J. Org. Chem. **1996,** *61,* 7784−7792

Iron Carbonyl-Promoted Isomerization of Olefin Esters to Their α,*β*-Unsaturated Esters: Methyl Oleate and Other Examples

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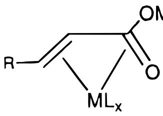
Received July 22, 1996⊗

Ultraviolet photolysis of stoichiometric amounts of methyl oleate and $Fe(CO)_5$ in hexanes solvent at 0 °C gives $Fe(CO)_3(\eta^4$-α,*β*-ester) in which the α,*β*-unsaturated ester isomer of methyl oleate is stabilized by η^4-oxadiene π coordination of the olefin and ester carbonyl groups to the $Fe(CO)_3$ unit. Treatment of the $Fe(CO)_3(\eta^4$-α,*β*-ester) with pyridine or CO liberates the free α,*β*-ester, methyl octadec-*trans*-2-enoate, in 70% yield. The $Fe(CO)_3$ unit both catalyzes the olefin isomerization and stabilizes the α,*β*-unsaturated ester, which results in the formation of the α,*β*-ester in a yield far above that (3.5%) observed for simple catalyzed methyl oleate isomerization. The much smaller olefin esters, methyl 3-butenoate and ethyl 4-methyl-4-pentenoate, are isomerized under the same conditions to their α,*β*-unsaturated esters in 94 and 90% yields, respectively. The effects of reaction conditions on the yield, the use of $Fe(CO)_3$(*cis*-cyclooctene)$_2$ as a nonphotolytic catalyst, and the mechanism of this useful synthetic process are discussed.

Introduction

The isomerization of olefins is catalyzed by a variety of agents including bases,[1] acids,[2] and a plethora of transition metal complexes.[2,3] These catalysts yield a thermodynamic mixture of isomeric olefins if the isomerizations are allowed to proceed to equilibrium. Non-thermodynamic distributions of products are obtained if equilibrium is not achieved, but it is rare[4] that olefin isomerization leads to high yields of one isomer unless it is highly favored thermodynamically. In the present study, we sought to develop a catalyst that would promote olefin isomerization of a mono-ene ester and drive this isomerization specifically to the α,*β*-unsaturated ester by coordinating this isomer as the oxadiene η^4 π complex **A**.



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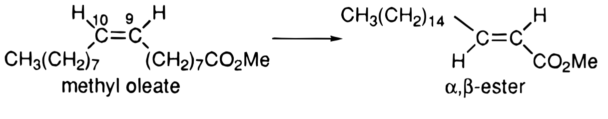
As there is considerable commercial interest in transformations of esters of oleic acid,[5−7] we sought to perform the isomerization in eq 1. This is a particularly challenging isomerization because of the many olefin isomers that are possible within the 17-carbon hydrocarbon chain; none of these isomers is highly favored thermodynamically. Any method that would promote the isomerization in eq 1 could presumably be used for the isomerization of other mono-ene esters to α,*β*-unsaturated esters; these reactive products would be useful intermediates for the synthesis of other new compounds. A few reactions of the α,*β*-ester (eq 1), prepared by more elaborate methods,[8,9] have been reported.[9,10]



(1)

Iron carbonyls have been used extensively as catalysts for the isomerization of olefins.[3c] For example, 1-pentene isomerizes to give an equilibrium mixture of *cis*-2-pentene (21%) and *trans*-2-pentene (76%) in the presence of $Fe(CO)_5$ in C_6H_6 solvent under ultraviolet photolysis.[11] The same product distribution is obtained when $Fe(CO)_3$(*cis*-cyclooctene)$_2$ catalyzes 1-pentene isomerization without photolysis.[12] A mixture of isomers is obtained from the $Fe_3(CO)_{12}$-catalyzed isomerizations of *n*-hexenes, *n*-pentenes, and methyl-1-pentenes under reflux.[13] Similarly, $Fe(CO)_5$ catalyzes the isomerization of *n*-alkenyl and cyclohexenyl carboxylate esters and ethers to a mixture of isomers when refluxed (125−150 °C) in hydrocarbon solvents or photolyzed at 20 °C.[14] Methyl oleate itself has been reported to give a very complex mixture of olefin isomers when heated at 185 °C with $Fe(CO)_5$;[15] in this mixture the amount of the α,*β*-ester isomer (eq 1) was too small to be detected.

Not only do the iron carbonyls catalyze olefin isomerization but also there is evidence that under the proper conditions they might weakly stabilize the α,*β*-ester isomer (eq 1) by coordinating it as an η^4-oxadiene to

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⊗ Abstract published in *Advance ACS Abstracts,* October 15, 1996.

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S0022-3263(96)01371-0 CCC: $12.00

$Fe(CO)_3$ as in **A**. Isolable $Fe(CO)_3$ complexes of η^4 α,β-unsaturated aldehydes ($RCH{=}CHC({=}O)H$), ketones ($RCH{=}CHC({=}O)R'$), and imines ($RCH{=}CHC({=}NR')H$) are well known.[16,17,18] The olefin esters, η^4 methyl acrylate and methyl *trans*-crotonate, also form η^4 complexes, $Fe(CO)_3(\eta^4\text{-}H_2C{=}CHCO_2Me)$ and $Fe(CO)_3(\eta^4\text{-}CH_3CH{=}CHCO_2Me)$, that have been detected in ultraviolet-irradiated, low-temperature matrices (10−12 K) containing $Fe(CO)_5$ and the α,β-unsaturated esters.[19] Even at −5 °C, $Fe(CO)_3(\eta^4\text{-}H_2C{=}CHCO_2Me)$ has been observed in *n*-hexane where it is in equilibrium with $Fe(CO)_3(\eta^2\text{-}H_2C{=}CHCO_2Me)_2$, whose concentration depends on the concentrations of the complex and added methyl acrylate.[20,21] These studies suggest that it may be possible to stabilize the α,β-ester isomer of methyl oleate by η^4 coordination to $Fe(CO)_3$ if the complex (of type **A**) is produced at relatively low temperatures. This, of course, means that $Fe(CO)_5$ must catalyze the isomerization at low temperature and that the inexpensive $Fe(CO)_5$ be used in stoichiometric amount so as to capture the α,β-ester as its η^4 complex.

In this paper, we show that $Fe(CO)_5$ under UV photolysis at 0 °C promotes the reaction in eq 1 by isomerizing methyl oleate to the α,β-ester isomer that is trapped as its η^4 complex, $Fe(CO)_3(\eta^4\text{-}\alpha,\beta\text{-ester})$. The α,β-ester is removed from this complex by reaction with more strongly coordinating ligands (CO or pyridine). This method also converts methyl 3-butenoate and ethyl 4-methyl-4-pentenoate to their α,β-unsaturated ester isomers in high yields.

Experimental Section

All reactions were performed under a nitrogen atmosphere in reagent-grade solvents using standard Schlenk techniques. Hexanes and toluene were distilled under N_2 from CaH_2; tetrahydrofuran (THF) was distilled from Na/benzophenone. Silica gel (Davisil 62; 150 mesh, 58 Å) was purchased from Davison Chemical. $Fe(CO)_5$ was purchased from Aldrich and used immediately after purification by bulb-to-bulb distillation. Methyl oleate (99%), methyl palmitate (99%), ethyl 4-methyl-4-pentenoate (98%), methyl *trans*-crotonate (98%), methyl 3-butenoate (97%), pyridine, *cis*-cyclooctene (99%), and $Fe_2(CO)_9$ (98%) were purchased from Aldrich and used without further purification.

