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Carbonylation of Dienes and Diols in the Presence of Copper(I) Carbonyl Catalysts

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Dienes and diols having carbon numbers of 6 to 12 reacted with carbon monoxide to give mixtures of lactones, dicarboxylic acids and monocarboxylic acids in the presence of copper(I) carbonyl catalysts at room temperature and at 1 atm of carbon monoxide. Dienes and diols having carbon numbers larger than 10 gave isomers of dicarboxylic acid, the main component of which was tetramethyl-substituted tertiary carboxylic acid. The yield increased for an increase of the carbon number. All starting materials gave mixtures of 1,4- and 1,5-lactones. Larger amounts of the lactones were obtained from diols than from dienes. Cyclic monocarboxylic acid and saturated monocarboxylic acid were obtained by the carbonylation of 1,7-octadiene. The appropriate reaction temperature of the dienes and diols was 0—10 and 20—30 °C, respectively.

Several results of carbonylation catalyzed by copper(I) carbonyl ion giving tertiary-carboxylic acids in high yields from olefins and alcohols at room temperature and in pure carbon monoxide at 1 atm were described in previous paper.[1–5)]

For the carbonylation of dienes and diols, strong acid catalysts and metal carbonyl catalysts were used. Schauerte and Koch have studied the carbonylation of dienes and diols in concd H_2SO_4 and $BF_3 \cdot H_2O$, and obtained mixtures of dicarboxylic acids, monocarboxylic acids and lactones.[6,7)] On the other hand, Kuvaev *et al.* have studied the carbonylation of butadiene in the presence of a $Co_2(CO)_8$ catalyst at 160—220 °C at 250 atm of carbon monoxide, and obtained mixtures of adipic, methylglutaric and alkylsuccinic acids.[8)] Paulik has also synthesized C_5—C_{22} dicarboxylic acids by the carbonylation of C_3—C_{20} non-vicinal glycols in the presence of rhodium and iridium complex catalysts at 200 °C at 70 atm of carbon monoxide.[9)] In all these reactions, the carbonylation was carried out at elevated pressures of carbon monoxide.

In this paper, carbonylation of dienes and diols in the presence of copper(I) carbonyl catalysts in strong acids at room temperature and at 1 atom of carbon monoxide are described. The effect of the carbon number of the starting materials upon the formation of the dicarboxylic acid or lactone was studied using C_6—C_{12} dienes and diols. The reaction mechanisms are briefly discussed.

Results and Discussion

An unstable copper(I) carbonyl ion $Cu(CO)_n^+$ is formed by the absorption of carbon monoxide in an H_2SO_4 or H_2SO_4–FSO_3H solution of cuprous oxide.[10)] Dienes and diols easily react with carbon monoxide at atmospheric pressure in the presence of copper(I) carbonyl ions.

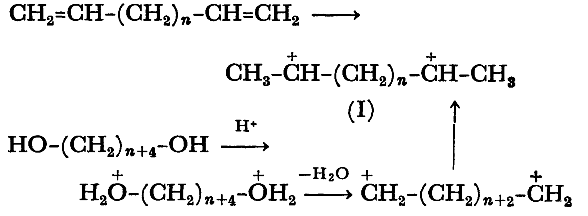
$$Cu^+ + CO \rightarrow Cu(CO)^+ \xrightarrow{CO} Cu(CO)_n^+ \quad n=3,\ 4$$

$$Cu(CO)_n^+ \rightleftharpoons Cu(CO)^+ + (n-1)CO$$

The copper(I) carbonyl ion behaves as a CO carrier from the gas phase to the H_2SO_4 solution, and has the same effect on the carbonylation as for elevated pressures of carbon monoxide. In general, the carbonylation of dienes in acid solutions is difficult because of their strong tendency to polymerization. However, the application of copper(I) carbonyl catalysts renders possible the carbonylation of diene in high yields even in strong acid solutions.

Dienes and diols having carbon numbers from 6 to 12 react with carbon monoxide and gave mixtures of monocarboxylic acids, dicarboxylic acids and lactones. The ratio of these components in the mixture varied with the carbon number of the starting material. The results are shown in Table 1. Dicarboxylic acids were obtained from starting materials having carbon numbers larger than 10. Lactones were obtained from all compounds. In general, larger amounts of lactones were obtained from diols than from dienes. Cyclic monocarboxylic acid and saturated monocarboxylic acid were obtained by the carbonylation of 1,7-octadiene. No hydroxycarboxylic acid and unsaturated carboxylic acid were identified in the strong acid solution. The carbonylation of diols was carried out at 20—30 °C, on the other hand, the carbonylation of dienes was carried out at 0—10 °C in order to prevent polymerization.

