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The Participation of Solvents in the Reaction of Alkenes with Manganese(III) Acetate*

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1-Hexene and 2-methyl-2-pentene were heated with manganese(III) acetate at 100 °C in two mixed solvents of glacial acetic acid and acetic anhydride and of propionic acid and propionic anhydride in a nitrogen flow. γ-Acyloxy carboxylic acids, γ-lactones and saturated and unsaturated carboxylic acids were obtained, these oxidative products being considered to be adducts of acetic and propionic acids. Additional investigations were carried out on a mutual reaction of the oxidant and the solvents and on the thermal analysis of manganese(III) acetate. The reaction was explained by a solvent-participating free-radical mechanism.

The present author has reported on the formation of γ-butyrolactones and acetates in the reaction of *d*-limonene, *i.e.*, 1-methyl-4-isopropyl-1-cyclohexene, with manganese(III) acetate in acetic acid.[2] He has subsequently reported on the formation of saturated mono- and diacetates and certain kinds of allylic acetates in the heating of *d*-carvomenthene with a reagent in glacial acetic acid[3] and the formation of carboxymethyl adducts in the heating of *d*-limonene, *d*-carvomenthene, 1-methylcyclohexene, cyclohexene and 1-decene in glacial acetic acid containing catalytic amounts of potassium acetate.[4]

In addition, the formation of γ-lactones has been reported by Bush[5] in refluxing phenyl- and methyl-substituted ethylenes with manganese(III) acetate in a mixed solvent of acetic acid and acetic anhydride, and by Heiba[6] in refluxing certain alkenes, such as *trans*-β-methylstyrene, 1-octene, *trans*-4-octene, cyclooctene, styrene and *trans*-stilbene with manganese(III) acetate in glacial acetic acid containing potassium acetate. Allylic acetate has also been detected by Gilmore and Kasahara[7] in the reaction of cyclohexene, 1-methylcyclohexene, α- and β-methylstyrene. Heiba[6] has described that in these reactions, manganese(III) acetate reacts with olefins *via* a free-radical pathway leading to γ-butyrolactone. Whether or not the solvent participates in the reaction and the detailed mechanism of this reaction, however, have not yet been reported.

Results and Discussion

Characterization of Reaction Products. 1-Hexene and 2-methyl-2-pentene were separately heated with manganese(III) acetate dihydrate at 100 °C in two kinds of mixed solvents of acetic acid and acetic anhydride (solvent A) and of propionic acid and propionic anhydride (solvent P) in flowing nitrogen; the compounds listed in Table 1 were obtained as reaction products. The characterization of the products from the reaction of 1-hexene in solvent A depends upon the establishment of the chemical correlation for structually-known compounds as follows.

*γ-Lactone of 4-Hydroxyoctanoic Acid (**2**):* The product with the lowest boiling point, $C_8H_{14}O_2$, from the reaction of 1-hexene in solvent A exhibited an IR absorption band characteristic of γ-lactone at 1775 cm^{-1}. Its reduction with lithium aluminum hydride furnished viscous 1,4-octanediol, which was converted into a methyl ester of a keto acid in a good yield by potassium permanganate oxidation followed by the treatment with diazomethane together with a small amount of the returned original γ-lactone. The keto ester was then subjected to Clemmensen reduction to give methyl octanoate. The structure of this compound is thus certain.

*3-Octenoic and 4-Octenoic Acids (**3**,**4**):* An acidic substance isolated from the middle fraction of the reaction products, after being methylated, was separated into two unsaturated methyl esters by means of preparative gas chromatography, the quickly eluted one being identified as methyl 3-octenoate and the other as an unsaturated methyl ester containing a *trans*-disubstituted double bond, which gave methyl octanoate after catalytic hydrogenation. On the other hand, potassium permanganate oxidation of the mixed acidic substance furnished butyric and valeric acids. This evidence indicates the presence of 3-octenoic and 4-octenoic acids.

*4-Acetoxyoctanoic Acid (**1**):* The product with the highest boiling point, $C_{10}H_{20}O_4$, was found to possess a carboxyl group (2670, 1710 cm^{-1}, 10.02 ppm) and an acetoxy group in its IR and NMR spectra. The compound was reduced *via* methylation with $LiAlH_4$ into 1,4-octanediol obtained in a similar treatment of **2**, and it was heated at 250 °C and converted into **2** and acetic acid in good yields together with a small amount of 3-octenoic and 4-octenoic acids.

The structures of the reaction products obtained in the other runs were determined based on spectral evidence and the structural analogy of the above-mentioned products.

Participation of the Solvent in the Reaction. Several kinds of products obtained from 1-hexene and 2-methyl-2-pentene in the manganese(III) acetate oxidation in two solvents are classified into acyloxy carboxylic acids, γ-lactones and unsaturated and saturated carboxylic acids; all the classes of these compounds were uniformly isolated in each run with the exception of acyloxy carboxylic acid which was not formed in the reaction of 2-methyl-2-pentene with solvent P. In these classes acyloxy carboxylic acids were a new class in the oxidation of alkenes with manganese(III) acetate. On the other hand, the reaction products from solvent A are considered as adducts of acetic acid, while those

