Preparation of Conjugated Soybean Oil and Other Natural Oils and Fatty Acids by Homogeneous Transition Metal Catalysis

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ABSTRACT: The use of as little as 0.1 mol% $[RhCl(C_8H_{14})_2]_2$, 0.25 mol% $PtCl_2(PPh_3)_2$, or 0.5 mol% $RuHCl(CO)(PPh_3)_3$, where Ph = phenyl, catalyzes the isomerization of soybean oil to conjugated soybean oil under mild reaction conditions and in high yields. No hydrogenation products are detected with any of these catalysts. Preliminary physical tests have shown that the conjugated soybean oil has exceptional drying properties and the resulting coatings exhibit good solvent resistance. The $[RhCl(C_8H_{14})_2]_2$ catalyst provides similarly high yields of other conjugated vegetable oils, conjugated linoleic acid, and conjugated ethyl linoleate. Other rhodium catalysts, such as $RhCl(PPh_3)_3$, have also been found to be effective for the conjugation of ethyl linoleate.

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KEY WORDS: Conjugated linoleic acid, conjugated soybean oil, conjugated vegetable oil, conjugation, drying oil, olefin isomerization, Wilkinson's catalyst.

The conversion of vegetable oils to their conjugated counterparts is known to produce better drying oils, which could prove valuable substitutes for the more expensive imported tung and castor oils (1,2). Conjugated soybean oil is of special interest owing to the low cost and ready availability of soybean oil. Conjugated soybean oil could also provide a valuable source of conjugated linoleic acid (CLA), which is found naturally in beef and dairy products. Recent research has shown that CLA is a possible anticarcinogen and as a nutritional supplement may decrease fat and increase muscle retention (3). CLA is currently produced from sunflower and safflower oils, both of which are more expensive than soybean oil.

Because of the importance of conjugated fatty acids and oils, there have been numerous reports on the isomerization of double bonds in fatty acids (4). A number of these methods have utilized homogeneous transition metal catalysts. For example, various arene chromium tricarbonyl complexes have been shown to effect 45–73% conjugation of polyunsaturated fats (5). These reactions require temperatures of 165–195°C and pressures of 70–200 psi, and hydrogenation and dehydrogenation side products have been observed. Two of the most useful catalysts so far reported are based on Wilkinson's catalyst, $RhCl(PPh_3)_3$, where Ph = phenyl. DeJarlais and Gast (6) reported that the reaction of methyl linoleate and catalytic amounts of $RhCl(PPh_3)_3$ in methanol at 65°C afforded conjugated dienes in 95% yield. However, the catalyst often dies after only a couple of hours, and the reaction has been irreproducible in our hands. Singer *et al.* (7,8) used the same catalyst in the presence of $SnCl_2{\cdot}2H_2O$, HCl, $FeCl_3$, $CrCl_3$, or LiCl to isomerize linoleic acid or its methyl ester to conjugated dienoic acids or esters in good yields. The disadvantages of this method are that high temperatures of 120–150°C are required in the absence of solvent and that the reaction yields 20–30% of hydrogenated products. Singer *et al.* (9) also reported that the isomerization reaction depends on the ligands present in the rhodium catalyst. Tri-*p*-tolylphosphine produced the most active catalyst among a number of phosphorus and nitrogen ligands studied. In using 0.8 mol% of the rhodium tri-*p*-tolylphosphine catalyst, conjugated dienes were obtained in a good yield at a temperature as low as 25°C. However, this catalyst is not commercially available, unlike Wilkinson's catalyst.

Another rhodium complex, $(Ph_3P)_2Rh$(norbornadiene)-ClO_4, has been reported to be an efficient isomerization catalyst for soybean oil and other polyunsaturated fatty acid derivatives according to an Indian patent (10). This catalyst effects 90% conversion of linoleates at 70°C and is easily recovered from the reaction without loss of activity.

In a U.S. patent, Sleeter (11) reported that various ruthenium catalysts in the presence of formic acid effectively isomerize linseed and soybean oils in 3 h using as little as 0.02 mol% ruthenium. Two major drawbacks of this method are the high temperature (180°C) required for the process and the presence of formic acid.

Other ruthenium catalysts have been reported by Krompiec *et al.* (12) to isomerize rapeseed, soybean, sunflower, and linseed oils in up to 54% yield without the use of acid. The most effective of these catalysts was $RuHCl(CO)(PPh_3)_3$. This process also requires high temperature (212–226°C), and up to 10% of polymerization products are observed.

In this paper, we report our efforts to develop improved catalysts for the isomerization of ethyl linoleate, linoleic acid, soybean oil, and other vegetable oils using homogeneous rhodium, ruthenium, and platinum catalysts under milder conditions.

EXPERIMENTAL PROCEDURES

Spectroscopic analyses. ^1H Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity spectrometer (Palo Alto, CA) operating at either 300 or 400 MHz. Gas

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chromatographic analyses were performed on an HP 5890 gas chromatograph Hewlett-Packard (Palo Alto, CA) equipped with an HP-1 Megabore column.

Reagents. Chlorobis(cyclooctene)rhodium dimer (13), dichlorobis(triphenylphosphine)platinum (14), and carbonylchlorohydridotris(triphenylphosphine)ruthenium (15) were prepared according to literature procedures. Chloro(ethylene)rhodium dimer, chlorotris(triphenylphosphine)rhodium, tri-*o*-tolylphosphine, tri-*p*-tolylphosphine, and tri(*p*-methoxyphenyl)phosphine were purchased from Strem Chemical Inc. (Newburyport, MA). Rhodium trichloride and triphenylphosphine were donated by Kawaken Fine Chemicals Co., Ltd. (Tokyo, Japan). Tin dichloride dihydrate was purchased from Fisher Scientific Company (Springfield, NJ). Vegetable oils from the following companies were purchased from local vendors: Wesson soybean, corn, and sunflower oils (Hunt-Wesson, Inc., Fullerton, CA); Hain safflower oil (The Hain Group, Inc., Uniondale, NY); Loriva sesame oil (Loriva Supreme Foods, Inc., Hauppauge, NY); and Planters peanut oil (Nabisco Foods, Inc., Planters Division, Winston-Salem, NC). Silica gel (230–400 mesh) was purchased from J.T. Baker (Phillipsburg, NJ).

Calculations for the percent conjugation. The percent conjugation for ethyl linoleate was determined by gas chromatography (GC). The GC trace gave four peaks: ethyl linoleate, and the *Z,E-, E,Z-* and *E,E*-conjugated dienes. We assigned each of the peaks according to the previous literature (6). The yield of conjugated vegetable oils was determined by ^{1}H NMR spectroscopy. The nonconjugated vinylic protons in the starting oil give peaks at about 5.30 ppm, and the peaks for the conjugated vinylic protons shift downfield to 5.30–6.29 ppm in the product. For the conjugated diene product, the vinylic protons usually appear as four sets of peaks, including one at the same position as the nonconjugated vinylic protons of the starting oil. Therefore, the percent conjugation can be calculated using the appropriate integration of these peaks and the fatty acid compositions of the oils (16).

