtani, T. Kusumi, Y. Kashman, H. Kakisawa, *J. Am. Chem. Soc.* **1991**, *113*, 4092–4096.

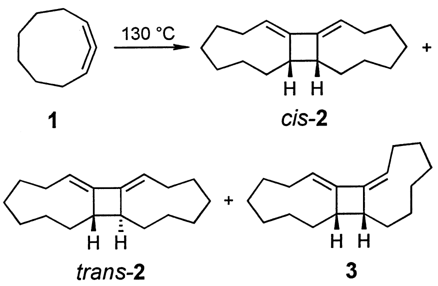
[10] H. A. Kirst, K. H. Michel, J. W. Martin, L. C. Creemer, E. H. Chio, R. C. Yao, W. M. Nakatsukasa, L. D. Boeck, J. L. Occolowitz, J. W. Paschal, J. B. Deeter, N. D. Jones, G. D. Thompson, *Tetrahedron Lett.* **1991**, *32*, 4839.

[11] S. Ito, Y. Hirata, *Tetrahedron Lett.* **1972**, 1185–1188.

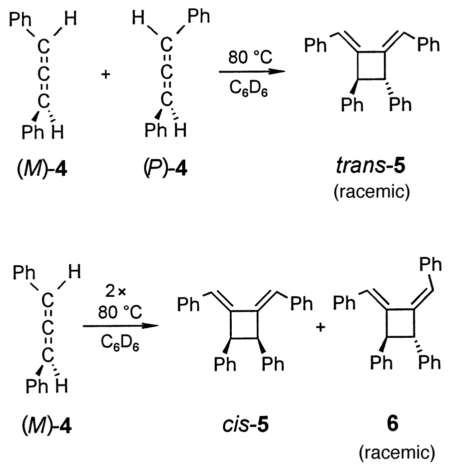
The Dimerization of Chiral Allenes: Pairs of Enantiomers and Pairs of Homomers Furnish Different Diastereomers**

Manfred Christl,* Stefan Groetsch, and Kurt Günther

At room temperature, cyclonona-1,2-diene (**1**) can be stored virtually unlimited. Proceeding at 130 °C, its dimerization furnishes the 1,2-bis(methylene)cyclobutane derivatives *cis*-**2**, *trans*-**2**, and **3** in the ratio of 5:10:1 in the case of the racemic mixture, whereas a nearly pure enantiomer affords almost only *cis*-**2**.[1] These findings suggest the interpretation that the combination of a pair of homomers in racemic **1** gives rise to *cis*-**2** and that of a pair of enantiomers provides preferentially *trans*-**2** and additionally **3**.



1,3-Diphenylallene (**4**) had been studied as a second example for the dimerization of chiral nonracemic allenes. By using a sample with an optical purity of 35 %, the optical rotation did decrease to zero, however, the ratio of products (*cis*-**5**, *trans*-**5**, and **6**) was unchanged compared to that from the dimerization of racemic **4**.[2] Assuming that the enantiomeric excess could have been too small for the observation of a deviation from the behavior of racemic **4**, we repeated the experiments. On heating in C_6D_6 at 80 °C for five days, racemic **4** was consumed to the extent of 93 % and yielded *cis*-**5**, *trans*-**5**, and **6** in the ratio of 44:28:28. The pure enantiomers of **4** were obtained by HPLC on Chiralcel OD[3] and dimerized to give predominantly *cis*-**5** and **6** and only a small proportion of *trans*-**5** (*cis*-**5**:*trans*-**5**:**6** = 46:4:50). Therefore, we conclude that in racemic **4** pairs of enantiomers prefer to form *trans*-**5**, while pairs of homomers produce mainly *cis*-**5** or **6**.



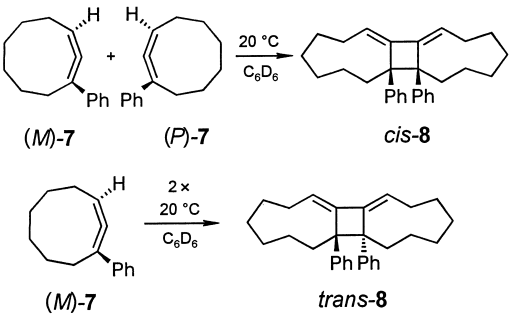
Recently, we reported on the dimerization of racemic 1-phenylcyclonona-1,2-diene (**7**) in $CDCl_3$, which occurs already at 20 °C with formation of *cis*- and *trans*-**8** in the ratio of about 1:2.[4] The reaction has now been conducted in C_6D_6 and the product ratio was found to be very close to 50:50. The pure enantiomers of **7** were obtained by HPLC of the racemic mixture on Chiralcel OD with hexane as eluant. Their dimerization in C_6D_6 (several weeks at 20 °C) gave *trans*-**8** with high preference (*cis*-**8**:*trans*-**8** = 8:92). These results

