Contribution from the Department of Chemistry,
University of Wisconsin, Madison, Wisconsin 53706

Thermal Decomposition of (*erythro*-2,3-Dimethylpentanoyl)pentacarbonylmanganese(I)

CHARLES P. CASEY,* CLIFFORD R. CYR, and JANET A. GRANT

Received July 13, 1973

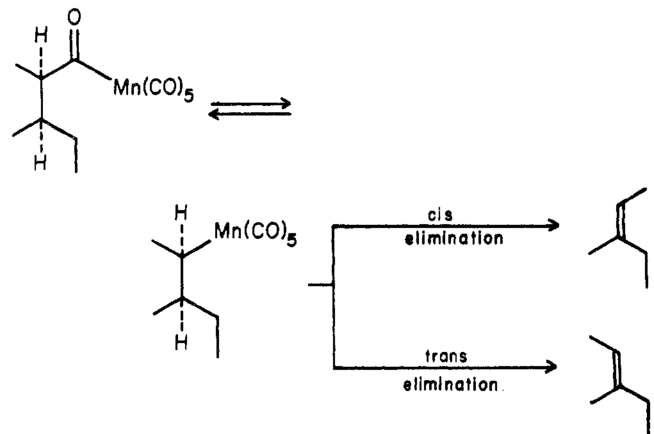
(*erythro*-2,3-Dimethylpentanoyl)pentacarbonylmanganese(I) (**5**), a mixture of **5** and the threo isomer **6**, and (4-methylhexanoyl)pentacarbonylmanganese(I) (**7**) all thermally decompose to give the same mixture containing 4–11% 3-methyl-1-pentene, 56–62% *trans*-3-methyl-2-pentene, and 31–32% *cis*-3-methyl-2-pentene. In contrast, (3-ethylpentanoyl)pentacarbonylmanganese(I) (**8**) thermally decomposed to give 78% 2-ethyl-1-butene and 22% of the same mixture of alkenes obtained from **5**, **6**, and **7**. Alkenes do not isomerize under these reaction conditions. These results are interpreted in terms of a mechanism involving interconversion of $RMn(CO)_4$ and (alkene)$Mn(CO)_4H$ species at a rate much faster than decomplexation of the alkene.

Introduction

Both the addition of transition metal hydrides to alkenes to give metal alkyls and the microscopic reverse of this process, the thermal decomposition of metal alkyls to alkenes and metal hydrides, constitute two of the most important processes in organometallic chemistry.[1] The thermal decomposition of metal alkyls is generally thought to proceed by the β elimination of a metal hydride, since metal hydrides have been isolated from the thermolysis of *n*-alkylplatinum(II),[2] -rhodium(I),[3] and -copper(I)[4] compounds.

Both the elimination of transition metal hydride from metal alkyls and the addition of metal hydrides to alkenes are generally considered to be cis processes. The products of cis addition of transition metal hydrides to acetylenes,[5] 1,3-dienes,[6] and unsaturated acids[7] have been observed. Furthermore, cis addition of metal hydrides has been proposed as an essential process in alkene isomerization,[8] homogeneous hydrogenation,[9] and hydroformylation reactions.[10] While there is abundant data consistent with the cis elimination or addition of transition metal hydrides, we felt that a *direct* determination of the stereochemistry of a transition metal hydride elimination from a simple system was desirable.

To obtain direct evidence for the stereochemistry of a metal hydride elimination reaction, we initiated a study of the thermal decomposition of (*erythro*-2,3-dimethylpentanoyl)pentacarbonylmanganese(I), **5**. Acylmanganese compounds readily undergo reversible stereospecific decarbonylation[11-14] and are an excellent source of alkylmanganese compounds. The



(*erythro*- and *threo*-2,3-dimethylpentanoyl)pentacarbonyl- since it constitutes the simplest system which would allow the determination of the stereochemistry of a metal hydride elimination without the use of isotopic labels. Cis elimination of metal hydride from (*erythro*-2,3-dimethylpentanoyl)-pentacarbonylmanganese(I) would give *cis*-3-methyl-2-pentene while trans elimination would lead to *trans*-3-methyl-2-pentene.

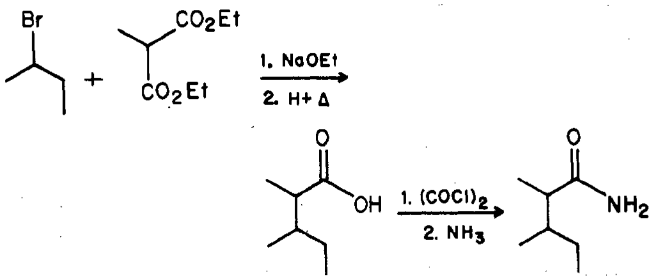
Here we report that both pure *erythro*- and a mixture of (*erythro*- and *threo*-2,3-dimethylpentanoyl)pentacarbonylmanganese(I) thermally decompose to give the same mixture of *cis*- and *trans*-3-methyl-2-pentene and 3-methyl-1-pentene under conditions which do not isomerize these alkenes. Further experiments demonstrated that this mixture of alkenes was obtained due to the interesting rapid multiple isomerization of the initially formed complexed alkene prior to decomplexation. Due to these rapid isomerization processes, the goal of directly determining the stereochemistry of a transition metal hydride elimination has remained elusive.

