# HIGHLY EFFICIENT OLEFIN ISOMERIZATION CATALYZED BY METAL HYDRIDES DERIVES FROM DIRHODIUM(II) CARBOXYLATES AND CATECHOLBORANE

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**Abstract**. Dirhodium(II) tetraacetate in combination with catecholborane catalyzes the isomerization of alkenes and dienes. Effective isomerization occurs at 80-135°C with the use of only 0.1 mol % rhodium acetate. With 2-methyl-1,5-hexadiene the disubstituted double bond is preferentially isomerized. In addition, hydrogen transfer hydrogenation occurs with 1,4-cyclohexadienes. The mechanism of these reactions is proposed to involve organoborane addition across a Rh-O bond which activates the catalyst for isomerization and hydrogenation.

## INTRODUCTION

Catalytic isomerization of alkenes is a characteristic transformation of transition metal hydrides that often accompanies hydrogenation[1] and is one of the most thoroughly studied catalytic reactions.[2-4] Compounds of cobalt, nickel, palladium, platinum, rhodium, and ruthenium are effective,[2] but other transition metal compounds have also been employed for catalytic isomerizations.[2-4] Although the nature of this transformation is dependent on the catalyst, selectivity for alkene isomerization generally favors reactions with monosubstituted ethylenes over di- and tri-substituted ethylenes. In the course of our investigations of the catalytic effectiveness of dirhodium(II) tetrakis(carboxylates) we have uncovered a useful methodology for the generation of rhodium hydride species that, as we now report, are surprisingly effective for the isomerization of alkenes as well as for hydrogen transfer hydrogenation.

## MATERIALS AND METHODS

Reactions were performed in a round bottom flask equipped with a screw cap that was fitted with a septum for convenient withdrawal of aliquots. The alkene or diene (5-10 mmol) and $Rh_2(OAc)_4$ (0.10 mol %) were added to the flask, and the flask was flushed with dry nitrogen. Freshly distilled catecholborane (3-4 mol %) was added by syringe, and the resulting solution was heated to the appropriate temperature until reaction was complete. After cooling at room temperature, distillation of the products afforded 75-95% isolated yields. Products were characterized by ^{1}H NMR (300 MHz) and mass spectral methods, and they were analyzed by GC generally in comparison with authentic samples.
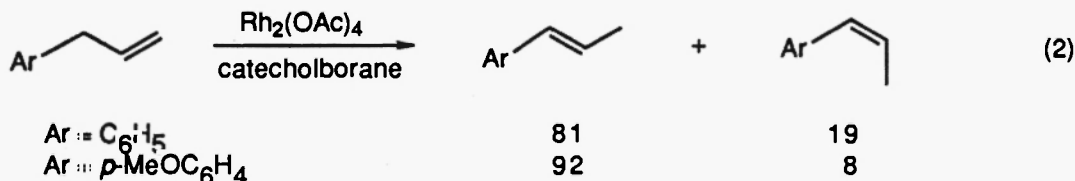
## RESULTS

Treatment of 2-methyl-1,5-hexadiene with rhodium(II) acetate (0.1 mol %) to which was added catecholborane (3.7 mol %) produced, after heating the mixture at reflux (92°C) for 11 d,
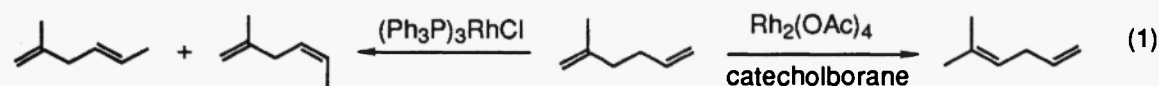


5-methyl-1,4-hexadiene as the sole product following distillation (eq 1). In contrast, use of Wilkinson's catalyst, $(Ph_3P)_3RhCl$ (0.1 mol %) under the same conditions produced the isomeric trans- and cis-2-methyl-1,4-hexadienes (57% conversion) without evidence for formation of 5-methyl-1,4-hexadiene. The isomerization of 2-methyl-1,4-pentadiene with diene-coordinated

cyclopentadienylrhodium(I) has been previously reported to yield 2-methyl-1,3-pentadiene as the dominant primary product,[6] where the driving force is conjugated diene formation. The contrasting behavior of two rhodium catalysts on a 1,5-diene (eq 1) is unique.

