$CH_2=CHCO_2C_2H_5$ was followed by measuring the disappearence of the signals due to $\mathbf{CH_2=CH}$ - at 5.2–6.2 ppm (relative to Me_4Si). The quartet due to $-CO_2CH_2CH_3$ at 4.0 ppm was employed as an internal standard. Hydrogenation of *trans*-$CH_3CH=CHCO_2C_2H_5$ was followed by measuring the disappearence of the signals at 6.3–6.5 ppm due to $-CH=CH-$ and using the quartet at 4.0 ppm due to $-CO_2CH_2CH_3$ as an internal standard. Hydrogenation of *trans*-$C_6H_5CH=CHCO_2C_2H_5$ was followed by measuring the disappearence of the signals at 6.3–6.4 ppm due to $-CH=CHCO_2-$ and using the quartet at 4.2 ppm due to $-CO_2CH_2CH_3$ as an internal standard.

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References

1. Submitted for publication.
2. H.M. Jeong and C.S. Chin, *Bull. Korean Chem. Soc.*, **5**, 199 (1984).
3. S.H. Park, H.-K. Park, and C.S. Chin, *Inorg. Chem.*, **24**, 1120 (1985).
4. S.H. Park, H.-K. Park, and C.S. Chin, *Bull. Korean Chem. Soc.*, **5**, 167 (1984).
5. Submitted for publication.
6. R. Brady, B.R. Flynn, G.L. Geoffroy, H.B. Gray, J. Peone, Jr. and L. Vaska, *Inorg. Chem.*, **15**, 1485 (1976).
7. L. Vaska, *Acc. Chem. Res.*, **1**, 335 (1968).
8. C.S. Chin, unpublished results (see ref. 9 of ref. 4).
9. J. Peone, Jr. and L. Vaska, *Angew. Chem. Int. Ed.*, **10**, 511 (1971).

Reactions, Hydrogenation and Isomerization of Unsaturated Esters with a Rhodium(I)–Perchlorato Complex

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The isolated products from the reactions of $Rh(ClO_4)(CO)(PPh_3)_2$ (**1**) with $CH_2=CHCO_2C_2H_5$ (**2**) and *trans*-$CH_3CH=CHCO_2C_2H_5$ (**3**) contain 80~90% of $[Rh(CH_2=CHCO_2C_2H_5)(CO)(PPh_3)_2]ClO_4$ (**4**) and $[Rh(\textit{trans}\text{-}CH_3CH=CHCO_2C_2H_5)(CO)(PPh_3)_2]ClO_4$ (**5**), respectively where **2** and **3** seem to be coordinated through the carbonyl oxygen. It has been found that complex **1** catalyzes the isomerization of $CH_2=CH(CH_2)_8CO_2C_2H_5$ (**6**) to $CH_3(CH_2)_nCH=CH(CH_2)_{7-n}CO_2C_2H_5$ (n=0~7) under nitrogen at 25°C. The isomerization of **6** is slower than that of $CH_2=CH(CH_2)_9CH_3$ to $CH_3(CH_2)_nCH=CH(CH_2)_{8-n}CH_3$ (n=0~8), which is understood in terms of the interactions between the carbonyl oxygen of **6** and the catalyst. It has been also observed that complex **1** catalyzes the hydrogenation of **2**, **3**, **6**, *trans*-$C_6H_5CH=CHCO_2C_2H_5$ (**7**), $CH_3(CH_2)_7CH=CH(CH_2)_7CO_2C_2H_5$ (**8**) and $CH_2=CH(CH_2)_9CH_3$ (**9**), and the isomerization (double bond migration) of **6** and **9** under hydrogen at 25°C. The interactions between the carbonyl oxygen of the unsaturated esters and the catalyst affect the hydrogenation in such a way that the hydrogenation of the unsaturated esters becomes slower than that of simple olefins.

