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ZIRCONOCENE-PROMOTED STEREOSELECTIVE BICYCLIZATION OF 1,6- AND 1,7-DIENES TO PRODUCE *TRANS*-ZIRCONABICYCLO[3.3.0]OCTANES AND *CIS*-ZIRCONABICYCLO[4.3.0]NONANES.

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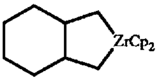
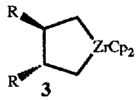
SUMMARY: The Zr-promoted bicyclization of 1,6- and 1,7-dienes can stereoselectively produce *trans*-zirconabicyclo[3.3.0]octanes and *cis*-zirconabicyclo[4.3.0]nonanes, respectively; these compounds can be readily converted into protonolysis, halogenolysis, and carbonylation products.

We have recently reported the Zr-promoted bicyclization reactions of enynes and diynes.[2,3] Our interest in the corresponding reaction of dienes was aroused by two seemingly conflicting reports on the reaction of 1,7-octadiene (**1a**) with zirconocene derivatives.[4,5] In one the formation of a 1:1 mixture of the cis and trans isomers of **2a** was reported,[4] while the other reported that the cis isomer was obtained to the extend of 90%.[5] These results became more puzzling in the light of the Zr-promoted coupling of 1-alkenes which gave stereoselectively *trans*-3,4-dialkylzirconacyclopentanes (**3**).[6]



2a



3 (R=alkyl)

We now report that the zirconocene-promoted bicyclization reaction of 1,7- and 1,6-dienes (**1** and **4**) can stereoselectively produce the corresponding zirconabicyclo[4.3.0]nonanes (**2**) and zirconabicyclo[3.3.0]octanes (**5**), respectively. Significant, although still puzzling, is the fact that the preferred stereochemistry in **2** is cis, while that in **5** is trans.

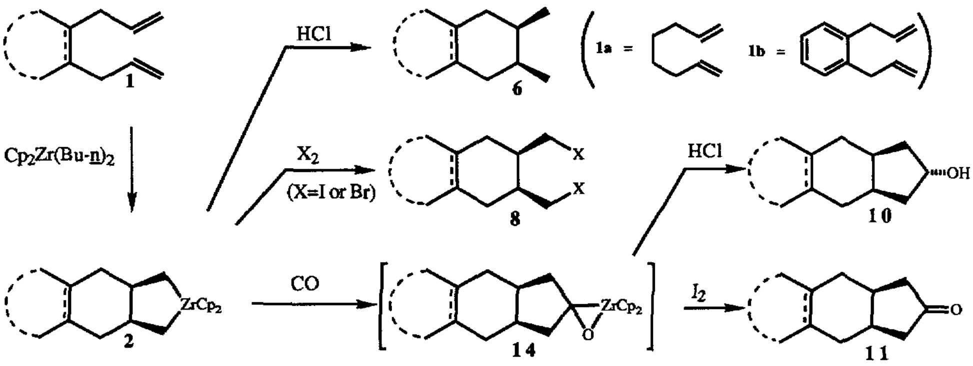
Protonolysis of **2** and **5** gives **6** and **7**, respectively, while their halogenolysis gives **8** and **9**, respectively. Their carbonylation cleanly provides either cycloalkanols or cycloalkanones **10** or **11** and **12** or **13**, respectively, depending on the method of quenching.[6] (Schemes 1 and 2 ; only the dominant stereochemistry is shown).