The photochemical reactions were performed in a quartz tube equipped with a nitrogen bubbler using a 450-W Hanovia high-pressure mercury UV lamp (Ace, cat. no. 7825-34). The temperatures (−35 to +20 °C) of the photochemical reaction solutions were maintained by a Lauda RK 20 constant temperature circulator. Infrared spectra were obtained on a Nicolet 710 FTIR spectrophotometer using a solution cell with NaCl salt plates (0.2 mm). A Varian 3400 GC interfaced to a Finnigan TSG 700 high-resolution magnetic sector mass spectrometer with electron ionization (70 eV) was used for all GC−MS measurements. Gas chromatographic analyses were performed with a temperature-programmed Varian 3400 GC using a 25 m HP-1 (cross-linked methylsilicone gum phase) capillary column (OV-101) with a flame ionization detector. Internal standards of reactants or products were used in representative reactions to determine product yields, which are reproducible within ±3%. For analyses of methyl oleate and its isomers, the GC column temperature was held at 120 °C for 1 min, followed by a 50 °C/min ramp to 200 °C. After a 1 min hold, a final ramp (2 °C/min) to 220 °C was used. For analyses of ethyl 4-methyl-4-pentenoate and its isomers, the column temperature was held at 50 °C for 5 min, followed by a 20 °C/min ramp to 150 °C. The ^1H NMR spectra were recorded on a Nicolet NT-300 spectrometer using a deuteriated solvent as the internal lock and internal reference ($CDCl_3$: δ 7.25 ppm; C_6D_6: δ 7.16 ppm for ^1H).

Irradiation (UV) of $Fe(CO)_5$ and Methyl *trans*-Crotonate. A solution of methyl *trans*-crotonate (28 μL, 0.27 mmol) and $Fe(CO)_5$ (35 μL, 0.27 mmol) in hexanes (20mL) was allowed to come to temperature equilibrium at 0 °C for 30 min. Irradiation (UV) of the slightly yellow solution with a continuous nitrogen flow over the surface of the solution to remove the evolved CO gave a red solution. Approximately every 30 min ca. 0.2 mL of the solution was removed by syringe for immediate FTIR analysis.

Irradiation of $Fe(CO)_5$ and Methyl 3-Butenoate. The same procedures were used for this reaction as for methyl *trans*-crotonate. After 6 h of irradiation, the solution was treated with CO first at 0 °C for 1 h and then at 50 °C for 12 h as described in detail below in order to liberate the free methyl crotonate; the resulting product mixture (with a capillary containing reference C_6D_6) was identified by its ^1H NMR spectrum as being 94% methyl *trans*-crotonate and 6% of the starting methyl 3-butenoate. Their ^1H NMR spectra are as follows: methyl *trans*-crotonate (δ 7.47, d of q, $J = 15.6$, 6.9 Hz, olefin H at C3; 6.35, d of q, $J = 15.6$, 1.7 Hz, olefin H at C2; 4.19, s, OCH_3) and 6% of the starting methyl 3-butenoate (δ 5.65, d of apparent q, J = 10.2, 1.5, 1.5 Hz, olefin H at C4; 5.66, d of apparent q, $J = 17.1$, 1.5, 1.5 Hz, olefin H at C4; 6.51, d of d of t, $J = 16.8$, 10.2, 6.9 Hz, olefin H at C3; 3.57, d of t, $J = 6.9$, 1.5 Hz, H at C2; 4.17, s, OCH_3). Although not observed in this reaction, the ^1H NMR spectrum of methyl *cis*-crotonate in C_6D_6 is as follows: δ 7.47 (d of q, $J = 15.6$, 6.9 Hz, olefin H at C3), 6.35 (d of q, $J = 15.6$, 1.7 Hz, olefin H at C2), 4.19 (s, OCH_3).

Irradiation of $Fe(CO)_5$ and Methyl Oleate. A solution of methyl oleate (90 μL, 0.27 mmol) and $Fe(CO)_5$ (35 μL, 0.27 mmol) in hexanes (20 mL) at 0 °C was irradiated under a continuous nitrogen flow. The solution turned from pale yellow to red during the irradiation. As the irradiation was prolonged, the color of the solution turned to deep red. Periodically, 0.5 mL of the solution was removed by syringe for analysis. A portion of the solution (0.2 mL) was syringed into the NaCl IR cell for immediate FTIR analysis. The other portion of the solution (0.3 mL) was added to a vial (1.5 mL) containing a 20-fold amount of pyridine; this solution was stirred at room temperature for 10 min and then analyzed by GC for the organic compounds. Similar procedures were used in irradiation experiments with different concentrations of $Fe(CO)_5$ and methyl oleate in different solvents (toluene and THF) and at a higher reaction temperature (20 °C).

Irradiation of $Fe(CO)_5$ and Ethyl 4-Methyl-4-pentenoate. This reaction was performed as described for methyl oleate.

Reaction of CO with an Irradiated Solution of $Fe(CO)_5$ and Methyl Oleate. A hexanes solution (20 mL) of $Fe(CO)_5$ (0.27 mmol) and methyl oleate (0.27 mmol) was irradiated at 0 °C for 3 h under a continuous N_2 flow to give $Fe(CO)_3(\eta^4\text{-}CH_3(CH_2)_{14}CH{=}CHCO_2Me)$ (**6**). Then CO was bubbled through the solution at 0 °C for 1 h, followed by stirring under the CO atmosphere at 50 °C for 12 h. The resulting $Fe(CO)_5$ and solvent were vacuum distilled (bulb-to-bulb) from the reaction mixture. The residue was then chromatographed in hexanes through a short (1 × 10 cm) column (silica gel) to remove the iron impurities. The composition of the resulting solution was analyzed by GC as described above. The compounds present in the mixture were identified by the following ^1H NMR spectra in $CDCl_3$, which are very similar to those reported in

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the literature.[22] Methyl octadec-*trans*-2-enoate: δ 2.18 (apparent q of d, J = 7.2, 7.2, 1.5 Hz, H at C4), 6.96 (d of t, J = 15.5, 7.2 Hz, olefin H at C3), 5.81 (d of t, J = 15.5, 1.5 Hz, olefin H at C2), 3.71 (s, OCH_3). Methyl octadec-*cis*-2-enoate: δ 2.63 (apparent q of d, J = 7.5, 7.5, 1.5 Hz, H at C4), 6.22 (d of t, J = 11.4, 7.5 Hz, olefin H at C3), 5.70 (d of t, J = 11.4, 1.5 Hz, olefin H at C2), 3.69 (s, OCH_3). Methyl octadec-*trans*-3-enoate: δ 2.02 (m, H at C5), 5.52 (m, H at C3 and C4), 3.02 (d, J = 5.4 Hz, H at C2), 3.67 (s, OCH_3). Methyl octadec-*cis*-3-enoate: δ 2.02 (m, H at C5), 5.52 (m, H at C3 and C4), 3.08 (d, J = 5.1 Hz, H at C2), 3.67 (s, OCH_3). The ^1H NMR spectrum of the starting methyl oleate in $CDCl_3$ follows: δ 5.32 (m, 2 H, olefin H), 1.99 (m, 4 H, CH_2 at C8 and C11), 1.60 (m, 2 H, CH_2 at C3), 2.28 (t, J = 7.5 Hz, 2 H, CH_2 at C2), 3.64 (s, 3 H, OCH_3), 0.86 (t, J = 6.6 Hz, 3 H, CH_3 at C18), 1.25−1.28 (m, 20 H, remaining CH_2 groups).

Reaction of CO with an Irradiated Solution of $Fe(CO)_5$ and Ethyl 4-Methyl-4-pentenoate. A hexanes solution (20 mL) of $Fe(CO)_5$ (35 μL, 0.27 mmol) and ethyl 4-methyl-4-pentenoate (43 μL, 0.27 mmol) was irradiated at 0 °C for 3 h with a continuous nitrogen flow to produce $Fe(CO)_3(\eta^4\text{-}Pr^iCH{=}CHCO_2Et)$ (**3**). The solution was then purged with CO at 0 °C for 1 h, followed by stirring under CO at 50 °C overnight. Volatile compounds including $Fe(CO)_5$ produced during the reaction, free ethyl 4-methyl-4-pentenoate and its isomers, and hexanes were transferred to another vessel by bulb-to-bulb vacuum distillation. The $Fe(CO)_5$ and hexanes in this transferred solution were then removed by distillation at 0 °C under vacuum (0.1 mmHg) leaving a mixture of esters, which were analyzed by GC and GC−MS. These compounds were identified by the following ^1H NMR spectra in $CDCl_3$, which are very similar to those reported in the literature.[23] Ethyl 4-methyl-4-pentenoate: δ 4.65 (s, olefin H at C5), 4.70 (s, olefin H at C5), 1.70 (s, CH_3 at C4), 2.40 (t, J = 7.8 Hz, CH_2 at C3), 2.29 (t, J = 7.8 Hz, CH_2 at C2), 4.09 (q, J = 7.2 Hz, OCH_2CH_3), 1.21 (t, J = 7.2 Hz, OCH_2CH_3). Ethyl 4-methyl-3-pentenoate: δ 1.74 (s, CH_3 at C4), 1.63 (s, CH_3 at C4), 5.31 (t, J = 6.9 Hz, olefin H at C3), 3.02 (d, J = 6.9 Hz, CH_2 at C2), 4.09 (q, J = 7.2 Hz, OCH_2CH_3), 1.21 (t, J = 7.2 Hz, OCH_2CH_3). Ethyl 4-methyl-*trans*-2-pentenoate: δ 1.06 (d, J = 6.6 Hz, CH_3 at C4), 2.45 (m, H at C4), 6.94 (d of d, J = 15.6, 6.6 Hz, olefin H at C3), 5.76 (d, J = 15.6 Hz, olefin H at C2). Ethyl 4-methyl-*cis*-2-pentenoate: δ 1.06 (d, J = 6.6 Hz, CH_3 at C4), 2.34 (m, H at C4), 6.00 (d of d, J = 11.4, 9.2 Hz, olefin H at C3), 5.65 (d, J = 11.4 Hz, olefin H at C2).