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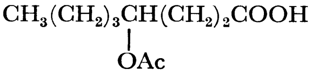
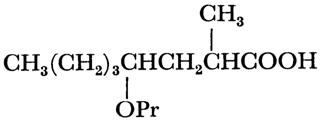
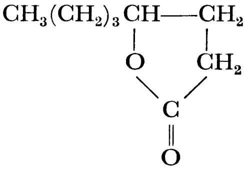
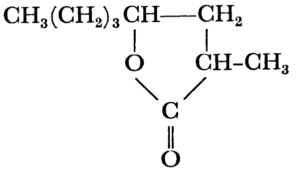
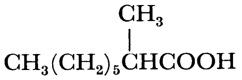
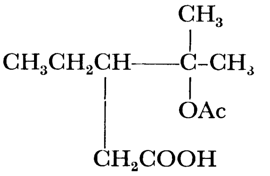
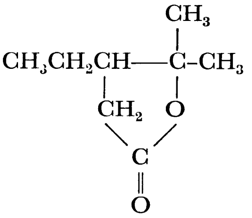
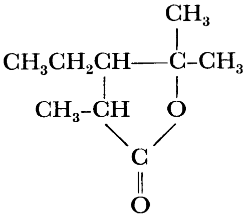
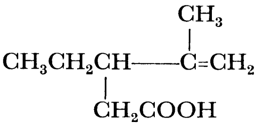
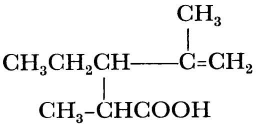
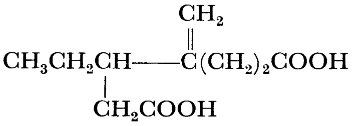
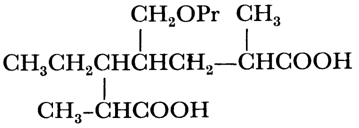
* A part of the result has been preliminarily reported.[1]

TABLE 1. PRODUCTS OF THE REACTION OF 1-HEXENE AND 2-METHYL-2-PENTENE WITH MANGANESE(III) ACETATE

	Solvent A (acetic acid and acetic anhydride)	Yield		Solvent P (propionic acid and propionic anhydride	Yield
	1-Hexene				
(1)	 $CH_3(CH_2)_3CH(OAc)(CH_2)_2COOH$	61%	(6)	 $CH_3(CH_2)_3CH(OPr)CH_2CH(CH_3)COOH$	44%
(2)		19%	(7)		15%
(3)	$CH_3(CH_2)_3CH{=}CHCH_2COOH$	5%	(8)	unsaturated carboxylic acid	trace
(4)	$CH_3(CH_2)_2CH{=}CH(CH_2)_2COOH$	8%			
(5)	$CH_3(CH_2)_6COOH$	7%	(9)	 $CH_3(CH_2)_5CH(CH_3)COOH$	41%
	2-Methyl-2-pentene				
(10)	 $CH_3CH_2CH(CH_2COOH)C(CH_3)(OAc)CH_3$	14%			
(11)		55%	(14)		35%[a]
(12)	 $CH_3CH_2CH(CH_2COOH)C(CH_3){=}CH_2$	22%	(15)	 $CH_3CH_2CH(CH_3\text{-}CHCOOH)C(CH_3){=}CH_2$	38%
(13)	 $CH_3CH_2CH(CH_2COOH)C({=}CH_2)(CH_2)_2COOH$	9%	(16)	 $CH_3CH_2CH(CH_3\text{-}CHCOOH)CH(CH_2OPr)CH_2\text{—}CH(CH_3)COOH$	27%[b]

a) This compound was separated into two diastereoisomers in relative amounts of 13 to 1. b) This compound was separated into two diastereoisomers in relative amounts of 5 to 1.

from solvent P are recognized to be adducts of propionic acid.

Furthermore, when the reaction of 1-methylcyclohexene with manganese(III) acetate was carried out in acetic acid containing acetic acid-^{14}C, radioactive γ-lactone[8,9] and acetates[9] were obtained. This indicates that the solvent participates in the reaction of alkenes with manganese(III) acetate.

Thermal Decomposition of Manganese(III) Acetate Dihydrate. The thermal analysis of manganese(III) acetate dihydrate was performed to determine the weight loss and differential thermal analysis curves, shown in Fig. 1 for a standard of silicone dioxide. In the weight loss curves about 50 to 100 °C corresponds to the loss of the two hydrated waters of manganese acetate molecule and about 100 to 130 °C to the loss of one acetic acid residue from the molecule. When manganese(III) acetate dihydrate itself was also heated in a flask by gradually raising the temperature in flowing nitrogen gas, violent evolution of carbon dioxide was observed at about 110 °C. Both results indicate that at the reaction temperature used in the present investigation manganese(III) acetate dihydrate decomposes into manganese(II) acetate *via* two steps: the first step is the release of the two hydrated waters, which may be promoted by the acetic anhydride, and the second is the rupture of one acetic acid residue.

Thermal Reaction of Manganese(III) Acetate Dihydrate in the Solvent. Manganese(III) acetate dihydrate was heated at 100 °C in solvent A and P without the

