

## An Efficient Hydride-Assisted Isomerization of Alkenes via Rhodium

### Catalysis

#### Supporting Information

Terence C. Morrill\* and Christopher A. D'Souza

Department of Chemistry, Rochester Institute of Technology, Rochester, New York 14623.

### I. GENERAL

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GC analysis was performed using Hewlett Packard 6890-5973 GC-MS system.

Column: HP-1MS – Crosslinked Methyl Siloxane, (HP 19091S-936) 60 m, 250  $\mu\text{m}$  diameter, 0.25  $\mu\text{m}$  thickness, He carrier, 15.6 psi initial pressure, 1.0 mL min<sup>-1</sup> flow, MS detector.

Oven Ramp	°C/min	Next °C	Hold (min)	Run time
Initial		35	5.00	5.00
Ramp 1	5.00	40	5.00	11.00
Ramp 2	5.00	50	4.00	17.00
Ramp 3	10.00	100	8.00	30.00
Post run	10.00	250	3.00	33.00

Solvent delay: 14.20 minutes.

#### Materials

1-octene, *trans*-2-octene, *trans*-3-octene, *trans*-4-octene, styrene, allylbenzene, 1-heptene,  $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ ,  $\text{RhBr}_3 \cdot n\text{H}_2\text{O}$ ,  $\text{RhCl}(\text{PPh}_3)_3$ ,  $[\text{RhCl}(\text{COD})]_2$  and  $\text{BH}_3$ -THF were obtained from Aldrich Chemical Co.; *cis*-2-octene from TCI America; THF and diethyl ether from Fisher Chemicals;  $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$  and  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  from Strem Chemicals.

## II. EXPERIMENTAL

### 1. Isomerization of 1-octene using $\text{RhCl}_3 \cdot n\text{H}_2\text{O}/\text{BH}_3\text{-THF}$ in THF.

A mixture of  $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$  (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 minutes, in an atmosphere of dry nitrogen. The  $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$  was partially soluble in the THF, imparting a reddish color to the solution. Using a syringe,  $\text{BH}_3\text{-THF}$  (0.3 mL, 0.3 mmol) was injected into the reaction flask at a very slow rate, over a period of 15 minutes. Within a few minutes the  $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$  dissolved completely resulting in a pale yellow solution, which slowly turned brownish-black. The reaction was allowed to continue for an additional 2 hrs, followed by alkaline peroxide oxidation, extraction, and purification. The above procedure was adopted for the isomerization of *cis*-2-octene, *trans*-2-octene, *trans*-3-octene, *trans*-4-octene, 1-heptene, and allylbenzene.

## **2. Isomerization of 1-octene using $\text{RhCl}_3 \cdot n\text{H}_2\text{O}/\text{BH}_3\text{-THF}$ in THF in the Presence of Traces of $\text{D}_2\text{O}$ [Labeling Studies].**

A mixture of  $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$  (10 mg, 0.048 mmol), 1-octene (0.5 mL, 3.19 mmol),  $\text{D}_2\text{O}$  (0.08 mL, 4.4 mmol) and THF (10 mL) was stirred in a three-necked round bottom flask, at room temperature ( $24^\circ\text{C}$ ) for 15 minutes, in an atmosphere of dry nitrogen. The  $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$  was partially soluble in the THF, imparting a reddish color to the solution. Using a syringe,  $\text{BH}_3\text{-THF}$  (0.3 mL, 0.3 mmol) was injected into the reaction flask at a very slow rate, over a period of 15 minutes. Within a few minutes the  $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$  completely dissolved resulting in a pale yellow solution, which slowly turned brownish-black. The reaction was allowed to continue for an additional 2 hrs, followed by alkaline peroxide oxidation, extraction and purification. The above procedure was adopted with styrene and cyclohexene. In yet another modification to the above procedure  $\text{BD}_3\text{-THF}$  (0.8 mL, 0.8 mmol) was used instead of  $\text{BH}_3\text{-THF}$ , under anhydrous conditions.

### 3. Migration Pattern

A mixture of  $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$  (10 mg, 0.048 mmol), 1-heptene (1.5 mL, 10.65 mmol), and THF (30 mL) was stirred in a three-necked round bottom flask, at room temperature (24°C) for 15 minutes, in an atmosphere of dry nitrogen. The  $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$  was partially soluble in the THF, imparting a reddish color to the solution. Using a syringe,  $\text{BH}_3$ –THF (0.3 mL, 0.3 mmol) was injected into the reaction flask at a very slow rate. Within a few minutes the  $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$  completely dissolved resulting in a pale yellow solution. At regular intervals 0.5 mL aliquots of the reaction mixture were extracted and quenched using a mixture of NaOH and  $\text{H}_2\text{O}_2$ . After 10 minutes the products were extracted using 3 mL of pentane and analyzed using GC-MS.