The reaction schemes are explained as follows. The reaction pathways of the dienes and diols are almost the same. A carbonium ion (I) is formed by protonation to the double bond of the diene, or by protonation and successive dehydration of the diol.



$$CH_2{=}CH\text{-}(CH_2)_n\text{-}CH{=}CH_2 \xrightarrow{H^+} CH_3\text{-}\overset{+}{C}H\text{-}(CH_2)_n\text{-}\overset{+}{C}H\text{-}CH_3 \ \text{(I)}$$

$$HO\text{-}(CH_2)_{n+4}\text{-}OH \xrightarrow{H^+} H_2\overset{+}{O}\text{-}(CH_2)_{n+4}\text{-}\overset{+}{O}H_2 \xrightarrow{-H_2O} \overset{+}{C}H_2\text{-}(CH_2)_{n+2}\text{-}\overset{+}{C}H_2 \rightarrow \text{(I)}$$

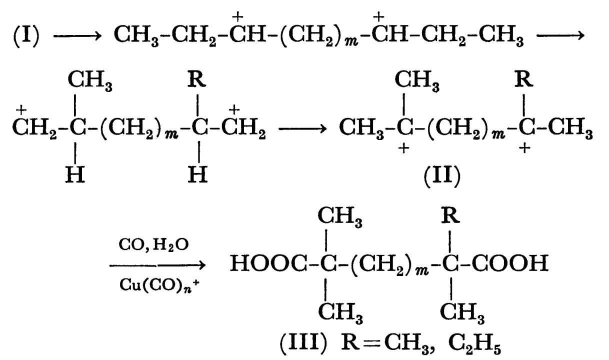
When the carbon number of I is larger than 10, the carbonium ion (I) isomerizes to the more stable *t*-carbonium ion (II) by Wagner-Meerwein rearrangement, and reacts with carbon monoxide. By this mechanism, *t*-dicarboxylic acid is obtained from a diene or diol having a carbon number larger than 10. In this case, the carbon number for the two tertiary carbonium ions is larger than 4. The yield of *t*-dicarboxylic acid increases when the carbon numbers of the starting materials increases to between

TABLE 1. CARBONYLATION PRODUCTS OF DIENES AND DIOLS[a)]

Substrates	Time h	Temp °C	Products	Abbr.	Yield %
1,5-Hexadiene	2	0— 5	2-Ethyl-4-pentanolide	(I)	46
1,7-Heptanediol	3	20—30	2,2-Dimethyl-4-hexanolide	(II)	40
			2-Methyl-2-ethyl-5-pentanolide	(III)	30
			2,2-Dimethyl-5-hexanolide	(IV)	10
1,7-Octadiene	2.5	3— 8	2,2-Dimethyl-4-heptanolide	(V)	15
			2,2-Dimethyl-5-heptanolide	(VI)	8
			2,2-Dimethylheptanoic acid		14
			2-Methyl-2-ethylhexanoic acid		6
			1,4-Dimethylcyclohexanecarboxylic acid		35
1,8-Octanediol	2.5	20—25	2,2-Dimethyl-4-heptanolide	(V)	35
			2,2-Dimethyl-5-heptanolide	(VI)	40
1,9-Nonanediol	3	15—25	2,2-Dimethyl-4-octanolide	(VII)	35
			2,2-Dimethyl-5-octanolide	(VIII)	25
			2,2-Diethyl-4-hexanolide		10
1,9-Decadiene[b)]	2.5	5—10	2-Methyl-2-ethyl-4-octanolide	(IX)	20
			2-Methyl-2-ethyl-5-octanolide	(X)	15
			2,2,7,7-Tetramethyloctanedioic acid	(XI)	45
			2-Ethyl-2,6,6-trimethylheptanedioic acid		10
1,10-Undecadiene[b)]	2	4— 8	1,4- and 1,5-Lactone[c)]		25
			2,2,8,8-Tetramethylnonanedioic acid	(XII)	49
			2-Ethyl-2,7,7-trimethyloctanedioic acid		8
1,12-Dodecanediol	3	20	1,4- and 1,5-Lactone[c)]		50
			2,2,9,9-Tetramethyldecanedioic acid	(XIII)	38
			2-Ethyl-2,8,8-trimethylnonanedioic	(XIV)	9

a) Reactions were carried out using 30 ml of 98% H_2SO_4, 1.144 g of Cu_2O and 30 mmol of dienes or diols.
b) During the carbonylation, 10 ml of FSO_3H was added. c) The structure of this substance was not determined.