Results

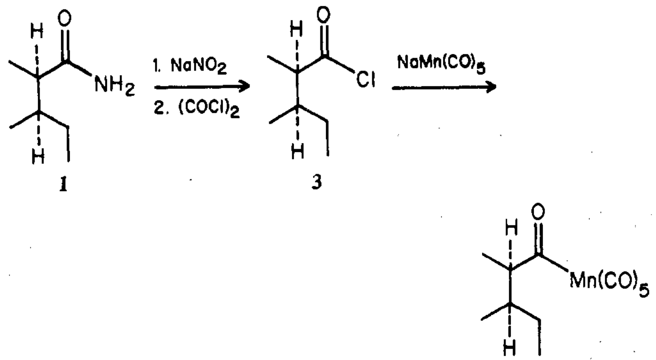
Synthesis. A mixture of *erythro*- (**1**) and *threo*-2,3-dimethylpentanamide (**2**) was synthesized by the procedure outlined in Scheme I. Pure erythro amide **1** was obtained by fractional crystallization of the mixture from methanol-water. Unequivocal stereochemical assignments of amides **1** and **2** had previously been made by Pino[15] on the basis of chemical correlations with meso and optically active 3,4-dimethyladipic acid.

(1) For reviews of transition metal hydride additions to alkenes see (a) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. 2, 3rd ed, Methuen and Co., London, 1968, Chapter 7; (b) G. W. Parshall and J. J. Mrowca, *Advan. Organometal. Chem.*, 7, 157 (1968); (c) C. A. Tolman in "Transition Metal Hydrides," Vol. 1, E. L. Muetterties, Ed., Marcel Dekker, New York, N. Y., 1971, Chapter 6.
(2) G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, 94, 5258 (1972), and references therein.
(3) R. Cramer, *Accounts Chem. Res.*, 1, 186 (1968).
(4) G. M. Whitesides, E. R. Stedronsky, C. P. Casey, and J. San Filippo, Jr., *J. Amer. Chem. Soc.*, 92, 1426 (1970); K. Wada, M. Tamura, and J. Kochi, *ibid.*, 92, 6656 (1970).
(5) H. C. Clark and W. S. Tsang, *J. Amer. Chem. Soc.*, 89, 529 (1967).
(6) C. A. Tolman, *J. Amer. Chem. Soc.*, 92, 6785 (1970).
(7) L. M. Jackman, J. A. Hamilton, and J. M. Lawlor, *J. Amer. Chem. Soc.*, 90, 1914 (1968).
(8) R. Cramer, *J. Amer. Chem. Soc.*, 88, 2272 (1966).
(9) J. A. Osborn, F. H. Jardine, J. F. Young, and G. F. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).
(10) W. F. Fichtman and M. Orchin, *J. Org. Chem.*, 34, 2790 (1969).
(11) For a review see A. Wojcicki, *Advan. Organometal. Chem.*, 11, 87 (1973).
(12) G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, 91, 4313 (1969).
(13) R. W. Johnson and R. G. Pearson, *Chem. Commun.*, 986 (1970).
(14) F. Calderazzo and K. Noack, *Coord. Chem. Rev.*, 1, 118 (1966).
(15) P. Pino, R. Rossi, and P. Bucci, *Tetrahedron Lett.*, 3295 (1966).

Scheme I. Synthesis of a Mixture of *erythro*- and *threo*-2,3-Dimethylpentanamide

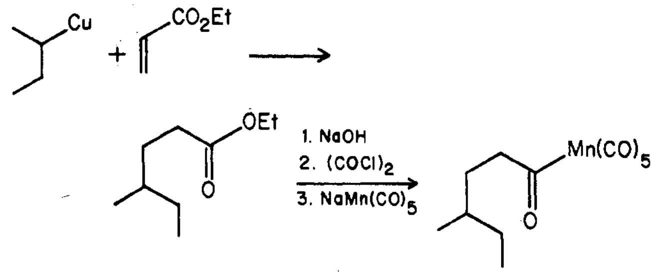


Scheme II. Synthesis of (*erythro*-2,3-Dimethylpentanoyl)pentacarbonylmanganese(I)



5

Scheme III. Synthesis of (4-Methylhexanoyl)pentacarbonylmanganese(I)



7

Erythro amide **1** was converted to *erythro*-2,3-dimethylpentanoyl chloride, **3**, as shown in Scheme II. Reaction of erythro acid chloride **3** with sodium pentacarbonylmanganate(–I) followed by preparative layer chromatography and low-temperature crystallization from pentane gave (*erythro*-2,3-dimethylpentanoyl)pentacarbonylmanganese(I), **5**, as a crystalline solid melting at 19–21°. The infrared spectrum of **5** in hexane had bands at 2110, 2040, and 2000 cm^{-1} for the $Mn(CO)_5$ unit and at 1650 cm^{-1} for the acyl group.

A 1.4:1 mixture of erythro (**3**) and threo (**4**) acid chlorides was similarly converted to a mixture of erythro (**5**) and threo (**6**) acylmanganese compounds.

