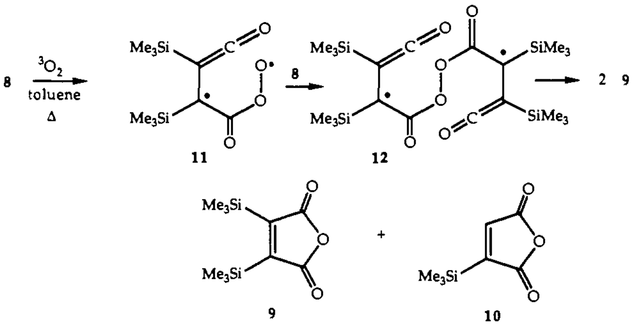
for ring opening of variously substituted cyclobutenes to 1,3-butadienes,[7] and of cyclobutenones to vinylketenes.[8] Theoretical studies of these latter reactions have appeared.[9,10]

Thus **8** is thermodynamically stable and persistent in the pure state at room temperature, as predicted,[3a] due to the effect of silyl substitution. The bisketene structure **1** is, however, calculated to be destabilized relative to ketene and butadiene; thus the isodesmic reaction of eq 1 has a calculated $\Delta E$ of −11.9 kcal/mol, based on the published[3a] energies of the individual species.

$$\underset{\mathbf{1}}{(\mathrm{CH{=}C{=}O})_2} + 2\mathrm{CH_2{=}CH_2} \xrightarrow{\Delta E\,=\,11.9\ \mathrm{kcal/mol}} 2\mathrm{CH_2{=}C{=}O} + (\mathrm{CH{=}CH_2})_2 \quad (1)$$

A degassed sample of **8** in $CDCl_3$ was unchanged after standing for 45 days at 2 °C, but bubbling $O_2$ into a refluxing solution of **8** in toluene gave bis(trimethylsilyl)maleic anhydride (**9**),[11] (trimethylsilyl)maleic anhydride (**10**),[11] and small amounts of other unidentified products. Previous reactions of ketenes[12] and strained alkenes[13] with $O_2$ have been interpreted as involving perepoxide and diradical intermediates.[12] A diradical pathway for reaction of **8** with $^3O_2$ could involve an initial triplet diradical **11** followed by reaction of a second molecule of **8** to give **12**, which could lead to **9** after intersystem crossing.



Various mono- and difunctional nucleophiles also react with **8** by unique pathways which will be reported shortly.

**Acknowledgment**. Financial support of this work by the Natural Sciences and Engineering Research Council of Canada and technical assistance by Annette D. Allen are gratefully acknowledged.

---

(7) (a) Cooper, W.; Walters, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 4220–4224. (b) Pomerantz, M.; Hartman, P. H. *Tetrahedron Lett.* **1968**, 991–993. (c) Frey, H. M.; Pope, B. M.; Skinner, R. F. *Trans. Faraday Soc.* **1967**, *63*, 1166–1170. (d) Brauman, J. I.; Archie, W. C., Jr. *Tetrahedron* **1971**, *27*, 1275–1280.

(8) (a) Huisgen, R.; Mayr, H. *J. Chem. Soc., Chem. Commun.* **1976**, 55–56. (b) Mayr, H.; Huisgen, R. *J. Chem. Soc., Chem. Commun.* **1976**, 57–58.

(9) (a) Breulet, J.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1984**, *106*, 1221–1226. (b) Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 2099–2111. (c) Rudolf, K.; Spellmeyer, D. C.; Houk, K. N. *J. Org. Chem.* **1987**, *52*, 3708–3710. (d) Bachrach, S. M.; Liu, M. *J. Org. Chem.* **1992**, *57*, 2040–2047.

(10) (a) Seidl, E. T.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1990**, *112*, 1493–1499. (b) Seidl, E. T.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1991**, *113*, 5195–5200. (c) Nguyen, M. T.; Ha, T.; More O'Ferrall, R. A. *J. Org. Chem.* **1990**, *55*, 3251–3256.