Thermal Reaction of $Fe(CO)_3(\eta^2\text{-}cis\text{-cyclooctene})_2$ with Methyl Oleate. *cis*-Cyclooctene (2.7 mmol) and $Fe(CO)_5$ (0.27 mmol) in hexanes (20 mL) were irradiated at −35 °C while a continuous N_2 flow was maintained over the surface of the solution in order to remove liberated CO. Irradiation was continued (2 h) until $Fe(CO)_5$ and the intermediate $Fe(CO)_4(\eta^2\text{-}cis\text{-cyclooctene})$ had largely disappeared, and $Fe(CO)_3(\eta^2\text{-cis-cyclooctene})_2$ was the only major product, as established by FTIR spectroscopy (Table 1).[12] Then, methyl oleate (2.7 mmol) was added to the solution, followed by warming to 0 °C. This solution was stirred at 0 °C for 3 h, during which time samples were removed periodically for FTIR and GC analysis.

Thermal Reaction of $Fe_2(CO)_9$ with Methyl Oleate. To a Schlenk tube containing $Fe_2(CO)_9$ (97 mg, 0.27 mmol) suspended in toluene (20 mL) was added methyl oleate (0.27 mmol). The mixture was stirred at 50 °C. Periodically, the solution was analyzed by GC for the organic compounds and by FTIR spectroscopy for the iron carbonyl compounds.

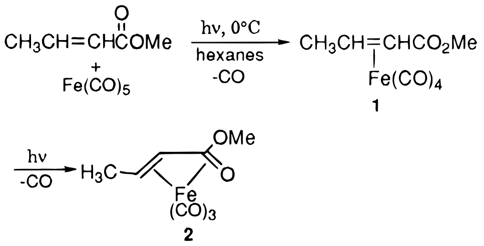
Table 1. IR Data for Relevant Compounds

compds	ν(CO) in hexanes (cm^{-1})
$CH_2{=}CHCH_2CO_2Me$	1752 (m)
$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2Me$	1749 (m)
$CH_2{=}C(CH_3)(CH_2)_2CO_2Et$	1745 (m)
trans-$CH_3CH{=}CHCO_2Me$	1735 (m)
$CH_3(CH_2)_{14}CH{=}CHCO_2Me$ (**7**)	1735 (m)
trans-$Pr^iCH{=}CHCO_2Et$	1731 (m)
$Fe(CO)_5$	2023 (s), 2000 (s)
$Fe(CO)_4(\eta^2\text{-}CH_3CH{=}CHCO_2Me)$ (**1**)	2096 (m), 2029 (s), 2014 (s), 1991 (s), 1717 (m)[a]
$Fe(CO)_4(\eta^2\text{-}CH_3(CH_2)_{14}CH{=}CHCO_2Me$ (**8**)	2094 (m), 2032 (s), 2014 (s), 1990 (s), 1717 (m)[a]
$Fe(CO)_4(\eta^2\text{-}Pr^iCH{=}CHCO_2Et)$ (**4**)	2095 (m), 2031 (s), 2014 (s), 1990 (s), 1713 (m)[a]
$Fe(CO)_4$(pyridine)	2051 (m), 1968 (s), 1942 (s)
$Fe(CO)_4(\eta^2$-*cis*-cyclooctene)[b]	2077 (m), 2000 (s), 1994 (s), 1973 (s)
$Fe(CO)_4(\eta^2$-methyl oleate)	2077 (m), 2036 (s), 1992 (s), 1973 (s)
$Fe(PF_3)_4(\eta^2\text{-}CH_2{=}CHCO_2Me)$[c]	1710 (m)[a]
$Fe(CO)_3(\eta^4\text{-}CH_2{=}CHCO_2Me)$[d]	2064 (m), 1994 (s), 1979 (s)
$Fe(CO)_3(\eta^4\text{-}CH_3CH{=}CHCO_2Me)$ (**2**)	2059 (m), 1991 (s), 1976 (s)
$Fe(CO)_3(\eta^4\text{-}CH_3(CH_2)_{14}CH{=}CHCO_2Me)$ (**6**)	2058 (m), 1990 (s), 1975 (s)
$Fe(CO)_3(\eta^4\text{-}Pr^iCH{=}CHCO_2Et)$ (**3**)	2058 (m), 1990 (s), 1973 (s)
$Fe(CO)_3(pyridine)_2$	1863 (s)
$Fe(CO)_3(\eta^2$-*cis*-cyclooctene$)_2$[b]	2043 (m), 1965 (s)
$Fe(PF_3)_3(\eta^4\text{-}CH_3CH{=}CHCO_2Me)$[c]	1379 (m)

[a] ν(C=O) of η^2-coordinated olefin ester. [b] See ref 12. [c] See ref 24. [d] See ref 20.

Results

Irradiation of $Fe(CO)_5$ and Methyl *trans*-Crotonate in Hexanes. When a hexanes solution of $Fe(CO)_5$ (13 mM) and methyl *trans*-crotonate (13 mM) at 0 °C is irradiated (eq 2) with UV light, the FTIR spectrum



(2)

(Figure 1a) of the solution after 0.5 h of irradiation shows a decrease in the intensities of the $Fe(CO)_5$ bands (Table 1) at 2023 and 2000 cm^{-1} due to the reaction of $Fe(CO)_5$. Figure 1a also shows the appearance of several new bands, indicating the formation of $Fe(CO)_4(\eta^2\text{-}CH_3CH{=}CHCO_2Me)$ (**1**) and $Fe(CO)_3(\eta^4\text{-}CH_3CH{=}CHCO_2Me)$ (**2**). The bands at 2059 (m), 1991 (s), and 1976 (s) cm^{-1} are assigned to the ν(CO) absorptions of $Fe(CO)_3(\eta^4\text{-}CH_3CH{=}CHCO_2Me)$ (**2**) by comparing them with ν(CO) bands of the known complex $Fe(CO)_3(\eta^4\text{-}CH_2{=}CHCO_2Me)$ at 2064 (m), 1994 (s), and 1979 (s) cm^{-1} (Table 1).[20] The absorptions at 2096 (m), 2029 (s), 2014 (s), and 1991 (s) cm^{-1} are assigned to the ν(CO) bands of $Fe(CO)_4(\eta^2\text{-}CH_3CH{=}CHCO_2Me)$ (**1**) following the previous assignments[19] for this compound. The decrease in intensity of the 1735 cm^{-1} ν(C=O) band for free methyl *trans*-crotonate after 0.5 h of irradiation indicates that ca. 28% of the methyl *trans*-crotonate has reacted. Compound **2** also exhibits a band at 1504 cm^{-1}, which is assigned to ν(C=C) of the η^4-coordinated $CH_3CH{=}CHCO_2CH_3$ in **2** on the basis of the analogous band in $Fe(PF_3)_3(\eta^4$-

