

Notes

Kinetics of the Isomerization of 1-Decene to *cis*- and *trans*-2-Decene

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In connection with other studies that are being carried out in our laboratory,¹ we are interested in the isomerization of 1-olefins to 2-olefins. One method reported in the literature involves the reaction of the olefin with strong bases such as potassium *tert*-butoxide or potassium methoxide.² For olefins with alkyl chains longer than 1-pentene, this method has the drawback that the double bond usually migrates to a more internal position of the alkyl chain and mixtures of isomers are obtained. Other methods which are more selective and give higher yields of the 2-olefin involve complexes formed between phosphines (triphenyl, diphenyl, triethyl, etc.) and salts of certain transition metals in the presence of a cocatalyst. For instance, nickel³ or cobalt⁴ halides or thiocyanates or nitrates with NaBH₄ as a cocatalyst have been found to be effective for the reaction with 1-olefins.

We report here a study on the isomerization of 1-decene to 2-decene which proceeds in quantitative yield to a mixture of *cis*- and *trans* 2-decene in homogeneous solution using [(Ph)₃P]₂Co(SCN)₂/BH₄Na as catalyst.

Results and Discussion

The reactions were carried out using THF and dioxane as solvents at 0 °C, and good care was taken to exclude humidity and oxygen. Samples were taken at regular periods of time and analyzed by gas chromatography. The percentage of product vs time is shown in Figure 1 where the amount of catalyst and the conditions for the reactions are also indicated. The *trans*/*cis* ratio remains almost constant up to 90% total conversion, and then it increases. Besides, there is about 6% of decane which is produced by reduction of the 2-decenes since this product appears when there is almost no 1-decene left. In the isomerization of 1-butene in a somewhat similar reaction system but with a higher ratio of catalyst/olefin, some reduction was also observed, but at the beginning of the reaction.⁵

The kinetic results are interpreted in terms of Scheme 1.

The expressions for the concentration of 1-decene (D), *cis*-2-decene (C), and *trans*-2-decene (T) are given by eqs 1–3 whose derivation is given in the Appendix.

$$\%[D] = 100e^{-(k_1+k_2)t} \quad (1)$$

Non linear adjustment of the data⁶ in eqs 1–3 yields the rate constants indicated in Table 1. In Figure 2 is

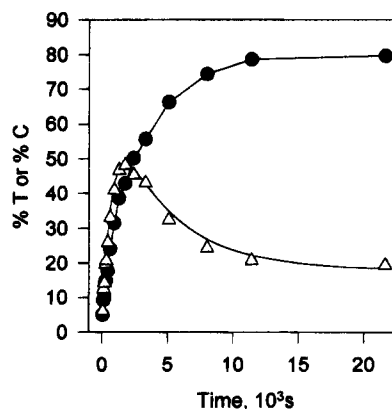
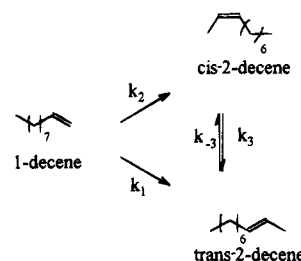


Figure 1. Percent of *cis*-2-decene (Δ) and *trans*-2-decene (\bullet) vs time. The lines are calculated with eqs 2 and 3 and the rate constants reported in Table 1. Temperature, 0 °C; solvent, dioxane:THF (50%); catalyst = 6.7 mM; [NaBH₄] = 13.4 mM; [(Ph)₃P] = 3.3 mM; [1-decene] = 0.67 M.

Scheme 1



$$\%[C] = 100[1 - e^{-A_2t} - A_1(e^{-A_2t} - e^{-A_3t}) + A_4(e^{-A_3t} - 1)] \quad (2)$$

$$\%[T] = 100[A_1e^{-A_2t} - (A_1 + A_4)e^{-A_3t} + A_4] \quad (3)$$

shown the plot of the logarithm of the 1-decene concentration vs time. The plot is linear up to 95% conversion and the sum $k_1 + k_2$ can be obtained from the slope. This value is in good agreement with the one obtained from a nonlinear fit of eq 1.

