

THE TRANSITION METAL COMPLEX PROMOTED
ISOMERIZATION OF *trans*-BICYCLO[4.1.0]HEPT-3-ENE
TO *cis*-BICYCLO[4.1.0]HEPT-3-ENE

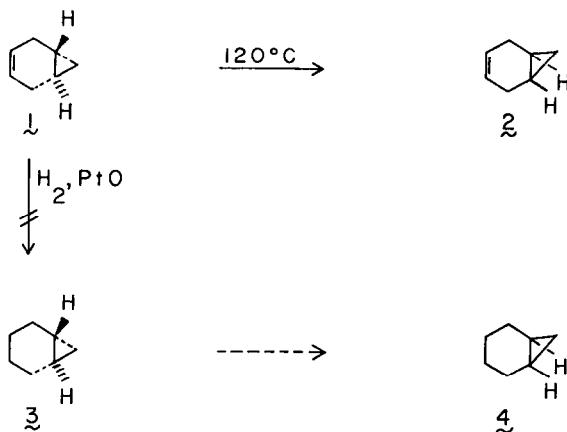
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Summary: An unprecedented isomerization of a *trans*-1,2-disubstituted cyclopropane to a *cis*-1,2-disubstituted cyclopropane has been achieved with both rhodium(I) and platinum(II) catalysts.

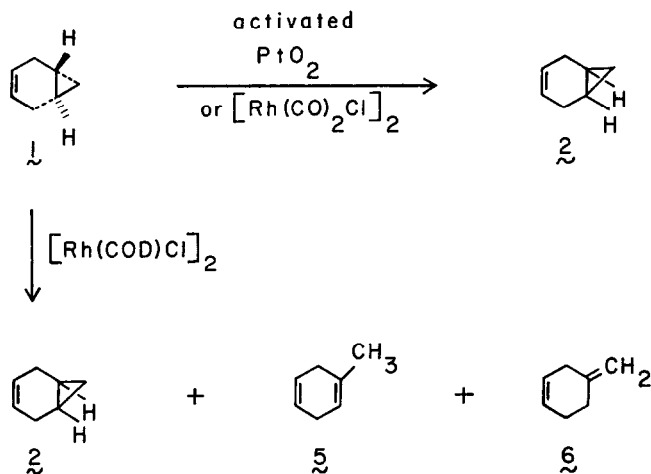
Although the interconversion of *cis* and *trans* olefins by transition metal catalysts is well established in the literature,¹ and although there are numerous examples of the isomerization of highly strained polycyclic cyclopropane derivatives to olefins in the presence of transition metal complexes,² we are unaware of any related *cis*-*trans* isomerization of cyclopropanes in the presence of transition metal complexes.³ We now report a unique example of such isomerization.

Recently, we reported the synthesis of *trans*-bicyclo[4.1.0]hept-3-ene (1) and its facile thermal isomerization to *cis*-bicyclo[4.1.0]hept-3-ene (2).⁴ We



were interested in studying the possible related thermal isomerization of *trans*-bicyclo[4.1.0]heptane (**3**) to *cis*-bicyclo[4.1.0]heptane (**4**) and, as a result, were concerned about the possible catalytic reduction of **4** to **3**. Being cognizant of the sensitivity of highly strained polycyclic hydrocarbons to activated catalytic species,² we first examined whether **4** would be stable to the conditions normally used for the catalytic reduction of carbon-carbon double bonds. We found that **4** was rapidly isomerized to **2** by activated (pre-reduced) platinum oxide catalyst.

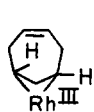
When 5 mg of platinum oxide in 1.5 mL of ethanol was activated with hydrogen and 100 mg of **4** was added followed by immediate workup, 95 mg of **2** was recovered.⁵ Similarly, when **4** was exposed to catalytic amounts (10 mol %) of di- μ -chlorotetracarbonyldirrhodium, a 65% yield of **2** was obtained in what appeared to be an instantaneous reaction at room temperature.⁶



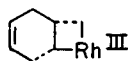
In contrast, treatment of **4** with 2.4 mol % of di- μ -chloro(di-1,5-cyclo-octadiene)dirrhodium at room temperature gave 51% of **2**, 43% of **5**, and trace amounts of **6**. The structure of **5** was established by comparison with an authentic sample prepared according to the method of Benkeser,⁹ which involved a Birch reduction of toluene. An authentic sample of **6**¹⁰ was prepared by the reaction of 4-hydroxymethylcyclohexene with σ -nitrophenyl selenocyanate¹¹ and tri-*n*-butylphosphine in tetrahydrofuran, followed by treatment of the resultant 4-[(2-nitrophenyl)selenomethyl]cyclohexene¹² with sodium periodate.¹³ The products obtained from **4** were identical in all respects to the independently synthesized samples. The formation of both **5** and **6** have precedent in the iridium(I) and rhodium(I) promoted rearrangements of *cis*-bicyclo[4.1.0]heptane (**4**) to 1-methylcyclohexene⁸ and methylenecyclohexane,² respectively, at ele-

vated temperatures. It was demonstrated that ζ and η were derived directly from ξ and not from a secondary reaction of ζ , since ζ was stable to the reaction conditions.