Introduction

Perchlorato ligand (ClO_4) in $M(ClO_4)(CO)(PPh_3)_2$ (M = Rh, Ir) is so labile that it is readily replaced even by various solvent molecules.[1] We recently reported that ClO_4 group in $M(ClO_4)(CO)(PPh_3)_2$ (M = Rh, Ir) is replaced with unsaturated nitriles,[2] unsaturated aldehydes[3] and unsaturated alcohols[4] to give cationic complexes, $[ML(CO)(PPh_3)_2]ClO_4$ (L = unsaturated nitriles, unsaturated aldehydes and unsaturated alcohols) which show catalytic activities for the hydrogenation, isomerization and oligomerization of the corresponding unsaturated compounds (L). We also found that $Rh(ClO_4)(CO)(PPh_3)_2$ (**1**) catalyzes the hydrogenation and isomerization of soybean oil which is a mixture of unsaturated esters and saturated esters.[5] The interactions between the rhodium in **1** and the carbonyl oxygen of soybean oil, however, could not be established in that study.[5]

Accordingly, we have decided to investigate the interaction between pure unsaturated esters and **1**. In this paper, we wish to report the formation of cationic rhodium(I) complexes of unsaturated esters and the catalytic activities of **1** for the hydrogenation and isomerization of unsaturated esters.

Results and Discussion

Reactions of $Rh(ClO_4)(CO)(PPh_3)_2$ (1) and unsaturated esters. Interaction is apparent between the rhodium in **1** and the carbonyl oxygen of the ester group in the unsaturated esters chosen in this study (see below) although pure complexes have not been isolated from the reactions of **1** and the unsaturated esters. The reactions of **1** with $CH_2=CHCO_2C_2H_5$ (**2**) and *trans*-$CH_3CH=CHCO_2C_2H_5$ (**3**) yield pale yellow solids, respectively (see Experimental for details), while no rhodium complexes have been isolated from the reactions of **1** with other unsaturated esters, *trans*-$C_6H_5CH=CHCO_2C_2H_5$, $CH_2=CH(CH_2)_8CO_2C_2H_5$ and $CH_3(CH_2)_7CH=CH(CH_2)_7CO_2C_2H_5$. The products obtained from the reaction of **1** with **2** and **3** lose **2** and **3**, respectively when they are dissolved

Table 1. Catalytic Isomerization (Double Bond Migration) of $CH_2=CH(CH_2)_8CO_2C_2H_5$ (6) to $CH_3(CH_2)_nCH=CH(CH_2)_{7-n}CO_2C_2H_5$ with $Rh(ClO_4)(CO)(PPh_3)_2$ (1) (0.04 mmole) in $CDCl_3$ (0.6 ml) at 25°C under nitrogen.

reactant	inner olefins (%)[a]			
	2 hr.	5 hr.	8 hr.	11 hr.
6 (0.5 mmole)	30	56	77	83
6 (0.5 mmole) + $CH_3CO_2C_2H_5$ (1.0 mmole)	23	46	60	36
$CH_2=CH(CH_2)_9CH_3$ (0.5 mmole)	48	92	95	96

[a] $CH_3(CH_2)_nCH=CH(CH_2)_{7-n}CO_2C_2H_5$ (n= 0~7) from **6** and $CH_3(CH_2)_nCH=CH(CH_2)_{7-n}CH_3$ (n= 0~8) from $CH_2=CH(CH_2)_9CH_3$.

^{1}H-NMR spectra. The amount of **2** dissociated in $CDCl_3$ from the pale yellow product (**4**) of the reaction of **1** with **2**, is always less than one (0.8~0.9) mole per mole of $Rh(PPh_3)_2$ moiety, which suggests that **4** is not a pure single compound. The product (**5**) obtained from the reaction of **1** with **3** also dissociates in $CDCl_3$ about 0.8 mole of **3** per mole of $Rh(PPh_3)_2$ moiety. Infrared spectrum of **4** shows two medium-strong $\nu_{c=o}$ at 1646 and 1587 cm^{-1} (Nujol) while that of free $CH_2=CHCO_2C_2H_5$ shows the bands at 1725 and 1625 cm^{-1}. These significant decreases in $\nu_{c=o}$ of $CH_2=CHCO_2C_2H_5$ upon coordination suggest that $CH_2=CHCO_2C_2H_5$ in **4** is coordinated through the carbonyl oxygen to rhodium. Significant decreases have been also found for $\nu_{c=o}$ of **3** in **5** (1620, 1599 cm^{-1}) compared with those of free **3** (1720, 1657 cm^{-1}). An unsaturated ester may be coordinated through the olefinic group or/and the carbonyl oxygen of the ester group (no transition metal complexes have been reported to contain unsaturated esters coordinated through the oxygen of C-O-C group). The infrared spectra of **2**~**5** do not provide information on whether **2** in **4** and **3** in **5** are also coordinated through the olefinic groups since $\nu_{c=c}$ are obscured by the strong $\nu_{c=o}$ near them.