C_{10} and C_{12}. The dicarboxylic acids obtained consist of structural isomers of which the main product is tetramethyl-substituted dicarboxylic acid and the by-product is ethyl-substituted dicarboxylic acid.

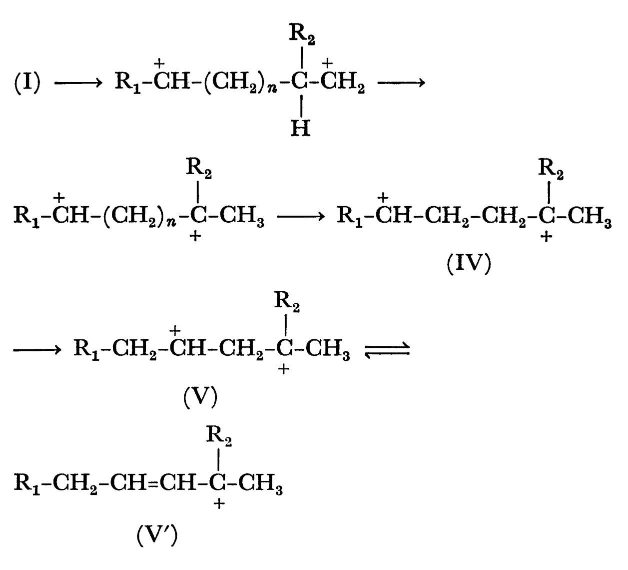


$$\text{(I)} \longrightarrow CH_3\text{-}CH_2\text{-}\overset{+}{C}H\text{-}(CH_2)_m\text{-}\overset{+}{C}H\text{-}CH_2\text{-}CH_3 \longrightarrow$$

$$\overset{+}{C}H_2\text{-}\underset{H}{\overset{CH_3}{C}}\text{-}(CH_2)_m\text{-}\underset{H}{\overset{R}{C}}\text{-}\overset{+}{C}H_2 \longrightarrow \underset{\text{(II)}}{CH_3\text{-}\underset{+}{\overset{CH_3}{C}}\text{-}(CH_2)_m\text{-}\underset{+}{\overset{R}{C}}\text{-}CH_3}$$

$$\xrightarrow[Cu(CO)_n^+]{CO,H_2O} HOOC\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}(CH_2)_m\text{-}\underset{CH_3}{\overset{R}{C}}\text{-}COOH \qquad \text{(III) } R{=}CH_3,\ C_2H_5$$

Lactone was always obtained for the carbonylation of the dienes or diols. The lactone obtained is a mixture of five-membered 1,4-lactones and six-membered 1,5-lactone derivatives. No four-membered lactones or large-ring lactones were obtained. In the formation of stable 1,4-lactone derivatives, the carbonium ions (I) rearrange to resonance-stabilized allyl cation intermediates (V′). The carbonium ions (V) undergo carbonylation and hydration, and subsequently 1,4-lactones are formed by intramolecular esterification. During the isomerization process to V, carbonium ions (IV) react with carbon monoxide, and then stable 1,5-lactone derivatives are obtained. Generally, the amount of 1,4-lactone is larger than the quantity of 1,5-lactone. Lactonization to five- and six-membered rings is fast, however ring-closure reactions to seven- and eight-membered rings are slow. Furthermore, the isomerization rate is higher than the ring-closure rate to large-ring lactones. For these reasons, it is understood that no large-ring lactones or four-membered lactone are obtained. In all lactones, the α-carbon of the carbonyl group has two alkyl substituents, and the carbon atom adjacent to the oxygen atom has one alkyl substituent.

