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Efficient Hydride-Assisted Isomerization of Alkenes via Rhodium Catalysis

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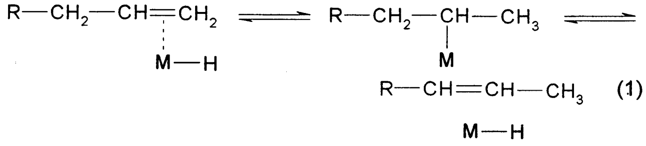
We find that alkenes isomerize rapidly in the presence of catalytic amounts of a hydroborating reagent and a rhodium compound. The hydroborating reagent is apparently responsible for the in situ generation of a metal hydride species, which has been implicated to account for the stepwise migration of the double bond. Labeling studies reveal a high degree of reversibility in the catalytic cycle. A mechanism involving reversible alkene metal hydride insertion followed by β-hydride elimination is consistent with our data. Generally, the final product favors the thermodynamic equilibrium mixture of isomeric alkenes. The methodology provides for an efficient and economical route to alkene isomerization.

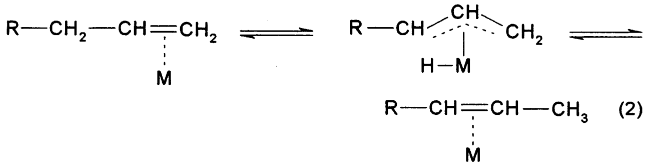
Introduction

It is known that transition-metal compounds are very effective isomerization catalysts.[1] Most of these isomerizations are accomplished by metal hydrides or by compounds that can be converted into a metal hydride (M−H) by a proton source.[2] Two general mechanisms have been proposed depending on the type of catalyst employed. These are addition/elimination reactions of metal hydride complexes,[3] M−H being present initially as catalyst or generated in situ (eq 1), versus a rearrangement through a transitory π-allyl complex, which proceeds by the coordination of the metal with the alkene, followed by a reversible hydrogen transfer to generate the π-allyl M−H intermediate (eq 2).

While most isomerizations appear to proceed via the addition/elimination mechanism,[4] iron carbonyl[5] and some palladium catalyzed isomerizations are believed to proceed via the π-allyl complex.[6] Mechanistic studies have revealed that the addition/elimination reaction follows a pathway that requires an open coordination site and a transition state involving a syn-coplanar arrangement of the α- and β-carbons, the β-hydrogen, and the metal center.[7]



$$R{-}CH_2{-}\underset{\underset{M-H}{\vdots}}{CH{=}CH_2} \rightleftharpoons R{-}CH_2{-}\underset{\underset{M}{|}}{CH}{-}CH_3 \rightleftharpoons \underset{M-H}{R{-}CH{=}CH{-}CH_3} \quad (1)$$



$$R{-}CH_2{-}\underset{\underset{M}{\vdots}}{CH{=}CH_2} \rightleftharpoons \underset{H-M}{R{-}CH\overset{CH}{\cdots\cdots}CH_2} \rightleftharpoons R{-}CH{=}\underset{\underset{M}{\vdots}}{CH}{-}CH_3 \quad (2)$$

Results and Discussion

During the course of our study on transition-metal-promoted hydroboration of alkenes, we noticed a reversal of the usual regioselectivity associated with oxidative hydroboration. Rather than the usual anti-Markovnikov hydration, 1-octene with $BH_3{\cdot}THF$ at room temperature in the presence of 1.5 mol % $RhCl_3{\cdot}nH_2O$ yielded 4-octanol (40.8%), 3-octanol (34.8%), 2-octanol (16.4%), and 1-octanol (2.2%) along with octane (5.0%) and octanones (0.8%). Under identical reaction conditions, the other isomeric octenes gave similar product distributions.[8]

To obtain a clear picture of the isomerization process, the hydroboration/oxidation was carried out using less than stoichiometric amounts of the hydroborating reagent, a procedure we refer to as "starved" hydroboration.[9] Analysis of the product mixture revealed the presence of 1-octene (0.6%) and isomeric internal octenes (87.0%), along with octane (6.6%) and octanols (5.8%). Under similar conditions allylbenzene[11] was isomerized into *cis*- and *trans*-1-phenyl-1-propene (10:90).