Electronic absorption spectra of **4** (349 nm) in **2** and **5** (348 nm) in **3** in the visible region also support the bonding between rhodium and the oxygen both in **4** and **5**. It is well-known that the four coordinated rhodium(I) complexes, $RhA(CO)(PPh_3)_2$ (A = monodentate anionic and neutral ligands which coordinate through oxygen atom) show an absorption band (350~360 nm) in the visible region.[3,6]

Infrared spectra of **4** and **5** show a strong $\nu_{c=o}$ at 1993 and 1991 cm^{-1}, respectively whereas that of **1** shows $\nu_{c=o}$ at 1999 cm^{-1}. A strong and broad band at *ca.* 1100 cm^{-1} observed for **4** and **5**, respectively is attributable to the tetrahedral (Td) anionic ClO_4^- group,[1] which suggests that the ClO_4 group is not directly coordinated to rhodium. Molar conductance values obtained for **4** in **2** and for **5** in **3** are *ca.* 100 ohm^{-1} cm^{2}mol^{-1} (see Experimental for details), which is in agreement with **4** and **5** being 1:1 electrolytes.

In summary based on the spectral data and conductance measurements, it may be said that (a) cationic rhodium(I) complexes of the unsaturated esters seem to form according to the equation (1) although the isolated products (**4** and **5**) seem to contain only *ca.* 80-90% of $[Rh(CH_2=CHCO_2C_2H_5)(CO)(PPh_3)_2]ClO_4$ and $[Rh(trans\text{-}CH_3CH=CHCO_2C_2H_5)(CO)(PPh_3)_2]ClO_4$, respectively, and (b) $CH_2=CHCO_2C_2H_5$ and *trans*-$CH_3CH=CHCO_2C_2H_5$ seem to be coordinated through the carbonyl oxygen in $[Rh(CH_2=CHCO_2C_2H_5)(CO)(PPh_3)_2]ClO_4$ and $[Rh(trans\text{-}CH_3CH=CHCO_2C_2H_5)(CO)(PPh_3)_2]ClO_4$, respectively. It may also be mentioned here that the similar rhodium(I) complexes, $[RhL(CO)(PPh_3)_2]ClO_4$ (L = unsaturated nitriles, unsaturated aldehydes, unsaturated alcohols coordinated through the nitrogen and oxygen atom but not through the olefinic group) have been prepared recently.[2b,2c,3,4]

$$Rh(ClO_4)(CO)(PPh_3)_2 + L \longrightarrow [RhL(CO)(PPh_3)_2]ClO_4 \quad (1)$$
$$L = CH_2=CHCO_2C_2H_5,\ trans\text{-}CH_3CH=CHCO_2C_2H_5$$

Catalytic Reactions of Unsaturated Esters with $Rh(ClO_4)(CO)(PPh_3)_2$ (1). Isomerization under Nitrogen. It has been found that **1** catalyzes the isomerization of terminal olefinic ester, $CH_2=CH(CH_2)_8CO_2C_2H_5$ (**6**) to inner olefinic esters under nitrogen (eq. 2). The isomerization identified by the signals at ca. 5.4 ppm (relative to Me_4Si in $CDCl_3$) due to $-CH=CH-$ which increase during the reaction at the expense of the signals at *ca.* 5.0 ppm due to $CH_2=$ or *ca.* 5.8 ppm ($=CH-$). The isomerization suggests that there should

$$CH_2=CH(CH_2)_8CO_2C_2H_5 \xrightarrow[CDCl_3,\ 25°C]{1,\ N_2}$$
$$CH_3(CH_2)_7\ CH=CH(CH_2)_{7-n}CO_2C_2H_5 \quad (2)$$
$$n = 0 \sim 7$$

be some interactions between the olefinic group of **6** and **1**. One can also expect the interaction between **1** and the carbonyl oxygen of **6** as observed for **2** and **3** (see above). The isomerization (eq. 2) was followed in the presence of $CH_3CO_2C_2H_5$ in order to determine the effect of an ester group on the isomerization, and it was found to be slower than that in the absence of $CH_3CO_2C_2H_5$ (see Table 1). The isomerization of **6** (eq. 2) is also slower than that of a simple terminal olefin, $CH_2=CH(CH_2)_9CH_3$ to inner olefins, $CH_3(CH_2)_nCH=CH(CH_2)_{8-n}CH_3$ (n= 0~8) (see Table 1). Accordingly, it is apparent that there are interations between the carbonyl group of **6** and **1**, due to which the isomerization of **6** is slower than that of simple terminal olefins.

