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OXIDATION OF OLEFINS BY MANGANESE(III) ACETATE IN A PROPIONIC ACID SOLVENT. FORMATION OF PROPIONIC ACID DERIVATIVES

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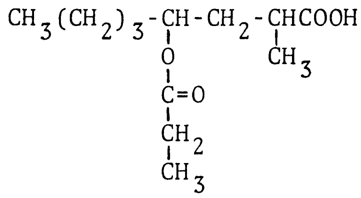
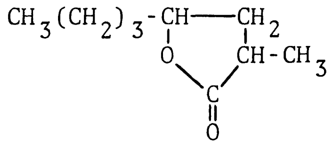
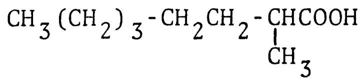
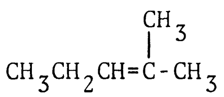
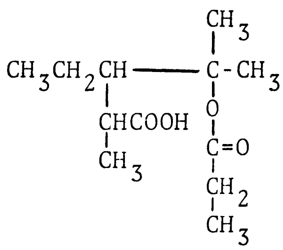
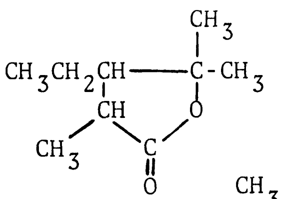
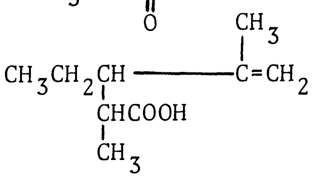
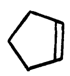
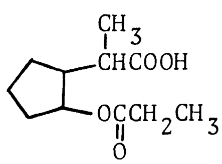
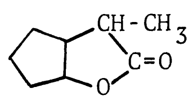
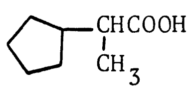
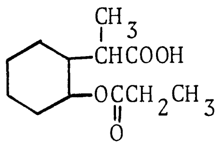
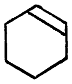
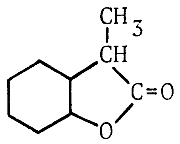
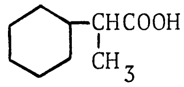
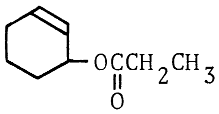
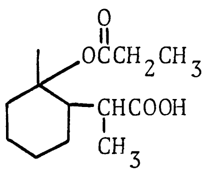
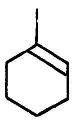
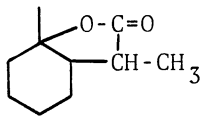
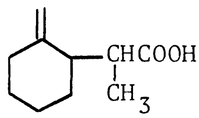
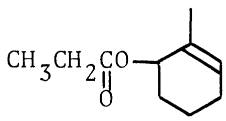
Oxidation of olefins by manganese(III) acetate was carried out using propionic acid as a solvent. The oxidation products obtained were propionic acid derivatives such as 2-methyl-4-propanoyloxyalkanoic acids, γ-lactones, alkanoic or alkenoic acids and propanoyloxyalkenes. Of these products, 2-methyl-4-propanoyloxyalkanoic acids underwent thermal cracking with ease to decompose into corresponding γ-lactones and propionic acid.

The manganese(III) acetate oxidation of olefins has been carried out in acetic acid to give various kinds of products, acetates[1,2,4,5], γ-lactones[1-5] and alkanoic and alkenoic acids[6]. All the products, however, are compounds to be characterized as acetic acid derivatives. Now, the oxidation was tried in a propionic acid solvent instead of acetic acid on five olefins of hex-1-ene, 2-methylpent-2-ene, cyclopentene, cyclohexene and 1-methylcyclohex-1-ene, and it is interesting that various kinds of propionic acid derivatives were obtained as shown in the Table.

$Mn(OAc)_3 \cdot 2H_2O$[7] (200 m mol) was previously heated up to 100°C in a mixture of propionic acid(200 ml) and its anhydride(200 ml) under an atmosphere of nitrogen. The addition of propionic anhydride increased the oxidation rate and improved the yield of the products. To this heated solution of the oxidant, a reactant olefin (100 m mol) was added with stirring, and the mixture was successively heated at the same temperature until the brown color of manganese(III) ion disappeared(*ca.* 20 min). Water was added to the oxidized mixture which was subsequently extracted with ether; the extract was separated into each component by combination of fractional distillation and preparative gas chromatography[8]. The following compounds were thus characterized as oxidized products[9].

Table Conversion of Each Olefin and Selectivity for Each Consurmed Olefin.