Isomerization of ethyl linoleate by $[RhCl(C_8H_{14})_2]_2$. To 0.616 g (2.0 mmol) of ethyl linoleate in 4 mL of EtOH was added 0.1 mol% (1.43 mg) of $[\mathrm{RhCl(C_8H_{14})_2}]_2$, 0.8 mol% (3.61 mg) of $\mathrm{SnCl_2{\cdot}2H_2O}$, and 0.4 mol% (2.41 mg) of $(p\text{-}\mathrm{CH_3C_6H_4})_3\mathrm{P}$. The resulting dark orange solution was flushed with argon and stirred at 60°C for 24 h. After removal of the solvent on a rotary evaporator, the crude products were purified by flash chromatography on a silica gel column. The mixture of *Z,E*-, *E,Z*-, and *E,E*-conjugated octadecadienoic esters was obtained in 97% yield. The ratio of *Z,E*- and *E,Z* - to *E,E*-stereoisomers is 95:5. ^{1}H NMR spectrum of conjugated ethyl linoleate ($\mathrm{CDCl_3}$): δ 0.89 (*m*, 3 H, $\mathrm{C}H_3\mathrm{CH_2}$), 1.23–1.63 (*m*, 21 H, $\mathrm{OCH_2C}H_3$, $\mathrm{C}H_2\mathrm{CH_2C{=}O}$, and other $\mathrm{CH_2}$ groups), 2.03–2.18 (*m*, 4 H, $\mathrm{{=}CHC}H_2$), 2.28 (*t*, J = 7.5 Hz, 2 H, $\mathrm{CH_2C{=}O}$), 4.12 (*q*, J = 7.5 Hz, 2 H, $\mathrm{OCH_2}$), 5.30 (*dt*, J = 10.5 Hz, J = 6.9 Hz, 1 H, *Z*- $\mathrm{{=}C\text{-}CH{=}C}H$), 5.63 (*dt*, J = 14.7 Hz, J = 7.2 Hz, 1 H, *E*- $\mathrm{{=}C\text{-}CH{=}C}H$), 5.94 (*dd*, J = 10.8 Hz, J = 10.8 Hz, 1 H, *E*- $\mathrm{{=}C\text{-}C}H\mathrm{{=}CH}$), 6.29 (*dd*, J = 15.0 Hz, J = 10.8 Hz, 1 H, *Z*- $\mathrm{{=}C\text{-}C}H\mathrm{{=}CH}$). ^{1}H NMR spectrum for ethyl linoleate itself ($\mathrm{CDCl_3}$): δ 0.90 (*t*, J = 7.5 Hz, 3 H, $\mathrm{C}H_3\mathrm{CH_2}$), 1.20–1.35 (*m*, 17 H, $\mathrm{OCH_2C}H_3$, and other $\mathrm{CH_2}$ groups), 1.60 (*m*, 2 H, $\mathrm{C}H_2\mathrm{CH_2C{=}O}$), 2.05 (*m*, 4 H, $\mathrm{{=}CHC}H_2$), 2.30 (*t*, J = 7.2 Hz, 2 H, $\mathrm{CH_2C{=}O}$), 2.78 (*t*, J = 6.9 Hz, 2 H, $\mathrm{{=}C\text{-}CH_2\text{-}C{=}}$), 4.14 (*q*, J = 7.2 Hz, 2H, $\mathrm{OCH_2}$), 5.37 (*m*, 4 H, =CH).

Isomerization of linoleic acid by $[RhCl(C_8H_{14})_2]_2$. Linoleic acid was 93% conjugated using the above procedure. ^{1}H NMR spectrum of CLA ($\mathrm{CDCl_3}$): δ 0.89 (*m*, 3 H, $\mathrm{C}H_3\mathrm{CH_2}$), 1.25 (*m*, 16 H, other $\mathrm{CH_2}$ groups), 1.54 (*m*, 2 H, $\mathrm{C}H_2\mathrm{CH_2C{=}O}$), 2.00–2.19 (*m*, 4 H, $\mathrm{{=}CHC}H_2$), 2.28 (*t*, J = 7.5 Hz, 2 H, $\mathrm{CH_2C{=}O}$), 5.30 (*dt*, J = 10.5 Hz, J = 6.9 Hz, 1 H, *Z*- $\mathrm{{=}C\text{-}CH{=}C}H$), 5.67 (*dt*, J = 14.7 Hz, J = 7.2 Hz, 1 H, *E*- $\mathrm{{=}C\text{-}CH{=}C}H$), 5.94 (*dd*, J = 10.8 Hz, J = 10.8 Hz, 1 H, *E*- $\mathrm{{=}C\text{-}C}H\mathrm{{=}CH}$), 6.29 (*dd*, J = 15.0 Hz, J = 10.8 Hz, 1 H, *Z*- $\mathrm{{=}C\text{-}C}H\mathrm{{=}CH}$), 11.50 (*br s*, 1 H, COOH). ^{1}H NMR spectrum of linoleic acid itself ($\mathrm{CDCl_3}$): δ 0.88 (*t*, J = 7.5 Hz, 3 H, $\mathrm{C}H_3\mathrm{CH_2}$), 1.20–1.35 (*m*, 14 H, other $\mathrm{CH_2}$ groups), 1.66 (*m*, 2 H, $\mathrm{C}H_2\mathrm{CH_2C{=}O}$), 2.07 (*q*, J = 5.1 Hz, 4 H, $\mathrm{{=}CHC}H_2$), 2.33 (*t*, J = 7.2 Hz, 2 H, $\mathrm{CH_2C{=}O}$), 2.77 (*t*, J = 6.9 Hz, 2 H, $\mathrm{{=}C\text{-}CH_2\text{-}C{=}}$), 5.36 (*m*, 4 H, =CH), 11.50 (*br s*, 1 H, COOH).