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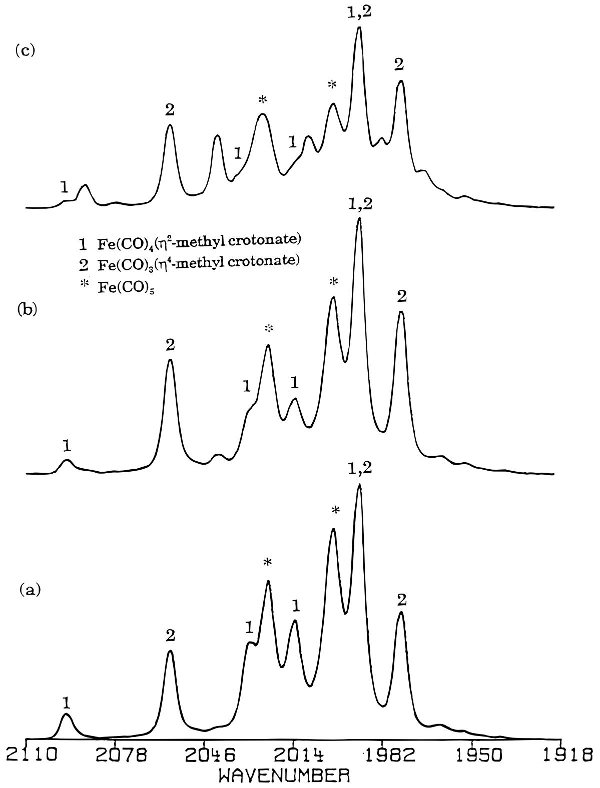


Figure 1. FTIR spectrum of the UV-irradiated solution of $CH_3CH{=}CHCO_2Me$ (13 mM) and $Fe(CO)_5$ (13 mM) in hexanes at 0 °C: (a) after 0.5 h irradiation; (b) after 1 h irradiation; (c) after 5 h irradiation.

$CH_3CH{=}CHCO_2CH_3$).[24] A new band at 1717 cm^{-1} is assigned to ν(C=O) of the η^2-coordinated methyl *trans*-crotonate in **1**; this assignment is based on the ν(C=O) value (1710 cm^{-1}) of the coordinated $CH_2{=}CHCO_2Me$ in $Fe(PF_3)_4(\eta^2\text{-}CH_2{=}CHCO_2Me)$.[21,24]

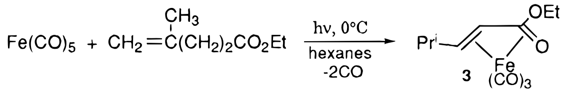
After 1 h of irradiation, the FTIR spectrum (Figure 1b) of the solution shows that the concentration of **2** increases while the concentration of **1** decreases, and about 24% of the free methyl crotonate is left in solution. Upon further irradiation (5 h) (Figure 1c), the concentrations of both **1** and **2** decrease, but free methyl crotonate increases (30%). A few bands in the spectra (Figure 1) could not be assigned to specific compounds. After the 5 h-irradiated solution was warmed to room temperature for 1 h, the concentration of **2** decreased significantly while the concentrations of **1** and $Fe(CO)_5$ increased. Irradiated hexanes solutions of $Fe(CO)_5$ and the other olefin-esters discussed in this paper exhibit FTIR spectra that are very similar to those in Figure 1.

Irradiation of Fe(CO)$_5$ and Methyl 3-Butenoate in Hexanes. In order to study olefin isomerization under the same conditions used in the formation (eq 2) of **2** from $Fe(CO)_5$ and methyl *trans*-crotonate, a hexanes solution of $Fe(CO)_5$ (13 mM) and methyl 3-butenoate (13 mM) was irradiated at 0 °C (eq 3). The ν(CO) bands

$$Fe(CO)_5 + CH_2{=}CHCH_2CO_2Me \xrightarrow[\text{hexanes}\ \text{-CO}]{h\nu,\ 0°C} 1^* \xrightarrow[\text{-CO}]{h\nu} 2 \qquad (3)$$

(Table 1) in the FTIR spectrum of the solution after 0.5 h of irradiation indicate that complexes **1*** and **2** are formed. The intermediate $Fe(CO)_4(\eta^2$-olefin ester) (**1***) is likely to be a mixture of **1**, as indicated by the ν(C=O) band at 1717 cm^{-1} and ν(CO) band at 2096 cm^{-1}, and $Fe(CO)_4(\eta^2\text{-}CH_2{=}CHCH_2CO_2Me)$, as indicated by the band at 2087 cm^{-1}. During the initial 0.5 h of irradiation, the decrease in intensity of the ν(C=O) band for free methyl 3-butenoate at 1752 cm^{-1} indicates that 33% of the methyl 3-butenoate remains uncoordinated. Free methyl *trans*-crotonate is also produced, as shown by a band at 1735 cm^{-1}. This establishes that the C=C double bond in methyl 3-butenoate isomerizes to the α,β-position during the irradiation in the presence of $Fe(CO)_5$. Upon longer irradiation, the concentration of **1** decreases while the concentration of **2** increases. The highest concentration of **2** was obtained after 1.5 h; it then decreased with further irradiation (6 h). The concentration of the free methyl 3-butenoate decreases throughout the irradiation also; only 12% of the free methyl 3-butenoate remains after 1.5 h, but its concentration does not increase upon prolonged irradiation (6 h). However, the concentration of free methyl *trans*-crotonate does increase during longer irradiation (6 h). When, after 6 h of irradiation, the solution was treated with CO to liberate the methyl crotonate from **2**, the reaction mixture consisted of 94% methyl *trans*-crotonate and 6% of the starting methyl 3-butenoate. When methyl 3-butenoate, in the absence of $Fe(CO)_5$, is irradiated under the same conditions (hexanes solvent, 0 °C, 6 h), no methyl *trans*-crotonate is produced. It might be noted that UV-photolysis (5 h) of methyl *trans*-crotonate in hexanes at 0 °C gave 27% methyl *cis*-crotonate, 4% methyl 3-butenoate, and 69% unreacted methyl *trans*-crotonate; UV-promoted isomerization of methyl *trans*-crotonate has been previously reported.[25]

Irradiation of Fe(CO)$_5$ and Ethyl 4-Methyl-4-pentenoate in Hexanes. When the branched-chain olefin-ester, ethyl 4-methyl-4-pentenoate (13 mM), is irradiated for 0.5 h with $Fe(CO)_5$ (13 mM) in hexanes at 0 °C, an FTIR spectrum shows that $Fe(CO)_3(\eta^4\text{-}Pr^iCH{=}CHCO_2Et)$ (**3**) is formed (eq 4) as indicated by



(4)

the ν(CO) peaks at 2058, 1990, and 1973 cm^{-1}; there are also bands for $Fe(CO)_4(\eta^2$-olefin ester) complexes. Upon treatment with excess pyridine, the bands for **3** completely disappear, and a strong ν(C=O) band at 1731 cm^{-1} for the free α,β-ester *trans*-$Pr^iCH{=}CHCO_2Et$ is observed; the formation of the α,β-ester was confirmed by a GC–MS analysis of the reaction solution.[26] The concentration of **3** increases initially and then decreases after longer irradiation times, as detected in FTIR spectra of the solution. The FTIR spectra show that the highest concentration of **3** is obtained after 3 h of irradiation; GC analysis of the pyridine-treated solution also shows that the highest yield of *trans*-$Pr^iCH{=}CHCO_2Et$ (90%) is obtained after 3 h of irradiation. The yield decreases to 69% after 6 h of irradiation. When the reaction was conducted at 20 °C (Table 2, entries 14 and 15), the maximum yield (83%) was lower than at 0 °C and was achieved in 1 h.

Reaction of CO with an Irradiated Solution of Fe(CO)$_5$ and Ethyl 4-Methyl-4-pentenoate. In order to release ethyl 4-methyl-2-pentenoate from **3** produced

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(24) Kruck, T.; Knoll, L. *Chem. Ber.* **1973**, *106*, 3578.

(25) Kropp, P. J.; Krauss, H. J. *J. Org. Chem.* **1967**, *32*, 3222.

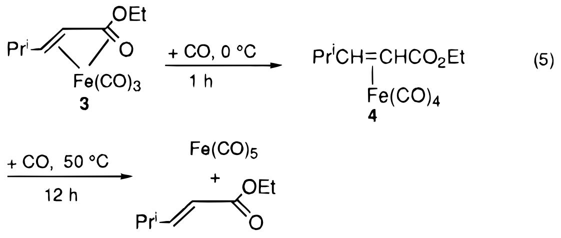
(26) (a) Lauwers, W.; Serum, J. W.; Vandewalle, M. *Org. Mass Spectrosc.* **1973**, *7*, 1027. (b) Bowles, A. J.; Brittain, E. F. H.; George, W. O. *Org. Mass Spectrosc.* **1969**, *2*, 809.