(11) Isolated yields of **9** and **10** after radial chromatography were 14 and 7%, respectively. **9**: mp 58–59.5 °C; $^1$H NMR ($CDCl_3$) $\delta$ 0.390; $^{13}$C NMR ($CDCl_3$) $\delta$ 0.03, 161.6, 168.5; IR ($CDCl_3$) 1830 (w), 1814 (w), 1752, 1747 (d, s) cm$^{-1}$; CIMS *m/z* 243 ($M^+ + 1$); EIMS *m/z* 227 ($M^+ - CH_3$, 11), 155 (100), 73 ($Me_3Si^+$, 47); HRMS *m/z* calcd for $C_{10}H_{18}O_3Si_2 - CH_3$ ($M^+ - CH_3$) 227.0560, found 227.0567. **10**: oil; $^1$H NMR ($CDCl_3$) $\delta$ 0.345, 6.985; $^{13}$C NMR ($CDCl_3$) $\delta$ −2.3, 142.8, 155.6, 164.7, 167.5; IR ($CDCl_3$) 1855 (w), 1816 (w), 1764 (s) cm$^{-1}$; CIMS *m/z* 171 ($M^+ + 1$, 100), 155 ($M^+ - CH_3$, 72); HRMS *m/z* calcd for $C_6H_7O_3Si$ ($M^+ - CH_3$) 155.0164, found 155.0152.

(12) (a) Bartlett, P. D.; McCluney, R. E. *J. Org. Chem.* **1983**, *48*, 4165–4168. (b) Wheland, R.; Bartlett, P. D. *J. Am. Chem. Soc.* **1970**, *92*, 6057–6058. (c) Turro, N. J.; Ito, Y.; Chow, M.; Adam, W.; Rodriquez, O.; Yang, F. *J. Am. Chem. Soc.* **1977**, *99*, 5836–5838. (d) Turro, N. J.; Chow, M.; Ito, Y. *J. Am. Chem. Soc.* **1978**, *100*, 5580–5582. (e) Turro, N. J.; Chow, M. *J. Am. Chem. Soc.* **1980**, *102*, 5058–5064. (f) Majerski, Z.; Vinkovic, V. *Synthesis* **1989**, 559–560.

(13) (a) Bartlett, P. D.; Banavali, R. *J. Org. Chem.* **1991**, *56*, 6043–6050. (b) Pasto, D. J.; Yang, S.; Muellerleile, J. A. *J. Org. Chem.* **1992**, *57*, 2976–2978.

---

# 8-Endo Cyclization of (Alkoxycarbonyl)methyl Radicals Generated from Bromoacetates

Eun Lee,* Cheol Hwan Yoon, and Tae Hee Lee

*Department of Chemistry, College of Natural*
*Sciences, Seoul National University*
*Seoul 151-742, Korea*

*Received September 2, 1992*

The radical cyclization reactions developed in the last decade are now firmly established as indispensable tools in synthetic chemistry. These reactions exhibit useful regio- and stereoselectivity employing a variety of functional groups as radical acceptors.[1]

Initial attempts to cyclize (alkoxycarbonyl)alkyl radical species from $\alpha$-haloalkanoate esters under standard radical-generating conditions with tributylstannane and AIBN led only to simple reduction products, and the results were attributed to the relative stability of these carbonyl conjugated radicals. Stork[2] and Ueno[3] solved this problem by developing tin hydride-mediated cyclization of $\alpha$-halo acetals as an indirect route to $\gamma$- and $\delta$-lactones. Another practical solution to this problem has been devised by Curran[4] based on the halogen atom transfer reactions. More recently, however, direct syntheses of $\gamma$- and $\delta$-lactones via 5-exo or 6-exo radical cyclizations using $\alpha$-haloalkanoates as substrates were reported.[5]

We report herein that (alkoxycarbonyl)methyl radicals generated from bromoacetates under standard high-dilution conditions undergo intramolecular cyclization in a regioselective 8-endo mode[6] to yield eight-membered-ring heptanolactones. This 8-endo cyclization is preferred over 5-exo cyclization as proved in competition experiments.

Slow addition (via a syringe pump) of a solution of tributylstannane (1.4 equiv) in benzene containing AIBN (0.1 equiv) over 5 h into a benzene solution (0.015 M) of the bromoacetate **2a** under reflux gave the acetate **2b** (24%) and the lactone **2c** (52%) (Scheme I). Further examples of 8-endo cyclization are presented in Table I.[7] On the contrary, lower and higher homologues **5a** and **6a** were transformed mainly into the corresponding acetates **5b** and **6b**, and cyclization products (6-exo or 7-endo mode for **5a** and 8-exo or 9-endo mode for **6a**) were not isolated.[8] These results indicate that the 8-endo mode of cyclization is the in-

---

(1) For reviews, see: (a) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon Press: Oxford, 1986. (b) Hart, D. J. *Science* **1984**, *223*, 883. (c) Neumann, W. P. *Synthesis* **1987**, 665. (d) Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541. (e) Curran, D. P. *Synthesis* **1988**, 417 and 489. (f) Curran, D. P. *Chem. Rev.* **1991**, *91*, 1237.