Isomerization of Wesson soybean oil by $[RhCl(C_8H_{14})_2]_2$. The modified soybean oil (100 g) was obtained with >95% conjugation using the above procedure. ^{1}H NMR spectrum of conjugated soybean oil ($\mathrm{CDCl_3}$): δ 0.88 (*m*, 9 H, $\mathrm{CH_3}$), 1.23 (*m*, 55.1 H, other $\mathrm{CH_2}$ groups), 1.58 (*m*, 6 H, $\mathrm{C}H_2\mathrm{CH_2C{=}O}$), 2.05 (*m*, 10 H, $\mathrm{{=}CHC}H_2$), 2.32 (*t*, J = 7.5 Hz, 6 H, $\mathrm{CH_2C{=}O}$), 4.15 (*dd*, J = 12.0 Hz, J = 6.0 Hz, 2 H, $\mathrm{OC}H_a\mathrm{H_bCHC}H_a\mathrm{H_bO}$), 4.31 (*dd*, J = 12.0 Hz, J = 4.5 Hz, 2 H, $\mathrm{OCH_a}H_b\mathrm{CHCH_a}H_b\mathrm{O}$), 5.37 (*m*, 4.2 H, *Z*- $\mathrm{{=}C\text{-}CH{=}C}H$, $\mathrm{OCH_2C}H\mathrm{CH_2O}$, and =CH), 5.56 (*m*, 1.6 H, *E*- $\mathrm{{=}C\text{-}CH{=}C}H$), 5.98 (*dd*, J = 22.5 Hz, J = 13.8 Hz, 1.8 H, *E*- $\mathrm{{=}C\text{-}C}H\mathrm{{=}CH}$), 6.29 (*t*, J = 12.6 Hz, 2 H, *Z*- $\mathrm{{=}C\text{-}C}H\mathrm{{=}CH}$). ^{1}H NMR spectrum of soybean oil itself ($\mathrm{CDCl_3}$): δ 0.89 (*m*, 9 H, $\mathrm{CH_3}$ groups), 1.30 (*m*, 50 H, other $\mathrm{CH_2}$), 1.61 (*m*, 6 H, $\mathrm{C}H_2\mathrm{CH_2C{=}O}$), 2.06 (*m*, 10 H, $\mathrm{{=}CHC}H_2$), 2.31 (*t*, J = 7.5 Hz, 6 H, $\mathrm{CH_2C{=}O}$), 2.77 (*t*, J = 6.0 Hz, 4 H, $\mathrm{{=}C\text{-}CH_2\text{-}C{=}}$), 4.15 (*dd*, J = 12.0 Hz, J = 6.0 Hz, 2 H, $\mathrm{OC}H_a\mathrm{H_b\text{-}CHC}H_a\mathrm{H_bO}$), 4.29 (*dd*, J = 12.0 Hz, J = 4.5 Hz, 2 H, $\mathrm{OCH_a}H_b\mathrm{\text{-}CHCH_a}H_b\mathrm{O}$), 5.35 (*m*, 10 H, $\mathrm{OCH_2C}H\mathrm{CH_2O}$ and =CH).

Isomerization of safflower oil by $[RhCl(C_8H_{14})_2]_2$. Safflower oil with >95% conjugation was obtained using the above procedure. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.88 (*m*, 9 H, $\mathrm{CH_3}$ groups), 1.30 (*m*, 51 H, other $\mathrm{CH_2}$), 1.61 (*m*, 6 H, $\mathrm{C}H_2\mathrm{CH_2C{=}O}$), 2.05 (*m*, 11 H, $\mathrm{{=}CHC}H_2$), 2.31 (*t*, J = 7.5 Hz, 6 H, $\mathrm{CH_2C{=}O}$), 4.14 (*dd*, J = 12.0 Hz, J = 6.0 Hz, 2 H, $\mathrm{OC}H_a\mathrm{H_bCHC}H_a\mathrm{H_bO}$), 4.29 (*dd*, J = 12.0 Hz, J = 4.5 Hz, 2 H, $\mathrm{OCH_a}H_b\mathrm{CHCH_a}H_b\mathrm{O}$), 5.32 (*m*, 4 H, *Z*- $\mathrm{{=}C\text{-}CH{=}C}H$, $\mathrm{OCH_2C}H\mathrm{CH_2O}$, and =CH), 5.65 (*m*, 2 H, *E*- $\mathrm{{=}C\text{-}CH{=}C}H$), 6.00 (*dd*, J = 22.5 Hz, J = 11.7 Hz, 2 H, *E*- $\mathrm{{=}C\text{-}C}H\mathrm{{=}CH}$), 6.29 (*dd*, J = 15.0 Hz, J = 14.4 Hz, 2 H, *Z*- $\mathrm{{=}C\text{-}C}H\mathrm{{=}CH}$). ^{1}H NMR spectrum of safflower oil itself ($\mathrm{CDCl_3}$): δ 0.89 (*m*, 9 H, $\mathrm{CH_3}$ groups), 1.31 (*m*, 47 H, other $\mathrm{CH_2}$), 1.61 (*m*, 6 H, $\mathrm{C}H_2\mathrm{CH_2C{=}O}$), 2.02 (*m*, 11 H, $\mathrm{{=}CHC}H_2$), 2.32 (*t*, J = 7.5 Hz, 6 H, $\mathrm{CH_2C{=}O}$), 2.77 (*t*, J = 6.0 Hz, 4 H, $\mathrm{{=}C\text{-}CH_2\text{-}C{=}}$), 4.14 (*dd*, J = 12.0 Hz, J = 6.0 Hz, 2 H, $\mathrm{OC}H_a\mathrm{H_b\text{-}CHC}H_a\mathrm{H_bO}$), 4.30 (*dd*, J = 12.0 Hz, J = 4.5 Hz, 2 H, $\mathrm{OCH_a}H_b\mathrm{\text{-}CHCH_a}H_b\mathrm{O}$), 5.35 (*m*, 10 H, $\mathrm{OCH_2C}H\mathrm{CH_2O}$ and =CH).

Isomerization of sunflower oil by $[\mathrm{RhCl}(C_8H_{14})_2]_2$. Sunflower oil with 93% conjugation was obtained using the above procedure. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.88 (*m*, 9 H, $\mathrm{CH_3}$ groups), 1.25 (*m*, 55 H, other $\mathrm{CH_2}$), 1.60 (*m*, 6 H, $\mathrm{C}H_2\mathrm{CH_2C{=}O}$), 1.97–2.19 (*m*, 11 H, $\mathrm{{=}CHC}H_2$), 2.31 (*t*, *J* = 7.5 Hz, 6 H, $\mathrm{CH_2C{=}O}$), 4.14 (*dd*, *J* = 12.0 Hz, *J* = 6.0 Hz, 2 H, $\mathrm{OC}H_\mathrm{a}\mathrm{H_bCHC}H_\mathrm{a}\mathrm{H_bO}$), 4.29 (*dd*, *J* = 12.0 Hz, *J* = 4.5 Hz, 2 H, $\mathrm{OCH_a}H_\mathrm{b}\mathrm{CHCH_a}H_\mathrm{b}\mathrm{O}$), 5.30 (*m*, 4.8 H, *Z*- =C-CH=C*H*, $\mathrm{OCH_2C}H\mathrm{CH_2O}$, and =CH), 5.65 (*m*, 2.4 H, *E*- =C-CH=C*H*), 6.02 (*dd*, *J* = 22.5 Hz, *J* = 11.7 Hz, 2.3 *H*, *E*- =C-C*H*=CH), 6.29 (*t*, *J* = 13.8 Hz, 1.8 H, *Z*- =C-C*H*=CH). ^{1}H NMR spectrum of sunflower oil itself ($\mathrm{CDCl_3}$): δ 0.88 (m, 9 H, $\mathrm{CH_3}$ groups), 1.30 (*m*, 51 H, other $\mathrm{CH_2}$), 1.59 (*m*, 6 H, $\mathrm{C}H_2\mathrm{CH_2C{=}O}$), 2.04 (*m*, 11 H, $\mathrm{{=}CHC}H_2$), 2.32 (*t*, *J* = 7.5 Hz, 6 H, $\mathrm{CH_2C{=}O}$), 2.77 (*t*, *J* = 6.0 Hz, 4 H, =C-$\mathrm{CH_2}$-C=), 4.16 (*dd*, *J* = 12.0 Hz, *J* = 6.0 Hz, 2 H, $\mathrm{OC}H_\mathrm{a}\mathrm{H_bCHC}H_\mathrm{a}\mathrm{H_bO}$), 4.31 (*dd*, *J* = 12.0 Hz, *J* = 4.5 Hz, 2 H, $\mathrm{OCH_a}H_\mathrm{b}\mathrm{CHCH_a}H_\mathrm{b}\mathrm{O}$), 5.39 (*m*, 10.3 H, $\mathrm{OCH_2C}H\mathrm{CH_2O}$ and =CH).