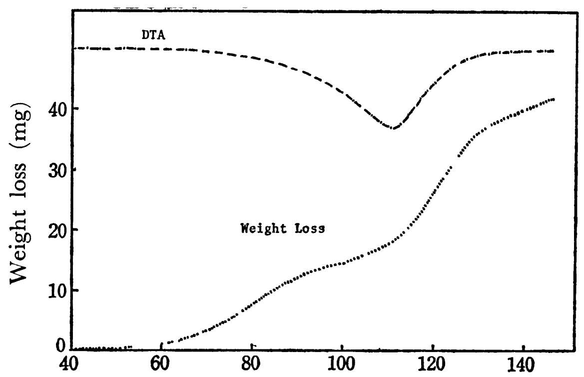
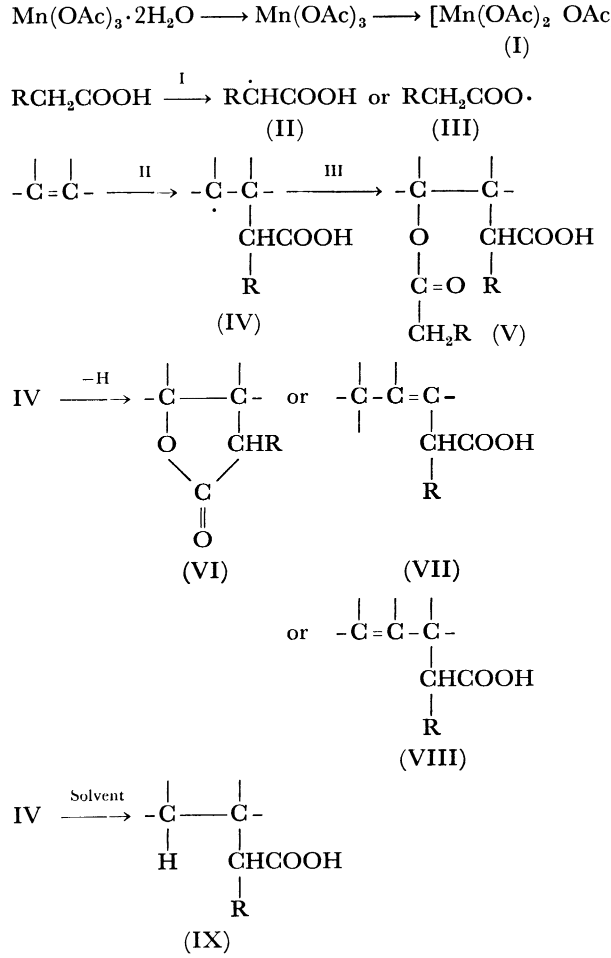


Fig. 1. Thermal analysis of $Mn(OAc)_3 \cdot 2H_2O$.*

reactant, an appreciable amount of succinic acid and a trace of acetoxyacetic acid being isolated in the heating with solvent A, and *dl*-2-propionyloxypropionic acid and 2,3-dimethylsuccinic acids which consisted of *dl*- and *meso*-isomers in a ratio of 3 : 1 being obtained in the heating with solvent P. Together with the fact that, in the above reaction of alkene in solvent P, only propionic acid adducts were isolated, this result demonstrates that $\cdot CH_2COOH$, $CH_3COO\cdot$, $\cdot\overset{CH_3}{C}HCOOH$ and $CH_3CH_2COO\cdot$ radicals were formed with the participation of the solvents in the manganese (III) acetate reaction.



Sceme 1. Reaction mechanism.

Reaction Mechanism. On the basis of this evidence, the reaction of alkenes with manganese(III) acetate in the solvent may be explained by the reaction mechanism presented in Scheme 1.

For the first time, hydrated water of manganese(III) acetate is abstracted by acid anhydride. The anhydrous molecule of manganese(III) acetate thus produced is thermally decomposed releasing an acetoxy radical, which should be stabilized within the coordination sphere of the manganous ion. This radical does not react directly with the substrate, but with a surrounding molecule of the solvent to furnish an alkyl carboxymethyl(II) or an acyloxy(III) radical. The addition of II to a double bond of alkene gives a radical intermediate (IV), which may be immediately stabilized by the following reactions: 1) the addition of an acyloxy radical(III) to give γ-acyloxy carboxylic acid (V), 2) the release of a hydrogen atom to give γ-lactone (VI) and unsaturated carboxylic acid (VII or VIII), and 3) the abstraction of a hydrogen atom from the solvent to give saturated carboxylic acid (IX).

Experimental

Analytical and preparative GLC were carried out on a Hitachi 023 gas chromatograph equipped with a thermocouple detector in connection with a stainless steel column (3 mm in diameter) which was packed with Celite 545 (40—60 mesh) impregnated with 20% PEG-20M or 25% DEGS. The NMR spectra were determined on a JEOL model JNM-MH-60 spectrometer in CCl_4, $CDCl_3$ or C_6D_6 with an internal reference of tetramethylsilane. The mass spectra were taken on a Hitachi RMS-4 instrument with a 70-eV ionization voltage and a 200 °C ionization chamber temperature. The molecular weight was determined on a Hitachi Perkin-Elmer 115 MW apparatus in benzene. Thermal analysis was carried out on a Shimadzu model DTB-2B DTA-TG apparatus.

Reagents. A Tokyo Kasei guaranteed reagent of 1-hexene and extra-pure reagent of 2-methyl-2-pentene were used. These materials each showed one peak in the GLC and the IR and NMR spectra were coincident with authentic samples.

Preparation of Manganese(III) Acetate Dihydrate. $Mn(OAc)_2 \cdot 4H_2O$ was oxidized with potassium permanganate according to a modification of the procedure of Heiba.[10] Crystallized $Mn(OAc)_3 \cdot 2H_2O$ filtering up from the reacted mixture was washed with ether, and preserved over sodium hydroxide *in vacuo* for a week. The purity was 99% according to iodometric titration.

Reaction of 1-Hexene and 2-Methyl-2-pentene with Manganese(III) Acetate. 1-Hexene and 2-methyl-2-pentene (8.4 g, 100 mmol of each) were added to a solution of manganese(III) acetate (53.6 g, 200 mmol) in a mixed solvent (400 ml) of acetic acid and acetic anhydride (v/v, 1 : 1, solvent A) or of propionic acid and propionic anhydride (v/v, 1 : 1, solvent P) drop by drop at 70 °C in flowing nitrogen, the mixture being stirred with a gradual increase of the reaction temperature up to 100 °C. When the brown color of the Mn(III) ions disappeared, the stirring was stopped, and the reaction mixture was cooled, diluted with water (*ca.* 300 ml)

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* 104.8 mg of $Mn(OAc)_3 \cdot 2H_2O$ was used.

and extracted with ether. Brown oily substances were obtained (from 1-hexene, 12 g in solvent A and 16 g in solvent P; from 2-methyl-2-pentene, 7 g in solvent A and 9 g in solvent P). The oily substances were then separated by a combination of fractionation and preparative gas chromatography into individual compounds whose characterizations were carried out as follows.