Table 2. Yields of α,β-Esters Obtained from UV-Promoted Isomerizations of Olefin Esters in the Presence of $Fe(CO)_5$

entry	olefin esters	concn[a] (mM)	*T* (°C)	solvent	time (h)	α,β-ester yield[d] (%)
1	methyl oleate	13	0	hexanes	0.5	45
2	methyl oleate	13	0	hexanes	3	70
3	methyl oleate	13	0	hexanes	7	60
4	methyl oleate	13	20	hexanes	1	58
5	methyl oleate	13	20	hexanes	4	49
6	methyl oleate	40	0	hexanes	5	42
7	methyl oleate	40	0	toluene	5	38
8	methyl oleate	40	0	THF	5	5
9	methyl oleate	40	0	hexanes[b]	5	36
10	methyl oleate	40	0	hexanes[c]	5	30
11	methyl oleate	40	20	hexanes	1.5	47
12	4-ethyl-4-pentenoate	13	0	hexanes	3	90
13	4-ethyl-4-pentenoate	13	0	hexanes	6	69
14	4-ethyl-4-pentenoate	13	20	hexanes	1	83
15	4-ethyl-4-pentenoate	13	20	hexanes	2	78

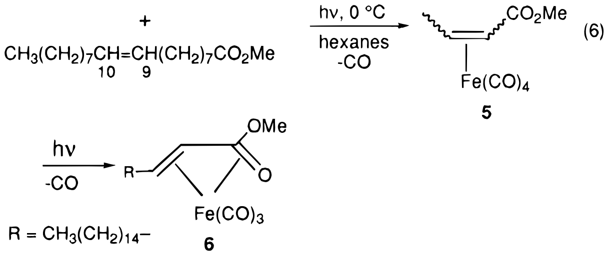
[a] Equal concentrations of $Fe(CO)_5$ and the olefin ester were used. [b] THF (80 mM) is present in the solution. [c] *cis*-Cyclooctene (40 mM) is present in the solution. [d] Determined by pyridine displacement method.

during the irradiation (eq 4) and to recycle the starting $Fe(CO)_5$, the hexanes solution of $Fe(CO)_5$ (13 mM) with ethyl 4-methyl-4-pentenoate (13 mM) that had been irradiated for 3 h at 0 °C was purged with CO at 0 °C (eq 5). An FTIR spectrum of the solution after 1 h of reaction with CO showed that **3** disappeared completely, and the concentration of the $Fe(CO)_4(\eta^2\text{-}\alpha,\beta\text{-ester})$ complex (**4**) increased significantly. Further purging (2 h) of the solution with CO at 0 °C did not convert **4** to $Fe(CO)_5$. However, after the CO-saturated solution had been stirred at 50 °C for 12 h, the FTIR spectrum of the solution then showed that **4** had completely disappeared. The major Fe product in the solution was $Fe(CO)_5$; its concentration was approximately 12 mM, which is slightly less than the 13 mM used in the initial reaction (eq 4). A GC analysis of the solution showed that 90% of the mixture was the α,β-ester, ethyl 4-methyl-*trans*-2-pentenoate; the other isomers were present in small amounts. An ^1H NMR spectrum of the ester mixture showed that more than 99% of the α,β-ester is the *trans* isomer as indicated by the characteristic chemical shifts and coupling constants of the C3 and C2 olefinic protons at δ 6.94 ($J = 15.6$, 6.6 Hz) and 5.76 ($J = 15.5$ Hz).

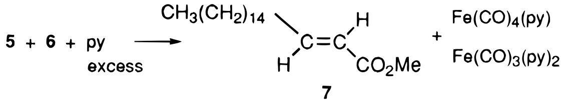


(5)

Irradiation of $Fe(CO)_5$ with Methyl Oleate in Hexanes. A hexanes solution of $Fe(CO)_5$ (13 mM) and the long-chain olefin ester methyl oleate (13 mM) was irradiated at 0 °C (eq 6). An FTIR spectrum of the solution after 0.5 h of irradiation showed that $Fe(CO)_3(\eta^4\text{-}CH_3(CH_2)_{14}CH{=}CHCO_2Me)$ (**6**) was the major product as indicated by bands at 2058, 1990, and 1975 cm^{-1}. A mixture of $Fe(CO)_4(\eta^2\text{-olefin ester})$ intermediates **5** was also observed; a ν(CO) band at 2077 cm^{-1} suggests that most of these compounds contain the non-α,β-unsaturated isomers, while the weak band at 2094 cm^{-1} indicates the presence of some of the η^2-α,β-unsaturated ester complex **8**. Complex **6** is stable at 0 °C for at least 1 h as FTIR spectra of the stirred solution in the dark for 1 h show no significant change. However, significant decomposition of **6** occurs when the solution is stirred at room temperature for 1 h, as the concentrations of $Fe(CO)_5$ and **5** increase. If the solution (eq 6) obtained from 0.5 h of irradiation at 0 °C is stirred with 20-fold pyridine (py) for 10 min, all of **6** disappears and new bands at 2051, 1968, 1942, and 1863 cm^{-1} are observed, indicating the formation[27] of $Fe(CO)_3(py)_2$ and $Fe(CO)_4(py)$ (eq 7). The band at 1717 cm^{-1} for ν(C=O) of the ester group in **8** disappears completely, and the intensity of the band at 1735 cm^{-1} for ν(C=O) of the free α,β-ester, methyl octadec-*trans*-2-enoate (**7**), increases significantly.



(6)



(7)

The identity of **7** formed in reaction 7 was confirmed by GC−MS studies. GC analysis of the reaction solution showed five peaks at retention times ranging from 9 to 11 min. The peak at 10.5 min showed lines in the mass spectrum at *m*/*e* 87 and 113 for methyl acrylate and an oxacyclohexadiene, respectively, which are characteristic[26] fragments observed in mass spectra of α,β-unsaturated methyl esters. Other GC fractions showed mass spectra characteristic of other isomers of methyl oleate in which the olefin is not in the α,β-position. These non-α,β-ester isomers in the four remaining GC peaks were not assigned to specific isomers. Quantitative GC analysis of the mixture showed that >97% of the original methyl oleate was recovered from reactions 6 and 7 as methyl oleate or its isomers; for this determination a known amount of methyl palmitate $CH_3(CH_2)_{14}CO_2CH_3$ was added to the reaction solution as the internal standard.

The reaction (eq 6) of $Fe(CO)_5$ (13 mM) and methyl oleate (13 mM) in hexanes at 0 °C was monitored by FTIR

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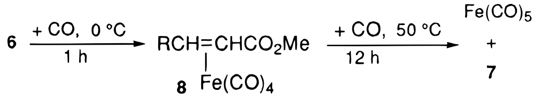
(27) (a) van Dijk, H. K.; Stufkens, D. J.; Oskam, A. *J. Organomet. Chem.* **1988**, *340*, 227. (b) Schubert, E. H.; Sheline, R. K. *Inorg. Chem.* **1966**, *5*, 1071.

spectroscopy for the production of the iron carbonyl complexes and examined by GC for the yield of **7** by treating samples from the reaction solutions with excess pyridine (eq 7) at times ranging from 0.5 to 7 h from the beginning of the reaction. FTIR spectra of the solutions showed that the concentration of **6** increases during the first three hours of irradiation but then decreases upon further irradiation (7 h). The ν(C=O) absorbance at 1749 cm^{-1} for methyl oleate and its non-α,β-ester isomers decreases during the first 3 h and then increases at longer irradiation times. Yields of the α,β-ester obtained from GC analyses parallel those obtained by FTIR using the ν(C=O) band of the free methyl oleate and $Fe(CO)_4$-(η^2-non-α,β-ester) at 1749 cm^{-1}; the intensity of this band decreases as methyl oleate is converted to **6**. The yields of the α,β-ester **7** increase from 45% after 0.5 h of irradiation to 70% after 3 h of irradiation and then drop to 60% after 7 h (Table 2, entries 1−3). When a solution of methyl oleate (13 mM) in hexanes was irradiated for 6 h *without* $Fe(CO)_5$, the α,β-ester **7** was not detected.