---

[*] Prof. Dr. M. Christl, Dipl.-Chem. S. Groetsch
Institut für Organische Chemie der Universität
Am Hubland, 97074 Würzburg (Germany)
Fax: (+49) 931-8884606
E-mail: christl@chemie.uni-wuerzburg.de

Dr. K. Günther
INFRACOR GmbH, Analytisch Technische Services
Postfach 1345, 63403 Hanau (Germany)

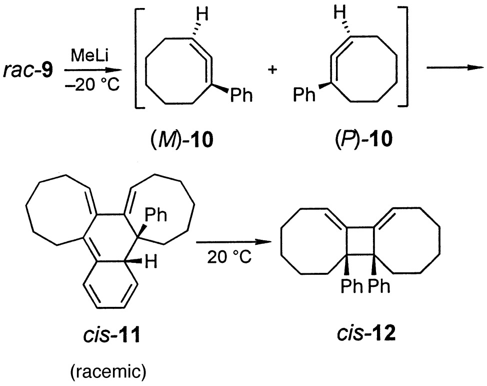
[**] Cycloallenes, Part 14. This work was supported by the Deutsche Forschungsgemeinschaft, by the Fonds der Chemischen Industrie, and by CHEMETALL GmbH. Part 13: M. Christl, S. Groetsch, *Eur. J. Org. Chem.* **2000**, 1871–1874.



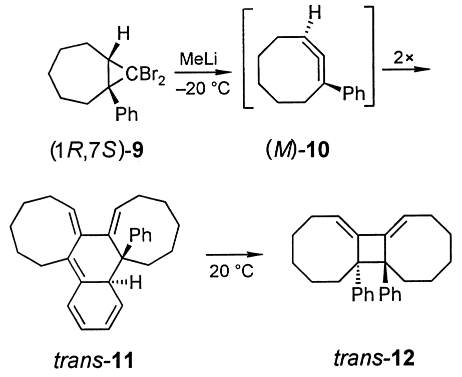
(absolute configuration unknown)

suggest the highly selective production of *cis*-**8** from pairs of enantiomers in racemic **7**, whereas pairs of homomers furnish *trans*-**8**; the ratio of the rate constants is 2:1. In comparison with the situation in **1**, the stereochemical course is reversed, as the *meso*-form (*cis*-**2** and *cis*-**8**, respectively) originates from pairs of homomers there and from pairs of enantiomers here. The optical activity of the *trans*-**8** products, obtained from (+)-**7** and (−)-**7**, does not support the formation of racemic mixtures.[5]

The above results with **7** aroused our curiosity about 1-phenylcycloocta-1,2-diene (**10**). Some time ago we had generated this cycloallene as a racemic mixture (*rac*-**10**) and obtained its unusual dimer *cis*-**11**, which probably emerges from the diradical intermediate **21** in a dead-end equilibrium and rearranges slowly to *cis*-**12** at 20 °C. Since *cis*-**12** is the only known *cis* dimer of a cycloallene with an eight-membered or a smaller ring, it has also to be considered as unusual.[6] Dimerizing rapidly even at −40 °C, **10** cannot be observed directly,[6] which is why only its precursor **9** could be employed in the form of pure enantiomers. Racemic **9** (*rac*-**9**) was resolved by HPLC on Chiralpak AD with hexane as eluant. Optically active samples of **4** and **1** can in fact be prepared via nonracemic *trans*-2,3-diphenylcyclopropylidene[7] and from nonracemic 9,9-dibromo-*trans*-bicyclo[6.1.0]nonane[8] by the Doering–Moore–Skattebøl reaction, but the stereochemical course of the conversion of (1*R*,7*S*)- and (1*S*,7*R*)-**9** into **10** was unclear because of the absence of C_2 symmetry in these substrates. The analysis of the ring opening of cyclopropylidene to allene by quantum-chemical calculations reveals a quite complex process.[9]



(racemic)

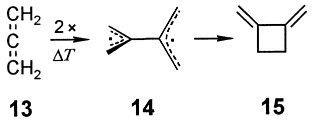


(absolute configuration unknown)

After treatment of the pure enantiomers of **9** with methyllithium in diethyl ether we indeed observed at best a very small quantity of *cis*-**11** and *cis*-**12** (error limit 6 %). The only identified product was *trans*-**12**, which we had observed previously on heating of *cis*-**12** to 160 °C.[6] For a short time after each of the experiments had been carried out, another product could be detected by ^1H NMR spectroscopy. This product rearranged completely to *trans*-**12** within one day at room temperature. Owing to the similarity of the data to those of *cis*-**11**, we assign structure *trans*-**11** to it. The optical activity as well as HPLC on Chiralpak AD with isohexane as eluant demonstrate the nonracemic nature of both *trans*-**12** samples.