The isomerization of alkenes by the combination of $Rh_2(OAc)_4$/catecholborane extends to simple olefins. For example, treatment at 80°C of neat allylbenzene with catalytic amounts of $Rh_2(OAc)_4$ (1.0 mol %) and catecholborane (3.0 mol %) resulted in its complete isomerization to (Z)- and (E)-1-phenyl-1-propene (eq 2, Z:E = 19:81 at 22h); under the same conditions neither

$$Ar \diagup\!\!\!\diagdown\!\!\!\diagup \xrightarrow[\text{catecholborane}]{Rh_2(OAc)_4} Ar\diagup\!\!\!\diagdown\!\!\!\diagup \quad + \quad Ar\diagdown\!\!\!\diagup \qquad (2)$$

Ar = $C_6H_5$         81          19
Ar = p-$MeOC_6H_4$    92          8

$Rh_2(OAc)_4$ nor catecholborane alone caused this isomerization. 4-Allylanisole gave similar results at 135°C with the use of only 0.1 mol % catalyst, but with a lower Z:E product ratio; under these conditions $Rh_2(OAc)_4$ alone catalyzes isomerization, but conversions occurred at much slower rates. The product from catalytic hydrogenation was not observed. For comparison, p-allylanisole is isomerized at 140°C to the arene conjugated olefin anethole with a catalytic amount of $Fe(CO)_5$,[7] but the E/Z ratio is 87:13 rather than the 92:8 observed with the $Rh_2(OAc)_4$-catecholborane combination. The reaction temperatures used for isomerization of these alkenes (80-135°C) are within the temperature ranges employed by others for similar substrates.[6-10]

The isomerization of 1-octene was followed as a function of time, and the results of this investigation are shown in Figure 1. Even with only 0.1 mol % $Rh_2(OAc)_4$, isomerization of 1-



**Figure 1.** Isomerization of 1-octene at 125°C catalyzed by $Rh_2(OAc)_4$ (0.10 mol %) in combination with catecholborane (4.0 mol %).
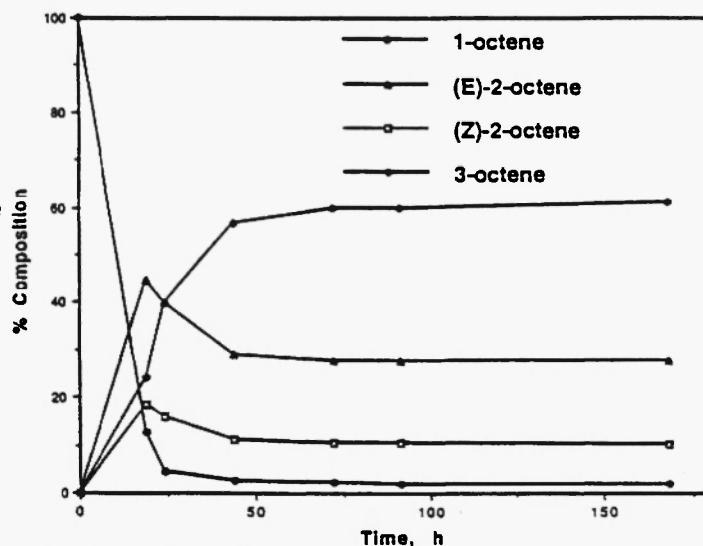
octene is virtually complete at 25 h. The first formed products are (E)- and (Z)-2-octene which undergo further isomerization to 3-octene, but they reach equilibrium at 50 h after which time no further change in the product ratio is observed. The product from replacement of hydride on catecholborane by acetate is formed, albeit in no more than 80% yield based on reactant $Rh_2(OAc)_4$. Under the same conditions, with $Rh_2(OAc)_4$ as the catalyst (0.1 mol %), isomerization of 1-octene is only 90% complete at 275 h. With $(Ph_3P)_3RhCl$ as the isomerization catalyst (0.1 mol %), the rate for isomerization of 1-octene is somewhat faster than that with $Rh_2(OAc)_4$/catecholborane, but although the Z/E product ratio for 2-octene is the same (E:Z = 2.5-2.7), the equilibrium ratio of 3-octene:2-octene is 0.85 (at 370 h) compared to 1.6 with $Rh_2(OAc)_4$/catecholborane.

Treatment of 4-vinyl-1-cyclohexene with $Rh_2(OAc)_4$ (0.1 mol %) and catecholborane (4.7 mol %) produced, instead of the expected isomerization products, a 66:34 mixture of ethylbenzene and ethylcyclohexane (eq 3) and no other detectable products (86% yield following distillation).

