Isomerization of olefin carboxylic esters catalyzed by nickel and palladium compounds

Xiaotai Wang, L. Keith Woo *

Department of Chemistry, Iowa State University, Ames, IA 50011-3111, USA

Abstract

The Group 10 complex *trans*-Pd$(C_6H_5CN)_2Cl_2$ and acidic solutions of Ni$[P(OEt)_3]_4$ effectively catalyze the stereoselective isomerization of C=C double bonds in olefinic esters. With acidic solutions of Ni$[P(OEt)_3]_4$, only 4-pentenoate is produced from 3-pentenoate at early times. However, in the presence of excess phosphite, 2-pentenoate is the only positional isomer produced (61% yield). In the absence of excess phosphite, a kinetically controlled process is proposed to explain the initial formation of 4-pentenoate. With the Pd catalyst, no 4-pentenoate is observed. For example, *trans*-Pd$(C_6H_5CN)_2Cl_2$ selectively produces 2-pentenoate from 3-pentenoate (58%). © 1998 Elsevier Science B.V.

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1. Introduction

It has long been known that protonated Ni(0) phosphine or phosphite complexes catalyze the double bond migration of olefins [1]. Early work by Tolman on simple olefins provided important mechanistic insight into catalytic isomerization of olefins such as 1-pentene [2]. It is generally believed that a nickel hydride species adds across the C=C bond to form a nickel alkyl complex. Subsequent β-hydrogen elimination reforms the C=C bond. Several cycles of hydride insertion and β-hydrogen elimination afford positional isomers. Also, Tolman has shown that the nickel hydride complex tends to decompose and probably generates a catalytically inactive Ni(II) species (Scheme 1) [3]. Miller reported that ethylenebis(*tri-o*-tolyl phosphite)nickel(0) treated with hydrogen chloride in hexane solution catalyzes isomerization of olefins having polar functional groups. Interestingly, this system results in the conversion of ethyl-4-pentenoate to *trans*- and *cis*-ethyl-3-pentenoate as the only products [4]. No conjugated isomers were observed. More recently, McKinney reported that the isomerization of 3-pentenenitrile with nickel hydride catalysts is kinetically controlled [5]. The kinetic product, 4-pentenenitrile, is initially produced in prefer-

$$NiL_4 + H^+ \rightleftharpoons [HNiL_4]^+$$

$$[HNiL_4]^+ \rightleftharpoons [HNiL_3]^+ + L$$

$$[HNiL_3]^+ + H^+ \rightleftharpoons Ni^{(II)}L_3 + H_2$$
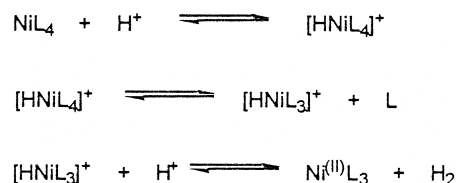
Scheme 1. Formation and decomposition of Ni hydrides.

* Corresponding author.
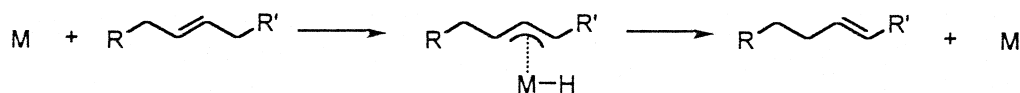
Scheme 2. Olefin isomerization through a π-allylic mechanism.

ence to the thermodynamically favored conjugated isomer, 2-pentenenitrile. Coordination of the nitrile function to nickel has been proposed to explain the observed kinetic preference. In addition to nickel complexes, other late transition metal complexes, particularly those of palladium, have been found to be effective catalysts for double bond and skeletal isomerizations [6–9]. For instance, *trans*-Pd(C$_6$H$_5$CN)$_2$Cl$_2$ catalyzes the isomerization of 1-pentene to 2-pentene in benzene solution [10]. This process is believed to proceed via π-allylic intermediates (Scheme 2) rather than the metal hydride addition mechanism proposed for the Ni(0) catalyst systems. Moreover, isomerization of allyl phenyl ethers with *trans*-Pd (C$_6$H$_5$CN)$_2$Cl$_2$ in boiling benzene gives phenyl prop-1-enyl ethers [11].