During the course of this investigation, it became desirable to study the thermal decomposition of the isomeric acylmanganese compounds possessing the same carbon backbone as **5** and **6**. Consequently, (4-methylhexanoyl)pentacarbonylmanganese(I), **7**, was synthesized as outlined in Scheme III. The key step in the synthesis was the conjugate addition of lithium di-*sec*-butylcuprate to ethyl acrylate. (3-Ethylpentanoyl)pentacarbonylmanganese(I), **8**, was routinely prepared from the corresponding acid chloride. However, reaction of 2-ethyl-2-methylbutanoyl chloride with $NaMn(CO)_5$ did not afford any of the desired acylmanganese compound **9** but gave only $Mn_2(CO)_{10}$ and $Mn(CO)_5Cl$.

8 9

Stereochemistry of Acylmanganese Compounds. The diastereomeric purity of the erythro acylmanganese compound **5** is supported by three independent lines of evidence. First, **5** was synthesized from pure erythro amide **1** by a route not involving steps which would be expected to give rise to epimerization. Second, the 100-MHz nmr spectrum of **5** did not exhibit the resonances at 72 and 78 Hz which occurred in the nmr spectrum of the mixture of diastereomeric manganese compounds **5** and **6**. Third, cleavage of **5** with chlorine in methanol gave only methyl *erythro*-2,3-dimethylpentanoate while the diastereomeric mixture of **5** and **6** prepared from a 1.4:1 mixture of erythro (**3**) and threo (**4**) acid chloride gave a 1.5:1 ratio of erythro and threo methyl esters. (See Scheme IV.) The diastereomeric purity of the methyl esters was readily determined by nmr since the CH_3CHCO resonance of the erythro isomer appears as a doublet centered at δ 1.12 while that of the threo isomer appears at δ 1.07.

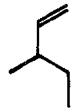
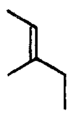
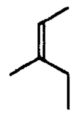
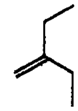
Thermal Decomposition of Acylmanganese Compounds. The thermal decomposition of acylmanganese compounds **5**, **6**, **7**, and **8** was complete within 18 hr at 100° in methylcyclohexane.[16] Thin-layer chromatography showed the complete disappearance of starting material and the formation of $Mn_2(CO)_{10}$. In the case of the decomposition of **7**, the yield of $Mn_2(CO)_{10}$ was found to be 71%. Gas chromatographic analysis showed that C_6 alkenes were the only hydrocarbon products formed. No C_6 or C_{12} alkanes or C_7 aldehydes were detected in the reaction mixtures. As indicated in Table I, the erythro manganese compound **5**, a 1.4:1 mixture of erythro (**5**) and threo (**6**) manganese compounds, and the primary manganese compound **7** all gave similar mixtures containing 3-methyl-1-pentene (4–12%), ~2:1 mixture of *trans*- and *cis*-3-methyl-2-pentene (88–94%), and only traces (<1.0%) of 2-ethyl-1-butene. In contrast, acylmanganese compound **8** gave 78.5% 2-ethyl-1-butene, only 19% of a 2:1 mixture of *trans*- and *cis*-3-methyl-2-pentene, and 4% 3-methyl-1-pentene.

To determine whether alkene isomerization was occurring under the conditions of the thermal decomposition of the acylmanganese compounds, 0.16 mmol of a mixture of **5** and **6** was decomposed in the presence of 0.32 mmol of *trans*-3-methyl-2-pentene. Gc analysis of the reaction mixture following decomposition indicated that no isomerization of *trans*-3-ethyl-2-pentene had occurred. Similarly, no isomerization of excess added 3-methyl-1-pentene was observed during the decomposition of a mixture of **5** and **6**. A further indication that alkene isomerization is not occurring under the conditions of the thermal decomposition is that the decomposition of **8** gave a mixture of alkenes drastically different from that obtained from the decompositions of either **5**, **6**, or **7**.

To determine whether acylmanganese compound **7** interconverted with erythro and threo acylmanganese compounds under the thermal decomposition conditions, the decomposition of **7** was carried to about 50% completion (30 min at 100°) and the unreacted acylmanganese compounds were

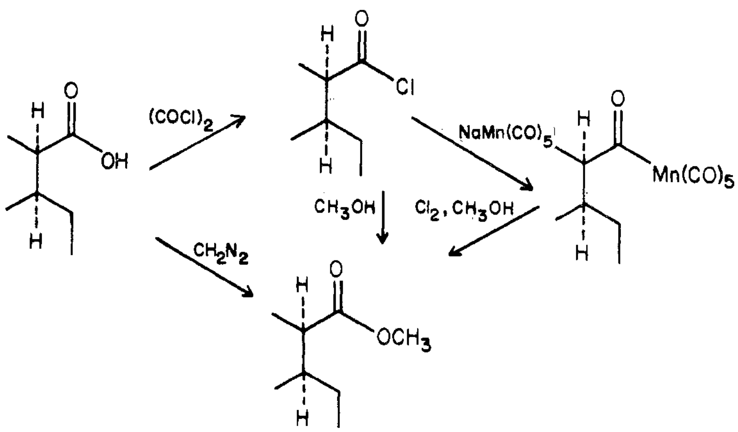
(16) The time required for ~50% decomposition at 100° was found to be 30 min by nmr.