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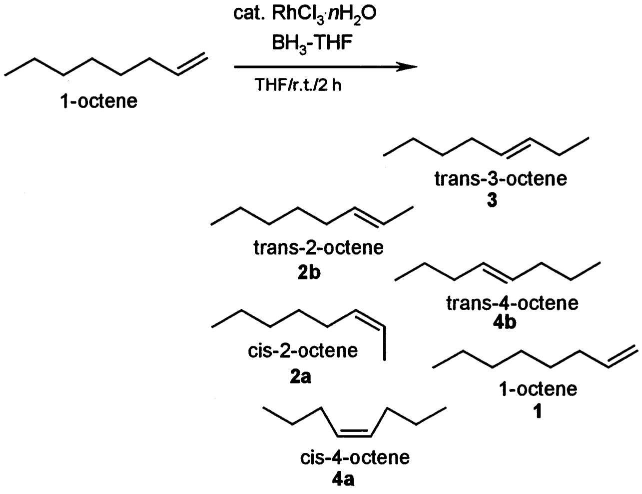
Table 1. Isomerization of Isomeric Octenes Using $RhCl_3$·nH_2O/BH_3·THF in THF[a]



entry	alkene	octene (%)[b]					
		1	2a	2b	3	4a	4b
1	1-octene	0.6	8.9	30.4	33.4	3.7	23.0
2	*cis*-2-octene	0.7	10.8	38.3	30.7	4.2	15.3
3	*trans*-2-octene	0.8	10.1	30.8	32.5	3.9	21.9
4	*trans*-3-octene	0.4	7.0	23.3	44.0	5.5	19.8
5	*trans*-4-octene	0.5	8.8	31.3	33.3	4.6	21.5

[a] Isomerization was carried out at room temperature for 2 h by the very slow addition of BH_3·THF (0.3 mL, 0.3 mmol) into a mixture of the isomeric octene (0.5 mL, 3.19 mmol) and $RhCl_3$·nH_2O (10 mg, 0.048 mmol) in THF, followed by oxidation with alkaline peroxide. [b] Product distributions were determined by GC. Products include octenes, octanols, and octane.

Typically, equilibration of alkenes favors structures with the double bond farther from the end of the carbon chain. Part of the driving force here is to produce the[11] highest possible substitution of the double bond.[10] However, we notice that, during the isomerization of 1-octene, *trans*-4-octene was not the major product. Further, when *trans*-4-octene was subjected to similar experimental conditions, the product ratio resembled that obtained with 1-octene. We had thus found that no matter which isomeric alkene one started with, the final product composition was virtually a thermodynamic equilibrium mixture of isomeric alkenes (Table 1). Examples of other catalytic systems are summarized in Table 2.

Table 3 compares the experimental values for isomer distribution of heptenes with the thermodynamic equilibrium values calculated by standard methods from the enthalpies of formation[12] at 25 °C. Clearly, the experimental data parallel the trend of the theoretical values.

Table 2. Effect of the Catalytic System on the Isomerization of 1-Octene

entry	catalytic system	octene (%)[c]					
		1	2a	2b	3	4a	4b
1	$RhCl_3$ + BH_3·THF[a]	0.6	8.9	30.4	33.4	3.7	23.0
2	$RhBr_3$ + BH_3·THF[a]	0.9	10.3	35.4	31.2	4.7	17.5
3	$RhCl(PPh_3)_3$ + BH_3·THF[a]	3.5	26.8	49.2	12.7	4.0	3.8
4	$RhCl_3$ + CB·THF[b]	0.8	11.4	36.6	30.4	4.1	16.7

[a] Isomerization was carried out at room temperature for 2 h by the very slow addition of BH_3·THF (0.3 mmol) into a mixture of the 1-octene (3.19 mmol) and the catalyst (10 mg) in THF, followed by oxidation with alkaline peroxide. [b] A 1 mL portion (1 mmol) of catecholborane−THF was used. [c] Product distributions were determined by GC. Products include octenes, octanols, and octane.