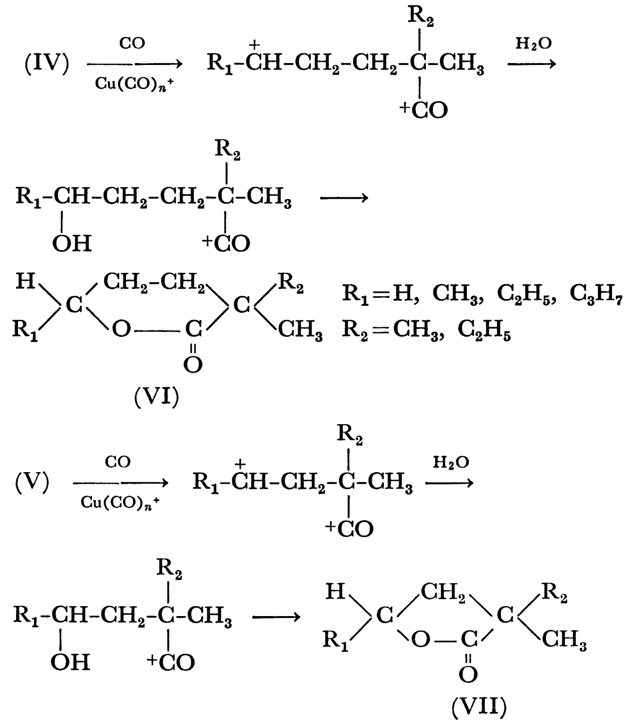


$$\text{(I)} \longrightarrow R_1\text{-}\overset{+}{C}H\text{-}(CH_2)_n\text{-}\underset{H}{\overset{R_2}{C}}\text{-}\overset{+}{C}H_2 \longrightarrow$$

$$R_1\text{-}\overset{+}{C}H\text{-}(CH_2)_n\text{-}\underset{+}{\overset{R_2}{C}}\text{-}CH_3 \longrightarrow \underset{\text{(IV)}}{R_1\text{-}\overset{+}{C}H\text{-}CH_2\text{-}CH_2\text{-}\underset{+}{\overset{R_2}{C}}\text{-}CH_3}$$

$$\longrightarrow \underset{\text{(V)}}{R_1\text{-}CH_2\text{-}\overset{+}{C}H\text{-}CH_2\text{-}\underset{+}{\overset{R_2}{C}}\text{-}CH_3} \rightleftharpoons$$

$$\underset{\text{(V')}}{R_1\text{-}CH_2\text{-}CH{=}CH\text{-}\underset{+}{\overset{R_2}{C}}\text{-}CH_3}$$



$$(IV) \xrightarrow[Cu(CO)_n^+]{CO} R_1-\overset{+}{C}H-CH_2-CH_2-\underset{+CO}{\overset{R_2}{C}}-CH_3 \xrightarrow{H_2O}$$

$$R_1-\underset{OH}{CH}-CH_2-CH_2-\underset{+CO}{\overset{R_2}{C}}-CH_3 \longrightarrow$$

(VI)

$R_1=H, CH_3, C_2H_5, C_3H_7$ $R_2=CH_3, C_2H_5$

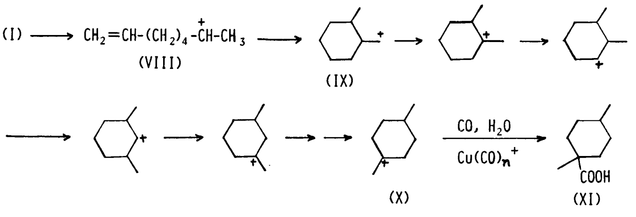
$$(V) \xrightarrow[Cu(CO)_n^+]{CO} R_1-\overset{+}{C}H-CH_2-\underset{+CO}{\overset{R_2}{C}}-CH_3 \xrightarrow{H_2O}$$

$$R_1-\underset{OH}{CH}-CH_2-\underset{+CO}{\overset{R_2}{C}}-CH_3 \longrightarrow$$

(VII)

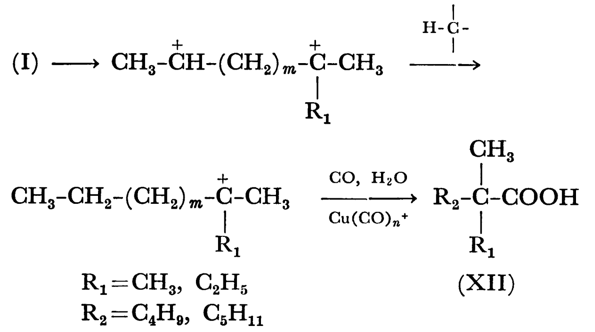
$R_1=CH_3, C_2H_5, C_3H_7, C_4H_9$
$R_2=CH_3, C_2H_5$

Cyclic monocarboxylic acid and *t*-monocarboxylic acid are obtained by the carbonylation of 1,7-octadiene. In the formation of cyclic monocarboxylic acid, the carbonium ion (VIII) undergoes a ring-closure reaction by means of the intramolecular attack of the cation on the double bond. After rearrangement from IX to X, the carbonium ion (X) reacts with carbon monoxide producing 1,4-dimethylcyclohexanecarboxylic acid.