Hydrogenation ahd Isomerization under Hydrogen. It has been found that complex **1** catalyzes the hydrogenation of unsaturated esters to the corresponding saturated esters and the isomerization of terminal olefinic esters to the inner olefinic esters under hydrogen (see eq. (3) and (4), and Figure 1). The data in Figure 1 are the rates of production of the corresponding esters. (1) The hydrogenation of $CH_2=CHCO_2C_2H_5$ (**2**) and *trans*-$CH_3CH=CHCO_2C_2H_5$ (**3**) is

$$RCH=CR'CO_2C_2H_5 \xrightarrow[CDCl_3,\ 25°C]{1,\ H_2} RCH_2CHR'CO_2C_2H_5 \quad (3)$$

compound no.	R	R′
2	H	H
3	CH_3	H
6	H	$H(CH_2)_8$
7	C_6H_5	H
8	$CH_3(CH_2)_7$	$H(CH_2)_7$

$$CH_2=CH(CH_2)_8CO_2C_2H_5 \xrightarrow[CDCl_3,\ 25°C]{1,\ H_2}$$
$$CH_3(CH_2)_nCH=CH(CH_2)_{7-n}CO_2C_2H_5 \quad (4)$$
$$n = 0 \sim 7$$

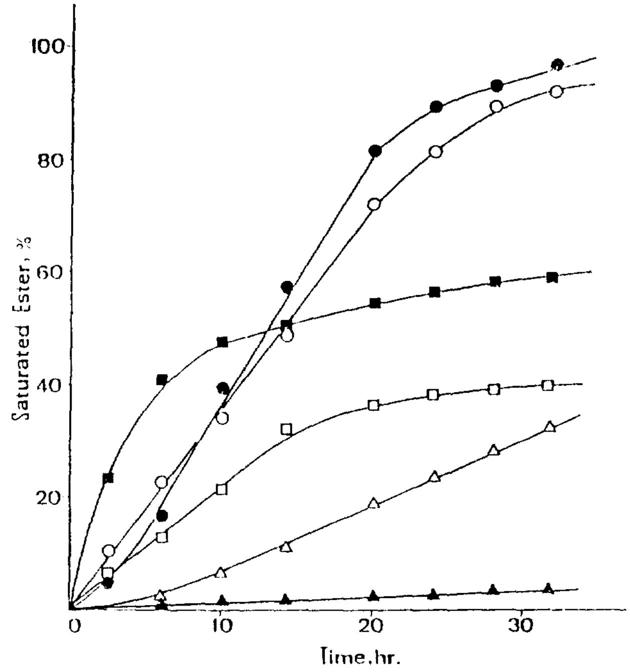

Figure 1. Hydrogenation of Unsaturated Esters (34 mmole) to the Corresponding Staturated Esters with $Rh(ClO_4)(CO)(PPh_3)_2$ (**1**) (0.1 mmole) in $CDCl_3$ (6.0 m*l*) at 25°C under Hydrogen (P_{H_2} + the vapor pressure of the solution = 1 atm). —○—○—, $CH_2=CHCO_2C_2H_5$ (**2**); —●—●—, *trans*-$CH_3CH=CHCO_2C_2H_5$ (**3**); —□—□—, $CH_2=CH(CH_2)_8CO_2C_2H_5$, (**6**) (see text for details); —△—△—, *trans*-$C_6H_5CH=CHCO_2C_2H_5$ (**7**); —▲—▲—, $CH_3(CH_2)_7CH=CH(CH_2)_7CO_2$-$C_2H_5$ (**8**); —■—■—, $CH_2=CH(CH_2)_9CH_3$ (**9**) ($CH_3(CH_2)_{10}CH_3$ production is plotted, see text for details).