Isomerization of walnut oil by $[\mathrm{RhCl}(C_8H_{14})_2]_2$. Walnut oil with >95% conjugation was obtained using the above procedure. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.88 (*m*, 9 H, $\mathrm{CH_3}$ groups), 1.26 (*m*, 55 H, other $\mathrm{CH_2}$ groups), 1.61 (*m*, 6 H, $\mathrm{C}H_2\mathrm{CH_2C{=}O}$), 2.05 (*m*, 11 H, $\mathrm{{=}CHC}H_2$), 2.33 (*t*, *J* = 7.5 Hz, 6 H, $\mathrm{CH_2C{=}O}$), 4.14 (*dd*, *J* = 12.0 Hz, *J* = 6.0 Hz, 2 H, $\mathrm{OC}H_\mathrm{a}\mathrm{H_bCHC}H_\mathrm{a}\mathrm{H_bO}$), 4.31 (*dd*, *J* = 12.0 Hz, *J* = 4.5 Hz, 2 H, $\mathrm{OCH_a}H_\mathrm{b}\mathrm{CHCH_a}H_\mathrm{b}\mathrm{O}$), 5.38 (*m*, 5.6 H, *Z*- =C-CH=C*H*, $\mathrm{OCH_2C}H\mathrm{CH_2O}$, and =CH), 5.66 (*m*, 1.5 H, *E*- =C-CH=C*H*), 6.01 (*t*, *J* = 10.8 Hz, 1.8 H, *E*- =C-C*H*=CH), 6.30 (*t*, *J* = 11.4 Hz, 1.1 H, *Z*- =C-C*H*=CH). ^{1}H NMR spectrum of walnut oil itself ($\mathrm{CDCl_3}$): δ 0.88 (*m*, 9 H, $\mathrm{CH_3}$), 1.36 (*m*, 51 H, other $\mathrm{CH_2}$), 1.59 (*m*, 6 H, $\mathrm{C}H_2\mathrm{CH_2C{=}O}$), 2.04 (*m*, 11 H, $\mathrm{{=}CHC}H_2$), 2.33 (*t*, *J* = 7.5 Hz, 6 H, $\mathrm{CH_2C{=}O}$), 2.81 (*t*, *J* = 6.0 Hz, 4 H, =C-$\mathrm{CH_2}$-C=), 4.17 (*dd*, *J* = 12.0 Hz, *J* = 6.0 Hz, 2 H, $\mathrm{OC}H_\mathrm{a}\mathrm{H_bCHC}H_\mathrm{a}\mathrm{H_bO}$), 4.31 (*dd*, *J* = 12.0 Hz, *J* = 4.5 Hz, 2 H, $\mathrm{OCH_a}H_\mathrm{b}\mathrm{CHCH_a}H_\mathrm{b}\mathrm{O}$), 5.33 (*m*, 10 H, $\mathrm{OCH_2C}H\mathrm{CH_2O}$ and =CH).

Isomerization of corn oil by $[\mathrm{RhCl}(C_8H_{14})_2]_2$. Corn oil with >95% conjugation was obtained using the above procedure. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.88 (*m*, 9H, $\mathrm{CH_3}$ groups), 1.28 (*m*, 56 H, other $\mathrm{CH_2}$), 1.61 (*m*, 6 H, $\mathrm{C}H_2\mathrm{CH_2C{=}O}$), 2.08 (*m*, 11 H, $\mathrm{{=}CHC}H_2$), 2.31 (*t*, *J* = 7.5 Hz, 6 H, $\mathrm{CH_2C{=}O}$), 4.14 (*dd*, *J* = 12.0 Hz, *J* = 6.0 Hz, 2 H, $\mathrm{OC}H_\mathrm{a}\mathrm{H_bCHC}H_\mathrm{a}\mathrm{H_bO}$), 4.31 (*dd*, *J* = 12.0 Hz, *J* = 6.0 Hz, 2 H, $\mathrm{OCH_a}H_\mathrm{b}\mathrm{CHCH_a}H_\mathrm{b}\mathrm{O}$), 5.32 (*m*, 3.7 H, *Z*- =C-CH=C*H*, $\mathrm{OCH_2C}H\mathrm{CH_2O}$, and =CH), 5.63 (*m*, 1.6 H, *E*- =C-CH=C*H*), 6.01 (*dd*, *J* = 19.5 Hz, *J* = 11.4 Hz, 1.9 H, *E*- =C-C*H*=CH), 6.27 (*t*, *J* = 12.6 Hz, 1.2 H, *Z*- =C-C*H*=CH). ^{1}H NMR spectrum of corn oil itself ($\mathrm{CDCl_3}$): δ 0.88 (*m*, 9 H, $\mathrm{CH_3}$ groups), 1.31 (*m*, 51 H, other $\mathrm{CH_2}$), 1.58 (*m*, 6 H, $\mathrm{C}H_2\mathrm{CH_2C{=}O}$), 2.04 (*m*, 11 H, $\mathrm{{=}CHC}H_2$), 2.32 (*t*, *J* = 7.5 Hz, 6 H, $\mathrm{CH_2C{=}O}$), 2.77 (*t*, *J* = 6.0 Hz, 3.4 H, =C-$\mathrm{CH_2}$-C=), 4.16 (*dd*, *J* = 12.0 Hz, *J* = 6.0 Hz, 2 H, $\mathrm{OC}H_\mathrm{a}\mathrm{H_bCHC}H_\mathrm{a}\mathrm{H_bO}$), 4.31 (*dd*, *J* = 12.0 Hz, *J* = 4.5 Hz, 2 H, $\mathrm{OCH_a}H_\mathrm{b}\mathrm{CHCH_a}H_\mathrm{b}\mathrm{O}$), 5.35 (*m*, 10 H, $\mathrm{OCH_2C}H\mathrm{CH_2O}$ and =CH).