### III. CALCULATIONS

Table 1. Calculated Product Distribution Based on Enthalpies of Formation of Liquid Heptenes

Isomeric heptene	$\Delta H_f$	$\Delta\Delta H_f$	$B_f$	D	$B_f \cdot D$	Calc.(%)	<sup>a</sup> Expt.(%)
1-heptene	-23.35	2.8	0.0088	2	0.0176	0.427	0.728
c-2-heptene	-25.31	0.84	0.242	2	0.484	11.743	12.724
t-2-heptene	-26.15	0	1	2	2.000	48.525	43.254
c-3-heptene	-25.00	1.15	0.143	2	0.286	6.939	7.262
t-3-heptene	-25.91	0.24	0.667	2	1.334	32.366	36.032

$\Delta H_f$  = Enthalpies of formation of isomeric heptenes in kcal/mol.<sup>12</sup>

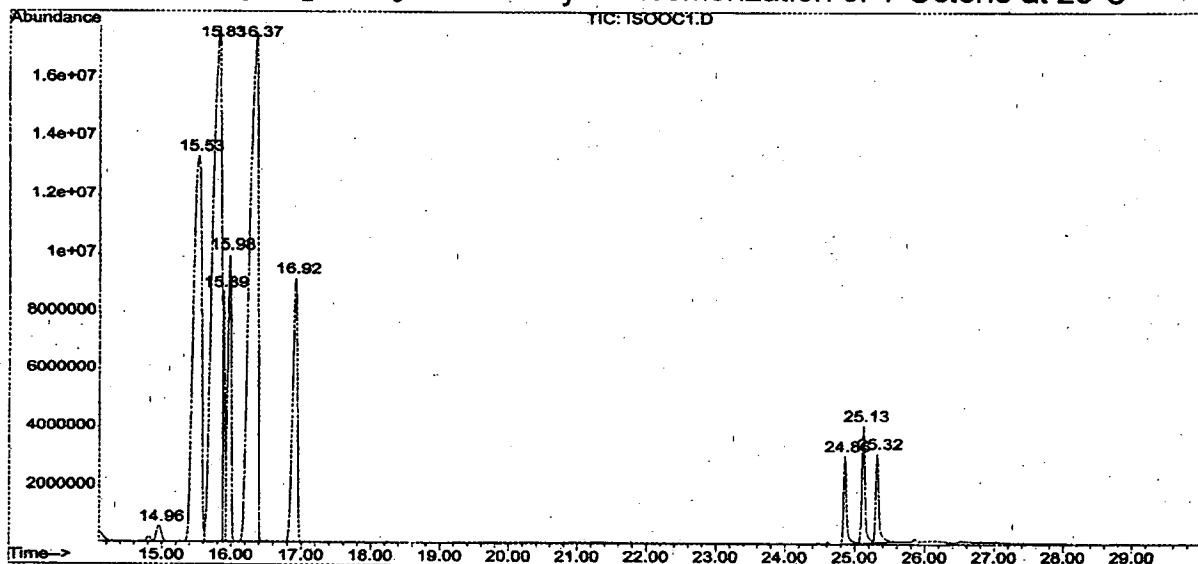
D = degeneracy.  $B_f$  = Boltzmann factor =  $\exp[-\Delta\Delta H_f \cdot 1000/\text{RT}]$ .

Calc. (%) =  $[B_f D / \sum B_f D] \times 100$ .

<sup>a</sup>Product distribution after 24 hours.