realtively fast and proceeds to near completion without any changes in rate (see Figure 1). The isomerization of *trans*-$CH_3CH=CHCO_2C_2H_5$ (**3**) to $CH_2=CHCH_2CO_2C_2H_5$ has not been observed under the experimental conditions in Figure 1. (2) The hydrogenatin of *trans*-$C_6H_5CH=CHCO_2C_2H_5$ (**7**) is slower than that of **2** and **3**, but it does not show a decrease in the rate for a certain period of time (see Figure 1). This observation may be understood both by the extended conjugated system of **7** which stabilizes the olefinic group ($-CH=CH-$) very much and by somewhat steric effect of the bulky phenyl group which may make the catalyst hard to interact with the olefinic group. (3) The hydrogenation of the inner olefinic ester, $CH_3(CH_2)_7CH=CH(CH_2)_7CO_2C_2H_5$ (**8**) is extremely slow due to steric reason (Figure 1). (4) It is noticed that the hydrogenation of the terminal olefinic ester, $CH_2=CH(CH_2)_8CO_2C_2H_5$ (**6**) which also undergoes the isomerization (eq. (4)), proceeds differently from that of **2**, **3**, **7** and **8** (see Figure 1). The hydrogenation of **6** is relatively fast at first and becomes very slow as the reaction proceeds further. The isomerization of **6** (eq. (4)) also occurs simultaneously during the hydrogenation of **6** (see Experimental for details). The hydrogenation data for **6** in Figure 1 is the rate of the CH_3-$(CH_2)_9CO_2C_2H_5$ production and is the combination of disappearance of **6** and that of $CH_3(CH_2)_nCH=CH(CH_2)_{7-n}$-$CO_2C_2H_5$ which are produced during the reaction (by the isomerization of **6** according to eq. (4)) (see Experimental for details). It has been observed that practically no terminal olefinic ester, **6** was left in the reaction mixture after *ca.* 14 hours under the catalytic conditions. According to ¹H-NMR measurements after *ca.* 14 hours, 32% of **6** (originally taken) was converted to the saturated ester, $CH_3(CH_2)_9CO_2C_2H_5$ while the rest, 68% was converted to the inner olefinic esters, $CH_3(CH_2)_nCH=CH(CH_2)_{7-n}CO_2C_2H_5$. Therefore, the hydrogenation curve after 14 hours for **6** in Figure 1 actually represents the hydrogenation of the inner olefinic esters, $CH_3(CH_2)_nCH=CH(CH_2)_{7-n}CO_2C_2H_5$ formed by the isomerization of the original reactant, **6**. (5) To establish the effect of the ester group on the hydrogenation of the unsaturated esters, the hydrogenation of a terminal olefin, $CH_2=CH(CH_2)_9CH_3$ (**9**) was measured under the same conditions and compared with that of the unsaturated esters (Figure 1). Hydrogenation of **9** is significantly faster than that of **6**, but shows the same trend as that of **6**. It is very fast at first and becomes very slow after a certain period of time. It was found that there was practically no starting meterial, **9** left in the mixture after 10 hours under the catalytic conditions. The hydrogenation curve for **9** after 10 hours in Figure 1 actually represents the hydrogenation of the inner olefins, $CH_3(CH_2)_nCH=CH(CH_2)_{8-n}$-$CH_3$ (n = 0~8) which were formed by the isomereization of the starting material, **9** (according to ¹H-NMR measurements). It is now evident that the interactions between the catalyst and the carbonyl oxygen of unsaturated esters affect the hydrogenation in such a way that the hydrogenation of the unsaturated esters becomes slower than that of simple olefins.

Experimental

Infrared, electronic absorption and ¹H-NMR spectra were obtained by Shimadzu IR-440, Shimadzu UV-240 and Varian 60 MHz (Model EM-360), respectively. Conductance measurements were obtained with Wiss-Tech Conductivity meter LBR at 25°C under nitrogen.

Standard vacuum line and Schlenk-type glassware were used in handling metal complexes. $Rh(ClO_4)(CO)(PPh_3)_2$ (**1**) was prepared according to the literature method.¹ $CH_2=CHCO_2C_2H_5$ (Aldrich), *trans*-$CH_3CH=CHCO_2C_2H_5$ (Fluka), *trans*-$C_6H_5CH=CHCO_2C_2H_5$ (Fluka) and $CH_2=CH(CH_2)_9CH_3$ (Aldrich) were distilled before use. $CH_2=CH(CH_2)_8CO_2C_2H_5$ and $CH_3(CH_2)_7CH=CH(CH_2)_7CO_2C_2H_5$ were prepared by the reatctions of the corresponding unsaturated acid and C_2H_5OH. $AgCl_4$ and PPh_3 were used as purchased from Aldrich. Nitrogen and hydrogen were supplied by Doyang Argon.