Table 3. Calculated Product Distribution Based on Enthalpies of Formation of Liquid Heptenes

isomeric heptene	ΔH_f[a]	calcd (%)	exptl (%)[b]
1-heptene	−23.35	0.427	0.728
cis-2-heptene	−25.31	11.743	12.724
trans-2-heptene	−26.15	48.525	43.254
cis-3-heptene	−25.00	6.939	7.262
trans-3-heptene	−25.91	32.366	36.032

[a] ΔH_f = enthalpy of formation of isomeric heptenes in kcal/mol.[12] [b] Product distribution after 24 h of the isomerization reaction.

Labeling Studies. Gratified by this success, we soon embarked upon an in-depth study of the reaction mechanism. Isomerization of 1-octene with BD_3·THF instead of BH_3·THF revealed a high level of deuterium incorporation into the products (octenes, octane, and octanols).[13] Deuterium labeling was also observed when the isomerization of 1-octene was carried out in the presence of small amounts of D_2O. These results suggest that (a) the metal hydride addition/elimination mechanism is the more prevalent pathway for these isomerizations and (b) the species causing the isomerization undergoes very rapid deuterium exchange with the deuterium source.

A high degree of reversed regioselectivity[14] has been observed during the $RhCl(PPh_3)_3$-catalyzed hydroboration of styrene using catecholborane (CBH). However, during the $RhCl_3$·nH_2O-promoted hydroboration of styrene using BH_3·THF,[8] we obtained anti-Markovnikov product ratios similar to those of the uncatalyzed hydroborations.[15] To verify if our in situ generated catalyst was indifferent toward substrates that did not possess an isomerizable double bond, we performed the "starved" hydroboration of styrene and cyclohexene in the presence of small amounts of D_2O. We were surprised when the mass spectrometry results revealed that some molecules of styrene had three deuterium atoms, while cyclohexene (Figure 1) had more than five deuterium atoms incorporated into the molecule. This result drives home the point that deuterium incorporation occurred whether alkene isomerization was the case.

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(9) *Representative experimental procedure*: A mixture of $RhCl_3$·nH_2O (10 mg, 0.048 mmol), 1-octene (0.5 mL, 3.19 mmol), and THF (10 mL) was stirred in a three-necked round-bottom flask at room temperature (24 °C) for 15 min, under an atmosphere of dry nitrogen. Using a syringe, BH_3·THF (0.3 mL, 0.3 mmol) was injected into the reaction flask at a very slow rate, over a period of 15 min. The reaction was allowed to continue for an additional 2 h, followed by alkaline peroxide oxidation, extraction, and purification.

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(15) We expected styrene to give us the high Markovnikov selectivity via the formation of a (η^3-benzyl)rhodium complex.