Table I. Thermal Decomposition of Acylmanganese Compounds[a]

	Ratio of alkene products[b]					
Acylmanganese compd					Total yield[b] of alkenes, %	Yield of $Mn_2(CO)_{10}$
5	11.4	56.6	31.7	0.3	37	
1.4:1, 5:6	9.8	58.6	31.6	0.1	32	
7	4.5	62.7	32.0	0.7	49	71[c]
8	3.8	11.7	6.1	78.5	56	

[a] Decomposition in methylcyclohexane at 100° for 18–24 hr. [b] Determined by gas chromatography using *n*-heptane as an internal standard. [c] Yield of material isolated by preparative thick-layer chromatography.

Scheme IV. Stereochemical Correlations for (*erythro*-2,3-Dimethylpentanoyl)pentacarbonylmanganese(I)



treated with chlorine in methanol at −78°. Analysis of the chlorination products by gas chromatography indicated a mixture containing 80% methyl 4-methylhexanoate and 20% methyl 2,3-dimethylpentanoate resulting from isomerization. In a similar experiment, a mixture of **5** and **6** was partially decomposed in methylcyclohexane at 100° for 25 min and the remaining acylmanganese compounds were treated with chlorine in methanol at −78°. Gas chromatographic analysis indicated a mixture of 98% methyl 2,3-dimethylpentanoate and only 2% methyl 4-methylhexanoate formed by isomerization.

Discussion

This study of the thermal decomposition of (*erythro*-2,3-dimethylpentanoyl)pentacarbonylmanganese(I), **5**, was initiated in an effort to determine the validity of the generally accepted cis stereochemistry of the elimination of metal hydrides from metal alkyls. If decomposition of **5** proceeded by a cis elimination of a metal hydride, then decomposition should lead to 3-methyl-1-pentene and *cis*-3-methyl-2-pentene as the only alkene products. However, it soon became obvious that a simple cis elimination of metal hydride was not occurring in this system since the decomposition of both pure erythro **5** and a 1.4:1 mixture of erythro (**5**) and threo (**6**) acylmanganese compounds produced the same mixture of alkenes containing a 2:1 ratio of *cis-:trans*-3-methyl-2-pentene.

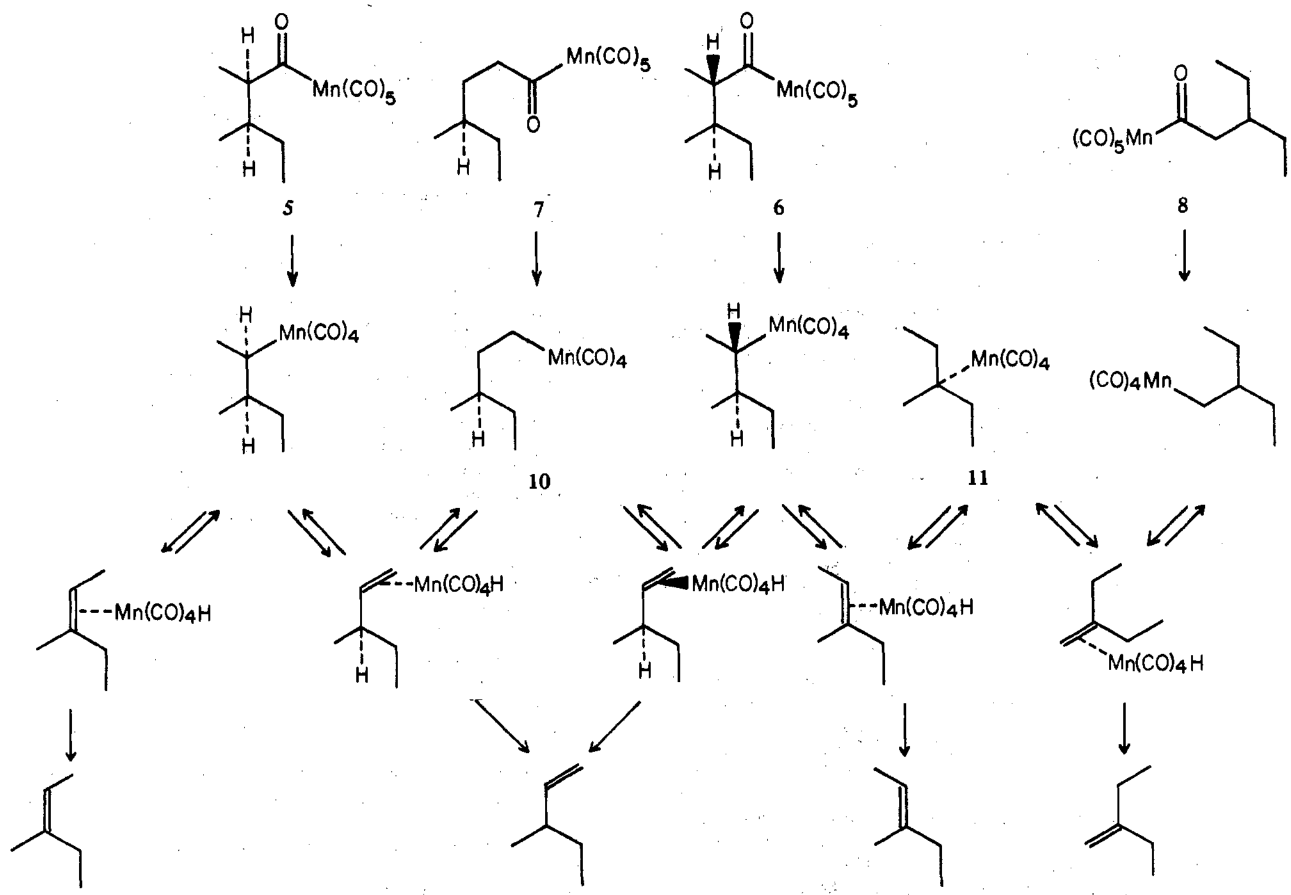
Obvious control experiments ruled out several trivial explanations for the above result. Chlorination of erythro **5** in methanol gave only methyl *erythro*-2,3-dimethylpentanoate and ruled out the possibility of an isomerization during the synthesis of **5**. The possibility that olefin isomerization was occurring under the thermal decomposition conditions was eliminated by the demonstration that both 3-methyl-1-pentene and *trans*-3-methyl-2-pentene do not isomerize under the conditions of thermal decomposition.