Reaction of 1-Hexene in Solvent A. *4-Acetoxyoctanoic Acid (**1**)*: The highest boiling product was isolated as a colorless viscous substance which showed a blue-violet spot after the spraying of a vanillin-sulfuric acid reagent and a yellow spot with a solution of BCG indicator in TLC using silica gel and a mixed solvent of hexane and ethyl acetate (v/v 1 : 4) at R_f: 0.0—0.3 (tailing). $\nu_{\max}^{\text{neat}}$ 2670 and 1710 (COOH), 1240 cm^{-1}(acetate); $\delta_{\text{ppm}}^{\text{CCl}_4}$ 0.91t(3H, $J=5$ Hz), 1.1—1.7 m(6H), 1.97s(4H), 1.8—2.1m(6H), 4.84t(1H, $J=6$ Hz), 10.02s(1H, exchangeable with D_2O)

It was treated with diazomethane to give a colorless liquid methyl ester. $C_{10}H_{20}O_4$(MS and elementaly analysis). *m/e* 173(7%, $M^+-C_2H_3O$), 142(4%, $M^+-C_3H_6O_2$), 117 (81%, $M^+-C_2H_3O-C_4H_7$), 85(42%, $M^+-C_3H_6O_2-C_4H_9$), 74 (17%, $C_3H_6O_2$), 55(35%, C_4H_7), 43(100%, C_2H_3O); $\nu_{\max}^{\text{neat}}$ 1740(ester), 1240 cm^{-1}(acetate); $\delta_{\text{ppm}}^{\text{CCl}_4}$ 0.92t(3H, $J=5$ Hz), 1.1—1.6 m(6H), 1.96 m(6H), 1.7—2.5 m(4H), 3.60s(3H), 4.80t(1H, $J=6$ Hz). Found: C, 61.30; H, 9.11%; mol wt, 216±2. Calcd for $C_{10}H_{20}O_4$: C, 61.11; H, 9.26%; mol wt, 216.

In the reduction of the methyl ester (0.4 g) with $LiAlH_4$ (LAH, 0.4 g), 1,4-octanediol (0.3 g) was obtained. $C_8H_{18}O_2$ (MS). *m/e* 89(18%, $M^+-C_4H_9$), 87(12%, $M^+-C_3H_7O$), 71(100%, $M^+-C_4H_9-H_2O$), 69(40%, $M^+-C_3H_7O-H_2O$) 59(5%, C_3H_7O), 57(15%, C_4H_9); $\nu_{\max}^{\text{neat}}$ 3330 cm^{-1} (OH); $\delta_{\text{ppm}}^{\text{CCl}_4}$ 0.91t(3H, $J=5$ Hz), 1.34bs(6H), 1.51bs(4H), 3.50bs(2H, exchangeable with D_2O).

In heating at 100 °C with solvent A, the compound showed no decomposition, but it (0.5 g) decomposed at 250 °C to give acetic acid (*ca.* 0.1 g) and the γ-lactone of 4-hydroxyoctanoic acid (*ca.* 0.30 g) described below. On the other hand, **1** was not obtained by refluxing **2** in solvent A.

*γ-Lactone of 4-Hydroxyoctanoic Acid (**2**)*: The compound was isolated as the oily product with lowest boiling point. The IR and NMR spectra were coincident with those of authentic samples. $C_8H_{14}O_2$(MS). *m/e* 142(2%, M^+), 85(100%, $M^+-C_4H_9$); $\nu_{\max}^{\text{neat}}$ 1775 cm^{-1} (γ-lactone); $\delta_{\text{ppm}}^{\text{CCl}_4}$ 0.93t(3H, $J=5$ Hz), 1.1—1.8 m(6H), 1.8—2.6 m (4H), 4.31 m(1H).

In reduction with LAH (0.4 g), it (0.4 g) gave 1,4-octanediol (0.38 g), which was also obtained by LAH reduction of **1**. The oxidation of 1,4-octanediol (0.20 g) with potassium permanganate (0.5 g) followed by treatment with diazomethane gave, together with a minor amount of returned **2**, methyl 4-oxooctanoate as a main product. $C_9H_{16}O_3$(MS). *m/e* 141(8%, M^+-CH_3O), 130(13%, $M^+-C_3H_6$), 98 (24%, $M^+-C_3H_6-CH_4O$), 115(22%, $M^+-C_4H_9$), 87(19%, $M^+-C_4H_9-CO$), 59(65%, $M^+-C_7H_{13}O$), 57(100%, C_4H_9); $\nu_{\max}^{\text{neat}}$ 1740(ester), 1720 cm^{-1} (ketone); $\delta_{\text{ppm}}^{\text{CCl}_4}$ 0.93t (3H, $J=5$ Hz), 2.3bs(2H), 2.51bs(2H), 3.59s(3H).

Methyl 4-oxooctanoate (0.10 g) was reduced to methyl octanoate in the Clemmensen reaction, which was indicated by admixing with the authentic sample in GLC and analysis of the MS, IR and NMR spectra.

*3-Octenoic Acid (**3**), 4-Octenoic Acid (**4**) and Octanoic Acid (**5**)*: The treatment of the middle fractions with diazomethane gave a mixture of three methyl esters which furnished common methyl octanoate by hydrogenation over a Raney nickel catalyst (W-2) in hexane in an autoclave. After three methyl esters were separated by preparative GLC, two were identified as methyl esters of **3** and **5** by gas chromatographic and spectrometric comparisons with authentic samples. The remaining methyl ester eluted in the middle position of the GLC exhibited and IR spectrum closely resembling that of methyl 3-octanoate, but the NMR spectrum was somewhat different. $\nu_{\max}^{\text{neat}}$ 1740(ester), 970 cm^{-1} (*trans*); $\delta_{\text{ppm}}^{\text{CCl}_4}$ 0.87t(3H, $J=6$ Hz), 1.1—2.1m(4H), 2.24s(4H), 3.54s(3H), 5.33t(2H, $J=3$ Hz).