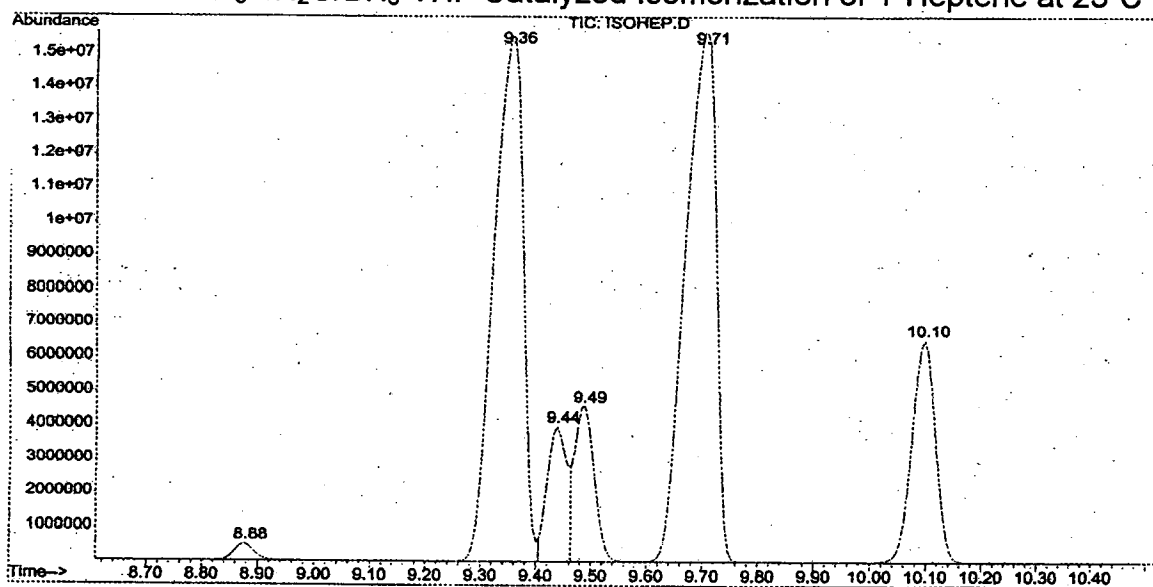
## IV. CHROMATOGRAMS

**Figure S1:** Gas Chromatographic Separation of the Product Mixture of the  $\text{RhCl}_3 \cdot n\text{H}_2\text{O}/\text{BH}_3\text{-THF}$  Catalyzed Isomerization of 1-Octene at 25°C



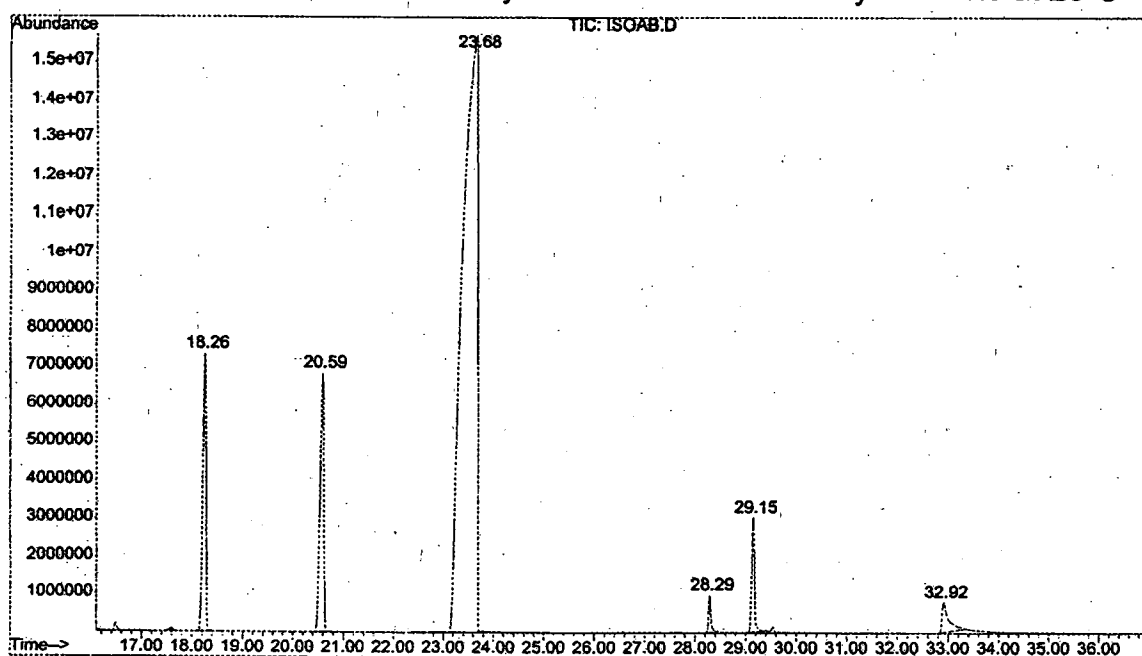
Retention time (minutes): 1-octene = 14.96; *trans*-4-octene = 15.53; *trans*-3-octene = 15.83; *cis*-4-octene = 15.89; octane = 15.98; *trans*-2-octene = 16.37; *cis*-2-octene = 16.92; 4-octanol = 24.86; 3-octanol = 25.13; 2-octanol = 25.32.