At this point, the nonstereospecific decomposition of **5** could be accounted for either by a mechanism involving a mixture of cis and trans elimination processes possibly involving free radicals or by a mechanism involving multiple isomerizations of a complexed alkene prior to decomplexation. To distinguish between these possibilities we studied the thermal decomposition of **7**, a compound possessing the same carbon framework as **5** and **6** but having a different site of attachment of the acylmanganese moiety. The thermal decomposition of **7** produced the same mixture of alkenes as obtained from **5** and **6**. The 3-methyl-2-pentenes could not be formed by a nonstereospecific elimination process but must be the result of a process which involves migration of manganese to different sites along the carbon chain. Since the same mixture of alkenes was obtained from **5**, **6**, and **7**, the isomerization processes interconverting the complexed alkenes must be occurring fast relative to decomplexation.

Scheme V illustrates the way in which an erythro manganese compound can isomerize to the corresponding threo isomer. The formation of a highly reactive coordinately unsaturated $RMn(CO)_4$ species which can undergo reversible metal hydride eliminations to give (alkene)$Mn(CO)_4H$ is the key to understanding the isomerization process. Isomerization of erythro to threo compounds cannot be achieved by a single metal hydride cis elimination and readdition since both the *cis*-3-methyl-2-pentene and the 3-methyl-1-pentene manganese hydride complexes formed from the erythro manganese alkyl can revert to the erythro but not the threo manganese alkyl. Isomerization from the erythro to the threo isomer can only occur *via* the symmetric primary 3-methyl-1-pentylmanganese compound (**10**) or the symmetric tertiary 3-methyl-3-pentylmanganese compound (**11**).

A distinction between isomerization *via* the primary manganese alkyl and isomerization *via* the tertiary manganese alkyl can be made on the basis of the results obtained in the

Scheme V. Thermal Decomposition of Acylmanganese Compounds



thermal decomposition of (3-ethylpentanoyl)pentacarbonylmanganese(I), **8**. Decomposition of **8** gave 78% 2-ethyl-1-butene and only 22% of the mixture of alkenes obtained from thermal decomposition of **5**, **6**, or **7**. Since a drastically different mixture of alkenes is obtained from decomposition of a potential precursor of the tertiary 3-methyl-3-pentylmanganese compound **11**, the interconversion of *erythro*- and *threo*-3-methyl-2-pentylmanganese compounds cannot be proceeding *via* **11**. The intervention of **11** in the decomposition of **5**, **6**, and **7** would have been expected to lead to the formation of substantial quantities of 2-ethyl-1-butene; however, less than 1% of this compound was obtained. Therefore, the 3-methyl-3-pentylmanganese species **11** is the high energy species which acts as a roadblock along the alkene isomerization pathway.

Apparently, the formation of free alkenes constitutes the major exit from the manifold of rapidly equilibrating $RMn(CO)_4$ and (alkene)$Mn(CO)_4H$ species, and the reversion to $RCOMn(CO)_5$ is only a minor exit from this manifold. Thus, less than 2% of **7** was formed after ~50% decomposition of a mixture of **5** and **6** and only 20% of a mixture of **5** and **6** was obtained after ~50% decomposition of **7**.

In summary, all of our results are consistent with the mechanism outlined in Scheme V. All of the addition and elimination steps interconverting $RMn(CO)_4$ and (alkene)$Mn(CO)_4H$ are very rapid with the exception of the steps leading to the formation of the tertiary 3-methyl-3-pentylmanganese compound **11**. The major exit from this manifold is the irreversible formation of alkenes which are stable under the reaction conditions. A minor exit from the manifold is reversion to isomeric $RCOMn(CO)_5$ compounds.

The isomerization of complexed alkenes and of metal alkyls *via* metal hydride addition-elimination sequences is beginning to be recognized as an important process in organometallic chemistry. Such processes have been observed to accompany the hydroformylation reaction,[17] the platinum-catalyzed isomerization of alkenes,[18] the decomposition of alkylplatinum compounds,[2] and the isomerization of alkylnickel[19,20] and -iridium compounds.[21]

Experimental Section

Nmr spectra were determined using Varian A-60A, T-60, and XL-100 spectrometers and a Joelco MH-100 spectrometer. Infrared spectra were recorded on a Beckman IR-8 spectrophotometer. Mass spectra were determined using an AEI-902 mass spectrometer. Gas chromatographic analyses were performed using a Hewlett-Packard Model 5750 research chromatograph; preparative gas chromatography was accomplished with a Varian 90-P gas chromatograph. *trans*-3-Methyl-2-pentene and a mixture of *cis*- and *trans*-2-pentene were obtained from Aldrich Chemical Co.