(2) (a) Stork, G.; Mook, R., Jr.; Biller, S. A.; Rychnovsky, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 3741. (b) Stork, G.; Sher, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 6765. (c) Stork, G.; Sher, P. M. *J. Am. Chem. Soc.* **1986**, *108*, 303. (d) Stork, G.; Sher, P. M.; Chen, H. L. *J. Am. Chem. Soc.* **1986**, *108*, 6384. (e) Stork, G. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 149.

(3) (a) Ueno, Y.; Chino, K.; Watanabe, M.; Moriya, O.; Okawara, M. *J. Am. Chem. Soc.* **1982**, *104*, 5564. (b) Ueno, Y.; Moriya, O.; Chino, K.; Watanabe, M.; Okawara, M. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1351.

(4) (a) Curran, D. P.; Chang, C. T. *Tetrahedron Lett.* **1987**, *28*, 2477. (b) Curran, D. P.; Chang, C. T. *J. Org. Chem.* **1989**, *54*, 3140. (c) Curran, D. P.; Chang, C. T. *Tetrahedron Lett.* **1990**, *31*, 933.

(5) (a) Belletire, J. L.; Mahmoodi, N. O. *Tetrahedron Lett.* **1989**, *30*, 4363. (b) Clough, J. M.; Pattenden, G.; Wight, P. G. *Tetrahedron Lett.* **1989**, *30*, 7469. (c) Hannesian, S.; Di Fabio, R.; Marcoux, J. F.; Prud'homme, M. *J. Org. Chem.* **1990**, *55*, 3436.

(6) For prior observations of 8-endo cyclizations of different radical systems, see: (a) Snider, B. B.; Merritt, J. E. *Tetrahedron Lett.* **1991**, *47*, 8663. (b) Sato, T.; Ishida, S.; Ishibashi, H.; Ikeda, M. *J. Chem. Soc., Perkin Trans. 1* **1991**, 353.

(7) All products in Tables I and II were separated by silica gel column chromatography, and the specified yields are *isolated* yields. In every case, separation was easily achieved even though products were isomeric compounds. For example, product (**8b–e**) from **8a** exhibited four well-separated spots on a silica gel TLC plate. Spectroscopic data for heptanolactone **1c** were reported in Matsubara, S.; Takai, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2029 and ref 15. Structural determination of other products is supported by a full set of spectroscopic data.

(8) The reaction of **5a** produced a complex product mixture from which **5b** was isolated in 42% yield. The conversion of **6a** into **6b** was accompanied by one major byproduct, which appeared to be a dimeric species formed by the intermolecular attack of the (alkoxycarbonyl)methyl radical and subsequent reduction.