Product (4) of the Reaction of $Rh(ClO_4)(CO)(PPh_3)_2$ (1) with $CH_2=CHCO_2C_2H_5$ (2). Addition of **1** (0.10 g, 0.15 mmol) into $CH_2=CHCO_2C_2H_5$ (20 m*l*) at 0°C under nitrogen immediately resulted in precipitatin of plae yellow solid (**4**) which was collected by filtration, washed with hexane (60 m*l*), and dried in vacuum for 24 hours at room temperature. The yield was 0.10 g. Λ_M = 100 ohm⁻¹ cm²mole⁻¹ ([Rh] = 5.0 × 10⁻⁵ **M** based on $[Rh(CH_2=CHCO_2C_2H_5)(CO)(PPh_3)_2]ClO_4$ in $CH_2=CHCO_2C_2H_5$ at 25°C).

Product (5) of the Reaction of $Rh(ClO)_4)(CO)(PPh_3)_2$ (1) with *trans*-$CH_3CH=CHCO_2C_2H_5$ (3). This compound was prepared by the same manner as described for **4**. 0.10 g of **1** and 20 m*l* of *trans*-$CH_3CH=CHCO_2C_2H_5$ were used to obtain 0.10 g of **5**. Λ_M = 100 ohm⁻¹cm²mole⁻¹ ([Rh] = 5.0 × 10⁻⁵ **M** based on [Rh (*trans*-$CH_3CH=CHCO_2C_2H_5$)(CO)$(PPh_3)_2$]-ClO_4 in *trans*-$CH_3CH=CHCO_2C_2H_5$ at 25°C).

Isomerization of $CH_2=CH(CH_2)_8CO_2C_2H_5$ (6) with $Rh(ClO_4)(CO)(PPh_3)_2$ (1) under Nitrogen. Complex **1** (0.03 g, 0.04 mmole) and **6** (0.11 g, 0.50 mmole) were dissolved in $CDCl_3$ (0.6 m*l*) in an NMR tube under nitrogen and the resulting yellow solution was continuously shaken at 25°C for 12 hours during which time, ^1H-NMR spectra were recorded at intervals. Isomerization was followed by measuring the disappearance of the signals due to $\mathbf{CH_2} =$ of **6** at 4.9 ~ 5.1 ppm (relative to Me_4Si) or appearance of the signals due to $-\mathbf{CH}=\mathbf{CH}-$ of the products, inner olefins at 5.3 ~ 5.5 ppm. Isomerization of **6** in the presence of $CH_3CO_2C_2H_5$ was measured in the same manner described above. Isomerization of $CH_2 = CH(CH_2)_9CH_3$ (**9**) was also followed by the same way measuring the disappearance of the signals due to $\mathbf{CH_2} =$ of the starting material, **9** at 4.9 ~ 5.1 ppm. A quartet at 4.1 ppm due to $-CO_2\mathbf{CH_2}CH_3$ was used as an internal standard.

Hydrogenation of $CH_2 = CHCO_2C_2H_5$ (2) with $Rh(ClO_4)(CO)(PPh_3)_2$ (1). Complex **1** (0.10 mmole) and **2** (34 mmole) were added in $CDCl_3$ (6.0 m*l*) in a 25 m*l* round bottomed flask and the resulting yellow solution was stirred under hydrogen (P_{H_2} + the vapor pressure of the solution = 1 atm) at 25°C for 32 hours during which time, a portion (0.5 m*l*) of the reaction mixture was taken out for ^1H-NMR measurement at intervals. Hydrogenation of **2** was followed by measuring the disappearnace of $\mathbf{CH_2}=\mathbf{CH}-$ signals of **2** at 5.2 ~ 6.2 ppm (relative to Me_4Si). A quartet at 4.0 ppm due to $-CO_2\mathbf{CH_2}CH_3$ was used as an internal standard.

Hydrogenation of *trans*-$CH_3CH = CHCO_2C_2H_5$ (3) with $Rh(ClO_4)(CO)(PPh_3)_2$ (1). This reaction was carried out in the same manner described above and followed by measuring the disappearance of the signals at 5.7 ~ 7.0 ppm due to $-\mathbf{CH}=\mathbf{CH}-$ of **3** and using the quartet at 4.0 ppm due to $-CO_2\mathbf{CH_2}CH_3$ as an internal standard.