(3)
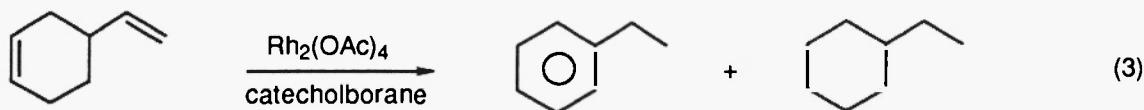
Under the same reaction conditions, $Rh_2(OAc)_4$ and $(Ph_3P)_3RhCl$ also gave these same products but as relatively minor components of a complex reaction mixture (at least five products). In the $(Ph_3P)_3RhCl$ catalyzed reaction, the ratio of ethylbenzene to ethylcyclohexane was also 2:1, but with $Rh_2(OAc)_4$ this ratio was the reverse. Bicyclo[4.3.0]nona-3,6(1)-diene underwent a similar disproportionation when treated with $Rh_2(OAc)_4$ (0.1 mol %) and catecholborane (3.7 mol %) at

(4)
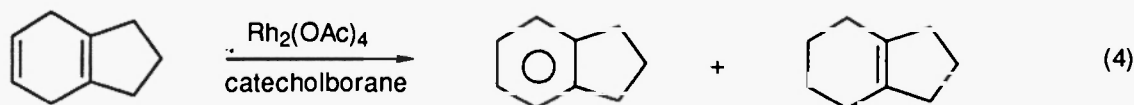
135°C (eq 4), and both indane and bicyclo[4.3.0]non-6(1)-ene were the sole reaction products observed following distillation (63:37). The tetrasubstituted double bond did not undergo reduction or isomerization. The same disproportionation reaction occurred when catalyzed by $(Ph_3P)_3RhCl$. When styrene was added to the reaction mixture from the $Rh_2(OAc)_4$-catalyzed process in the same molar amount as bicyclo[4.3.0]nona-3,6(1)-diene, conversion of styrene to ethylbenzene occurred to the virtual exclusion of bicyclo[4.3.0]non-6(1)-ene. Attempts to isomerize 5-vinyl-2-norbornene to a single product were unsuccessful; multiple products were obtained of which 5-ethylidene-2-norbornene was not the major component.
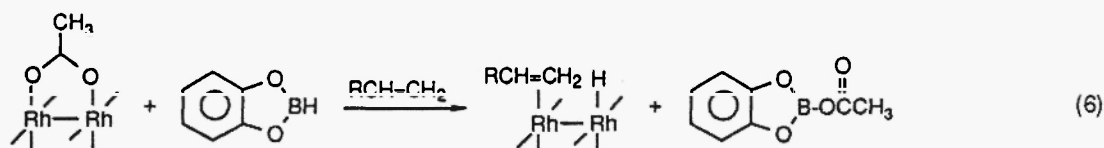
## DISCUSSION

We have previously reported that rhodium(II) perfluorobutyrate in combination with triethylsilane catalyzed the isomerization of 1-decene to 2- and 3-decene and of allylbenzene to 1-phenyl-1-propene.[11] These reactions occurred at room temperature, were performed with 1.0 mol % of catalyst, and they required 15 mol % of triethylsilane. Isomerization was explained by the intervention of a rhodium hydride species which was generated through hydrolysis of the rhodium coordinated triethylsilane[12] by water present in the reaction medium. Rhodium(II) acetate was relatively ineffective because of its inability to coordinate triethylsilane.

In the present investigation we have employed catecholborane as the hydride donor and have been able to effectively isomerize alkenes with the use of only 0.1 mol % $Rh_2(OAc)_4$. Catecholborane undergoes $Rh_2(OAc)_4$-catalyzed hydroboration of alkenes in refluxing dichloromethane in high yield and with a high degree of selectivity for placement of the boron functional group at the terminal position of monosubstituted ethylenes (e.g., eq 5).[13] However, the process is

(5)
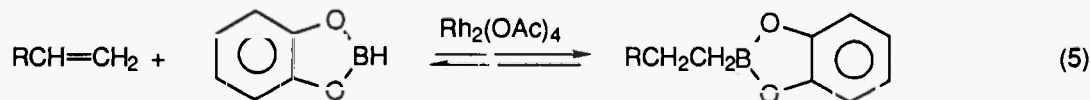
reversible at higher temperatures[14] and thereby provides a convenient source of hydride by slow release of catecholborane. Activation of $Rh_2(OAc)_4$ for catalytic isomerization is proposed to occur either via hydride transfer in the manner reported for organosilane induced isomerization or by addition of the organoborane across the Rh-O bond which releases hydride onto rhodium and opens a coordination site on the adjacent rhodium for olefin coordination (eq 6). Since $Rh_2(OAc)_4$

*Vol. 17, No. 6, 1994*

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$$\tag{6}$$

is not recovered after isomerization has taken place and the acetylborate derived from catecholborane is observed, the pathway for dirhodium activation described by eq 6 is more likely. Subsequent steps involving addition-elimination (for isomerization) or hydrogen elimination (to a $\pi$-allyl complex) and transfer (hydrogenation) are expected to proceed by previously reported pathways.[2-4]

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