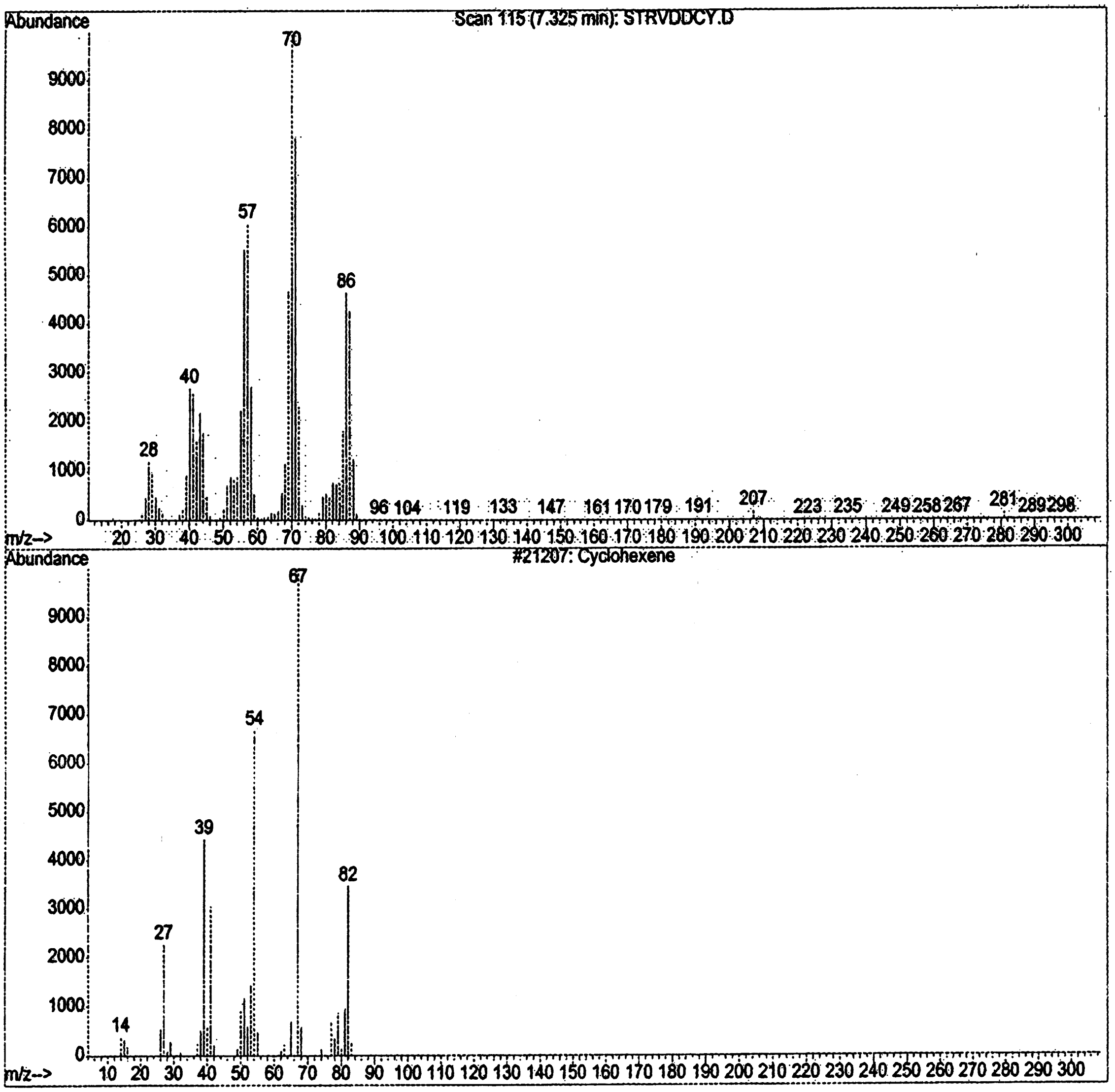

Figure 1. Isomerization/deuteration of cyclohexene with $RhCl_3/BH_3$ in D_2O.

Migration Pattern. To get a better idea of how the double bond migrates down the alkyl chain, the in situ catalyst was generated in the presence of 1-heptene[16] and aliquots of the reaction mixture were quenched using $NaOH/H_2O_2$. After 10 min the products were extracted using pentane and subjected to GC-MS analysis. Figure 2 clearly indicates that the migration of the double bond takes place in a stepwise manner. During the initial stages, 1-heptene is converted predominantly into *cis*-2-heptene, which undergoes rapid isomerization to *trans*-2-heptene. After 20 min, we notice that *cis*-2-heptene and *trans*-2-heptene are present in equal proportions. It is the *cis*- and *trans*-2-heptene that subsequently isomerize to *cis*- and *trans*-3-heptene. Although the initial products are kinetically controlled, both kinetic and thermodynamic control play a very important role in determining product distribution. A kinetic study would be very challenging, considering the many (estimated to be 16) intrinsic rate constants governing the process.