Hydrogenation of *trans*-$C_6H_5CH = CHCO_2C_2H_5$ (7) with $Rh(ClO_4)(CO)(PPh_3)_2$ (1). This reaction was carried out in the same manner described above and followed by measuring the disappearance of the signals at 6.3 ~ 6.5 ppm due to $-CH=CHCO_2-$ of **7** and using the quartet at 4.0 ppm due to $-CO_2\mathbf{CH_2}CH_3$ as an internal standard.

Hydrogenation of $CH_3(CH_2)_7CH = CH(CH_2)_7CO_2C_2H_5$ (8) with $Rh(ClO_4)(CO)(PPh_3)_2$ (1). This reaction was carried out in the same manner described above and followed by measuring the disappearance of the signals due to $-\mathbf{CH}=\mathbf{CH}-$ at 5.3 ~ 5.5 ppm and using the quartet at 4.0 ppm due to $-CO_2\mathbf{CH_2}CH_3$ as an internal standard.

Hydrogenation and Isomerization of $CH_2 = CH(CH_2)_8CO_2C_2H_5$ (6) with $Rh(ClO_4)(CO)(PPh_3)_2$ (1). This reaction was carried out in the same manner described above. The hydrogenation was followed by measuring the disappearance of the total signals at 4.9 ~ 6.0 ppm due to $\mathbf{CH_2}=\mathbf{CH}-$ of **6** and $-\mathbf{CH}=\mathbf{CH}-$ of the inner olefinic esters ($CH_3(CH_2)_nCH = CH(CH_2)_{7-n}CO_2C_2H_5$) formed during the reaction (see text for details), while the isomerization was followed by measuring the appearance of the signals at 5.3 ~ 5.5 ppm due to $-\mathbf{CH}=\mathbf{CH}-$ of the products, $CH_3(CH_2)_nCH = CH(CH_2)_{7-n}CO_2C_2H_5$. A quartet at 4.2 ppm due to $CO_2\mathbf{CH_2}CH_3$ was used as an internal standard.

Hydrogenation and Isomerization of $CH_2 = CH(CH_2)_9CH_3$ (9) with $Rh(ClO_4)(CO)(PPh_3)_2$ (1). This reaction was carried out in the same manner described above. The hydrogenation of **9** was followed by measuring the appearance of the signals at 5.0 ~ 6.0 ppm due to $\mathbf{CH_2}=CH-$ of **9** and $-\mathbf{CH}=\mathbf{CH}-$ of the inner olefins, $CH_3(CH_2)_nCH = CH-(CH_2)_{8-n}-CH_3$ formed during the catalysis, while the isomerization was followed by measuring the appearance of the signals at 5.3 ~ 5.5 ppm due to $-\mathbf{CH}=\mathbf{CH}-$ of the inner olefins. A quartet at 4.1 ppm due to $-CO_2\mathbf{CH_2}CH_3$ was used as an internal standard.

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References

1. J. Peone Jr. and L. Vaska, *Angew. Chem. Int. Ed. Engl.*, **10**, 511 (1971).
2. (a) S.H. Park, H.-K. Park, and C.S. Chin, *Inorg. Chem.*, **24**, 1120 (1985). (b) M.K. Lee, I.B. Kim, and C.S. Chin, *J. Organomet. Chem.*, **290**, 115 (1985). (c) T. Kwon, J.C. Woo, and C.S. Chin, *Polyhedron*, **2**, 1125 (1983). (d) J.C. Woo, S.H. Kim, and C.S. Chin, *J. Polymer Sci. Chem. Ed.*, **20**, 1947 (1982).
3. I.B. Kim and C.S. Chin, *Polyhedron*, **3**, 1151 (1984).
4. J. Park and C.S. Chin, submitted for publication.
5. H.M. Jeong and C.S. Chin, *Bull. Korean Chem. Soc.*, **5**, 199 (1984).
6. J. Brady, B.R. Flynn, G.L. Geoffroy, H.B. Gray, J. Peone, Jr., and L. Vaska, *Inorg. Chem.*, **15**, 1485 (1976).
7. Hydrogenation of $CH_2 = CH_2$ to C_2H_6 with **1** was briefly mentioned previously[1], but the hydrogenation of other olefins has not studied before.