Isomerization of sesame oil by $[\mathrm{RhCl}(C_8H_{14})_2]_2$. Sesame oil with 92% conjugation was obtained using the above procedure. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.89 (*m*, 9 H, $\mathrm{CH_3}$ groups), 1.25 (*m*, 56.4 H, other $\mathrm{CH_2}$ groups), 1.65 (*m*, 6 H, $\mathrm{C}H_2\mathrm{CH_2C{=}O}$), 2.04 (*m*, 11 H, $\mathrm{{=}CHC}H_2$), 2.31 (*t*, *J* = 7.5 Hz, 6 H, $\mathrm{CH_2C{=}O}$), 4.15 (*dd*, *J* = 12.0 Hz, *J* = 6.0 Hz, 2 H, $\mathrm{OC}H_\mathrm{a}\mathrm{H_bCHC}H_\mathrm{a}\mathrm{H_bO}$), 4.31 (*dd*, *J* = 12.0 Hz, *J* = 4.5 Hz, 2 H, $\mathrm{OCH_a}H_\mathrm{b}\mathrm{CHCH_a}H_\mathrm{b}\mathrm{O}$), 5.36 (*m*, 6 H, *Z*- =C-CH=CH, $\mathrm{OCH_2C}H\mathrm{CH_2O}$, and =CH), 5.65 (*m*, 1 H, *E*- =C-CH=C*H*), 5.98 (*t*, *J* = 14.2 Hz, 1.2 H, *E*- =C-C*H*=CH), 6.29 (*t*, *J* = 14.4 Hz, 0.4 H, *Z*- =C-C*H*=CH). ^{1}H NMR spectrum of sesame oil itself ($\mathrm{CDCl_3}$): δ 0.89 (*m*, 9 H, $\mathrm{CH_3}$), 1.26 (*m*, 52 H, other $\mathrm{CH_2}$), 1.66 (*m*, 6 H, $\mathrm{C}H_2\mathrm{CH_2C{=}O}$), 2.04 (*m*, 11 H, $\mathrm{{=}CHC}H_2$), 2.31 (*t*, *J* = 7.5 Hz, 6 H, $\mathrm{CH_2C{=}O}$), 2.79 (*t*, *J* = 6.0 Hz, 3 H, =C-$\mathrm{CH_2}$-C=), 4.15 (*dd*, *J* = 12.0 Hz, *J* = 6.0 Hz, 2 H, $\mathrm{OC}H_\mathrm{a}\mathrm{H_bCHC}H_\mathrm{a}\mathrm{H_bO}$), 4.31 (*dd*, *J* = 12.0 Hz, *J* = 4.5 Hz, 2 H, $\mathrm{OCH_a}H_\mathrm{b}\mathrm{CHCH_a}H_\mathrm{b}\mathrm{O}$), 5.35 (*m*, 10 H, $\mathrm{OCH_2C}H\mathrm{CH_2O}$ and =CH).

Isomerization of peanut oil by $[\mathrm{RhCl}(C_8H_{14})_2]_2$. Peanut oil with 88% conjugation was obtained using the above procedure. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.88 (*m*, 9 H, $\mathrm{CH_3}$), 1.25 (*m*, 62 H, other $\mathrm{CH_2}$), 1.61 (*m*, 6 H, $\mathrm{C}H_2\mathrm{CH_2C{=}O}$), 1.96 (*m*, 12 H, $\mathrm{{=}CHC}H_2$), 2.31 (*t*, *J* = 7.5 Hz, 6 H, $\mathrm{CH_2C{=}O}$), 4.15 (*dd*, *J* = 12.0 Hz, *J* = 6.0 Hz, 2 H, $\mathrm{OC}H_\mathrm{a}\mathrm{H_bCHC}H_\mathrm{a}\mathrm{H_bO}$), 4.31 (*dd*, *J* = 12.0 Hz, *J* = 4.5 Hz, 2 H, $\mathrm{OCH_a}H_\mathrm{b}\mathrm{CHCH_a}H_\mathrm{b}\mathrm{O}$), 5.34 (*m*, 5.2 H, *Z*- =C-CH=CH, $\mathrm{OCH_2C}H\mathrm{CH_2O}$, and =CH), 5.62 (*m*, 1.2 H, *E*- =C-CH=C*H*), 6.02 (*m*, 1.6 H, *E*- =C-C*H*=CH), 6.29 (*m*, 0.7 H, *Z*- =C-C*H*=CH). ^{1}H NMR spectrum of peanut oil itself ($\mathrm{CDCl_3}$): δ 0.88 (*m*, 9 H, $\mathrm{CH_3}$), 28 (*m*, 60 H, other $\mathrm{CH_2}$), 1.61 (*m*, 6 H, $\mathrm{C}H_2\mathrm{CH_2C{=}O}$), 2.00 (*m*, 12 H, $\mathrm{{=}CHCH_2}$), 2.31 (*t*, *J* = 7.5 Hz, 6 H, $\mathrm{CH_2C{=}O}$), 2.82 (*t*, *J* = 6.0 Hz, 1.7 H, = C-$\mathrm{CH_2}$-C=), 4.15 (*dd*, *J* = 12.0 Hz, *J* = 6.0 Hz, 2 H, $\mathrm{OC}H_\mathrm{a}\mathrm{H_bCHC}H_\mathrm{a}\mathrm{H_bO}$), 4.31 (*dd*, *J* = 12.0 Hz, *J* = 4.5 Hz, 2 H, $\mathrm{OCH_a}H_\mathrm{b}\mathrm{CHCH_a}H_\mathrm{b}\mathrm{O}$), 5.34 (*m*, 9 H, $\mathrm{OCH_2C}H\mathrm{CH_2O}$ and =CH).

Isomerization of Wesson soybean oil by $\mathrm{RuHCl(CO)(PPh_3)_3}$. To a solution of 1.5 g (1.7 mmol) of Wesson soybean oil in 5 mL of benzene was added 0.5 mol% (25 mg) $\mathrm{RuHCl(CO)(PPh_3)_3}$ under an argon atmosphere. The resulting light yellow solution was stirred at 60°C for 24 h. After removal of the solvent on a rotary evaporator, the ^{1}H NMR spectrum of the residue indicated >95% conversion to the conjugated oil.

Isomerization of Wesson soybean oil by $\mathrm{PtCl_2(PPh_3)_2/SnCl_2{\cdot}2H_2O}$ *under a hydrogen atmosphere.* To 1.5 g (1.7 mmol) of Wesson soybean oil in 5 mL of benzene was added 0.25 mol% (5.1 mg) $\mathrm{PtCl_2(PPh_3)_2}$ and 2.5 mol% (13 mg) of $\mathrm{SnCl_2{\cdot}2H_2O}$ under a hydrogen atmosphere. The resulting light yellow solution was stirred at 100°C for 24 h under 1 atm of hydrogen. The ^{1}H NMR spectrum of the residue indicated 88% conversion to the conjugated oil.