To form saturated *t*-monocarboxylic acid, some of the carbonium ions (I) are saturated by hydride abstraction from other molecules. It appears that the secondary carbonium ions are more susceptible to saturation than *t*-carbonium ions.

Actually, the main alkyl chain of the carboxylic acid obtained is linear.



$$(I) \longrightarrow CH_3-\overset{+}{C}H-(CH_2)_m-\underset{R_1}{\overset{+}{C}}-CH_3 \xrightarrow{H-\overset{|}{\underset{|}{C}}-}$$

$$CH_3-CH_2-(CH_2)_m-\underset{R_1}{\overset{+}{C}}-CH_3 \xrightarrow[Cu(CO)_n^+]{CO,\ H_2O} R_2-\underset{R_1}{\overset{CH_3}{C}}-COOH$$

(XII)

$R_1=CH_3, C_2H_5$
$R_2=C_4H_9, C_5H_{11}$

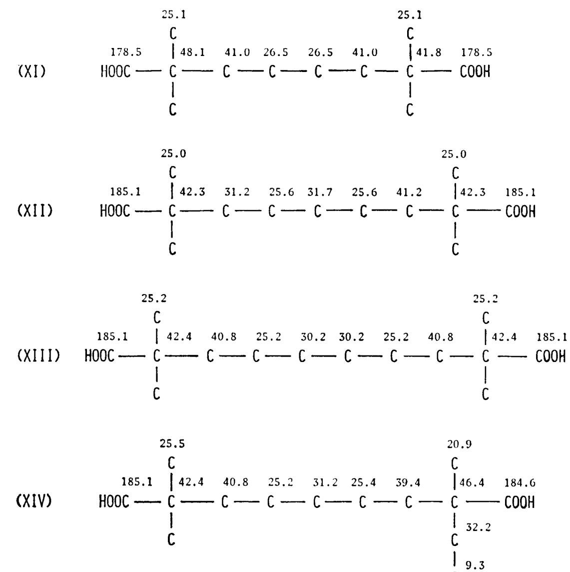


Chart 1. ^{13}C NMR chemical shifts of tertiary-dicarboxylic acids.

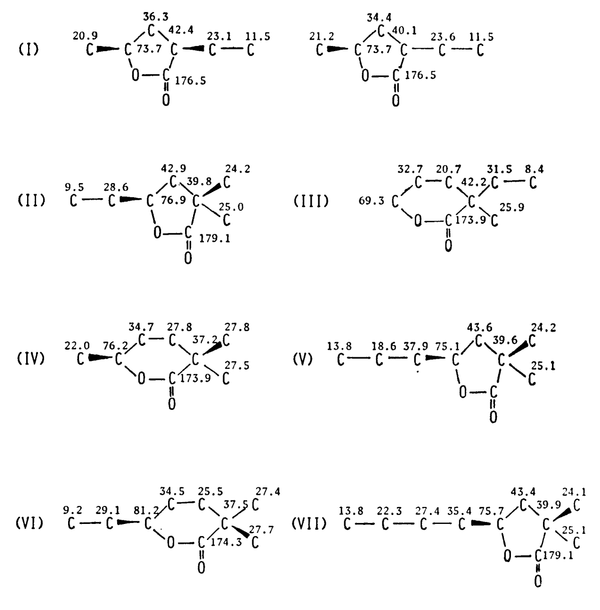


Chart 2. ^{13}C NMR chemical shifts of lactones.

Dicarboxylic acid was separated as crystals from lactone and recrystallized from a mixed solvent of petroleum ether and acetone. Since the isomers of the dicarboxylic acids could not be separated, the mixtures were analyzed by ^{13}C NMR. Lactone and monocarboxylic acid were isolated by preparative GLPC, and the structures were determined by ^{1}H NMR, ^{13}C NMR, IR, GC-MS and elemental analysis. The ^{13}C NMR chemical-shift assignments of the dicarboxylic acids and lactones are shown in Charts 1 and 2. From the ^{13}C NMR analysis, other isomers coexisted with the compound shown in Charts 1 and 2, however, the amount of other isomers was so few that the determination of their structures was not successful.