When technical-grade methyl oleate (containing 76% methyl oleate as determined by GC) and $Fe(CO)_5$ were irradiated under the same conditions (13 mM, hexanes solvent, 0 °C, followed by pyridine displacement), the maximum yield (67%, based on the initial methyl oleate) of the α,β-ester (**7**) was achieved after 3 h. The yields after 2 and 4 h were 62% and 61%, respectively.

In addition to pyridine (eq 7), CO was also used to liberate (eq 8) the α,β-ester **7** from its iron complex (**6**) produced during the irradiation; this treatment also regenerates the starting $Fe(CO)_5$. A hexanes solution of $Fe(CO)_5$ (13 mM) and methyl oleate (13 mM) that had been irradiated for 3 h at 0 °C was purged with CO at 0 °C. An FTIR spectrum of the solution, after reaction with CO for 1 h, showed that **6** disappeared completely while the concentration of $Fe(CO)_4(\eta^2$-α,β-ester) **8** increased significantly. Further purging of the solution with CO for 2 h at 0 °C did not convert **8** to $Fe(CO)_5$; nor did stirring the CO-saturated solution at room temperature for 12 h. However, stirring the CO-saturated solution at 50 °C for 12 h resulted in the complete disappearance of $Fe(CO)_4(\eta^2$-α,β-ester) **8** as indicated by the FTIR spectrum. The major iron product in the solution was $Fe(CO)_5$, and its concentration as determined by the intensity of its 2023 cm^{-1} band was approximately 12 mM, which is 92% of the initial $Fe(CO)_5$ used in reaction 6. GC analysis of the solution showed that more than 99% of the initial methyl oleate was recovered as its isomeric esters (primarily **7**). An ^1H NMR spectrum of the ester mixture demonstrated that more than 98% of the α,β-ester **7** was the *trans* isomer; this assignment is based on the chemical shifts and characteristically large coupling constants of the *trans* olefinic protons at δ 6.96 (J = 15.5, 7.2 Hz) and 5.81 (J = 15.5, 1.5 Hz).[23]



$$\mathbf{6}\ \xrightarrow[\text{1 h}]{+\text{CO, 0 °C}}\ \underset{\mathbf{8}\ \ Fe(CO)_4}{RCH{=}CHCO_2Me}\ \xrightarrow[\text{12 h}]{+\text{CO, 50 °C}}\ \begin{matrix}Fe(CO)_5\\+\\\mathbf{7}\end{matrix} \qquad (8)$$

Concentration Effects. When a hexanes solution of relatively high concentration $Fe(CO)_5$ (40 mM) and methyl oleate (40 mM) was irradiated (eq 6) at 0 °C, yellow $Fe_2(CO)_9$ precipitated from solution. Its FTIR spectrum (Nujol mull) contained ν(CO) bands at 2081 (s), 2017 (vs), 1985 (sh), and 1826 (s) cm^{-1} that are identical to those obtained of a known sample of $Fe_2(CO)_9$.[28] The yield of **7** obtained by GC analysis of the solution treated with excess pyridine increases during irradiation and reaches its highest value of 42% after 5 h (Table 2, entry 6); this is less than the 70% yield of the α,β-ester **7** obtained from the reaction at lower concentrations (13 mM) of $Fe(CO)_5$ and methyl oleate.

Solvent Effect. In an attempt to improve the yield of the α,β-ester and inhibit the formation of $Fe_2(CO)_9$ at the higher reactant concentrations, toluene and THF solutions of $Fe(CO)_5$ (40 mM) and methyl oleate (40 mM) were irradiated at 0 °C (Table 2, entries 7 and 8). In the experiment using toluene as the solvent, a large amount of yellow $Fe_2(CO)_9$ precipitated, and the highest yield (38%) of the α,β-ester was obtained after 5 h of irradiation. In the experiment using THF as the solvent, there was no yellow precipitate, presumably due to the formation of $Fe(CO)_4$(THF),[29] but the FTIR spectrum of the irradiated solution showed no bands indicating the formation of **8** or **6**. GC analysis of the solution showed that the methyl oleate isomerized, but the yield of the α,β-ester (5% after 5 h) was very low. In another experiment, no solvent was used. Equal volumes of $Fe(CO)_5$ (0.25 mL) and methyl oleate (0.25 mL) were mixed and then irradiated. Much precipitation of $Fe_2(CO)_9$ occurred and the maximum yield of the α,β-ester was ca. 5%. On the basis of these studies, hexanes solvent gave the highest yield of the α,β-ester.

Irradiation of $Fe(CO)_5$ with Methyl Oleate in the Presence of THF or *cis*-Cyclooctene. In an attempt to improve the yield of the α,β-ester and prevent the formation of $Fe_2(CO)_9$ at relatively high reactant concentrations, the weakly coordinating ligands THF (80 mM) or *cis*-cyclooctene (40 mM) were added to the hexanes solution of $Fe(CO)_5$ (40 mM) and methyl oleate (40 mM) for irradiation at 0 °C (Table 2, entries 9 and 10). Added THF (80 mM) gave a maximum yield (36%) of the α,β-ester, which is lower than that (42%) obtained in the absence of THF. With *cis*-cyclooctene (40 mM), the maximum yield was only 30%. In both experiments, a yellow precipitate of $Fe_2(CO)_9$ was observed.

Temperature Effect. The temperature of the reaction also had an important effect on the yield (Table 2, entries 4 and 5). During the irradiation of 13 mM $Fe(CO)_5$ and methyl oleate in hexanes at 20 °C, the highest yield (58%) of the α,β-ester **7** was obtained after 1 h; this is a lower yield than that (70%) obtained after 3 h of irradiation at 0 °C. Prolonged irradiation (4 h) reduces the yield of the α,β-ester to 49%. Stirring the solution (after 4 h of irradiation) in the dark at 20 °C for 1 h lowers the yield of **7** to only 42%.

In an experiment at 20 °C using higher concentrations (40 mM) of $Fe(CO)_5$ and methyl oleate, only a small amount of $Fe_2(CO)_9$ precipitate was observed during irradiation. However, the highest yield (47%) of **7**, obtained after 1.5 h of irradiation, was only slightly larger than that obtained at 0 °C (42%). When another portion of $Fe(CO)_5$ (40 mM) was added to the solution after 1.5 h of irradiation, a large amount of $Fe_2(CO)_9$ precipitated during further irradiation (1 h), but the yield of **7** did not improve.

Thermal Isomerization of Methyl Oleate Promoted by $Fe(CO)_3$(*cis*-cyclooctene)$_2$. $Fe(CO)_3$(*cis*-

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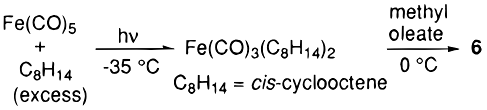
[28] (a) Griffith, W. P.; Wickham, A. J. *J. Chem. Soc. A* **1969**, 834. (b) Kristoff, J. S.; Shriver, D. F. *Inorg. Chem.* **1974**, *13*, 499.

[29] Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 3438.

cyclooctene)$_2$ was synthesized *in situ* by irradiating a hexanes solution of $Fe(CO)_5$ (13 mM) and 20 equiv of *cis*-cyclooctene (266 mM) at −35 °C (eq 9). After the addition of methyl oleate (133 mM), the solution was warmed to 0 °C during which time the color of the solution gradually turned from pale yellow to red. The FTIR spectrum of the solution after stirring at 0 °C for 0.5 h showed that most of the $Fe(CO)_3$(*cis*-cyclooctene)$_2$ had reacted with methyl oleate to give **6** and several unidentified complexes with ν(CO) bands ranging from 2100 to 1900 cm^{-1}. Some $Fe(CO)_5$ is also produced. GC analysis of a sample of the solution pretreated with excess pyridine gave a 30% yield of the α,β-ester **7** based on the amount of $Fe(CO)_5$ used. Further stirring of the solution for 4 h did not improve the yield of the α,β-ester, although isomerization of methyl oleate into the other non-α,β-ester isomers continued to proceed as shown from the GC data.



$$\begin{array}{c}Fe(CO)_5\\+\\C_8H_{14}\\\text{(excess)}\end{array} \xrightarrow[-35\ ^\circ C]{h\nu} Fe(CO)_3(C_8H_{14})_2 \xrightarrow[0\ ^\circ C]{\text{methyl oleate}} \mathbf{6} \qquad (9)$$

C_8H_{14} = *cis*-cyclooctene

In a similar experiment, $Fe(CO)_3$(*cis*-cyclooctene)$_2$ was synthesized by irradiation of $Fe(CO)_5$ (13 mM) with a lesser amount of *cis*-cyclooctene (53 mM). When this solution was reacted in the dark at 0 °C with methyl oleate (13 mM), the highest yield of the α,β-ester was 18% based on the amount of $Fe(CO)_5$ used.