2,3-Dimethylpentanoic Acid. Following a procedure similar to that of Kondakowa,[22] 39.5 g (33%) of a mixture of diastereomers of 2,3-dimethylpentanoic acid was prepared by dropwise addition of 2-bromobutane (136 g, 0.99 mol) to a solution of diethyl methylmalonate (162 g, 0.93 mol) and sodium (22 g, 0.96 mol) in dry ethanol followed by saponification and acid-catalyzed decarboxylation: bp 100° (5 mm); ir ν_{max}^{neat} 2950 (broad), 1700 cm^{-1}; nmr $\delta_{TMS}^{CCl_4}$ 0.6–2.0 (m, 9 H),

(17) C. P. Casey and C. R. Cyr, *J. Amer. Chem. Soc.*, **95**, 2240 (1973).
(18) H. C. Clark and H. Kurosawa, *Inorg. Chem.*, **12**, 1567 (1973).
(19) A. Yamomoto, T. Yamomoto, Y. Saruyama, and Y. Nakamura, *J. Amer. Chem. Soc.*, **95**, 4073 (1973).
(20) K. Tamao, Y. Kiso, K. Sumitani, and M. Kumada, *J. Amer. Chem. Soc.*, **94**, 9268 (1972).
(21) M. A. Bennett and R. Charles, *J. Amer. Chem. Soc.*, **94**, 666 (1972).
(22) M. S. Kondakowa and M. M. Katznelson, *Dokl. Akad. Nauk SSSR*, **18**, 271 (1938); *Chem. Zentralbl.*, **109**, 4444 (1938).

1.1 (d, 3 H, CH_3CHCO_2H), 2.4 (q, 1 H, CH_3CHCO_2H), and 12.3 (s, 1 H, CO_2H).

Methyl 2,3-Dimethylpentanoate. A mixture of diastereomers of methyl 2,3-dimethylpentanoate was prepared by the addition of diazomethane in ether to 2,3-dimethylpentanoic acid in ether: ir ν_{max}^{neat} 1735 cm^{-1}; nmr $\delta_{TMS}^{CCl_4}$ 0.87 (t, 3 H, CH_3CH_2), 0.88 (d, 3 H, CH_3CHCH), 1.03 (d of d, 3 H, $CH_3CHCO_2CH_3$ (diastereomeric CH_3's)), 1.0–1.85 (m, 3 H, CH_2, CH), 2.3 (q, 1 H, $CH_3CHCO_2CH_3$), and 3.6 (s, 3 H, CO_2CH_3). The ratio of erythro to threo isomers was found to be 1.4:1 by measurement of the relative intensities of the doublets in the nmr spectrum at δ 1.03.

2,3-Dimethylpentanoyl Chloride (3 and 4). Oxalyl chloride (17.6 g, 0.14 mol) was added slowly to 2,3-dimethylpentanoic acid (9.1 g, 0.07 mol). The mixture was stirred at 25° for 16 hr. Distillation under vacuum gave 7.68 g (75%) of a diastereomeric mixture of 3 and 4: bp 57–58° (17 mm); ir ν_{max}^{neat} 1780 cm^{-1}; nmr $\delta_{TMS}^{CCl_4}$ 0.7–1.6 (m, 8 H), 1.2 (d of d, 3 H, $CH_3CHCOCl$ (diastereomeric CH_3's)), 1.6–2.2 (m, CH_3CHCH), and 2.7 (m, $CH_3CHCOCl$).

2,3-Dimethylpentanamide (1 and 2). A diastereomeric mixture of 3 and 4 (8.3 g, 0.056 mol) in 25 ml of dry benzene was added dropwise to 125 ml of hot, ammonia-saturated benzene. After completion of the addition, ammonia gas was bubbled through the hot reaction mixture for 30 min. The hot reaction mixture was filtered. The amide (5.87 g, 81%) crystallized upon dropwise addition of pentane to the hot benzene solution and cooling: mp 104–109°; ir ν_{max}^{KBr} 3340 (broad), 3160, 2950, 1625 (broad); nmr $\delta_{TMS}^{CDCl_3}$ 0.7–1.0 (m, 6 H, $2CH_3$), 1.1 (d of d, 3 H, CH_3CH (diastereomeric CH_3's)), 1.1–1.9 (m, 3 H, CH_2, CH), 2.15 (m, 1 H, $CH_3CHCONH_2$), and 5.4–6.4 (broad d, 2 H, $CONH_2$).

erythro-**2,3-Dimethylpentanamide (1).** 1 was obtained by repeated fractional recrystallization from 40% methanol–water of the mixture of amides prepared above: mp 122–123° (lit.[15] mp 123–124°); nmr $\delta_{TMS}^{CDCl_3}$ 0.88 (t, 3 H, CH_3CH_2), 0.92 (d, 3 H, CH_3CH), 1.1 (d, 3 H, $CH_3CHCONH_2$), 1.0–1.3 (m, 2 H, CH_3CH_2CH), 1.35–1.8 (m, $CHCH_3$, 2.1 (q, 1 H, $CH_3CHCONH_2$), and 5.4–6.3 (broad d, 2 H, $CONH_2$).

erythro-**2,3-Dimethylpentanoic Acid.** A saturated aqueous solution of sodium nitrite (1.12 g, 16.3 mmol) was added dropwise to a 0° solution of 1 (0.49 g, 3.8 mmol) in 6 ml of concentrated sulfuric acid. The mixture was stirred at 0° for 30 min, heated at 60–70° for 1 hr, poured into 50 ml of water, and extracted with ether. Removal of the ether and preparative gas chromatography gave the acid.