The kinetically favored product is the *cis* isomer with $k_2 > k_1$, and toward the end of the reaction, the ratio changes in favor of the *trans* isomer, consistent with the values of $k_3 > k_{-3}$. Besides, the ratio of *trans*/*cis* at the beginning of the reaction (~ 0.7) is in good agreement with the ratio $k_1/k_2 = 0.6$. The final equilibrium of the two isomers is reached in about 6 hours to give a ratio of 4 in good agreement with the ratio k_3/k_{-3} . The rate constants are pseudo-first-order rate constants since they should involve the catalyst concentration. At a lower catalyst/

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(3) (a) Kanai, H. *J. Chem. Soc., Chem. Comm.* **1972**, 203–204. (b) Otsuka, S.; Nakamura, A.; Yoshida, T.; Naruto, M.; Ataka, K. *J. Am. Chem. Soc.* **1973**, *95*, 3180–3188. (c) D'aniello, M. J.; Barenfield, E. K. *J. Am. Chem. Soc.* **1978**, *100*, 1474.

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(5) Reference 4a.

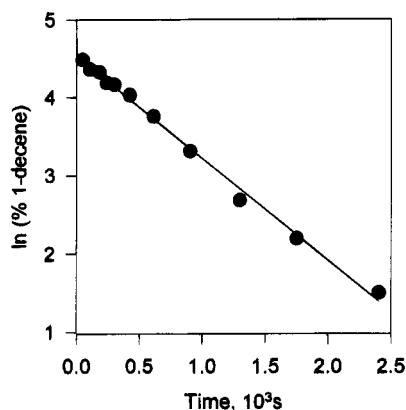
(6) *Sigmaplot DOS*, Version 6.0; 1993.

(1) Aymar, M. L. Magister Thesis, Universidad Nacional de Córdoba, Córdoba, Argentina, 1994.

Table 1. Calculated Rate Constants for the Isomerization of 1-Decene to 2-Decenes^a

$k_1 \times 10^4, \text{s}^{-1}$	$k_2 \times 10^4, \text{s}^{-1}$	$k_3 \times 10^4, \text{s}^{-1}$	$k_{-3} \times 10^6, \text{s}^{-1}$
5.19 ± 0.70^b	9.25 ± 0.84^b	1.67 ± 0.14^b	4.21 ± 0.26^b
5.33 ± 0.30^c	9.10 ± 0.37^c	1.63 ± 0.17^c	4.11 ± 0.13^c

^a Temperature, 0 °C; errors are the average deviation from the mean of three determinations. ^b Values calculated from the change in concentration of *cis*-2-decene with time, eq 2. ^c Values calculated from the change in concentration of *trans*-2-decene with time, eq 3.

**Figure 2.** Semilogarithmic plot for the consumption of 1-decene.

olefin ratio, the reaction becomes slower, although the ratio of *trans*/*cis* olefin is about the same. For instance, with the ratio of catalyst/olefin = $1/200$ and $1/150$, the conversion at 160 s is 4.6 and 8.6%, respectively, and the *trans*/*cis* ratio is 0.6. Under the conditions of the kinetic experiments, the catalyst/olefin ratio is $1/100$ and the conversion at the same reaction time is 21% with a *trans*/*cis* ratio of 0.7.

These results indicate that the method is suitable for the isomerization of 1-decene, and good yields of the thermodynamically less stable product can be obtained if the reaction is stopped after about half an hour where there is more than 90% conversion and the *cis* to *trans* ratio is about 1. Other methods of isomerization such as near-ultraviolet irradiation of $\text{Fe}(\text{CO})_5$ in the presence of linear olefins lead to isomerization to give a common equilibrium mixture of the alkenes, irrespective of the starting isomer.⁷ Thermal isomerization of terminal olefins using the same catalyst renders mixtures of internal isomers.⁸ The catalyst used not only is effective for the migration of the double bond from the 1- to the 2-position but also catalyzes the isomerization of the *cis* olefin to the *trans* olefin. The reactions are reproducible, provided that oxygen and humidity are excluded. Three runs were carried out under the same reaction conditions, and the plots of percentage of product or reactant vs time were superposable. The average deviation of the calculated rate constants is given in Table 1. The reaction can be carried out in larger scale, about 5 times the amount indicated in the Experimental Section, and the results are the same in regard to yields and product ratio, which is important for the synthesis of large quantities. Furthermore, similar behavior is observed when 1-octene is used as substrate.