Thermal Reaction of Methyl Oleate and $Fe_2(CO)_9$. A toluene solution of methyl oleate (13 mM) was stirred at 50 °C with $Fe_2(CO)_9$ (13 mM) suspended in the solution. After 2 h of stirring, only 1% of the α,β-ester was observed from a GC analysis of the solution. Prolonged stirring (12 h) at 50 °C does not increase the yield of the α,β-ester, but methyl oleate is isomerized to its non-α,β-ester isomers as determined by GC. When the same mixture was allowed to react at 0 °C, only a very low yield (1%) of **7** was obtained.

In other attempts to generate $Fe(CO)_3(\eta^4$-α,β-ester) **6** by nonphotolytic methods, equimolar (13 mM) methyl oleate and $Fe(CO)_5$ were reacted with excess (40 mM) Me_3NO[30] at 0 °C in toluene solvent. After 1 h, most of the $Fe(CO)_5$ had reacted; $Fe(CO)_4(NMe_3)$ was the major product based on the strong band at 2047 cm^{-1};[31] $Fe(CO)_4$-(η^2-methyl oleate) was the minor product based on the band at 2074 cm^{-1}. There was no change in their concentrations during 24 h, but warming to 20 °C resulted in slow decomposition of both species. There was no evidence for **6**, and GC analysis of the mixture, after pyridine treatment, showed that the α,β-ester **7** was not formed. When iodosobenzene, PhIO,[30] was used as the decarbonylating agent (26.6 mM in CH_2Cl_2 at 0 °C) in the reaction of $Fe(CO)_5$ with methyl oleate, the $Fe(CO)_5$ slowly disappeared but no new iron carbonyl complexes were formed. Thus, the oxide decarbonylating agents were unsuccessful for converting methyl oleate to its α,β-ester **7**.

Thermodynamic Amount of α,β-Ester (7) from Isomerization of Methyl Oleate. Using a procedure similar to that reported[32] for the isomerization of other olefin esters, the equilibrium amount of **7** generated by isomerization of methyl oleate was determined by using $RhCl(PPh_3)_3$ (12 mg, 1.3 × 10^{-5} mol) and $SnCl_2{\cdot}2H_2O$ (5.3 × 10^{-5} mol) as the catalyst system for the isomerization of methyl oleate (88 μL, 2.6 × 10^{-4} mol) in chlorobenzene (4 mL) at 115 °C. The GC traces showed six peaks for various isomers of methyl oleate, but only the α,β-ester **7** was identified. At times longer than 2 d, there was no change in the amount (3.5%) of **7**. To further confirm that equilibrium had been achieved, another portion of methyl oleate (88 μL, 2.6 × 10^{-4} mol) was added to the reaction mixture. After 3 d, the equilibrium amount of **7** was again 3.5% of the reacting methyl oleate.

Discussion

Synthesis of α,β-Unsaturated Esters by Isomerization of Olefin Esters. The conversion of an olefin ester to its α,β-unsaturated ester isomer depends on the ability of both the ester carbonyl and α,β-olefin groups to coordinate to $Fe(CO)_3$ in the $Fe(CO)_3(\eta^4$-α,β-ester) complex. Treatment of the complex with a more strongly coordinating ligand, e.g., pyridine or CO, gives the free *trans*-α,β-ester in 70−90% yield. To achieve these yields, the following conditions were used: 13 mM olefin ester and 13 mM $Fe(CO)_5$ in hexanes solvent at 0 °C under UV photolysis for approximately 3 h. Ultraviolet photolysis is necessary to promote the dissociation of the CO groups. This occurs via initial dissociation of one CO group and coordination of the olefin group of the olefin ester to the $Fe(CO)_4$ unit (eqs 3 and 6).[19−21,33,34] Additional photolysis removes another CO ligand, which allows the double bond to migrate to the α,β-position and the ester carbonyl group to bind to the metal to give the $Fe(CO)_3(\eta^4$-α,β-ester) complex. For our conditions, photolysis times shorter than approximately 3 h give lower yields (Table 2), because of incomplete reaction between $Fe(CO)_5$ and the olefin ester (eqs 3, 4, and 6). Longer reaction times result in decomposition of the $Fe(CO)_3(\eta^4$-α,β-ester) complex to unknown products; this decomposition is accompanied by isomerization of the α,β-ester to a mixture of olefin ester isomers. The 0 °C temperature of the reaction is also important because the $Fe(CO)_3(\eta^4$-α,β-ester) complex decomposes thermally at a moderate rate at 20 °C; this decomposition is likewise accompanied by isomerization of the α,β-ester to a mixture of isomers and lower yields of the desired α,β-ester. Concentrations of the $Fe(CO)_5$ and olefin ester reactants must not be too high because photolysis of $Fe(CO)_5$ produces insoluble $Fe_2(CO)_9$ in a reaction that competes with the formation of $Fe(CO)_3(\eta^4$-α,β-ester). The $Fe_2(CO)_9$ itself reacts with methyl oleate, but the yields of the α,β-ester (**7**) are very low. Thus, much higher yields of the α,β-ester (**7**) of methyl oleate are obtained when the concentrations of $Fe(CO)_5$ and methyl oleate are 13 mM (70%) rather than 40 mM (42%). Other solvents, toluene and THF, do not improve the yields of the 40 mM-scale reactions, nor do additions of THF or *cis*-cyclooctene to the hexanes reaction solutions (Table 2). Both THF and *cis*-cyclooctene presumably compete for coordination sites with methyl oleate, thereby reducing the yields of **7**.

In all of the above reactions, the free α,β-ester is most conveniently displaced from the $Fe(CO)_3(\eta^4$-α,β-ester)

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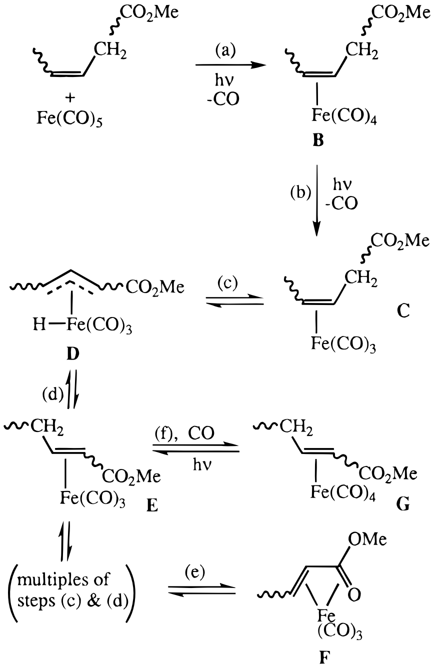
complex by treatment with a 20-fold excess of pyridine for 10 min at room temperature. The α,β-ester was also displaced by PMe$_3$, although the higher cost and air-sensitivity of this ligand make it less attractive than pyridine. The α,β-ester may also be displaced by CO in reactions (eqs 5 and 8) that regenerate the volatile Fe(CO)$_5$, which may be separated from the α,β-ester product by distillation. In order to prevent isomerization of the α,β-ester during decomposition of Fe(CO)$_3$(η^4-α,β-ester) at higher temperatures, CO is added to the reaction mixture at 0 °C. This treatment results in CO displacement of the coordinated ester group from the metal to give Fe(CO)$_4$(η^2-α,β-ester). In order to completely displace the α,β-ester, this complex is heated under 1 atm of CO at 50 °C for 12 h (eqs 5 and 8).