Several characteristics are clarified by the results of the analysis of the lactones. On the GLPC chromatogram, two large peaks were observed for every sample. The first peak corresponds to the 1,4-lactone derivatives, and the second peak to the 1,5-lactone derivatives. In the IR spectra, the $\nu_{C=O}$ of 1,4-lactone and 1,5-lactone were observed at 1775 and 1725 cm^{-1}, respectively. In the ^{1}H NMR chemical shifts of 1,4-lactones, characteristic signals for methylene of the lactone ring were observed at 2.0—2.3 ppm as the AB part of the ABX spin system. From ^{13}C NMR analysis, the chemical shifts for the carbonyl carbons of 1,4-lactone and 1,5-lactone were determined to be at 176—179 ppm and at *ca.* 174 ppm, respectively.

Using silver carbonyl ions instead of copper(I) carbonyl ions as catalysts, the same catalytic effect was observed and the same reaction products were obtained.

Experimental

GLPC analysis was performed using a 3-m Free Fatty Acid Polyester column. The infrared spectra were taken with neat samples using a JASCO IRA-1 spectrophotometer. The ^{1}H NMR spectra were taken using a JEOL PS-100 at 100 MHz with CCl$_4$ as the solvent. Chemical shifts are given in δ units (ppm) downfield from the tetramethylsilane internal standard. The ^{13}C NMR spectra were measured using the pulsed Fourier-transform technique with a JEOL PS-100 instrument, an FT-100 FT unit, a DP-1 pulse programmer, and an EC-100 computer, at a resonance frequency of 25.15 MHz. Proton noise decoupling was normally used. Mass spectra were obtained using a JEOL JMS-06 gas chromatograph-mass spectrometer with a 20-eV ionizing voltage.

Preparation of the Cu(I) Carbonyl Catalysts. In a 300-ml three-necked flask equipped with a thermometer and a carbon monoxide gas burette, 1.144 g of Cu$_2$O and 30 ml of 98% H$_2$SO$_4$ were placed. The apparatus was evacuated by a rotary pump, and then carbon monoxide was introduced from the gas burette. The mixture was stirred vigorously and a heterogeneous solution of Cu(CO)$_n^+$ was prepared.

Carbonylation of Dienes and Diols. From a syringe, 30 mmol of dienes or diols were added dropwise to the Cu(I) carbonyl catalyst solution for 2 h. Absorption of the carbon monoxide was completed within 2 — 3 h, and the reaction mixture was poured over ice-water. The mixture was shaken with hexane, and the reaction products were isolated by preparative GLPC or by recrystallization. The structures of the products were determined by ^{1}H NMR, ^{13}C NMR, IR and mass spectra and by elemental analysis.

In order to determine the monocarboxylic acid, dicarboxylic acid and lactone yield in the mixture, first the total amount of the carboxylic acids was determined by titrating a 1/10 volume of hexane extract with a 1/10 M NaOH ethanol solution. The monocarboxylic acid yield was determined using gas chromatography by adding a known amount of an internal standard. The dicarboxylic acid yield was calculated from the difference between the total carboxylic acid yield and the monocarboxylic acid yield. The lactone yield was determined by measuring the saponification value. The excess of the 1/10 M NaOH ethanol solution was added to the hexane extract, and the mixture was refluxed for 3 h, then titrated with a standard 1/10 M HCl solution. The lactone yield was found from the difference between saponification value and the total amount of carboxylic acids.

2,2-Dimethyl-4-hexanolide was obtained from 1,7-heptanediol. IR: 2960, 1760 (C=O), 1460, 1205 cm^{-1}. NMR δ 0.98 (3H, t, J=7Hz, $-CH_2-\mathbf{CH_3}$), 1.20 (6H, s, $-\overset{|}{\underset{|}{C}}-\mathbf{CH_3}$) 1.43—1.80 (2H, m, $-\mathbf{CH_2}-CH_2$), 2.00—2.30 (2H, m, $-O\overset{|}{C}H-\mathbf{CH_2}-$), 4.25(1H, m, $-O-\overset{|}{C}\mathbf{H}-CH_2-$). Found: C, 67.23; H, 9.78%. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92%.