We are interested in studying the potential directing effect of the carboxylic functional group in naturally occurring molecules including fatty acids and their esters, hoping to convert these agricultural products into industrial feed stocks via double bond isomerization. In this model study, we choose three olefinic esters as substrates, and Ni[P(OEt)$_3$]$_4$ and *trans*-Pd(C$_6$H$_5$CN)$_2$Cl$_2$ as catalysts. Not only can these late transition metal complexes be readily prepared [12,13], but they should also tolerate functionalities such as ester groups.

2. Experimental

2.1. General considerations

Reagent grade methanol and benzene were used without further purification. The materials Ni[P(OEt)$_3$]$_4$ and *trans*-Pd(C$_6$H$_5$CN)$_2$Cl$_2$ were prepared by literature procedures, from commercially purchased reagents. The substrates methyl *trans*-3-pentenoate, methyl *trans*-2-butenoate and methyl *trans*-3-butenoate were purchased from Aldrich, while methyl 4-pentenoate was prepared from 4-pentenoic acid by standard esterification methods [14]. All reactions were conducted under nitrogen using standard Schlenk techniques. GC analyses were performed on a HP 5890 gas chromatograph using a 30 m DB-5 column. Retention times of the products were compared to those of authentic samples. Confirmation of a product was achieved by co-injection of a known sample. NMR spectra were obtained on a Varian VXR-300 spectrometer.

2.2. Isomerization reactions

In a typical experiment, Ni[P(OEt)$_3$]$_4$ (14 mg, 0.019 mmol) was dissolved in ca. 2 ml of methanol and the solution was heated to 50°C. Following addition of 117 μl (0.95 mmol) of methyl *trans*-3-pentenoate, 0.2 ml of 0.10 M CF$_3$SO$_3$H in methanol was injected into the flask and the solution immediately turned from colorless to pale yellow. Aliquots of 10–20 μl of reaction solutions were taken out at 40 s, 15 min and 80 min of reaction time and analyzed by GC. The 40 s sample showed only two components: methyl *trans*-3-pentenoate and methyl-4-pentenoate with a ratio of 14:1. The 15 min sample showed four components: methyl *trans*-3-pentenoate, methyl *cis*-3-pentenoate, methyl *trans*-2-pentenoate and methyl-4-pentenoate with a ratio of 9.6:6.3:1.0:1.0. The 80 min sample showed no significant difference from the 15 min sample.

The experiment using Ni[P(OEt)$_3$]$_4$ and excess P(OEt)$_3$ was identical with the above procedure except that the reaction scale was doubled and a 40-fold excess of free P(OEt)$_3$ (550 mg, 0.76 mmol) was added before the injection of the CF$_3$SO$_3$H solution. GC analyses were done at 40 min, 3 h and 4 h of reaction. The 40

min sample showed no reaction, while the others showed three components: methyl *trans*-2-pentenoate, methyl *cis*-3-pentenoate, methyl *trans*-3-pentenoate with a ratio of 2.1:1.0:2.9 for the 4 h sample. After 18 h, the reaction solution was loaded on a 6 by 3 cm (length by diameter) silica gel column and eluted with approximately 30 ml of diethyl ether. Removal of the solvent under reduced pressure afforded the product mixture. A 300 MHz ^{1}H NMR spectrum indicated a 61% yield for the positional isomer methyl *trans*-2-pentenoate. No *cis*-2-pentenoate was detected by GC or ^{1}H NMR.

In the isomerization reaction of methyl *trans*-3-butenoate catalyzed by *trans*-Pd(C$_6$H$_5$CN)$_2$Cl$_2$, 14.6 mg (0.038 mmol) of the catalyst was dissolved in ca. 4 ml of benzene at 50°C to give a light yellow brown solution to which 120 μl (1.13 mmol) of the olefin substrate was added. The isomer methyl *trans*-2-butenoate was detected by GC after 20 min, and its ratio to methyl *trans*-3-butenoate reached a maximum of 1.8 at 48 h.