The above method was applied to the isomerization of methyl 3-butenoate to give methyl crotonate (eq 3) in 94% yield. This isomerization is favored thermodynamically as indicated by the following reported[35] equilibrium distribution for this system at 250 °C: methyl *trans*-crotonate (83%), methyl *cis*-crotonate (12%), and methyl 3-butenoate (5%). At 0 °C, the equilibrium amount of methyl *trans*-crotonate is likely to be even greater.[36] In the Fe(CO)$_5$-promoted reaction, stabilization of *trans*-methyl crotonate as the Fe(CO)$_3$(η^4-α,β-ester) complex **2** is not necessary for the formation of this product.

On the other hand, the isomerization of ethyl 4-methyl-4-pentenoate to ethyl *trans*-4-methyl-2-pentenoate is not favored thermodynamically. In fact, the equilibrium distribution of isomers at 25 °C is as follows:[1] ethyl 4-methyl-3-pentenoate (90%) and ethyl 4-methyl-2-pentenoate (10%). Despite this adverse equilibrium, ethyl 4-methyl-*trans*-2-pentenoate is obtained in (eq 4) 90% yield, which demonstrates the effect of η^4-α,β-ester binding in **3** on the preferred formation of this isomer. The isomerization of ethyl 4-methyl-4-pentenoate also shows that this method accommodates the isomerization of olefin esters that contain a tertiary carbon.

Finally, the Fe(CO)$_5$-promoted isomerization of methyl oleate to its α,β-isomer **7** occurs in 70% yield (eq 6), which is far greater than that predicted from thermodynamic considerations. It is known[14,36] that the effect of the ester group on the thermodynamic stabilization of the α,β-ester would lead to only a low yield of this isomer. In order to establish more precisely the thermodynamic amount of **7** among the many possible isomers derived from methyl oleate, we used RhCl(PPh$_3$)$_3$/SnCl$_2$ to catalyze the isomerization of methyl oleate at 115 °C in chlorobenzene solvent until equilibrium was achieved. The amount of the α,β-ester **7** at equilibrium was only 3.5%. Although the equilibrium studies were performed under different conditions (C$_6$H$_5$Cl solvent, 115 °C) than those used in the Fe(CO)$_5$-promoted isomerization (hexanes solvent, 0 °C), it is evident that **7** is produced in far higher yield (70%) using Fe(CO)$_5$ than would be obtained from a thermodynamic distribution of isomers. The methyl octadec-2-enoate **7** is obtained as the *trans* isomer (>98%). While a broader range of olefin esters has not yet been investigated, the above results suggest that this method may be of general use for the isomerization of olefin esters to their α,β-ester isomers.

Scheme 1. Mechanism of Olefin Ester Isomerization to the α,β-Unsaturated Ester



Mechanism of Olefin Ester Isomerization to α,β-Unsaturated Esters. The mechanism proposed (Scheme 1) for the isomerization of methyl 3-butenoate (eq 3), ethyl 4-methyl-4-pentenoate (eq 4), and methyl oleate (eq 6) to their α,β-unsaturated esters involves both double bond isomerization and trapping of the α,β-unsaturated ester as the Fe(CO)$_3$(η^4-α,β-ester) product. All of our observations are consistent with the mechanism proposed by Schroeder and Wrighton[11] for the photoassisted Fe(CO)$_5$-catalyzed isomerization of 1-pentene and other olefins. Photolysis of Fe(CO)$_5$ in the presence of the olefin esters initially (<0.5 h) produces primarily Fe(CO)$_4$(η^2-olefin ester), which does not undergo isomerization (Scheme 1). This was shown by noting that Fe(CO)$_4$(η^2-α,β-ester) **8**, produced in the reaction (eq 8) of Fe(CO)$_3$(η^4-α,β-ester) **6** with CO, undergoes no isomerization under the conditions of the reactions (0 °C) or even at 50 °C. Intermediate **B** probably contains unisomerized olefin, although it is not possible to distinguish it spectroscopically (ν(CO) = 2077 cm^{-1}) from other non-α,β-ester isomers. However, a small amount of the isomerized α,β-ester complex of methyl oleate, Fe(CO)$_4$(η^2-α,β-ester) **8**, was detected by its ν(C=O) band at 1717 cm^{-1}, characteristic of the η^2-coordinated α,β-ester of methyl oleate; this complex presumably results from isomerization of the olefin (see discussion below) followed by reaction of the Fe(CO)$_3$(η^2-α,β-ester) with CO to give **8**. The observation of **8** suggests that the other olefin isomers of Fe(CO)$_4$(η^2-olefin ester) **G** are present in the initial stages due to isomerization and capture (step f) of intermediate **E** with CO. All of these Fe(CO)$_4$(η^2-olefin ester) complexes (**B**) lose an additional CO (step b) under photolysis to generate unsaturated complex **C**. As previously shown,[11,12] it is the formation of the Fe(CO)$_3$ unit that is critical to the catalyzed isomerization. The isomerization itself is not photocatalyzed as shown by the thermal reaction (eq 9) of Fe(CO)$_3$(*cis*-cyclooctene)$_2$ with methyl oleate, which gives the α,β-ester **7** in 30% yield; this low yield, which is less than that (70%) observed in the photolytic reaction (eq 6), is presumably due to

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competition of *cis*-cyclooctene with methyl oleate for coordination sites on the $Fe(CO)_3$.

Although there is no spectroscopic evidence in this or previous work[11,12] for intermediates **C** or **E**, an analog of **D**, $Fe(CO)_3(H)(\eta^3\text{-allyl})$, has recently been identified[37] at −100 °C in the photolysis of $Fe(CO)_4(\eta^2\text{-}CH_2{=}CHCH_3)$; its existence is consistent with the mechanism in Scheme 1. Transfer (step c) of a hydrogen from a CH_2 group in **C** gives the allyl hydride **D**. Migration of the hydrogen back to the same carbon regenerates **C**, but transfer to the other terminal allyl carbon produces the isomeric olefin in **E**. Multiple hydrogen migrations between olefin-CH_2 groups and the iron in steps c and d provide a mechanism for the isomerization of the double bond along the entire hydrocarbon chain of methyl oleate and the other olefin esters. This isomerization occurs rapidly as shown[12] by the turnover rate (12.2 min^{-1} at 0 °C) for the $Fe(CO)_3$(*cis*-cyclooctene)$_2$-catalyzed isomerization of 1-pentene. Presumably, the rates in the present system are even faster since *cis*-cyclooctene is not present and therefore will not competitively bind to the $Fe(CO)_3$.

Of the possible $Fe(CO)_3$(olefin ester) species (**C**−**F**), the product $(CO)_3Fe(\eta^4\text{-}\alpha,\beta\text{-ester})$ **F** is the most stable thermodynamically, and it is in this form that the α,β-ester is stabilized at 0 °C. However, complexes **F** are not stable at 20 °C where they decompose to give $Fe(CO)_4(\eta^2\text{-olefin ester})$ (**B**, **G**), $Fe(CO)_5$, and other unidentified products. During this decomposition, considerable isomerization of the α,β-ester **7** occurs. The mechanism of this isomerization is not clear. It could occur by decomposition of **C**, **D**, or **E**, which would draw **F** into the isomerization manifold (**C**−**E**) or by some other uncharacterized mechanism. The yield of **F** is also reduced by extended photolysis at 0 °C; this decomposition is likewise accompanied by isomerization of the α,β-ester to the other isomers probably by a mechanism other than that in Scheme 1; this may involve photolytic dissociation of a CO group from **F**.[38]

Concluding Comments

In this paper, we describe a useful synthetic method for the isomerization of olefin esters to their α,β-unsaturated ester isomers. Yields are reasonably high (70−94%), and the method even applies to such long-chain olefin esters as methyl oleate. It should be mentioned that the method would not be useful for esters with two olefinic units since $Fe(CO)_5$ under UV photolysis catalyzes their isomerization to give conjugated dienes that form very stable $Fe(CO)_3(\eta^4\text{-diene})$ complexes;[34] thus, the $Fe(CO)_3(\eta^4\text{-}\alpha,\beta\text{-ester})$ would not form. Nevertheless, the $Fe(CO)_5$-catalyzed mono-olefin ester isomerization provides easy access to the highly reactive α,β-unsaturated esters.

Acknowledgment. We are grateful to the Iowa Soybean Promotion Board (Des Moines, IA) for funding this research.

JO961371U

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