Olefin	Conversion(%)	Product		Selectivity(%)
$CH_3(CH_2)_3CH=CH_2$	81		(1)	40
			(2)	15
			(3)	37
	43		(4)	28
			(5)	28
			(6)	30
	48		(7)	40
			(8)	13
			(9)	35

Olefin	Conversion(%)	Product		Selectivity(%)
			(10)	30
	34		(11)	5
			(12)	30
			(13)	35
			(14)	30
	25		(15)	28
			(16)	22
			(17)	20

2-Methyl-4-propanoyloxyoctanoic acid(1): bp 162°C/3.5 mm Hg; n_D^{25} 1.4391; ν_{max} 2650, 1730, 1705 and 1180 cm^{-1}; δ_{ppm} 0.87(t, J=5 Hz, 3H), 1.06(t, J=7 Hz, 3H), 2.23(q,J=7Hz, 2H), 1.15(d, J=7 Hz, 3H), 2.3(m), 4.86(m, 1H) and 11.2(s, 1H); m/e 156(M^+ - CH_3CH_2COOH, 2%), 99(M^+ - CH_3CH_2COOH - $CH_3CH_2CH_2CH_2$, 34%). The methyl ester was prepared by reaction with diazomethane in the ether solution: n_D^{25} 1.4298, ν_{max} 1740 and 1190 cm^{-1};δ_{ppm} 0.88(t, J=5 Hz, 3H), 1.06(t, J=7 Hz, 3H), 2.26(q, J=7 Hz, 2H), 1.11(d, J=7 Hz, 3H),4.92 (m, 1H) and 3.62(s, 3H); m/e 187(M^+ - CH_3CH_2CO, 5%). Found: C, 63.95; H, 9.82. Calcd for $C_{13}H_{24}O_4$: C, 63.93; H, 9.84.

Lactone of 2-methyl-4-hydroxyoctanoic acid(2): bp 78°C/2.5 mm Hg; n_D^{25} 1.4380, ν_{max}1770 cm^{-1}; δ_{ppm} 0.92(t, J=5 Hz, 3H), 1.20(d, J=7 Hz, 3H), 2.1-2.8(m, 1H) and 4.0-4.5(m, 1H); m/e 156(M^+, 1%) and 99(M^+ - $CH_3CH_2CH_2CH_2$, 100%).

2-Methyloctanoic acid(3): bp 110°C/2.5 mm Hg; n_D^{25} 1.4285(lit.[10] n_D^{25} 1.4281); ν_{max}1770 and 1705 cm^{-1};δ_{ppm} 0.88(t, J=5 Hz, 3H), 1.15(d, J=7 Hz, 3H), 2.30(m, 1H) and 12.0(s,1H); m/e 158(M^+, 1%). Amide: mp 80-81°C(lit.[10] mp 80-81°C).

2,4-Dimethyl-3-ethyl-4-propanoyloxypentanoic acid(4): This compound was isolated from the distillation residue. ν_{max} 2650, 1740, 1710 and 1200 cm^{-1}. Methyl ester: n_D^{25} 1.4469; ν_{max} 1740 and 1195 cm^{-1}; m/e 171(M^+ - CH_3CH_2COO, 8%).

Lactone of 2,4-dimethyl-3-ethyl-4-hydroxypentanoic acid(5): bp 58-59°C/3.5 mm Hg; n_D^{25} 1.4420; ν_{max} 1770, 1390 and 1380 cm^{-1}; δ_{ppm} 1.0(t, J=6 Hz, 3H), 1.14(d, J=5 Hz, 3H), 1.20(s, 3H), 1.38(s, 3H) and 2.35(m, 1H); m/e 141(M^+ - CH_3, 25%), 112(M^+ - CH_3 - CO_2, 18%) and 97(M^+ - CH_3 - CO_2 - CH_3, 12%).

2,4-Dimethyl-3-ethyl-4-pentenoic acid(6): bp 68°C/3.5 mm Hg; n_D^{25} 1.4455; ν_{max} 2650,1710, 1650 and 890 cm^{-1}; δ_{ppm} 0.77(t, J=6 Hz, 3H), 1.14(d, J=6 Hz, 3H), 1.53(s, 3H), 2.31(m) and 4.78(broad s, 2H); m/e 156(M^+, 9%).

2-(2-Propanoyloxypentyl) propanoic acid(7): This compound was isolated from the distillation residue. ν_{max} 2650, 1735 1705 and 1185 cm^{-1}. Methyl ester: n_D^{25} 1.4520; ν_{max} 1740 cm^{-1}; m/e 228(M^+, 4%) and 169(M^+ - $COOCH_3$, 26%).

Lactone of 2-(2-hydroxycyclopentyl) propanoic acid(8): n_D^{25} 1.4619; ν_{max} 1770 cm^{-1}; δ_{ppm} 1.25(d, J=6 Hz, 3H), 2.3(m) and 4.76(broad s, 1H); m/e 140(M^+, 4%), 96(M^+ - CO_2, 22%) and 81(M^+ - CO_2 - CH_3, 29%).

2-Cyclopentyl propanoic acid(9): bp 62°C/2 mm Hg; n_D^{25} 1.4561; ν_{max} 2650 and 1710 cm^{-1}; δ_{ppm}1.13(d, J=6 Hz, 3H), 2.25(m, 1H) and 11.1(s, 1H); m/e 142(M^+, 4%). Amide: mp 136 -137°C(lit.[11] mp 136.5-137.0°C).