RESULTS AND DISCUSSION

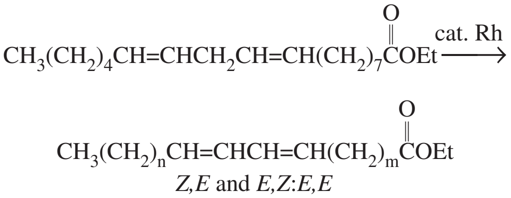
Rhodium-catalyzed isomerization of ethyl linoleate. We began our studies using rhodium catalysts with a simple model for soybean oil, ethyl linoleate (Eq. 1). Three mol% $\mathrm{RhCl_3{\cdot}3H_2O}$ was first employed in the presence of EtOH as a solvent. Only a trace amount of conjugated product was obtained (Table 1, entry 1). Adding the Lewis acid $\mathrm{SnCl_2{\cdot}2H_2O}$ improved the yield to 48% (Table 1, entry 2). The next catalyst employed was $[\mathrm{RhCl(C_2H_4)_2}]_2$. The highest yield ob-

TABLE 1
Isomerization of Ethyl Linoleate (0.5 mmol scale)[a]

Entry	Catalyst (mol%)	Additive(s) (mol%)	Temp. (°C)	Solvent	Yield (%)	*Z,E* or *E,Z/E,E*
1	$RhCl_3·2H_2O$ (3)	None	80	EtOH	3	—
2	$RhCl_3·2H_2O$ (3)	$SnCl_2·2H_2O$ (12)	80	EtOH	48	84:16
3	$[Rh(C_2H_4)_2Cl]_2$ (1.5)	None	80	EtOH	18	38:62
4	$[Rh(C_2H_4)_2Cl]_2$ (1.5)	$SnCl_2·2H_2O$ (12)	80	EtOH	48	62:38
5	$[Rh(C_2H_4)_2Cl]_2$ (1.5)	$SnCl_2·2H_2O$ (12) + PPh_3 (6)	80	EtOH	57	36:63
6	$RhCl(PPh_3)_3$ (3)	$SnCl_2·2H_2O$ (12)	60	EtOH	93	95:5
7	$RhCl(PPh_3)_3$ (3)	$SnCl_2·2H_2O$ (12)	80	EtOH	94	70:30
8	$RhCl(PPh_3)_3$ (3)	$SnCl_2·2H_2O$ (12)	100	EtOH	93	67:33
9	$RhCl(PPh_3)_3$ (3)	$SnCl_2·2H_2O$ (12)	120	EtOH	85	60:40
10	$RhCl(PPh_3)_3$ (3)	$SnCl_2·2H_2O$ (12)	60	Toluene	95	91:9
11	$RhCl(PPh_3)_3$ (3)	$SnCl_2·2H_2O$ (12)	60	MeOH	79	88:12
12	$RhCl(PPh_3)_3$ (3)	$SnCl_2·2H_2O$ (12)	60	95% EtOH	94	75:25
13	$RhCl(PPh_3)_3$ (3)	$SnCl_2·2H_2O$ (9)	60	EtOH	94	92:8
14	$RhCl(PPh_3)_3$ (3)	$SnCl_2·2H_2O$ (7.5)	60	EtOH	93	91:9
15	$RhCl(PPh_3)_3$ (3)	$SnCl_2·2H_2O$ (6)	60	EtOH	91	91:9
16	$RhCl(PPh_3)_3$ (3)	$SnCl_2·2H_2O$ (3)	60	EtOH	72	93:7
17	$RhCl(PPh_3)_3$ (1)	$SnCl_2·2H_2O$ (2.5)	60	EtOH	93	92:8
18	$RhCl(PPh_3)_3$ (1)	$SnCl_2·2H_2O$ (2.5)	60	95% EtOH	93	75:25
19	$RhCl(PPh_3)_3$ (0.5)	$SnCl_2·2H_2O$ (1.25)	60	EtOH	85	94:6
20	$RhCl(PPh_3)_3$ (0.5)	$SnCl_2·2H_2O$ (1.25)	60	95% EtOH	55	77:23
21	$RhCl(PPh_3)_3$ (0.25)	$SnCl_2·2H_2O$ (0.67)	60	EtOH	45	92:8
22	$RhCl(PPh_3)_3$ (0.25)	$SnCl_2·2H_2O$ (0.67)	80	EtOH	51	88:12
23	$[RhCl(C_8H_{14})_2]_2$ (0.5)	$SnCl_2·2H_2O$ (4) + PPh_3 (2)	60	EtOH	88	92:8
24	$[RhCl(C_8H_{14})_2]_2$ (0.5)	$SnCl_2·2H_2O$ (4) + $(p\text{-}FC_6H_4)_3P$ (2)	60	EtOH	85	94:6
25	$[RhCl(C_8H_{14})_2]_2$ (0.5)	$SnCl_2·2H_2O$ (4) + $(p\text{-}CH_3OC_6H_4)_3P$ (2)	60	EtOH	90	94:6
26	$[RhCl(C_8H_{14})_2]_2$ (0.5)	$SnCl_2·2H_2O$ (4) + $(o\text{-}CH_3C_6H_4)_3P$ (2)	60	EtOH	92	95:5
27	$[RhCl(C_8H_{14})_2]_2$ (0.5)	$SnCl_2·2H_2O$ (4) + $(p\text{-}CH_3C_6H_4)_3P$ (2)	60	EtOH	97	95:5
28	$[RhCl(C_8H_{14})_2]_2$ (0.25)	$SnCl_2·2H_2O$ (2) + $(p\text{-}CH_3C_6H_4)_3P$ (1)	60	EtOH	97	90:10
29	$[RhCl(C_8H_{14})_2]_2$ (0.1)	$SnCl_2·2H_2O$ (0.8) + $(p\text{-}CH_3C_6H_4)_3P$ (0.4)	60	EtOH	95	92:8
30	$[RhCl(C_8H_{14})_2]_2$ (0.05)	$SnCl_2·2H_2O$ (0.4) + $(p\text{-}CH_3C_6H_4)_3P$ (0.2)	60	EtOH	68	93:7
31	$[RhCl(C_8H_{14})_2]_2$ (0.05)	$SnCl_2·2H_2O$ (0.4) + $(p\text{-}CH_3C_6H_4)_3P$ (0.2)	60	EtOH	65	82:18

[a] Reactions were run under argon for 24 h with 2.0 mmol of methyl linoleate and 4 mL of solvent.

served was 57% using 3 mol% $[RhCl(C_2H_4)_2]_2$, 12 mol% $SnCl_2·2H_2O$, and 6 mol% PPh_3 (Table 1, entry 5). The conjugated product consisted of a mixture of *Z,E-*, *E,Z-*, and *E,E-*stereoisomers.