**Scheme I**

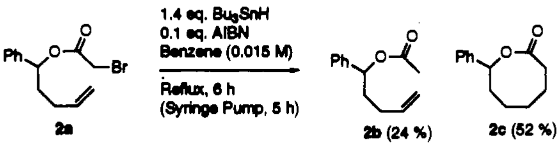


**Table I**

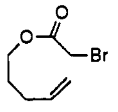
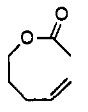
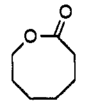
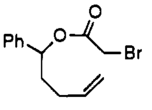
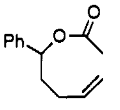
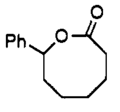
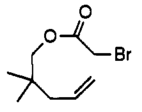
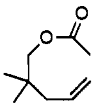
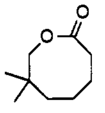
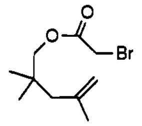
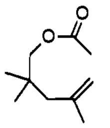
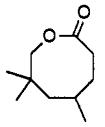
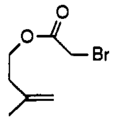
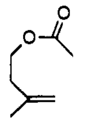
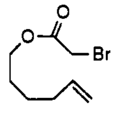
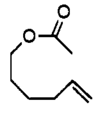
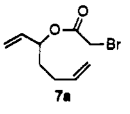
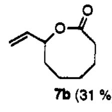
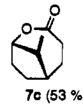
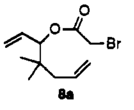
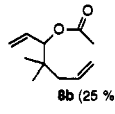
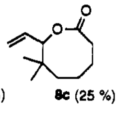
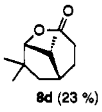
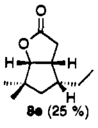
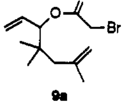
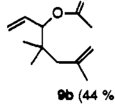
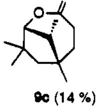
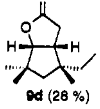
| Substrates | Products (Isolated Yield) | |
|---|---|---|
| <br>1a | <br>1b (31 %) | <br>1c (38 %) |
| <br>2a | <br>2b (24 %) | <br>2c (52 %) |
| <br>3a | <br>3b (16 %) | <br>3c (53 %) |
| <br>4a | <br>4b (50 %) | <br>4c (25 %) |
| <br>5a | <br>5b (42%) | |
| <br>6a | <br>6b (79%) | |

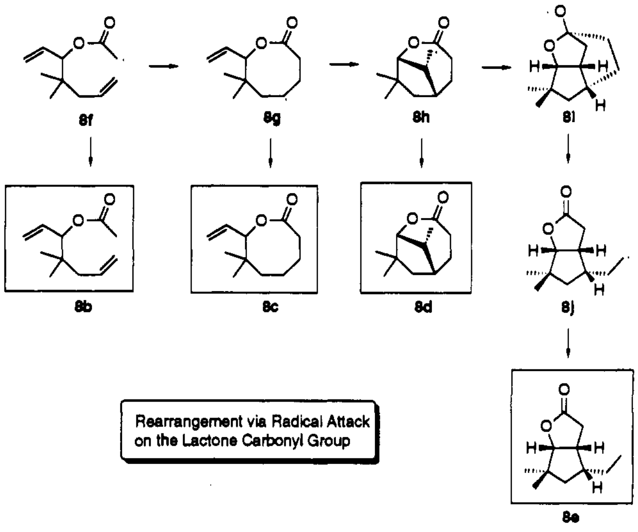
**Table II**

| Substrates | Products (Isolated Yield) | | | |
|---|---|---|---|---|
| <br>7a | | <br>7b (31 %) | <br>7c (53 %) | |
| <br>8a | <br>8b (25 %) | <br>8c (25 %) | <br>8d (23 %) | <br>8e (25 %) |
| <br>9a | <br>9b (44 %) | | <br>9c (14 %) | <br>9d (28 %) |

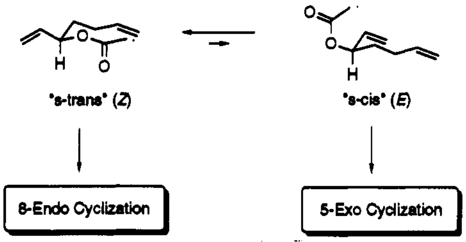
trinsically favored pathway for (alkoxycarbonyl)methyl radicals.

Next, substrates **7a–9a** were reacted under the same conditions for 5-exo/8-endo competition experiments (Table II). In the event, cyclization of radicals from bromoacetates **7a–9a** proceeded exclusively in the 8-endo mode to yield eight-membered lactones **7b** and **8c**. Bridged lactones **7c**, **8d**, and **9c**[9] were also obtained, which are products of 8-endo/5-exo tandem radical cyclizations.[10] No simple 5-exo mode cyclization products were obtained. Interestingly, butyrolactones **8e** and **9d**[11] were also isolated. It is assumed that the reaction proceeds from the methyl radical **8h** via transannular attack to the lactone carbonyl group and fragmentation of the oxy radical **8i** to the ethyl radical **8j** as outlined in Scheme II. We believe this is the first clear-cut example of radical rearrangements involving ester or lactone carbonyl functionalities.[12]