Experimental Section

The catalyst was synthesized following literature procedures.⁹ $\text{Co}(\text{SCN})_2$ was synthesized from 2.37 g (18.2 mmol) of CoCl_2 (anhyd) and 3.54 g (36.5 mmol) of KSCN in distilled acetone. The KCl was filtered and the acetone evaporated to dryness. The residue was extracted with ethyl ether, the ether evaporated, and the residue dissolved in acetone. To this solution was added dropwise for about 1 h 11.0 g (42 mmol) of Ph_3P (Aldrich) in 50 mL of acetone. The solution was evaporated, and the dry residue was dissolved in dichloromethane, to which hexane was added, to precipitate the green compound $[(\text{Ph})_3\text{P}]_2\text{Co}(\text{SCN})_2$. The solid was recrystallized in dichloromethane/hexane: yield 70%; mp 140.5 °C (lit.⁹ 140 °C).

The THF was dried with KOH and then with Na/K alloy and finally stored over AlH_4Li . Before each reaction, the solvent was filtered and refluxed with sodium benzophenone until the blue color of the benzophenone radical anion appeared and persisted. It was then distilled prior to use.

The dioxane was refluxed over Na and then distilled and stored over LiAlH_4 . Before each reaction, it was treated with sodium benzophenone as indicated above.

In a typical reaction 0.139 g (0.2 mmol) of the catalyst and 22 mg (0.1 mmol) of triphenylphosphine dissolved in 15 mL of THF were placed in a three-necked round-bottomed flask, and dioxane (15 mL) was added. The solution was cooled to 0 °C, and 14.7 mg (0.4 mmol) of NaBH_4 was added, followed by 1-decene (2.82 g, 20.1 mmol). The reaction mixture was continuously stirred under nitrogen, and the reaction was quenched with water upon completion. The organic layer was separated and analyzed by GC using a Sigma-Aldrich SA-1 capillary column: yield 99%. The quantification was done assuming equal response factors. The gas chromatograph used was a Konik KNK-3000-HRGC equipped with a FID detector.

To identify the *cis* and *trans* isomers, a reaction mixture, which by GC gave 73 and 27% of the peaks of the shorter and longer retention times, respectively, was analyzed by ^{13}C NMR without NOE.¹⁰ The δ values for the relevant carbons are 114.0 for C-1, 139.2 for C-2, and 33.8 for C-3 for 1-decene; 12.5 for C-1, 130.9 for C-2, and 123.6 for C-3 for *cis* 2-decene; and 17.9 for C-1, 131.7 for C-2, 124.5 for C-3 for *trans* 2-decene. The relative percentages of the *cis* and *trans* isomers were 28 ± 2 and 72 ± 2 , respectively. These values are coincident with the GC peaks of the longer and shorter retention times, indicating that they belong to the *cis* and *trans* isomers, respectively.

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Appendix

The change in concentration of D, T, and C is given by eqs A1–A3.

$$\frac{d[\text{D}]}{dt} = -(k_1 + k_2)[\text{D}] \quad (\text{A1})$$

$$\frac{d[\text{C}]}{dt} = k_2[\text{D}] - k_3[\text{C}] + k_{-3}[\text{T}] \quad (\text{A2})$$

$$\frac{d[\text{T}]}{dt} = k_1[\text{D}] - k_{-3}[\text{T}] + k_3[\text{C}] \quad (\text{A3})$$

Integration of eq A1 yields eq A4 which can be transformed into eq 1, considering that $\%[\text{D}] = 100[\text{D}]/[\text{D}]_0$.