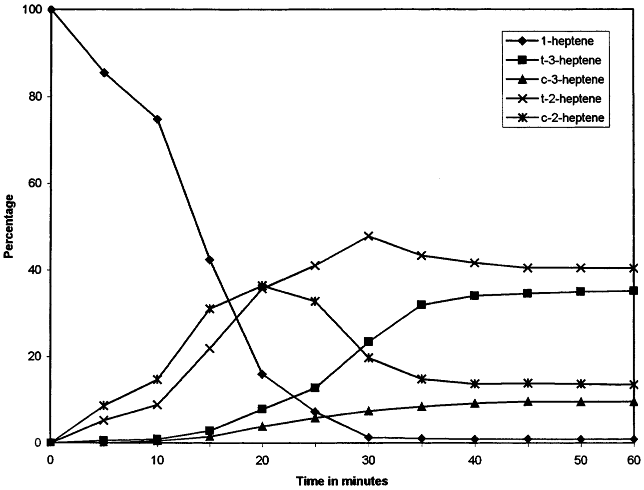

Figure 2. Isomerization of 1-heptene using $RhCl_3 \cdot nH_2O/BH_3 \cdot THF$ in THF.

Role and Fate of the Catalyst. A clear understanding of the role, efficiency, and fate of the catalyst is now at hand. The slow addition of $BH_3 \cdot THF$ into a mixture of the alkene and catalyst in THF appears to be of critical importance in achieving the desired isomerization. This modified procedure facilitates the generation of the in situ catalyst, presumably a rhodium hydride

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[16] 1-Heptene was chosen, since we were able to separate all the possible regioisomers successfully. In the octene system, *cis*-3-octene could not be isolated.

species, which is responsible for alkene isomerization, since $RhCl_3 \cdot nH_2O$ alone cannot isomerize alkenes rapidly enough. This "Rh−H" species adds reversibly across a double bond in a Markovnikov fashion, thus facilitating the formation of internal akenes. In many cases, it has been observed that the hydrogen in metal hydride complexes ionizes as a proton.[17] A rhodium dihydride species may be implicated to account for the alkene hydrogenation.[18] Additional $BH_3 \cdot THF$ finally reduces the catalyst into its elemental state, which appears as a fine black suspension in our reaction mixture.[19] This black suspension is also known to be a very efficient hydrogenation catalyst.[20]

In situ catalyst generation via slow addition of $BH_3 \cdot THF$ allows for the fine tuning of the isomerization aptitude of the catalyst. Catalyst deactivation and ultimate destruction can be achieved very easily, either by the addition of excess $BH_3 \cdot THF$, thus reducing the metal to its elemental state, or by quenching the reaction using $NaOH/H_2O_2$.

Conclusions

The combination of catalytic amounts of $RhCl_3 \cdot nH_2O$ and $BH_3 \cdot THF$ offers an excellent route for the isomerization of alkenes. Isomerization can also be achieved using a combination of other rhodium compounds such as $RhBr_3 \cdot nH_2O$ and $RhCl(PPh_3)_3$ in the presence of catalytic amounts of a hydroborating reagent. The rapid reversibility of the alkene insertion/β-hydride elimination step in the mechanism is the key to alkene isomerization. Generation of the catalyst in the presence of D_2O gives us a versatile procedure to label alkenes. We hope that this methodology will be useful to study the elegant dance of the double bond.

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Supporting Information Available: Text, tables and figures giving experimental procedures and compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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