The potassium permanganate oxidation of the fraction (0.20 g) followed by a treatment with diazomethane gave methyl esters (*ca.* 0.15 g) of butyric acid, valeric acid and unchanged octanoic acid, which were identified by admixing the authentic samples and analysis by GLC.

Reaction of 1-Hexene in Solvent P. *2-Methyl-4-propionyloxyoctanoic Acid (**6**)*: The product with the highest boiling in the reaction. $C_{12}H_{22}O_4$(MS). *m/e* 156(2%, $M^+-C_3H_6O_2$), 74(100%, $C_3H_6O_2$); $\nu_{\max}^{\text{neat}}$ 2650 and 1705(COOH), 1735(ester), 1180 cm^{-1} (propionate); $\delta_{\text{ppm}}^{\text{CCl}_4}$ 0.87t(3H, $J=5$ Hz), 1.0—2.0(14H), 1.06t($J=7$ Hz), 1.15d($J=7$ Hz), 2.23q (2H, $J=7$ Hz), 4.86 m(1H), 11.18 s(1H).

In heating at 260 °C, the acid (0.5 g) decomposed into propionic acid and the lactone (**7**) described in the following section.

After methylation, the substance was separated into equivalent amounts of diastereoisomers by means of preparative GLC. The quickly eluted isomer: $C_{13}H_{24}O_4$ (MS). *m/e* 187(19%, $M^+-C_3H_5O$), 88(78%, $C_4H_8O_2$), 57(100%, C_3H_5O); $\nu_{\max}^{\text{neat}}$ 1735(ester), 1190 cm^{-1} (propionate); $\delta_{\text{ppm}}^{\text{CCl}_4}$ 0.90t (3H, $J=5$ Hz), 1.10t(3H, $J=7$ Hz), 1.12d(3H, $J=7$ Hz), 2.19q (3H, $J=7$ Hz), 3.56s(3H), 4.72m(1H). Found: C, 64.04; H, 9.91%. Calcd for $C_{13}H_{24}O_4$: C, 63.88; H, 9.91%. The slowly eluted isomer: $C_{13}H_{24}O_4$(MS). *m/e* 187(16%, $M^+-C_3H_5O$), 88(100%, $C_4H_8O_2$), 57(100%, C_3H_5O); $\nu_{\max}^{\text{neat}}$ 1735(ester), 1185 cm^{-1} (propionate); $\delta_{\text{ppm}}^{\text{CCl}_4}$ 0.90t(3H, $J=5$ Hz), 1.10t(3H, $J=7$ Hz), 1.12q(3H, $J=7$ Hz), 2.21q (3H, $J=7$ Hz), 3.54s(3H), 4.78s(1H).

*γ-Lactone of 4-Hydroxy-2-methyloctanoic Acid (**7**)*: The oily product with the lowest boiling in the reaction. $C_9H_{16}O_2$ (MS). *m/e* 156(1%, M^+), 99(100%, $M^+-C_4H_9$); $\nu_{\max}^{\text{neat}}$ 1770 (γ-lactone); $\delta_{\text{ppm}}^{\text{CCl}_4}$ 0.92t (3H, $J=5$ Hz), 1.0—2.0 (11H), 1.20d($J=6$ Hz), 2.45m(1H), 4.24m(1H); $\delta_{\text{ppm}}^{C_6D_6}$ 0.82t (3H, $J=5$ Hz), 0.95d(1.5 H, $J=6$ Hz), 1.00d(1.5 H, $J=6$Hz), 1.0—1.5 m(4H), 2.08m(2H), 3.80m(1H). These spectral data suggest the γ-lactone to be a mixture of two diastereoisomers.

*2-Methyloctanoic Acid (**9**)*: Colorless oil. $C_9H_{18}O_2$ (MS). *m/e* 158(1%, M^+), 74(100%, $C_3H_6O_2$); $\nu_{\max}^{\text{neat}}$ 2650 and 1705 (COOH); $\delta_{\text{ppm}}^{\text{CCl}_4}$ 0.88t(3H, $J=5$ Hz), 1.0—1.6(13H), 1.15d ($J=7$ Hz), 1.28bs(10H), 2.30m(1H), 11.96s(1H); amide mp 80—81 °C (lit,[11] 80—81 °C).

Reaction of 2-Methyl-2-pentene in Solvent A. *4-Acetoxy-3-ethyl-4-methylpentanoic Acid (**10**)*: Upon treatment with diazomethane, the acid was converted into a colorless liquid methyl ester. $C_{11}H_{20}O_4$ (MS and elementaly analysis). *m/e* 157(5%, $M^+-C_2H_4O_2$), 127(15%, $M^+-C_2H_4O_2-CH_3O$), 97(21%, $M^+-C_2H_4O_2-C_2H_3O_2$), 96(41%, $M^+-2C_2H_4O_2$), 59(38%, $C_2H_3O_2$), 55(91%, $M^+-2C_2H_4O_2-C_3H_5$), 43 (100%, $C_2H_3O_2$), 41(62%, C_3H_5); $\nu_{\max}^{\text{neat}}$ 1735(ester), 1250 cm^{-1} (acetate); $\delta_{\text{ppm}}^{\text{CDCl}_3}$ 0.97t(3H, $J=5$ Hz), 1.0—2.1 (5H), 1.92s (3H), 1.40s (3H), 1.48s (3H), 3.66s (3H).

The methyl ester (0.1 g) was reduced with LAH (0.1 g) to give a diol which was identical with that obtained in the LAH reduction of **11**.