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(10) NMR experiments were carried out on a Bruker 200 instrument. Technical assistance by Dr. Virginia Sosa is acknowledged.

$$[\mathbf{D}] = [\mathbf{D}]_0 e^{-(k_1+k_2)t} \quad (\text{A4})$$

To find the expression for the concentration of \mathbf{T} , eq A2 is combined with the mass balance, namely $[\mathbf{C}] = [\mathbf{D}]_0 - [\mathbf{D}] - [\mathbf{T}]$, and eq A4 which yields eq A5.

$$\frac{d[\mathbf{T}]}{dt} = (k_1 - k_3)[\mathbf{D}]_0 e^{-(k_1+k_2)t} - (k_3 + k_{-3})[\mathbf{T}] + k_3[\mathbf{D}]_0 \quad (\text{A5})$$

Equation A5 is a first-order linear differential equation which can be solved by working with separated variables.¹¹ In order to do that, we used eqs A6–A11.

$$S = (k_1 - k_3)[\mathbf{D}]_0 \quad (\text{A6})$$

$$S_1 = k_1 + k_2 \quad (\text{A7})$$

$$S_2 = k_3 + k_{-3} \quad (\text{A8})$$

$$S_3 = k_3[\mathbf{D}]_0 \quad (\text{A9})$$

$$[\mathbf{T}] = uv \quad (\text{A10})$$

$$\frac{d[\mathbf{T}]}{dt} = u \frac{\delta v}{\delta t} + v \frac{\delta u}{\delta t} \quad (\text{A11})$$

Combining eqs A5–A11 results in eq A12.

$$u \left(\frac{\delta v}{\delta t} + S_2 v \right) + v \frac{\delta u}{\delta t} = S e^{-S_1 t} + S_3 \quad (\text{A12})$$

To find the value of v , the term in parentheses is set equal to 0; therefore, eq A13 holds and can be integrated to give eq A14.

$$\frac{\delta v}{v} = -S_2 \delta t \quad (\text{A13})$$

$$v = e^{-S_2 t} \quad (\text{A14})$$

Replacing v in eq A12 for eq A14 and rearranging results in eq A15.

$$\delta u = S e^{(S_2-S_1)t} \delta t + S_3 e^{S_2 t} \delta t \quad (\text{A15})$$

The integral of eq A15 is given by eq A16 where K is an integration constant

$$u = \frac{S}{S_2 - S_1} e^{(S_2-S_1)t} + \frac{S_3}{S_2} e^{S_2 t} + K \quad (\text{A16})$$

Replacing in eq A10 the values of u and v given by eqs A14 and A16 results in eq A17.

$$[\mathbf{T}] = \frac{S}{S_2 - S_1} e^{-S_1 t} + K e^{-S_2 t} + \frac{S_3}{S_2} \quad (\text{A17})$$

Equation A17 has infinite solutions, but when the conditions are imposed so that at $t = 0$, $[\mathbf{T}]_0 = 0$, the value of K is given by eq A18

$$K = -\frac{S}{S_1 - S_2} - \frac{S_3}{S_2} \quad (\text{A18})$$

Replacing K in eq A17 and then replacing the values of S , S_1 , S_2 , and S_3 given by eqs A6–A9 results in eq A19, with A_1 – A_4 defined in eqs A20–A23. Considering that

$$[\mathbf{T}] = [\mathbf{D}]_0 (A_1 e^{A_2 t} - (A_1 + A_4) e^{-A_3 t} + A_4) \quad (\text{A19})$$

$$A_1 = \frac{k_1 - k_3}{k_3 + k_{-3} - k_1 - k_2} \quad (\text{A20})$$

$$A_2 = k_1 + k_2 \quad (\text{A21})$$

$$A_3 = k_3 + k_{-3} \quad (\text{A22})$$

$$A_4 = \frac{k_3}{k_3 + k_{-3}} \quad (\text{A23})$$

$\%[\mathbf{T}] = 100[\mathbf{T}]/[\mathbf{D}]_0$, eq A19 is transformed into eq 3. Equation 2 is obtained by combining the mass balance with eqs A19 and A4.

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