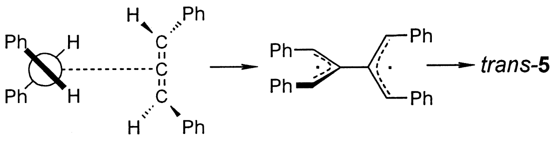
These experiments prove the highly selective conversion of (1*R*,7*S*)- and (1*S*,7*R*)-**9** into one enantiomer of **10** each (presumably (*M*)-**10** is formed from (1*R*,7*S*)-**9**). Giving rise to the dimers *trans*-**12**, the pure enantiomers **10** exhibit, at variance with the racemic mixture, a behavior typical for small-ring cycloallenes. Careful analysis of the crude product from *rac*-**9** indicated the presence of a small amount of *trans*-**12**; the ratio of (*cis*-**11** + *cis*-**12**):*trans*-**12** was 95:5. Thus, *rac*-**10** is a remarkable example for molecular recognition with significant selectivity; pairs of enantiomers react 38 times faster than pairs of homomers.

To rationalize these phenomena, we first consider the energetics of the dimerization of the parent allene (**13**). Roth and Schaffers[10] determined $\Delta H^{\neq}$ and $\Delta S^{\neq}$ with high precision to be 26.9 kcal mol^{-1} and 25.9 cal mol^{-1} K^{-1}, respectively, and located the intermediate tetramethyleneethane diradical **14** about 32 and about 8 kcal mol^{-1}, respectively, below the transition state of its generation from two molecules of **13** and the transition state en route to the final product, that is 1,2-(bismethylene)cyclobutane (**15**). Quantum-chemical calculations attribute to the singlet state of **14** the conformation with the allyl-radical subunits arranged perpendicularly to each other.[11]

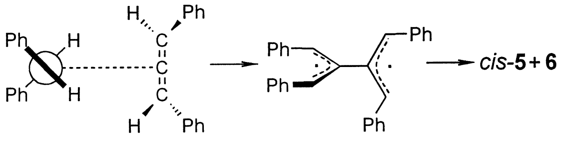


Previously, we had proposed such diradicals as intermediates for the dimerization of *rac*-**7** and *rac*-**10**, in the course of which the ring closures should occur as least-motion processes, corresponding to a conrotation. Accordingly, it must be assumed that stereoisomeric diradicals are generated selectively from pairs of enantiomers and homomers, respectively, and are transformed to the products without extensive isomerization.

En route to *trans*-**5**, the most likely diradical is **16**, which should be formed on the approach of (*M*)-**4** and (*P*)-**4** with their sterically unhindered faces in the crossed arrangement along their C_2 axes. The corresponding transition state shows equal interactions between the hydrogen atoms of one allene subunit and the phenyl groups of the other with the effect that the phenyl groups of **16** are as far away as possible from the other half of the molecule.



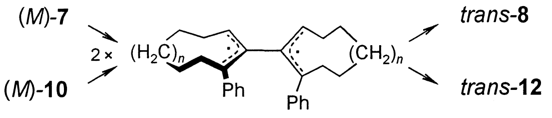
(*M*)-**4** (*P*)-**4** **16**



(*M*)-**4** (*M*)-**4** **17**

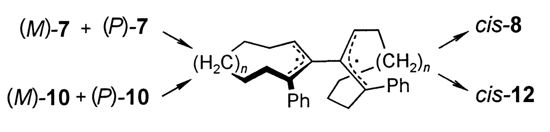
The diradical **17** should be the precursor of *cis*-**5** and **6**. In the corresponding transition state from two homomers of **4**, the hydrogen atoms of the allene subunits approach each other in pairs rather closely. Forced by the steric crowding, one hydrogen atom moves out of the way such that an allyl radical moiety with an *E*,*Z* configuration is generated. With regard to the formation of **5** and **6**, the diradicals **16** and **17** as well as their four diastereomers had been discussed in detail previously, but without a definite conclusion.[2, 12]