*γ-Lactone of 3-Ethyl-4-hydroxy-4-methylpentanoic Acid (**11**)*: Colorless oil. $C_8H_{14}O_2$ (MS). *m/e* 142(5%, M^+), 127(44%, M^+-CH_3), 69(40%, C_5H_9), 59(100%, C_3H_7O); $\nu_{\max}^{\text{neat}}$ 1775 (γ-lactone), 1390 and 1375 cm^{-1}(*gem*-dimethyl); $\delta_{\text{ppm}}^{\text{CCl}_4}$ 0.96t(3H,

J=5 Hz), 1.20s(3H), 1.39s(3H), 2.25d(2H, J=7 Hz).

Upon reduction with LAH (1.0 g), the compound (0.1 g) gave 3-ethyl-4-methyl-1,4-pentanediol, mp 44—45 °C, (*ca.* 0.9 g). $C_8H_{18}O_2$(MS). *m/e* 131(2%, M^+-CH_3), 113(14%, $M^+-CH_3-H_2O$), 84(6%, $M^+-CH_3-H_2O-C_2H_5$), 57 (100%, C_3H_7O); ν_{max}^{neat} 3330(OH), 1150(*tert.* OH), 1050 (*prim.* OH), 1380 and 1355 cm^{-1} (*gem*-dimethyl); $\delta_{ppm}^{CCl_4}$ 0.98t (3H, J=6 Hz), 1.05s(3H), 1.20s(3H), 1.56m(3H), 3.52m (2H), 5.02bs(2H, exchangeable with D_2O).

The diol (0.2 g) was oxidized with potassium permanganate (0.5 g) and returned to the original γ-lactone. It (0.6 g) was also treated with a mixture (5 ml) of acetic anhydride and pyridine (1 : 3, v/v) to give 3-ethyl-4-hydroxy-4-methylpentyl acetate as a colorless oily substance (*ca.* 0.6g). $C_{10}H_{20}O_3$ (MS). *m/e* 113 (21%, $M^+-C_2H_4O_2-CH_3$), 110 (17%, $M^+-C_2H_4O_2-H_2O$), 59(92%, $C_2H_3O_2$), 43(100%, C_2H_3O); ν_{max}^{neat} 3450(OH), 1740(ester), 1250(acetate), 1150 cm^{-1} (*tert.* OH); $\delta_{ppm}^{CCl_4}$ 0.93t(3H, J=5 Hz), 1.03s(3H), 1.13s (3H), 1.80s(1H, exchangeable with D_2O), 1.93s(3H), 4.03t (2H, J=7 Hz). Dehydration of this acetate (0.5 g) with acetic anhydride (1 ml) at 250 °C gave 3-isopropenyl-1-pentyl acetate as a colorless liquid (*ca.* 0.4 g). $C_{10}H_{18}O_2$ (MS). *m/e* 110(35%, $M^+-C_2H_4O_2$), 69(37%, $M^+-C_2H_4O_2-C_3H_5$), 43(100%, C_2H_3O), 41(80%, C_3H_5); ν_{max}^{neat} 3070, 1640 and 890 (C=C), 1740(ester), 1245 cm^{-1} (acetate); $\delta_{ppm}^{CCl_4}$ 0.83t(3H, J=7 Hz), 1.60s(3H), 1.92s(3H), 3.90t(2H, J= 7 Hz), 4.72m(2H).

Upon treatment with LAH (0.3 g), the above acetate (0.3 g) was reduced to 3-isopropenyl-1-pentanol (0.2 g). Colorless oil. $C_8H_{16}O$ (MS). *m/e* 128(3%, M^+), 113(2% M^+-CH_3), 110(3%, M^+-H_2O), 84(64%, $M^+-CH_3-C_2H_5$) 81(23%, $M^+-H_2O-C_2H_5$), 69(80%, $M^+-H_2O-C_3H_5$), 41(100%, C_3H_5); ν_{max}^{neat} 3340 and 1055 (*prim.* OH), 3080, 1640 and 890cm^{-1} (C=C). The unsaturated primary alcohol (0.1 g) was hydrogenated over a Raney nickel catalyst in ethanol to give 3-isopropyl-1-pentanol which was identified by means of gas chromatographic and IR and NMR spectrometric comparisons with an authentic sample synthesized as the final description.

*3-Isopropenylpentanoic Acid (**12**)*: After methylation, the acid was isolated as a colorless liquid in a highly homologous state from the highest fraction of the reaction product together with a dimethyl ester of the following dibasic acid (**13**). $C_9H_{16}O_2$ (MS). *m/e* 156 (7%, M^+), 141(6%, M^+-CH_3), 125(9%, M^+-CH_3O), 124(13%, M^+-CH_4O), 97 (20%, $M^+-C_2H_3O_2$), 96(48%, $M^+-C_2H_4O_2$), 59(27%, $C_2H_3O_2$), 55(100%, $M^+-C_2H_4O_2-C_3H_5$), 41(59%, C_3H_5); ν_{max}^{neat} 3070, 1645 and 890 (C=C), 1740 cm^{-1} (ester); $\delta_{ppm}^{CCl_4}$ 0.82t (3H, J=6 Hz), 1.65s(3H), 2.40s(2H), 3.64s(3H), 4.74bs(2H).

Upon reduction with LAH (0.1 g), the methyl ester (0.1 g) gave 3-isopropenyl-1-pentanol as a colorless oil, which was also derived from **11**.