2-(2-Propanoyloxycyclohexyl) propanoic acid(10): This compound was isolated from the distillation residue. ν_{max} 2650, 1735, 1705 and 1185 cm^{-1}; δ_{ppm} 1.06(t, J=6 Hz), 2.2 (q, J=6 Hz), 1.10(t, J=6 Hz) and 9.1(s). Methyl ester: n_D^{25}1.4560; ν_{max}1735 and 1185 cm^{-1}; m/e 185(M^+ - CH_3CH_2CO, 4%).

Lactone of 2-(2-hydroxycyclohexyl) propanoic acid(11): ν_{max} 1780, 1175 and 975 cm^{-1}; δ_{ppm} 1.14(d, J=6 Hz, 3H) and 4.38(m, 1H); m/e 154(M^+, 1%), 153(M^+ - H, 1%), 110(M^+ - CO_2, 25%) and 95(M^+ - CO_2 - CH_3, 29%). The IR and NMR spectra coincided with those of cis-2-hydroxy-cis-α-methylcyclohexaneacetic acid[12].

2-Cyclohexyl propanoic acid(12): bp 114°C/2 mm Hg; n_D^{25} 1.4644; ν_{max}2650 and 1705 cm^{-1}; δ_{ppm} 1.12(d, J=7 Hz, 3H), 2.16(q, J=6 Hz, 1H) and 11.8(s, 1H). Methyl ester: n_D^{25} 1.4486; ν_{max} 1740 cm^{-1}; m/e 111(M^+ - $COOCH_3$, 5%) and 88(M^+ - $CH_3CH_2COOCH_3$, 100%). Amide: mp 155-156°C(lit.[13] mp 156-157°C).

3-Propanoyloxycyclohex-1-ene(13): bp 42°C/2 mm Hg; n_D^{25} 1.4480; ν_{max} 1735 and 1185 cm^{-1}; δ_{ppm} 1.05(t, J=7 Hz, 3H), 2.20(q, J=7 Hz, 2H), 5.11(m, 1H) and 5.7(m, 2H); m/e 154(M^+, 5%).

2-(2-Methyl-2-propanoyloxycyclohexyl) propanoic acid(14): This compound was isolated from the distillation residue. ν_{max} 2650, 1735, 1705 and 1185 cm^{-1}; δ_{ppm} 1.03(t, J=7 Hz), 1.16(d, J=6 Hz) and 10.3(s). Methyl ester: n_D^{25} 1.4668; ν_{max} 1740 cm^{-1}.

Lactone of 2-(2-methyl-2-hydroxycyclohexyl) propanoic acid(15): bp 110°C/3 mm Hg; n_D^{25} 1.4730; ν_{max} 1770 cm^{-1}; δ_{ppm} 1.05(d, J=7 Hz, 3H) and 1.30(s, 3H); m/e 168(M^+, 7%), 153 (M^+ - CH_3, 13%), 124(M^+ - CO_2, 38) and 109(109(M^+ - CO_2 - CH_3, 36%).

2-(2-Methylenecyclohexyl) propanoic acid(16): n_D^{25} 1.4810; ν_{max} 2650, 1705, 1650 and 890 cm^{-1}; δ_{ppm} 1.09(d, J=6 Hz, 3H), 2.4(m, 1H) and 4.64(broad s, 2H); m/e 168(M^+, 4%).

1-Methyl-6-propanoyloxycyclohex-1-ene(17): bp 62°C/3 mm Hg; n_D^{25} 1.4505; ν_{max} 1735, 1185 and 804 cm^{-1}; δ_{ppm} 1.07(t, J=7 Hz, 3H), 2.22(q, J=7 Hz, 2H), 1.58(s, 3H), 5.10(broad s, 1H) and 5.55(broad s, 1H); m/e 168(M^+, 2%).

The above products are classified into five types of 2-methyl-4-propanoyloxyalkanoic acids(type I)[(1),(4),(7),(10) and (14)], γ-lactones(type II)[(2),(5),(8),(11) and (15)], alkanoic acids(type III)[(3),(9) and (12)], alkenoic acids(type IV)[(6) and(16)] and propanoyloxyalkenes(type V)[(13) and (17)]. Of these products, although the compounds of II-V are the types which have already been obtained[1-6], compounds of type I were detected for the first time in the present oxidation. When compounds of type I were heated at 210-260°C, it was observed for the compounds to decompose into corrsponding γ-lactones(type II) and propionic acid in good yields. Therefore, the formation of γ-lactones(type II) may be due to the pyrolysis of compounds of type I during the reaction course.

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7) Prepared by a modification of the procedure of O.T.Christensen, Z. Anorg. Allgem. Chem., 27, 325(1901).

8) Preparative gas chromatography was achieved with a Shimadzu Model GC-1B gas chromatograph utilizing the column packed with 20% PEG-20M on Celite.

9) NMR spectra were measured on a JEOL Model JNM-MH-60II spectrometer in CCl_4 with tetramethylsilane as an internal standard. Mass spectra were recorded on a Hitachi Model RMS-4 spectrometer at 200°C and 80 eV.

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