Transition states from two allene molecules in the crossed arrangement have to be assumed also for the dimerization of **7** and **10**. However, because of the variety of the possibilities and of the steric interactions—even methylene groups not directly linked to the allene moiety can impair the close contact with the other molecule—the situation is not easily comprehensible. Within the discussed mechanistic concept though, there is no doubt that pairs of homomers of **7** and **10** give rise to the diradicals **18** and **19**, respectively, which eventually collapse to give *trans*-**8** and *trans*-**12**, whereas pairs of enantiomers of **7** and **10** generate the diradicals **20** and **21**, respectively, from which *cis*-**8** and *cis*-**12** result. The non-racemic nature of the *trans* products supports a considerable conformative stability of **18** and **19**, and the only small admixtures of *cis*-**8** and *cis*-**12** confirm their configurative persistence as well, that is only insignificant proportions of **18** and **19** isomerize to **20** and **21**, respectively.



$n = 2$: **18**
$n = 1$: **19**

(absolute configuration unknown)



$n = 2$: **20**
$n = 1$: **21**

Received: March 14, 2000 [Z14847]

[1] W. R. Moore, R. D. Bach, T. M. Ozretich, *J. Am. Chem. Soc.* **1969**, *91*, 5918–5919.

[2] E. V. Dehmlow, G. C. Ezimora, *Tetrahedron Lett.* **1972**, 1265–1270.

[3] W. R. Roth, T. Bastigkeit, *Liebigs Ann.* **1996**, 2171–2183; in each case, the proportion of the other enantiomer was <1%.

[4] M. Christl, D. Moigno, E.-M. Peters, K. Peters, H. G. von Schnering, *Liebigs Ann.* **1997**, 1791–1796.

[5] (+)-**7**→(+)-**8**: $[\alpha]_{\mathrm{D}}^{20} = +97°$ ($c = 2.02$, CH_2Cl_2); (−)-**7**→(−)-**8**: $[\alpha]_{\mathrm{D}}^{20} = -109°$ ($c = 1.81$, CH_2Cl_2, unpurified sample in each case); according to the HPLC analysis with Chiralcel OJ with isohexane as eluant, the *ee* values were at least 90%.

[6] M. Christl, M. Rudolph, E.-M. Peters, K. Peters, H. G. von Schnering, *Angew. Chem.* **1995**, *107*, 2931–2934; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2730–2732.

[7] J. M. Walbrick, J. W. Wilson, Jr., W. M. Jones, *J. Am. Chem. Soc.* **1968**, *90*, 2895–2901.

[8] A. C. Cope, W. R. Moore, R. D. Bach, H. J. S. Winkler, *J. Am. Chem. Soc.* **1970**, *92*, 1243–1247.

[9] H. F. Bettinger, P. R. Schreiner, P. von R. Schleyer, H. F. Schaefer III, *J. Phys. Chem.* **1996**, *100*, 16147–16154; H. F. Bettinger, P. von R. Schleyer, P. R. Schreiner, H. F. Schaefer III, *J. Org. Chem.* **1997**, *62*, 9267–9275.

[10] T. Schaffers, Dissertation, Universität Bochum, **1992**.

[11] P. Nachtigall, K. D. Jordan, *J. Am. Chem. Soc.* **1993**, *115*, 270–271.

[12] A. J. Brattesani, E. Maverick, O. J. Muscio, Jr., T. L. Jacobs, *J. Org. Chem.* **1992**, *57*, 7346–7349.

Five-Coordinate Carbides in Ti-Al-C Complexes**

James E. Kickham, Frédéric Guérin, Jeffrey C. Stewart, and Douglas W. Stephan*

Fifty years after the discovery of catalytic olefin polymerization by Ziegler and Natta, polyolefin products are commodity chemicals. The production of these materials is a significant driving force in our economy; one that continues to inspire research. Over the last twenty years much effort has been directed towards tunable "single-site catalysts".[1–6] The

---

[*] Prof. Dr. D. W. Stephan, Dr. J. E. Kickham, Dr. F. Guérin,
J. C. Stewart
School of Physical Sciences, Chemistry and Biochemistry
University of Windsor
Windsor, ON, N9B 3P4 (Canada)
Fax: (+1) 519-973-7098
E-mail: Stephan@uwindsor.ca

[**] Financial support from NSERC of Canada and Nova Chemicals Corporation is gratefully acknowledged. F.G. is grateful for the award of an NSERC Postdoctoral Fellowship.