*3-Ethyl-4-methyleneheptanedioic Acid (**13**)*: The compound was isolated from the highest fraction after methylation. $C_{12}H_{20}O_4$(MS and elementaly analysis). *m/e* 196(9%, M^+-CH_3O), 168(9%, $M^+-C_2H_3O_2$), 166(5%, M^+-2CH_3O), 116(8%, $M^+-2C_2H_3O_2$), 59(100%, $C_2H_3O_2$); ν_{max}^{neat} 3075, 1640 and 890 (C=C), 1735 cm^{-1} (ester); $\delta_{ppm}^{CCl_4}$ 0.84t(3H, J=6 Hz), 1.0—1.9 m(3H), 2.41bs(6H), 3.64s(3H), 3.66s(3H), 4.81bs (2H). Found: C, 62.94; H, 9.16%. Calcd for $C_{12}H_{20}O_4$: C, 63.11; H, 8.84%. Reduction of the methyl ester (0.1 g) with LAH (0.1 g) gave 3-ethyl-4-methylene-1,7-heptanediol as a colorless oily substance. ν_{max}^{neat} 3330 and 1055 (*prim.* OH).

Reaction of 2-Methyl-2-pentene in Solvent P. *γ-Lactone of 2,4-Dimethyl-3-ethyl-4-hydroxypentanoic Acid (**14**)*: From the lowest boiling fraction of the reaction products two colorless liquids determined to be diastereoisomers were separated in the relative amounts of 13 : 1 by preparative GLC. Quickly eluted isomer: $C_9H_{16}O_2$ (MS). *m/e* 141 (25%, M^+-CH_3), 112(18%, M^+-CO_2), 97(12%, $M^+-CO_2-CH_3$), 55(100%); ν_{max}^{neat} 1770 (γ-lactone), 1390 and 1375 cm^{-1} (*gem*-dimethyl); $\delta_{ppm}^{CCl_4}$ 0.8—1.8(15H), 1.02t(3H, J=5 Hz), 1.20d(3H, J= 7 Hz), 1.21s(3H), 1.41s(3H), 2.17m(1H); $\delta_{ppm}^{C_6D_6}$ 0.60t(3H, J= 5 Hz), 0.81s(3H), 1.10s(3H), 1.05d(3H, J=6 Hz), 0.5—1.5 m(3H), 1.87m(1H). Slowly eluted isomer:$C_9H_{16}O_2$ (MS). *m/e* 141(25%, M^+-CH_3), 112(16%, M^+-CO_2), 97(12%, $M^+-CO_2-CH_3$), 55(100%); ν_{max}^{neat} 1765 (γ-lactone), 1390 and 1375(*gem*-dimethyl); $\delta_{ppm}^{CCl_4}$ 0.81—1.7 m(2H), 0.97t(3H, J=6 Hz), 1.20d(3H, J=7 Hz), 1.26s(3H), 1.39s(3H), 2.11m (1H), 2.57m(1H); $\delta_{ppm}^{C_6D_6}$ 0.55t(3H, J=6 Hz), 0.91s(3H), 1.02s(3H), 0.97d(3H, J=6 Hz), 1.58q(2H), 2.31q(1H, J= 8 Hz).

*3-Ethyl-2,4-dimethyl-4-pentenoic Acid (**15**)*: Colorless oily substance. $C_9H_{16}O_2$ (MS). *m/e* 156 (9%, M^+), 83(75%, $M^+-C_3H_5O_2$), 55(100%); ν_{max}^{neat} 2650 and 1710(COOH), 1650 and 895 (C=C); $\delta_{ppm}^{CCl_4}$ 0.7—1.6 (11H), 0.77t(3H, J= 6 Hz), 1.14d(3H, J=6 Hz), 1.53s(3H), 2.31m(2H), 4.78s (1H), 4.87s(1H), 11.3s(1H). Upon treatment with diazomethane, it gave a colorless oily methyl ester: ν_{max}^{neat} 3080, 1640 and 895 (C=C), 1735 cm^{-1} (ester); $\delta_{ppm}^{CCl_4}$ 0.75t(3H, J=6 Hz), 0.96d(3H, J=6 Hz), 1.0—1.4m(2H), 1.50s(3H), 2.10m (2H), 3.48s(3H), 4.61s(1H), 4.67s(1H).

*3-Ethyl-2,6-dimethyl-4-propionyloxymethyl-1,7-heptanedioic Acid (**16**)*: By preparative GLC of the fraction with the highest boiling point (0.5 g) of the reaction products, two colorless isomeric esters were separated in a ratio of 5 : 1 after treatment with diazomethane. Quickly eluted ester: $C_{17}H_{30}O_6$ (MS). *m/e* 154 (7%, $M^+-2C_4H_8O_2$), 139(13%, $M^+-2C_2H_3O_2-C_3H_5O_2$), 95(18%, $M^+-2C_4H_8O_2-C_2H_3O_2$), 88 (18%, $C_4H_8O_2$), 59 (8%, $C_2H_3O_2$), 57(100%, $C_3H_5O_2$); ν_{max}^{neat} 1735(ester), 1195 cm^{-1} (propionate); $\delta_{ppm}^{CCl_4}$ 1.05t(3H, J=6 Hz), 1.14d(6H, J=7 Hz), 1.68 m(7H), 2.20q(4H, J=7 Hz), 3.56s(6H), 4.80m(2H). Slowly eluted ester: $C_{17}H_{30}O_6$ (MS) *m/e* 154 (3%, $M^+-2C_4H_8O_2$), 139(11%, $M^+-2C_2H_3O_2$), 95(63%, $M^+-2C_4H_8O_2-C_2H_3O_2$), 88(48%, $C_4H_8O_2$), 59 (19%, $C_2H_3O_2$), 57(100%, $C_3H_5O_2$); ν_{max}^{neat} 1735(ester), 1195 cm^{-1} (propionate); $\delta_{ppm}^{CCl_4}$ 1.07t(3H, J=6 Hz), 1.14d(6H, J= 7 Hz), 1.70m(7H), 2.18q(4H, J=7 Hz), 3.56s(6H), 5.02m (2H). Since sixteen isomers are possible for 3-ethyl-2,6-dimethyl-4-propionyloxymethyl-1,7-heptanedioic acid, these substances should still be mixed esters.