**Scheme II**



**Scheme III**



---

[9] The second methyl group in **7c** was determined to be exo oriented whereas the secondary methyl groups in **8d** and **9c** were assigned to be endo oriented. The NOE difference spectrum of **9c** showed that the intensity of the signals (AB q, $\delta$ 1.692 and 1.568, $J$ = 14.1 Hz) from the protons of the isolated methylene group of the carbocyclic ring did not change upon irradiation of the secondary methyl group signals (d, $\delta$ 0.935, $J$ = 7.2 Hz), but the signals (dd, $\delta$ 1.671, $J$ = 13.5, 4.5 Hz) from one of the methylene protons $\beta$ to the carbonyl group were enhanced. Apparently, the transition-state conformations for the 5-exo cyclization of the heptanolactone radicals formed by 8-endo cyclization of the initial (alkoxycarbonyl)methyl radicals from **8a** and **9a** are much influenced by the presence of the *gem*-dimethyl moieties, so that the ensuing methyl radical centers are directed to the lactone rings, enticing further rearrangements.

[10] It is to be noted that the combined yield (84%) of **7b** and **7c** from **7a** for 8-endo cyclization is substantially higher than the yield (38%) of **1c** from **1a**. This could be the effect of an extra substituent on the reactive conformation. One alternative explanation is that (alkoxycarbonyl)methyl radical 8-endo cyclization is reversible under the reaction conditions, and the relative amounts of **1b** and **1c** may represent the equilibrium ratio of the (alkoxycarbonyl)methyl radical and heptanolactone radical. On the other hand, the heptanolactone radical generated from **7a** may be more effectively consumed by the 5-exo cyclization, in effect increasing the total yield of the 8-endo cyclization. In support of the equilibrium hypothesis, the reaction of **2a** under higher dilution conditions (syringe pump addition in 14 h) produced the same yield of **2b** and **2c**.

[11] The mechanism delineated in Scheme II calls for the cis relationship of the lactone ring and the ethyl group in **9d**. This was convincingly shown in the NOE difference spectrum: irradiation of the lactone methylene proton signals (d, $\delta$ 2.490, $J$ = 7.8 Hz) resulted in the enhancement of the signals (q, $\delta$ 1.285, $J$ = 7.2 Hz) from the methylene protons of the ethyl group.

[12] For some examples of intramolecular addition of alkyl radicals to aldehyde and ketone carbonyl groups, see: (a) Tsang, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1986**, *108*, 2116. (b) Tsang, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1986**, *108*, 8102. (c) Tsang, R.; Dickson, J. K., Jr.; Park, H.; Walton, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1987**, *109*, 3484. (d) Dowd, P.; Choi, S. C. *J. Am. Chem. Soc.* **1987**, *109*, 3493. (e) Dowd, P.; Choi, S. C. *J. Am. Chem. Soc.* **1987**, *109*, 6548.

The preferred 8-endo mode of cyclization of (alkoxycarbonyl)methyl radicals reflects the conformational bias of these radicals favoring *Z* conformation (s-trans) over *E* conformation (s-cis) (Scheme III). In line with many theoretical and experimental studies corroborating the relative stability of *Z* ester conformations, the *Z* conformation of the (alkoxycarbonyl)alkyl radicals was also judged to be more stable than the *E* conformation.[13,14] The selective formation of eight-membered-ring heptanolactones in these cyclization reactions is probably also connected with the finding that the heptanolactone is the smallest lactone for which *Z* conformers are found as low-energy conformers.[15]

In conclusion, 8-endo cyclization is the fundamentally preferred mode of reaction for (alkoxycarbonyl)methyl radicals, and eight-membered heptanolactones are obtained in reasonably good yields from bromoacetates. Further mechanistic details and the synthetic utility of these unique reactions will be reported in due course.

**Acknowledgment.** The authors thank the Organic Chemistry Research Center (KOSEF) and Ukong Corporation for financial support.

---

(13) (a) Fisher, H.; Wu, L. M. *Helv. Chim. Acta* **1983**, *66*, 138. (b) Beckwith, A. L. J.; Glover, S. A. *Aust. J. Chem.* **1987**, *40*, 157.

(14) Atom-transfer cyclization of allyl iodoacetates is much more efficient at 80 °C than at 25 °C. This beneficial effect of temperature arises because at higher temperature there is a relatively larger population of the less stable *E* conformer (which can cyclize in 5-exo mode) of [(allyloxy)carbonyl]methyl radicals than at lower temperature. See: Curran, D. P.; Tamine, J. *J. Org. Chem.* **1991**, *56*, 2746.

(15) Wiberg, K. B.; Waldron, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 7697.