To probe the scope of the Zr-promoted bicyclization of nonconjugated dienes we initially chose 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene and treated them with 1 equiv of $Cp_2Zr(Bu\text{-}n)_2$ generated in situ by the reaction of Cp_2ZrCl_2 with 2 equiv of *n*-BuLi [2b] at -78 to 0°C. Whereas the reactions of 1,5-hexadiene and 1,8-nonadiene failed to give monomeric cyclic products in significant yields, those of 1,7-octadiene and 1,6-heptadiene proceeded in high yields to give **2a** and **5a**, respectively. The ^1H NMR spectrum of **2a** indicated it to be a ca. 5:1 mixture of the cis and trans isomers obtained in nearly quantitative yield. The cis isomer showed the Cp signals at δ 6.36 and 6.38 ppm, while the trans isomer showed a singlet at δ 6.35 ppm. Protonolysis (3N HCl, 0°C) of **2a** gave a 5:1 mixture of the *cis*- and *trans*-**6a** in 67% yield , while its treatment with I_2 (3 equiv, 0-25°C) provided a 4:1 mixture of *cis*- and *trans*-**8a** in 52% yield. Carbonylation of **2a** (CO, 1.1 atm, -78°C) provided a product tentatively identified as **14a** (δ 5.78 ppm). Its protonolysis (3N HCl) cleanly provided a ca. 6:1 mixture of *cis*- and *trans*-**10a** in 65% yield, the former of which was a 20:1 mixture of the exo and endo isomers. On the other hand, iodinolysis of **14a** gave a 7:1 stereoisomeric mixture of **11a** in 43% yield. These results indicate that the cyclization reaction is >80% stereoselective in favor of the cis fusion.

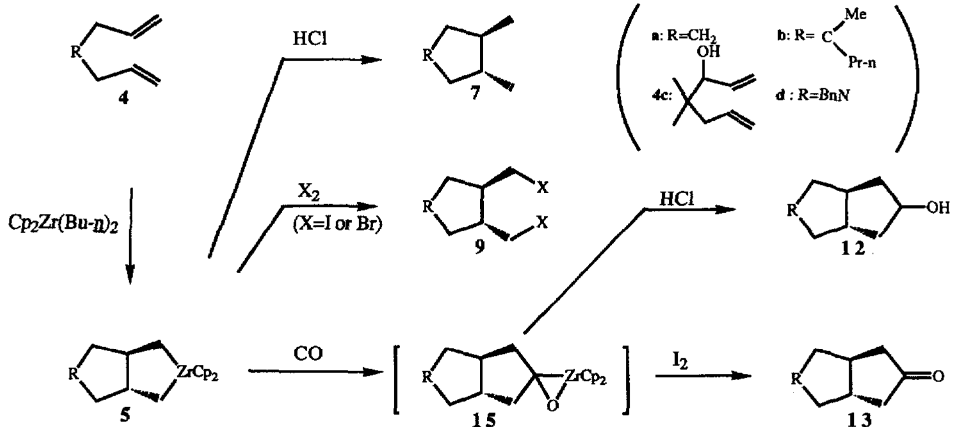
The corresponding reaction with $Cp_2Zr(Bu\text{-}n)_2$ of **4a** also proceeded in >90% yield by ^1H NMR. The Cp signal appeared as a singlet at δ 6.22 ppm, strongly suggesting the trans stereochemistry of **5a**. A few minor signals were also seen in the region. Treatment of **5a** with CO (1.1 atm) at -78°C cleanly shifted the Cp signal to δ 5.78 ppm, indicating nearly quantitative conversion into a carbonylation product tentatively identified as **15a**. Its protonolysis gave a 9:1 mixture of *trans*- and *cis*-**12a** in 83% yield, while iodinolysis (I_2, 3 equiv, 0°C) provided a 14:1 mixture of *trans*- and *cis*-**13a** in 53% yield.[7] The results clearly indicate that **5a** is largely trans.

Similar results were obtained with **1b** and **4b**-**4d**, as indicated by the data summarized in **Table I**. Although further confirmation is desirable, it appears that formation of **2** favors trans fusion, while that of **5** favors cis fusion. At present, we cannot offer a simple qualitative explanation for the contrasting behavior. In the reaction of **4c**, the use of 2 equiv of $Cp_2Zr(Bu\text{-}n)_2$ was necessary to obtain a 3:1 mixture of (1α,4α,5β)- and (1β,4α,5β)-2,2,4,5-tetramethylcyclopentanols in 67% combined yield[7] . In a similar way, the trimethylsilyloxy derivative cyclized under the influence of 1 equiv of $Cp_2Zr(Bu\text{-}n)_2$ to produce a 4:1 mixture of the two isomers in 65% yield.The reaction of **4d** initially gave an essentially 1:1 mixture of **5d**. Over 18 h at 25°C, however, the ratio increased to 4:1 and stayed at this level thereafter. In sharp contrast, the reaction of diallyl ether (**16**) with $Cp_2Zr(Bu\text{-}n)_2$ led only to the generation of a mixture of **17**-**19**, in which **17** initially dominated. Iodinolysis followed by the usual workup of the mixture gave allyl iodide and allyl alcohol. The preperation of **17** was independently achieved by treating **18** with allylmagnesium bromide, and the identity of **17**-**19** was further established by comparison of ^1H and ^{13}C NMR spectra of the reaction mixture with those of their independently prepared samples. We suggest that **17** may arise as shown in eq 1 and that it disproportionates to give **18** and **19**. Our brief investigation suggests that a similar decomposition occurs with diallyl sulfide as well.