$$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7\overset{O}{\overset{\|}{C}}OEt \xrightarrow{\text{cat. Rh}} \qquad [1]$$

$$CH_3(CH_2)_nCH{=}CHCH{=}CH(CH_2)_m\overset{O}{\overset{\|}{C}}OEt$$

Z,E and *E,Z*:*E,E*

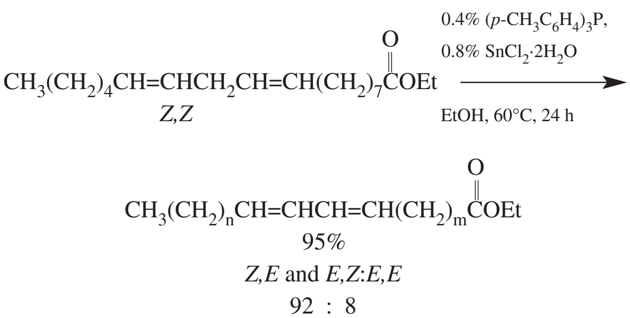
Since these catalysts afforded only moderate yields of conjugated product, another rhodium complex, $RhCl(PPh_3)_3$, was examined. This catalyst was found to be much more effective; 3 mol% $RhCl(PPh_3)_3$ provided conjugated products in 93% yield at only 60°C (Table 1, entry 6). To further improve the reaction conditions, variation of the temperature (Table 1, entries 7–9), solvent (Table 1, entries 10–12), and amount of $SnCl_2·2H_2O$ (Table 1, entries 13–16) were examined. While several procedures gave essentially identical results, the procedure described in Table 1, entry 14, is perhaps the most appealing, since it employs less tin reagent and an environmentally more attractive solvent, ethanol. The major difference between this method and Singer's is the use of solvent (7–9). In the presence of EtOH, the reaction proceeds at a much lower temperature (60 vs. 120–150°C), gives increased conjugation, and fails to generate hydrogenated products.

The amount of $RhCl(PPh_3)_3$ needed to effect conjugation was then examined. One mol% of $RhCl(PPh_3)_3$ still provided excellent results (Table 1, entries 17 and 18), and 0.5 mol% $RhCl(PPh_3)_3$ gave only a slightly lower yield (Table 1, entry

19). However, the yield dropped to only 45% when the amount of the catalyst was further reduced to 0.25 mol% (Table 1, entry 21).

The rhodium complex $[RhCl(C_8H_{14})_2]_2$ (C_8H_{14} = cyclooctene) was found to be an even more effective catalyst than $RhCl(PPh_3)_3$, when combined with $SnCl_2{\cdot}2H_2O$ and an appropriate phosphine ligand. Several phosphine ligands have been examined, and tri-*p*-tolylphosphine has proven most effective (Table 1, entry 27). As little as 0.1 mol% of $[RhCl(C_8H_{14})_2]_2$ (0.2 mol% Rh) provided conjugated products in 95% yield (Table 1, entry 29).

As a result of these studies, the following optimal procedure was developed for the isomerization of ethyl linoleate: 0.1 mol% $[RhCl(C_8H_{14})_2]_2$, 0.4 mol% $(p\text{-}CH_3C_6H_4)_3P$, 0.8 mol% $SnCl_2{\cdot}2H_2O$ in EtOH at 60°C (Eq. 2). The concentration of ethyl linoleate is 0.5 mmol/mL of solvent.



$$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7\overset{O}{\overset{\|}{C}}OEt \xrightarrow[\text{EtOH, 60°C, 24 h}]{\substack{0.1\%\ [RhCl(C_8H_{14})_2]_2,\\ 0.4\%\ (p\text{-}CH_3C_6H_4)_3P,\\ 0.8\%\ SnCl_2\cdot 2H_2O}} \quad [2]$$

$$\underset{Z,Z}{}$$

$$\underset{\substack{95\%\\ Z,E \text{ and } E,Z{:}E,E\\ 92\ :\ 8}}{CH_3(CH_2)_nCH{=}CHCH{=}CH(CH_2)_m\overset{O}{\overset{\|}{C}}OEt}$$

The stereochemistry of the conjugated isomers is noteworthy. Usually, the proportion of the *E,E*-isomer increases as the temperature increases. At the same temperature, $[RhCl(C_8H_{14})_2]_2$ and $RhCl(PPh_3)_3$ give much higher ratios of the *Z,E*- and *E,Z*-isomers to the *E,E*-isomer than $[RhCl(C_2H_4)_2]_2$ or $RhCl_3{\cdot}3H_2O$. The stereochemistry is also affected by the solvents when the $RhCl(PPh_3)_3$ catalyst is used. Much more *E,E*-isomer was obtained when 95% EtOH was used as the solvent (Table 1, entries 18 and 20).

Some of the reaction conditions in Table 1 were applied to the isomerization of ethyl linoleate on a larger scale (Table 2). In general, results similar to those on the smaller scale were obtained. Once again, the reaction conditions shown in Equation 2 provided the highest yield (Table 2, entry 4).

CLA was also obtained from linoleic acid in high yield (93%) under our optimal procedure. This appears to be a particularly attractive route to the commercial nutrient.

Isomerization of Wesson soybean oil by $[RhCl(C_8H_{14})_2]_2$/(p-$CH_3C_6H_4)_3P/SnCl_2{\cdot}2H_2O$. The isomerization of Wesson soybean oil was examined using our optimal procedure. A 100-g sample of soybean oil gave >95% conjugation (Eq. 3). A complete study of the drying properties of this conjugated oil will be reported elsewhere later.

$$\substack{\text{Soybean oil,}\\ \text{100 g}} \xrightarrow[\text{EtOH, 60°C, 24 h}]{\substack{0.1\%\ [RhCl(C_8H_{14})_2]_2,\\ 0.4\%\ (p\text{-}CH_3C_6H_4)_3P,\\ 0.8\%\ SnCl_2\cdot 2H_2O}} \text{>95\% conjugation} \qquad [3]$$

Conjugation of other vegetable oils. The $[RhCl(C_8H_{14})_2]_2$/$(p\text{-}CH_3C_6H_4)_3P/SnCl_2{\cdot}2H_2O$ system was employed in the isomerization of other vegetable oils that have a high linoleic acid content (Table 3). Other oils, such as corn oil, sunflower oil and safflower oil, provided high yields of conjugated products.

Isomerization of soybean oil by $PtCl_2(PPh_3)_2/SnCl_2{\cdot}2H_2O$ under a hydrogen atmosphere. An 89% conversion to conjugated soybean oil was obtained upon reaction of soybean oil with 0.25 mol% $PtCl_2(PPh_3)_2$ and 2.5 mol% $SnCl_2{\cdot}2H_2O$ under 1 atm of H_2 for 24 h at 100°C (Table 4, entry 3). Lowering the catalyst concentrations to 0.1 mol% $PtCl_2(PPh_3)_2$ and 1.0 mol% $SnCl_2{\cdot}2H_2O$ resulted in a significantly lower yield of 28% (Table 4, entry 2). Despite the utilization of a hydrogen atmosphere, no hydrogenation products were detected. Previous studies using this reaction system have shown that only olefin isomerization occurs when the reaction is carried out under a low pressure of hydrogen (17).