---

# Intramolecular [2 + 2] Cycloaddition of Bis(alkenylcyclopentadienyl)zirconium Dihalides: A Novel Way of Synthesizing *ansa*-Metallocene Complexes

Gerhard Erker* and Stephan Wilker

*Organisch-Chemisches Institut der*
*Universität Münster, Corrensstrasse 40*
*D-4400 Münster, Germany*

Carl Krüger and Richard Goddard

*Max-Planck-Institut für Kohlenforschung*
*Kaiser-Wilhelm-Platz 1*
*D-4330 Mülheim a.d. Ruhr, Germany*

*Received August 26, 1992*

*ansa*-Metallocene complexes of the group 4 transition metals have played a decisive role for the development of homogeneous Ziegler-type catalysts for stereoselective $\alpha$-olefin polymerization.[1] Two-carbon containing bridges between the metal bound $\eta^5$-cyclopentadienyl units (or analogues thereof) are usually prepared by means of substitution reactions[2] or coupling of $C_1$-substituted cyclopentadienyls.[3] We here describe a novel method of synthesizing $C_2$-bridged *ansa*-metallocene complexes by photochemically induced [2 + 2] cycloaddition of bis(alkenyl-Cp)$MX_2$ complexes.[4] The two-carbon bridge in these compounds is part of a cyclobutane ring. A representative example is described here.

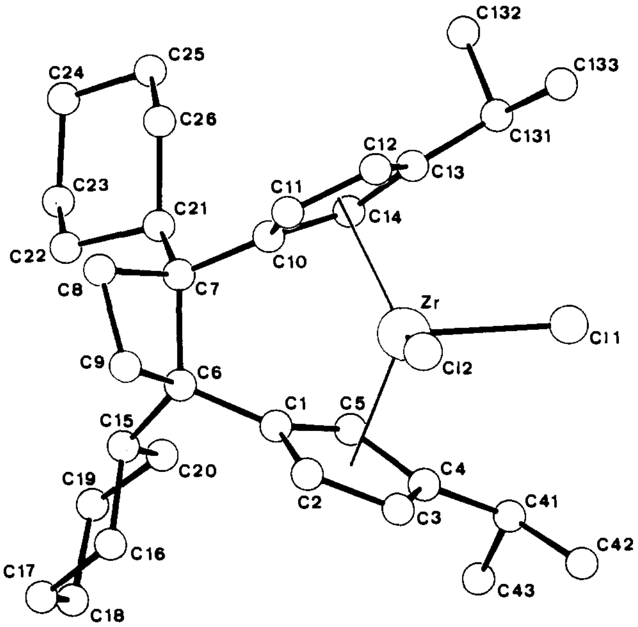


**Figure 1.** A view of the molecular structure of *meso*-**5**.

Bis(1-(cyclohexylethenyl)-3-isopropylcyclopentadienyl)zirconium dichloride (*rac*- and *meso*-**4**) was prepared by reacting the substituted alkenylcyclopentadienyllithium reagent **2** [generated by treatment of the 3-isopropyl-6-cyclohexylfulvene isomers (**1**) with LDA[5]] with 0.5 M equiv of $ZrCl_4(THF)_2$ (**3**). The isomers of **4** were separated by fractional crystallization from pentane (the pure diastereomers were isolated in ca. 10% yield each) and then irradiated with UV/vis light.[6] Irradiation of *meso*-**4** with Pyrex-filtered light from a high-pressure mercury lamp (Philips HPK 125, room temperature, 60 min, benzene solution) gave a 90:10

---

(1) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem.* **1985**, *97*, 507. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507.

(2) Schnutenhaus, H.; Brintzinger, H. H. *Angew. Chem.* **1979**, *91*, 837. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 777. Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233. Recent examples: Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *Organometallics* **1988**, *7*, 1828. Collins, S.; Hong, Y.; Taylor, N. J. *Organometallics* **1990**, *9*, 2695. Röll, W.; Brintzinger, H. H.; Rieger, B.; Zolk, R. *Angew. Chem.* **1990**, *102*, 339. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 279 and references cited therein. Bandy, J. A.; Green, M. L. H.; Gardiner, I. M.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1991**, 2207. Grossman, R. B.; Doyle, R. A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 1501. Lang, H.; Seyferth, D. *Organometallics* **1991**, *10*, 347. Collins, S.; Gauthier, W. J.; Holden, D. A.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. *Organometallics* **1991**, *10*, 2061. Collins, S.; Hong, Y.; Ramachandran, R.; Taylor, N. J. *Organometallics* **1991**, *10*, 2349. Rheingold, A. L.; Robinson, N. P.; Whelan, J.; Bosnich, B. *Organometallics* **1992**, *11*, 1869.