Scheme 1



Scheme 2



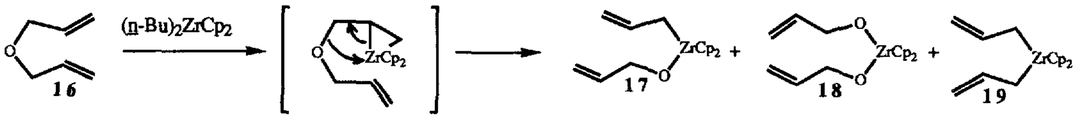
 (1)

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Table I. Zirconocene-Promoted Bicyclization of Nonconjugated Dienes.^{a}

	Zirconabicycle		Carbonylation Product				Protonolysis		Iodinolysis	
Diene	Product	Yield^{b} (%)	Protonolysis	Yield^{c} (%)	Iodinolysis	Yield^{c} (%)	Product	Yield^{c} (%)	Product	Yield^{c} (%)
1a	**2a**(1/5)	>90	**10a**(1/6)	65	**11a**(1/7)	43	**6a**(1/5)	67	**8a**(1/4)	52
1b	**2b**(1/20)	>90	*d*		**11b**(1/20)	70	**6b**(1/20)	69	**8b**(1/20)	71
4a	**5a**(>10)	>90	**12a**(9)	83	**13a**(14)	53	*d*		**9a**	63
4b	**5b**	>90	*d*		**13b**(9)	92	**7b**(5)	41	**9b**(9)	81
4c	**5c** *e*		*d*		*d*		**7c**(3)	67	*d*	
4d	**5d**(4^{f})	>90	*d*		**13d**(20^{f})	50	**7d**(4^{f})	62	*d*	

^{a}The numbers in parentheses indicate the trans/cis ratios. ^{b}By ^{1}H NMR using benzene as an internal standard. ^{c} Isolated yields. ^{d}Not performed. ^{e}Not determined. ^{f}This ratio was attained after equilibration for 18h at 25°C.

REFERENCES AND NOTES

(1) Metal-Promoted Cyclization. 31. Part 30. Negishi, E.; Zhang, Y.; Shimoyama, I.; Wu, G. Submitted for publication.

(2) (a) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**,*107*, 2568. (b) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829. (c) Negishi, E.; Zhang, Y.; Cederbaum, F. E.; Webb, M.B. *J. Org. Chem.* **1986**, *51*, 4080. (d) Negishi, E.; Swanson, D. R.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1987**, *28*, 917. (e) Takahashi, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1987**, 623. (f) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336.

(3) For related works by other workers, see (a) Nugent, W. A.; Thorn, D. L.;Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788. (b) RajanBabu, T. V.; Nugent, W. A.; Taber, D. F.; Fagen, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 7128.

(4) Gell, I.; Schwartz, J. *J. Chem. Soc. Chem. Comm.*.**1979**, *244; J. Am. Chem. Soc.* **1981**,*103*, 2687.

(5) Yasuda, H.; Nagasuna, K.; Akita, M.; Lee, K.; Nakamura, A. *Organometallics* **1984**, *3*, *1470*.

(6) Swanson, D. R.; Rousset,C. J.; Negishi, E.; Takahashi, T.; Seki, T.; Saburi, M.; Uchida, Y. *J. Org. Chem.* **1989**, *54*, 3521.

(7) **Fleming, I.; Rowley, M.** *Tetrahedron* **1986**, *42*, 3181.

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