**Figure S2:** Gas Chromatographic Separation of the Product Mixture of the  $\text{RhCl}_3 \cdot n\text{H}_2\text{O}/\text{BH}_3\text{-THF}$  Catalyzed Isomerization of 1-Heptene at 23°C



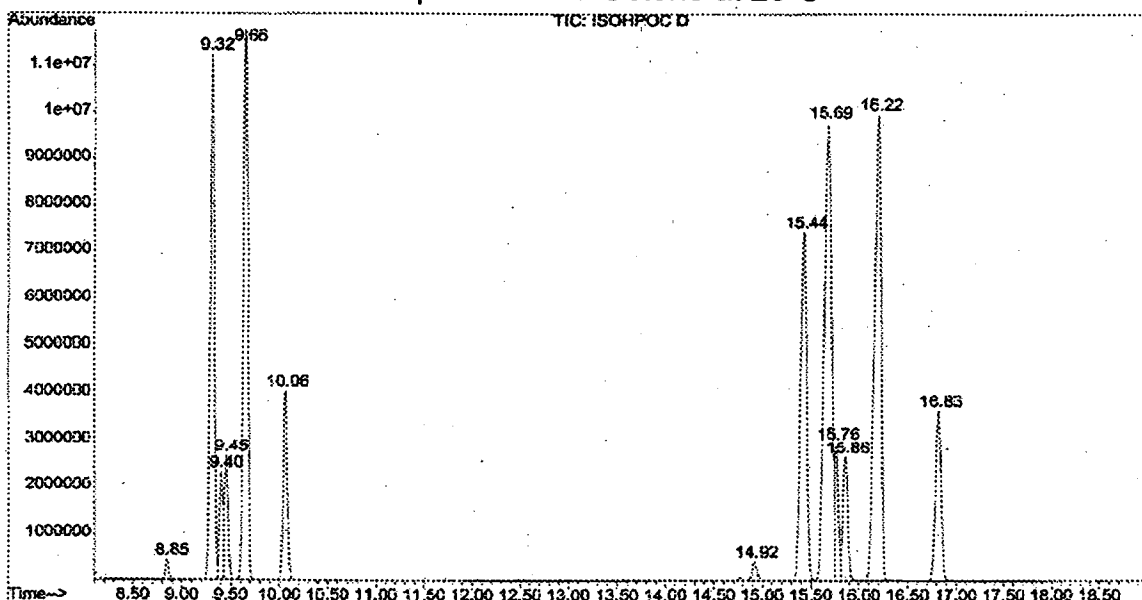
Retention time (minutes): 1-heptene = 8.88; *trans*-3-heptene = 9.36; heptane = 9.44; *cis*-3-heptene = 9.49; *trans*-2-heptene = 9.71; *cis*-2-heptene = 10.10.

**Figure S3:** Gas Chromatographic Separation of the Product Mixture of the  $\text{RhCl}_3 \cdot n\text{H}_2\text{O}/\text{BH}_3\text{-THF}$  Catalyzed Isomerization of Allylbenzene at 23°C



Retention time (minutes): propyl benzene = 18.26; *cis*-1-phenyl-1-propene = 20.59; *trans*-1-phenyl-1-propene = 23.68; 1-phenyl-2-propanol = 28.29; 1-phenyl-1-propanol = 29.15; 3-phenyl-1-propanol = 32.92.

**Figure S4:** Gas Chromatographic Separation of the Product Mixture of the  $\text{RhCl}_3 \cdot n\text{H}_2\text{O}/\text{BH}_3\text{-THF}$  Catalyzed Isomerization of 1-Heptene and 1-Octene at 28°C



Retention time (minutes): 1-heptene = 8.85; *trans*-3-heptene = 9.32; heptane = 9.40; *cis*-3-heptene = 9.45; *trans*-2-heptene = 9.66; *cis*-2-heptene = 10.06; 1-octene = 14.92; *trans*-4-octene = 15.44; *trans*-3-octene = 15.69; *cis*-4-octene = 15.76; octane = 15.86; *trans*-2-octene = 16.22; *cis*-2-octene = 16.83.