An advantage of this system is that no solvent is required. Surprisingly, the utilization of solvents, such as ethanol, methylene chloride or benzene, failed to produce any conjugated soybean oil with this platinum system, although the reactions were run at somewhat lower temperatures. One possible explanation is that the solvents used contained sufficient water to kill the catalyst, which is known to be water-sensitive (17), or the reaction may just be very sensitive to the temperature at which it is run. A disadvantage of this catalyst is the slightly higher temperature of 100°C needed for conjugation. When the reaction was carried out at 80°C with no sol-

TABLE 2
Isomerization of Ethyl Linoleate (larger scale)[a]

Entry	Catalyst (mol%)	Additive(s) (mol%)	Scale (mmol)	Yield (%)	*Z,E* or *E,Z/E,E*
1	$RhCl(PPh_3)_3$ (0.5)	$SnCl_2{\cdot}2H_2O$ (1.25)	60	85	95:5
2	$RhCl(PPh_3)_3$ (0.5)	$SnCl_2{\cdot}2H_2O$ (1.25)	80	88	70:30
3	$[RhCl(C_8H_{14})_2]_2$ (0.25)	$SnCl_2{\cdot}2H_2O$ (2) + $(p\text{-}CH_3C_6H_4)_3P$ (1)	60	94	92:8
4	$[RhCl(C_8H_{14})_2]_2$ (0.1)	$SnCl_2{\cdot}2H_2O$ (0.8) + $(p\text{-}CH_3C_6H_4)_3P$ (0.4)	60	96	94:6
5	$[RhCl(C_8H_{14})_2]_2$ (0.05)	$SnCl_2{\cdot}2H_2O$ (0.4) + $(p\text{-}CH_3C_6H_4)_3P$ (0.2)	60	65	94:6

[a] All reactions were run under argon at 60°C for 24 h in ethanol (2 mL/g of ethyl linoleate).

TABLE 3
Isomerization of Vegetable Oils with $[RhCl(C_8H_{14})_2]_2$[a]

Vegetable oil	Linoleic acid (%)	Polyunsaturated (%)	Monounsaturated (%)	Saturated (%)	Conjugation (%)
Soybean	54	63	22	15	>95
Safflower	78	78	13	9	>95
Sunflower	75	75	14	11	93
Walnut	64	64	22	14	>95
Corn	59	60	27	13	>95
Sesame	43	43	43	14	92
Peanut	31	31	51	18	88

[a] All reactions were run under argon at 60°C for 24 h in EtOH (5 mL per 1.5 g of oil) using 0.1 mol% $[RhCl(C_8H_{14})_2]_2$, 0.4 mol% $(p\text{-}CH_3C_6H_4)_3P$, and 0.8 mol% $SnCl_2 \cdot 2H_2O$.

TABLE 4
Isomerization of Soybean Oil[a,b]

Entry	Catalyst (mol%)	Additive(s) (mol%)	Solvent	Temp. (°C)	Yield (%)
1	$[RhCl(C_8H_{14})_2]_2$ (0.1)	$(p\text{-}CH_3C_6H_4)_3P$ (0.4) $SnCl_2 \cdot 2H_2O$ (0.8)	EtOH	60	>95
2	$PtCl_2(PPh_3)_2$ (0.1)	$SnCl_2 \cdot 2H_2O$ (1)	None	100	28
3	$PtCl_2(PPh_3)_2$ (0.25)	$SnCl_2 \cdot 2H_2O$ (2.5)	None	100	89
4	$PtCl_2(PPh_3)_2$ (0.5)	$SnCl_2 \cdot 2H_2O$ (5)	None	100	89
5	$PtCl_2(PPh_3)_2$ (1)	$SnCl_2 \cdot 2H_2O$ (10)	None	100	86
6	$PtCl_2(PPh_3)_2$ (1)	$SnCl_2 \cdot 2H_2O$ (10)	EtOH	60	0
7	$PtCl_2(PPh_3)_2$ (1)	$SnCl_2 \cdot 2H_2O$ (10)	CH_2Cl_2	40	0
8	$PtCl_2(PPh_3)_2$ (1)	$SnCl_2 \cdot 2H_2O$ (10)	None	60	0
9	$PtCl_2(PPh_3)_2$ (1)	$SnCl_2 \cdot 2H_2O$ (10)	None	80	0
10	$RuHCl(CO)(PPh_3)_3$ (0.1)	None	Benzene	60	42
11	$RuHCl(CO)(PPh_3)_3$ (0.25)	None	Benzene	60	65
12	$RuHCl(CO)(PPh_3)_3$ (0.5)	None	Benzene	60	88
13	$RuHCl(CO)(PPh_3)_3$ (1)	None	Benzene	60	95
14	$RuHCl(CO)(PPh_3)_3$ (1)	None	EtOH	60	51
15	$RuHCl(CO)(PPh_3)_3$ (1)	None	None	60	40

[a] All reactions were under an argon atmosphere except entries 2–9 where a hydrogen atmosphere was employed.
[b] If a solvent was used, 5 mL of the solvent was used per 1.5 g of soybean oil.

vent, no conjugated product was observed. The absence of conjugation is believed to be due to the low solubility of the catalyst at this temperature.

Isomerization of soybean oil by $RuHCl(CO)(PPh_3)_3$. A known olefin isomerization catalyst, $RuHCl(CO)(PPh_3)_3$ (18), was also found to be effective for the isomerization of soybean oil. Nearly quantitative conversion to conjugated soybean oil was obtained using 1 mol% $RuHCl(CO)(PPh_3)_3$ in benzene at 60°C for 24 h (Table 4, entry 13). The yield dropped only slightly to 88% when 0.5 mol% of the ruthenium catalyst was used (Table 4, entry 12). Lowering the amount of ruthenium further to 0.25 mol% resulted in a further drop in yield to 65% (Table 4, entry 11).

Although more metal catalyst is required compared to the $[RhCl(C_8H_{14})_2]_2/(p\text{-}CH_3C_6H_4)_3P/SnCl_2 \cdot 2H_2O$ and $PtCl_2(PPh_3)_2/SnCl_2 \cdot 2H_2O$ catalysts, one advantage of the Ru system is the lower cost of ruthenium compared to rhodium and platinum. Another advantage is that $SnCl_2 \cdot 2H_2O$ is not required. One disadvantage is the need to employ benzene as the solvent to dissolve the catalyst. Significantly lower yields were obtained using ethanol or no solvent (Table 4, entries 14 and 15), probably due to the low solubility of the catalyst under these conditions. Krompiec *et al.* (12) reported that the use of 0.05 mol% $RuHCl(CO)(PPh_3)_3$ without any solvent produced 54% conjugated product, but much higher temperatures (212–226°C) were required.

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