(*erythro*-2,3-Dimethylpentanoyl)pentacarbonylmanganese(I) (5). erythro acid chloride 3 (0.57 g, 3.9 mmol) was added to a tetrahydrofuran solution of $NaMn(CO)_5$ (8.0 ml, 0.58 *M*, 4.6 mmol) at 0°. The mixture was stirred for 3 hr at 25°. Solvent was removed on a rotary evaporator and the oily residue was dissolved in ether. The ether solution was washed with water, dried (Na_2SO_4), and concentrated. Preparative thick-layer chromatography (silica gel, hexane) gave the crude acylmanganese compound which was further purified by recrystallization from pentane at −78° to give 5 (0.21 g, 20% yield): mp 22–23°; ir ν_{max}^{hexane} 2110, 2040, 2000, 1650 cm^{-1}; nmr $\delta_{TMS}^{CS_2}$ 2.8 (quintet, 1 H, CHCO), 1.9–1.0 (m, 3 H), 1.0–0.8 (5 lines, 9 H); mass spectrum *m/e* (intensity, assignment) 308 (0.03, M), 223 (22, $Mn(CO)_6$), 195 (10, $Mn(CO)_5$), 112 (37, $C_7H_{12}O$), 85 (100, C_6H_{13}), 83 (10, MnCO), 69 (19), 58 (16), 57 (19), 56 (13), 55 (31, Mn), 43 (62), 41 (37), 39 (12).

2,3-Dimethylpentanoylpentacarbonylmanganese(I) (5 and 6). A 1.4:1 mixture of erythro and threo acid chlorides 3 and 4 (0.84 g, 5.65 mmol) was added dropwise to a tetrahydrofuran solution of $NaMn(CO)_5$ (11.4 ml, 0.58 *M*, 6.6 mmol) at 0° and the mixture was stirred at 25° for 1 hr. Workup of the reaction mixture by a procedure similar to the one described above for the isolation of the pure erythro isomer gave a mixture of 5 and 6 (1.03 g, 59%), mp 19–21°. The 100-MHz nmr spectrum (CS_2) of the mixture of isomers differed from that of the pure erythro acylmanganese compound in that it contained two additional sharp high-field resonances at 72 and 78 Hz.

Ethyl 4-Methylhexanoate. Reaction of lithium di-*sec*-butylcuprate prepared from *sec*-butyllithium (91 ml, 1.1 *M*, 0.10 mol) and CuI (9.5 g, 0.05 mol) in 150 ml of ether at −25° and ethyl acrylate (5 g, 0.05 mol) at −25° gave, after standard workup, ethyl 4-methylhexanoate (4.5 g, 57%): ir ν_{max}^{neat} 1740 cm^{-1}.

4-Methylhexanoic Acid. Hydrolysis of ethyl 4-methylhexanoate (4.5 g, 28 mmol) was accomplished by refluxing for 12 hr in 1 *M* KOH in 50% aqueous ethanol to give after workup 4-methylhexanoic acid (1.3 g, 35%): bp 110–116° (8 mm); ir ν_{max}^{neat} 1710 cm^{-1}.

4-Methylhexanoyl Chloride. Reaction of 4-methylhexanoic acid (1.3 g, 10 mmol) with neat oxalyl chloride (2.0 g, 16 mmol) for 10 hr gave 4-methylhexanoyl chloride (1.1 g, 75%): bp 78° (25 mm), ir ν_{max}^{neat} 1810 cm^{-1}.

(4-Methylhexanoyl)pentacarbonylmanganese(I) (7). 4-Methylhexanoyl chloride (0.50 g, 3.4 mmol) was stirred with a tetrahydrofuran solution of $NaMn(CO)_5$ (5.8 ml, 0.58 *M*, 3.4 mmol) for 4 hr at 0°. Preparative thick-layer chromatography (silica gel, hexane) gave 7 (0.51 g, 49%) as a white solid: mp 65–67°; ir $\nu_{max}^{heptane}$ 2110 (m), 2050 (m), 2010 (vs), and 1660 (m) cm^{-1}; nmr $\delta_{TMS}^{CS_2}$ 2.84 (2 H, t, J = 7, CH_2CH_2CO), 1.0–1.7 (5 H, broad m), 0.85 (6 H, m, $2CH_3$'s).