Reactions of $Mn(OAc)_3\cdot 2H_2O$ in Solvents A and P. $Mn(OAc)_3\cdot 2H_2O$ (26.8 g, 100 mmol) was heated with solvent A (200 ml) without a reactant for 6 h in a manner similar to the above reaction in flowing nitrogen. The reacted mixture was concentrated as a viscous liquid, which produced a small amount of white crystals when allowed to stand. The crystals, mp 184—186 °C, 1.3 g, showed no depression during a mixed mp determination with an authentic sample of succinic acid and the IR spectrum was coincident with that of an authentic sample. The liquior remaining after filtration of the crystals was methylated and then the reacted mixture was separated by preparative gas chromatography. Together with succinic acid, acetoxyacetic acid was isolated and it was identified based on gas chromatographic and spectrometric comparisons with an authentic sample prepared from hydroxyacetic acid. During heating, the nitrogen gas passing through the reaction flask passed into a saturated aqueous solution of calcium hydroxide (200 ml); although the solution became slightly cloudy, no precipitate was formed.

$Mn(OAc)_3\cdot 2H_2O$ (53.6 g, 200 mmol) was also heated with solvent P (400 ml). A similar treatment of the reacted mixture gave a mixture (1.7 g) of *meso*- (2 mmol, mp 196—

198 °C, lit,[11] 198 °C) and *dl*-2,3-dimethylsuccinic acid (6 mmol) and *dl*-2-propionyloxypropionic acid (2 mmol). They were separated by preparative GLC after methylation. *dl*-2-Propionyloxypropionic acid was identified by IR and NMR spectral comparisons with an authentic sample synthesized from *dl*-lactic acid. Similarly *dl*-2,3-dimethylsuccinic acid was identified by its MS, IR and NMR spectra. $C_8H_{14}O_4$ (MS). *m/e* 143 (28%, M^+-CH_3O), 115(30%, $M^+-C_2H_3O_2$), 59(100%, $C_2H_3O_2$); ν_{max}^{neat} 1740 cm^{-1} (ester); $\delta_{ppm}^{CCl_4}$ 1.11d(6H, *J*=6Hz), 2.71m(2H), 3.65s(6H).

Thermal Analysis of Mn(OAc)$_3$·2H$_2$O. The thermal analysis of $Mn(OAc)_3 \cdot 2H_2O$(104.8 mg) was carried out with a Shimadzu DTA-TG apparatus with temperature programming of 2°C/min in flowing nitrogen, and the weight loss (mg) and differential thermal analysis were recorded using a standard of fused SiO_2 (Fig. 1). On the other hand, $Mn(OAc)_3 \cdot 2H_2O$ (26.8 g, 100 mmol) was gradually heated up to 130 °C in flowing nitrogen, and the emerging gas from a reaction flask was bubbled into a saturated solution (200 ml) of calcium hydroxide. When the temperature reached 110 °C, the formation of a white precipitate was observed.

Synthesis of 3-Isopropyl-1-pentanol. 2-Methyl-3-pentanol (9.0 g, 88 mmol) which was prepared from propionaldehyde and isopropylmagnesium bromide[12] was oxidized with Jones reagent at room temperature for 6 h to give 2-methyl-3-pentanone, bp 113—118 °C (lit,[11] 115—116 °C), as a colorless liquid (7.5 g, yield 85%). The Reformatsky reaction[13] of 2-methyl-3-pentanone (7.5 g, 75 mmol) thus obtained with methyl bromoacetate(12.2 g, 80 mmol) gave methyl 3-hydroxy-3-isopropylpentanoate (8.5 g, 48.8 mmol); ν_{max}^{neat} 3530(OH), 1730 and 1715 (ester), 1385 and 1370 cm^{-1} (isopropyl); $\delta_{ppm}^{CCl_4}$ 0.87t(3H, *J*=7 Hz), 1.50q(2H, *J*=6 Hz), 1.90 d(6H, *J*=7 Hz), 2.40bs(2H), 3.69s(3H), 3.15bs(1H, exchangeable with D_2O). The alcohol, after dehydration with acetic anhydride, was subjected to catalytic hydrogenation to give methyl 3-isopropylpentanoate as a colorless liquid (bp 163—164 °C, 2.4 g, yield 59%). $C_9H_{18}O_2$ (MS). *m/e* 127(11%, M^+-CH_3O), 84(17%, $M^+-C_3H_6O_2$), 74 (100%, $C_3H_6O_2$), 59(31%, $C_2H_3O_2$); ν_{max}^{neat} 1745 (ester), 1390 and 1370 cm^{-1} (isopropyl); $\delta_{ppm}^{CCl_4}$ 0.91t(3H, *J*=4 Hz), 0.86d (3H, *J*=6 Hz), 0.89d(3H, *J*=6Hz), 2.15 m(2H), 3.59s(3H). Reduction of this methyl 3-isopropylpentanoate (1.0 g) with LAH(1.0 g) gave 3-isopropyl-1-pentanol (*ca.* 0.9 g). $C_8H_{18}O$ (MS). *m/e* 112 (2%, M^+-H_2O), 84(23%, $M^+-H_2O-C_2H_4$), 44(100%, C_3H_8), 40(96%, C_3H_4); ν_{max}^{neat} 3340 and 1055 (*prim.* OH), 1385 and 1367 cm^{-1} (isopropyl); $\delta_{ppm}^{CCl_4}$ 0.84d(6H, *J*=6 Hz), 3.46t(2H, *J*=7 Hz), 3.18s(1H, exchangeable with D_2O).

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