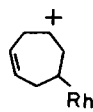
The details of the mechanism, whereby ξ was converted into ζ in a transition metal complex promoted rearrangement, are not established at this time. However, it seems unlikely that a one-step "oxidative addition" process such as has been postulated for other systems,¹⁴ would be involved in this case. Such an oxidative addition process would require the formation of a metallocyclobutane such as ζ or η . Since "reductive elimination" should, in most instances, be the microscopic reverse of oxidative addition, the reversal of the addition process should produce starting material.¹⁵ This suggests that ζ or η , or the corresponding radical species, may be involved as intermediates¹⁶ in the rhodium(I) promoted isomerization.



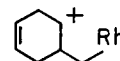
ζ



η



ζ



η

We are continuing to study the details of this facile rearrangement.

Acknowledgement. We are indebted to the National Science Foundation for Grant CHE81-14772 which supported this investigation.

References and Footnotes

1. For selected examples see: G.C. Bond and M. Hellier, *J. Catal.*, **4**, 1 (1965); J.C. Bailar and H. Itatani, *J. Am. Chem. Soc.*, **89**, 1592 (1967); R. Cramer, *J. Am. Chem. Soc.*, **88**, 2272 (1966); K. Tanaka, K. Tanaka, and K. Miyahara, *J.C.S. Chem. Comm.*, 666 (1980); J.L. Bilkou, J.M. Basset, R. Mutin, and W.F. Graydon, *J.C.S. Chem. Comm.*, 970 (1976).
2. For leading references see: K.C. Bishop, III, *Chem. Rev.*, **76**, 461 (1976); P.G. Gassman and F.J. Williams, *J. Am. Chem. Soc.*, **94**, 7733 (1972); P.G. Gassman, G.R. Meyer, and F.J. Williams, *ibid.*, **94**, 7741 (1972); P.G. Gassman and T.J. Atkins, *ibid.*, **94**, 7748 (1972); L.A. Paquette and G. Zon, *ibid.*, **96**, 224 (1974) and references contained therein.
3. A recent report of Lewis acid-catalyzed cis-trans interconversions of specifically substituted cyclopropanes has appeared. H.-U. Reissig and I. Böhm, *Tetrahedron Lett.*, **24**, 715 (1983). For a two step process for the inversion of cyclopropane stereochemistry which involved the reaction of a cyclopropane with an equivalent amount of bisbenzotrile palladium dichloride see M.F. Rettig, D.E. Wilcox, and R.S. Fleischer, *J. Organometal. Chem.*, **214**, 261 (1981).
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5. The reaction mixture and product were maintained below 25°C throughout this procedure.
6. In addition to **2**, a yellow-orange powder was obtained: mp 147-149°C (dec.); IR (CDCl₃) 3030, 2910, 2840, 2045, 1745, 1730, 1645, 1605, 1435, 1380, 1195, 1155, 1135, 1110, 1070, 995, 955, 815, and 780 cm⁻¹. This spectral data can be compared to the starting rhodium complex which showed sharp bands at 2100, 2090, and 2030 cm⁻¹. Because of the analogy of the carbonyl bonds to those exhibited by the adduct formed from di- μ -chlorotetracarbonyldirrhodium and quadricyclane (2070, 2010 and 1735 cm⁻¹),⁷ it seemed possible that the insoluble material may be an adduct formed from **1** and the rhodium complex. In addition, McQuillin and Powell⁸ have demonstrated that *cis*-bicyclo[4.1.0]heptane (**4**) reacts with di- μ -chlorotetracarbonyldirrhodium to produce a dimeric 1:1 adduct which has carbonyl absorptions at 2050, 1755 and 1735 cm⁻¹.
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11. K.B. Sharpless and M.W. Young, *J. Org. Chem.*, **40**, 947 (1975).
12. Satisfactory elemental analyses and/or exact mass molecular weights have been obtained on all new compounds. In all cases the spectral data were consistent with the structures indicated.
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15. This assumes that oxidative addition and reductive elimination, to and from strained carbon-carbon sigma bonds, respectively, are concerted processes. If a stepwise process involving discrete intermediates, such as **9** or **10**, is involved, transient metallocyclobutane type intermediates could be generated.
16. This refers to the initially generated species only. Cyclization of such intermediate carbocations (or radicals) must be considered as a possibility.

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