In the isomerization reaction of methyl 4-pentenoate catalyzed by *trans*-Pd(C$_6$H$_5$CN)$_2$Cl$_2$, 10.4 mg (0.027 mmol) of the catalyst was dissolved in ca. 4 ml of benzene at 50°C to give a light yellow brown solution to which ca. 94 mg (0.815 mmol) of the olefin substrate was added. GC analyses were taken at 40 min, 2, 4.5, 8, 24, and 30 h of reaction, which showed three components: methyl *trans*-3-pentenoate, methyl *cis*-3-pentenoate and methyl *trans*-2-pentenoate. The ratio of the first two remained approximately constant (1.0:0.3), while that of methyl *trans*-2-pentenoate kept growing to reach 1.8.

3. Results and discussion

3.1. Isomerization of trans-3-pentenoate catalyzed by Ni[P(OEt)$_3$]$_4$: Kinetic vs. thermodynamic control

When a methanolic solution of *trans*-3-pentenoate containing 2 mol% Ni[P(OEt)$_3$]$_4$ was treated with triflic acid (1 equiv/Ni) at 50°C, isomerization occurred in less than a minute. During this short period of time, the terminal 4-pentenoate was the only positional isomer detected by GC, albeit in low yield (7%). As the reaction proceeded, the conjugated *trans*-2-pentenoate and *cis*-3-pentenoate were also detectable. After ca. 15 min of reaction, the catalyst became inactive. The overall conversion of starting material was 47% and the ratio of 4-pentenoate:*trans*-2-pentenoate:*cis*-3-pentenoate was 1.0:1.0:6.3.

In another experiment, the effect of excess of P(OEt)$_3$ was examined. The presence of a 40-fold excess of phosphite resulted in a 40 min induction period before the onset of any catalytic activity. In addition, the reaction rate decreased at least 20-fold and the product distribution changed significantly. Moreover, the catalyst remained active for several hours in the presence of excess free P(OEt)$_3$ and throughout the catalysis, *trans*-2-pentenoate was the only positional isomer detected with no terminal isomer 4-pentenoate observed by GC analysis. After workup of the reaction mixture, a ^{1}H NMR spectrum confirmed that *trans*-2-pentenoate was the only positional isomer. The isolated product yield was 61%.

The catalytic isomerization of olefin esters by acidic solutions of Ni[P(OEt)$_3$]$_4$ shows striking differences in behavior in the presence or absence of excess P(OEt)$_3$. A key intermediate in the presumed catalytic cycle, HNi[P(OEt)$_3$]$_4^+$, is an 18-electron, coordinatively saturated complex. The observation of an induction period in the presence of excess phosphite is consistent with the need to dissociate a phosphite in order to generate an open coordination site on the catalyst to bind the substrate. This dissociation process (Eq. (2), Scheme 1) is inhibited by excess phosphite. Moreover, the longer lived catalyst in the presence of excess phosphite is also related to the inhibition of Eq. (2). Maintaining a higher steady state concentration of the Ni center in a coordinatively saturated environment minimizes protonolysis of the hydride

complex (Eq. (3), Scheme 1) and reduces the deactivation of the catalyst.

An explanation of the initial production of only the 4-pentenoate isomer by $HNi[P(OEt)_3]_4^+$ in the absence of excess phosphite also relies on how the catalyst maintains coordinative saturation during the early stages of the catalytic cycle. Possible events that illustrate this point involve five-coordinate alkyl Ni(II) species as shown in Scheme 3. Note that an analogous pentacoordinate phosphine complex, $[CH_3Ni(PMe_3)_4]^+$, has been structurally characterized by single-crystal X-ray diffraction [15].