(3-Ethylpentanoyl)pentacarbonylmanganese(I) (8). 3-Ethylpentanoyl chloride (0.50 g, 3.38 mmol) was stirred with a tetrahydrofuran solution of $NaMn(CO)_5$ (7.0 ml, 0.51 *M*, 3.57 mmol) for 2 hr at room temperature. Preparative thick-layer chromatography (silica gel, 1:1 hexane:benzene) gave 8: mp 55–56°; ir $\nu_{max}^{heptane}$ 2120 (m), 2050 (m), 2005 (vs), 1660 (m) cm^{-1}; nmr $\delta_{TMS}^{CS_2}$ 2.84 (2 H, d, J = 6, $CHCH_2CO$)), 1.78 (1 H, 5 lines, J = 6.5, CH), 2.26 (4 H, 5 lines, CH_2CH_3), 0.82 (6 H, t, CH_2CH_3).

Chlorination of 5. Chlorine was bubbled through a solution of the erythro manganese compound 5 (0.16 g, 0.52 mmol) in 5 ml of methanol at −78°. The solution was stirred for 30 min at 25° and worked up with water and pentane. Methyl 2,3-dimethylpentanoate was isolated from the dried, concentrated pentane extract by gas chromatography on an SE-30 column at 150°. The 100-MHz nmr spectrum of the methyl ester had a doublet centered at δ 1.12 for the CH_3CHCO protons of the erythro ester but no observable doublet centered at δ 1.07 indicating that the erythro ester was contaminated by <5% of the threo ester.

Similarly, chlorination of the mixture of erythro and threo manganese compounds 5 and 6 prepared from a 1.4:1 mixture of acid chlorides gave a 1.5:1 mixture of erythro:threo methyl esters as shown by the ratio of intensities of the doublets at δ 1.12 and 1.07 in the nmr spectrum of the esters.

Thermal Decomposition of Acylmanganese Compounds. A 0.5 *M* methylcyclohexane solution of the acylmanganese compound containing heptane as an internal standard for gas chromatographic analysis was degassed by three freeze–thaw cycles. The mixture was sealed in a test tube and heated at 100° for 18–24 hr. Tlc analysis (silica gel, hexane) indicated the complete disappearance of acylmanganese compound and the formation of $Mn_2(CO)_{10}$. The gas chromatographic analysis of hexenes was carried out on a 10 ft × $^1/_8$ in. 20% UCON 50 HB-280X column at 40°; retention times were as follows: 3-methyl-1-pentene, 5.6 min; 2-ethyl-1-butene, 8.4 min; *cis*-3-methyl-2-pentene, 9.3 min; *trans*-3-methyl-2-pentene, 10.2 min; *n*-heptane, 17.2 min. The alkenes produced in the thermal decomposition of the acylmanganese compounds were identified by comparison of gc retention times and mass spectral fragmentation patterns (obtained on a Varian CH-7 gc mass spectrometer) with those of authentic samples.

2-Ethyl-1-butene. 2-Ethyl-1-butene was obtained by the Wittig reaction of 3-pentanone (2.5 g, 0.031 mol) with methylenetriphenylphosphorane, generated by the addition of methyltriphenylphosphonium iodide (13.0 g, 0.032 mol) to dimsyl anion in DMSO. Bulb-to-bulb distillation of the reaction mixture gave 2.3 g (94%) of the crude olefin. A sample was purified by preparative gas chromatography; nmr $\delta_{TMS}^{CCl_4}$ 1.0 (t, 6 H, CH_3CH_2), 2.0 (q, 4 H, CH_3CH_2), and 4.67 (broad s, 2 H, $C{=}CH_2$).

3-Methyl-1-pentene. 3-Methyl-1-pentene was obtained by the Wittig reaction of 3-methyl-1-pentanal (2.0 g, 0.023 mol) with methylenetriphenylphosphorane, which was generated by the addition of methyltriphenylphosphonium iodide (13.0 g, 0.023 mol) to dimsyl anion in DMSO. Bulb-to-bulb distillation of the reaction mixture gave 1.1 g (56%) of the olefin, contaminated with some benzene. A sample was purified by preparative gas chromatography; nmr $\delta_{TMS}^{CCl_4}$ 0.86 (t, 3 H, CH_3CH_2), 0.93 (d, 3 H, CH_3CH), 1.0–1.5 (m, 2 H, CH_2), 1.6–2.2 (m, 1 H, CH), and 4.5–5.9 (m, 3 H, $CH{=}CH_2$).

Registry No. 1, 19138-85-3; 2, 51064-33-6; 3, 50599-92-3; 4, 50599-93-4; 5, 50600-98-1; 6, 50600-99-2; 7, 50601-00-8; 8, 50601-01-9; *erythro*-methyl-2,3-dimethylpentanoate, 50599-90-1; *threo*-methyl-2,3-dimethylpentanoate, 50599-91-2; *erythro*-2,2-dimethylpentanoic acid, 19138-84-2; ethyl 4-methylhexanoate, 1561-10-0; 4-methylhexanoylchloride, 50599-73-0; 4-methylhexanoic acid, 1561-11-1; 3-methyl-1-pentene, 760-20-3; 2-ethyl-1-butene, 760-21-4; *cis*-3-methyl-2-pentene, 922-62-3; *trans*-3-methyl-2-pentene, 616-12-6; lithium di-*sec*-butylcuprate, 23402-73-5; ethyl acrylate, 140-88-5; 3-ethoxypentanoylchloride, 50599-74-1; 3-pentanone, 96-22-0; 3-methyl-1-pentanal, 15877-57-3; methylenetriphenylphosphorane, 3487-44-3; $NaMn(CO)_5$, 13859-41-1.