(3) Schwemlein, H.; Brintzinger, H. H. *J. Organomet. Chem.* **1983**, *254*, 69. Wiesenfeldt, H.; Reinmuth, A.; Barsties, E.; Evertz, K.; Brintzinger, H. H. *J. Organomet. Chem.* **1989**, *369*, 359. Kawase, T.; Nisato, N.; Oda, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1145. Recknagel, A.; Edelmann, F. T. *Angew. Chem.* **1991**, *103*, 720. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 693. Burger, P.; Brintzinger, H. H. *J. Organomet. Chem.* **1991**, *407*, 207. Burger, P.; Hortmann, K.; Diebold, J.; Brintzinger, H. H. *J. Organomet. Chem.* **1991**, *417*, 9. Burger, P.; Diebold, J.; Gutmann, S.; Hund, H.-U.; Brintzinger, H. H. *Organometallics* **1992**, *11*, 1319. Dorer, B.; Diebold, J.; Weyand, O.; Brintzinger, H. H. *J. Organomet. Chem.* **1992**, *427*, 245 and references cited therein. For coupling reactions leading to $C_1$-bridged *ansa*-metallocene systems, see: Ewen, J. A.; Haspeslagh, L.; Atwood, J. L.; Zhang, H. *J. Am. Chem. Soc.* **1987**, *109*, 6544. Mallin, D. T.; Rausch, M. D.; Lin, Y.-G.; Dong, S.; Chien, J. C. W. *J. Am. Chem. Soc.* **1990**, *112*, 2030. Llinas, G. H.; Dong, S.-H.; Mallin, D. T.; Rausch, M. D.; Lin, Y.-G.; Winter, H. H.; Chien, J. C. W. *Macromolecules* **1992**, *25*, 1242 and literature cited in these references.

(4) For examples of remotely related organometallic [2 + 2] cycloaddition reactions, see: Nakanishi, K.; Mizuno, K.; Otsuji, Y. *J. Chem. Soc., Perkin Trans. 1* **1990**, 3362. Nakadira, Y.; Sakurai, H. *Tetrahedron Lett.* **1971**, 1183. Bichler, R. E. J.; Booth, M. R.; Clark, H. C. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 71. See, also: Nesmeyanov, A. N.; Sazonova, V. A.; Romanenko, V. I.; Rodionova, N. A.; Zolnikova, G. P. *Dokl. Akad. Nauk. SSSR* **1963**, *149*, 1354; *Chem. Abstr.* **1963**, *59*, 3460. Related reviews: Bozak, R. E. *Adv. Photochem.* **1971**, *8*, 227. Seebach, D. In *Houben-Weyl, Methoden der Organischen Chemie*; Müller, E., Ed.; Thieme: Stuttgart, 1971, Vol. IV/4. Kaupp, G. In *Houben-Weyl, Methoden der Organischen Chemie*; 1975; Vol. IV/5a, pp 278–412.

(5) For leading references concerning the synthetic procedures involved, see: Huang, Q.; Qian, Y. *Synthesis* **1987**, 710. Fiaud, J. C.; Malleron, J. L. *Tetrahedron Lett.* **1980**, *21*, 4437. Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849. Erker, G.; Aul, R. *Chem. Ber.* **1991**, *124*, 1301 and references cited therein.

(6) UV/vis absorptions in $CH_2Cl_2$: *meso*-**4**, $\lambda_{max}$ = 242 nm ($\epsilon$ = 20 400), 265 (sh, $\epsilon$ = 14 600), 340–375 (br, $\epsilon \approx$ 3000); *rac*-**4**, $\lambda_{max}$ = 239 nm ($\epsilon$ = 22 200), 265 (sh, $\epsilon$ = 17 200), 340–370 (br, $\epsilon \approx$ 4000); *meso*-**5**, $\lambda_{max}$ = 240 nm ($\epsilon$ = 49 000); *rac*-**5**: $\lambda_{max}$ = 234 nm ($\epsilon$ = 56 000).

0002-7863/92/1514-10983$03.00/0