In addition, five-coordinate Ni(II) alkyl species have been proposed as key intermediates in reductive elimination reactions [16]. The first phosphite dissociation from $HNi[P(OEt)_3]_4^+$ allows the catalyst to bind the substrate. The migratory insertion of the hydride ligand into the coordinated olefin can produce two different intermediates. In one case, Ni is bound to C3 of the pentanoate and in the other, Ni is bound to C4. In either case, the hydride migration step opens a new vacant coordination site on Ni. Proximity of the ester group allows for the facile binding of the carbonyl oxygen to form a
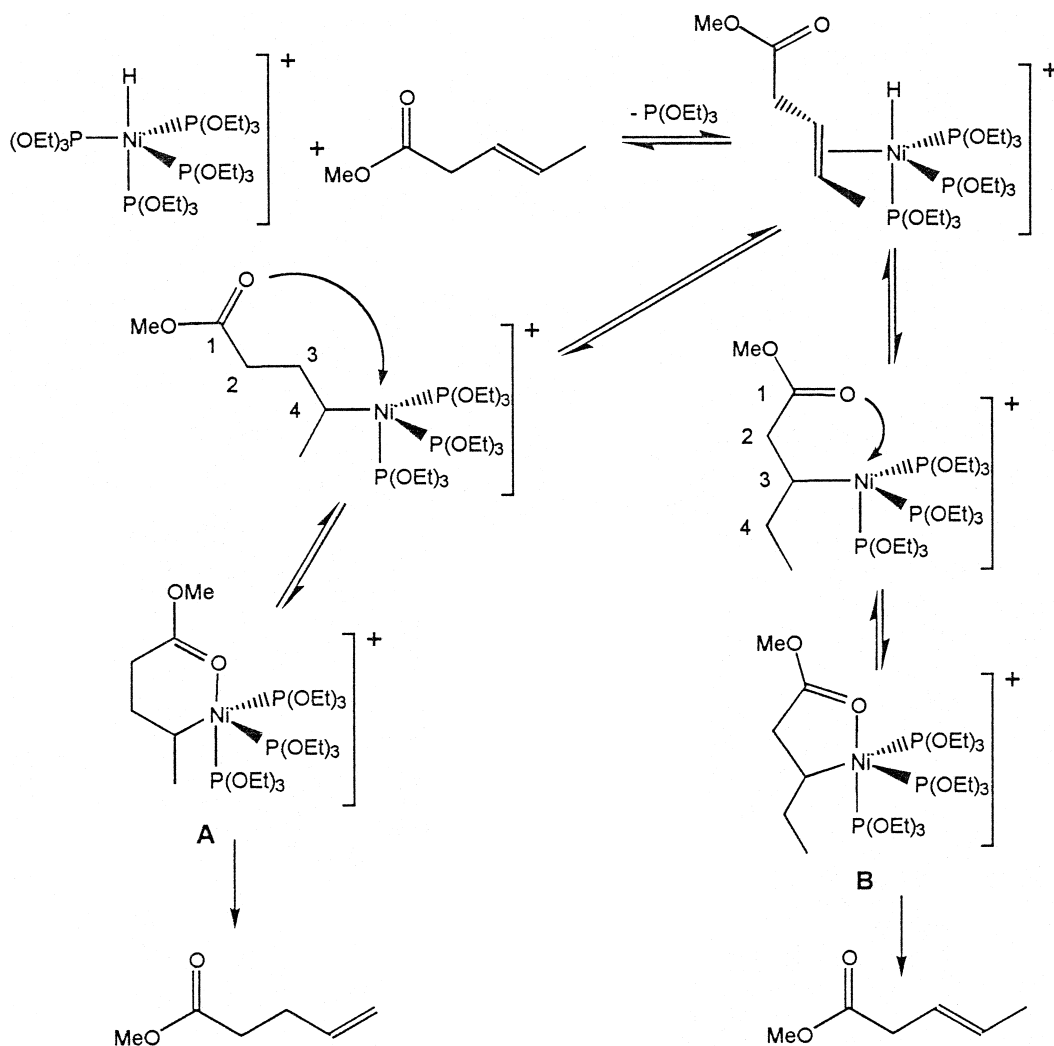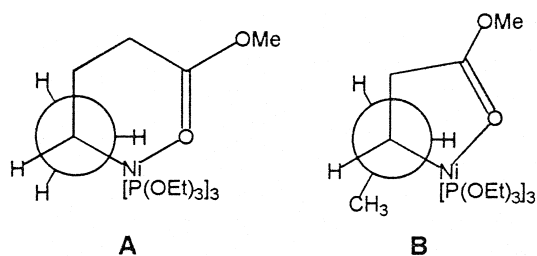

Scheme 3.

Fig. 1. Newman projections of proposed intermediates illustrating preference for β-hydrogen elimination.

coordinatively saturated intermediate. The C4 isomer results in the formation of a 6-membered ring (**A**) while the C3 isomer produces a 5-membered ring intermediate (**B**). Subsequent β-hydrogen elimination, which reforms a C=C double bond, requires that the Ni–C–C–H fragment involved in this process form a *cis* planar arrangement [17]. Geometrical constraints of a small cyclic system reduce the tendency for C–H units that are part of the ring from forming this planar arrangement [18]. Thus, it is more likely for β-hydrogen elimination to involve a C–H unit that is external to the ring. For example, in intermediate **B**, β-hydrogen elimination is more likely to occur from C4 than C2 (see Fig. 1). Hence, **B** preferentially results in reformation of the starting material (a non-productive path) with the double bond in the 3-position. However, in **A**, β-hydrogen elimination is more likely to occur from C5, generating the 4-pentenoate isomer (Fig. 1). Consequently, the ester coordination kinetically controls the formation of the 4-pentenoate product at early times.

When excess phosphite is present, ester coordination is inhibited. In this case, the isomerization is under thermodynamic control and the conjugated product, 2-pentenoate is exclusively formed.

The nature of Ni-ester coordination is not clear; no complex intermediate species have been isolated or spectroscopically detected. Detailed studies involving nickel complexes in the isomerization of olefin carboxylic esters are underway.

3.2. Isomerization of methyl 3-butenoate and trans-4-pentenoate catalyzed by trans-Pd(C6H5CN)2Cl2

In contrast to the Ni(0)/H$^+$ system, *trans*-Pd(C$_6$H$_5$CN)$_2$Cl$_2$ catalyzes olefin isomerization without the requirement of a co-catalyst, presumably through a π-allylic mechanism. When a benzene solution of methyl 3-butenoate containing 3.3 mol% of *trans*-Pd(C$_6$H$_5$CN)$_2$Cl$_2$ was heated at 50°C, the conjugated isomer *trans*-2-butenoate was detected by GC after 20 min of reaction, and its ratio to the 3-butenoate kept increasing over a period of 48 h, eventually reaching 1.8 (yield = 64%), as shown in Table 1. In another controlled experiment employing *trans*-2-butenoate as substrate, no isomerization was observed. These results suggest that *trans*-Pd(C$_6$H$_5$CN)$_2$Cl$_2$ has prolonged catalytical activity and strongly favors the formation of thermodynamically stable conjugated isomers. Thus, it may be better suited to catalytically move double bonds along an aliphatic chain. In an attempt to test this, methyl 4-pentenoate was used as a substrate. Rapid isomerization occurred and after 40 min of reaction, three isomers were detected with no starting material left (Table 1). While the ratio of *cis*- and *trans*-3-

Table 1
Isomerization of olefin esters catalyzed by *trans*-Pd(C$_6$H$_5$CN)$_2$Cl$_2^{a,b}$

Olefin substrate	Reaction time, h	Products (yield)
	48	(64%)
	30	(32%)
		(10%)
		(58%)

[a]All experiments were conducted under nitrogen in reagent-grade benzene at 50°C and yields were determined by GC or ^{1}H NMR.
[b]The molar ratio of substrate to catalyst was 30:1.

pentenoate remained approximately constant; the conjugated *trans*-2-pentenoate kept growing over a period of 30 h.

4. Conclusions

In examining the acid-promoted, Ni-catalyzed isomerization of double bonds in olefinic esters, we have observed a strong regiochemical influence in the presence and absence of excess phosphite. We propose that in the absence of free ligand, the isomerization of *trans*-3-pentenoate with $[HNi[P(OEt)_3]_4]^+$ may be kinetically controlled. Subsequent to metal hydride insertion of the olefin, ester coordination to nickel forms a small ring chelate complex which may dispose the β-hydrogen elimination step, towards the formation of the terminal, 4-pentenoate isomer at early times. The presence of excess phosphite inhibits ester chelation, thus favoring the production of the thermodynamically more stable *trans*-2-pentenoate. Note that at early times, none of the 2-pentenoate isomer is observed.

We have also found that Pd-based catalysts are also good catalysts for the isomerization of olefin esters. With *trans*-Pd$(C_6H_5CN)_2Cl_2$ as a catalyst, isomerization of mono-ene esters to the conjugated isomer occurs with good yield and good selectivity.

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