2-Methyl-2-ethyl-5-heptanolide was obtained from 1,7-heptanediol. IR: 2980, 1735 (C=O), 1380, 1260, 1140 cm^{-1}. NMR (CCl$_4$) δ 0.90 (3H, t, J=7Hz, $-CH_2-\mathbf{CH_3}$), 1.20 (3H, s, $-\overset{|}{\underset{|}{C}}-\mathbf{CH_3}$), 1.40—2.00 (6H, m, $-\mathbf{CH_2}-$), 4.28 (2H, m, $-O-\mathbf{CH_2}-$). Mass spectrum *m/e* (%) 142 (M$^+$, 8) 127(9), 113(100), 55(46). Found: C, 67.11; H, 9.89%. Calcd for $C_8H_{14}O_2$; C, 67.57; H, 9.92%.

2,2-Dimethyl-4-heptanolide was obtained from 1,7-octadiene and 1,8-octanediol. IR: 2970, 1770 (C=O), 1460, 1385, 1205, 1115 cm^{-1}. NMR (CCl$_4$) δ 1.00 (3H, t, J=7 Hz, $-CH_2-\mathbf{CH_3}$), 1.20 (6H, s, $\mathbf{CH_3}-\overset{|}{\underset{|}{C}}-\mathbf{CH_3}$), 1.36—2.20 (6H, m, $-\mathbf{CH_2}-$), 4.35 (1H, m, $-\overset{|}{C}\mathbf{H}-O-$). Mass spectrum *m/e* (%) 156 (M$^+$, 21), 113(100), 85(82), 69(86). Found: C, 69.07; H, 10.64%. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32%.

2,2-Dimethyl-5-heptanolide was obtained from 1,7-octadiene and 1,8-octanediol. IR: 2970, 1725(C=O), 1385, 1280, 1120 cm^{-1}. NMR (CCl$_4$) δ 1.02 (3H, t, J=7 Hz, $-CH_2-\mathbf{CH_3}$), 1.22 (6H, s, $\mathbf{CH_3}-\overset{|}{\underset{|}{C}}-\mathbf{CH_3}$), 1.40—1.95 (6H, m, $-\mathbf{CH_2}-$), 4.14 (1H, m, $-\overset{|}{C}\mathbf{H}-O-$). Mass spectrum *m/e* (%) 156 (M$^+$, 9), 127(14), 81(28) 70(25), 56(100). Found: C, 69.22; H, 10.73%. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32%.

2,2-Dimethyl-4-octanolide was obtained from 1,9-nonanediol. IR: 2960, 1765 (C=O), 1460, 1200, 1115 cm^{-1}. NMR (CCl$_4$) δ 0.94 (3H, t, J=6Hz, $-CH_2-\mathbf{CH_3}$), 1.20 (6H, s, $\mathbf{CH}-\overset{|}{\underset{|}{C}}-\mathbf{CH_3}$), 1.40—2.40 (8H, m, $-\overset{|}{C}\mathbf{H_2}-$), (1H, m, $-\mathbf{CH}-O-$). Mass spectrum *m/e* (%) 170(M$^+$, 14), 140(13), 112 (76), 70(100). Found: C, 70.35; H, 10.46%. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.65%.

2,2-Dimethyl-5-octanolide was obtained from 1,9-nonanediol. IR: 2960, 1725 (C=O), 1380, 1120 cm^{-1}. NMR (CCl$_4$) δ 0.98 (3H, t, J=7 Hz, $-CH_2-\mathbf{CH_3}$), 1.20 (6H, s, $\mathbf{CH_3}-\overset{|}{\underset{|}{C}}-\mathbf{CH_3}$), 1.40—1.80 (8H, $-\mathbf{CH_2}-$), 4.20 (1H, m, $-\overset{|}{C}\mathbf{H}-O-$). Mass spectrum *m/e* (%) 170 (M$^+$, 10), 126 (33), 70 (55), 56(100). Found: C, 70.48; H, 10.49%. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.65%.

C_{12} t-Dicarboxylic Acids (a mixture of 2,2,7,7-tetramethyloctanedioic acid and 2-ethyl-2,6,6-trimethylheptanedioic acid) were obtained from 1,9-decadiene. Mp 152—156 °C. IR (KBr): 2970, 1680 (C=O), 1465, 1380, 1250, 1170 cm^{-1}. NMR (CCl$_4$) δ 0.88 (t, J=7 Hz, $\mathbf{CH_3}-CH_2-$), 1.08, 1.12, 1.16 (s, $\overset{|}{\underset{|}{C}}-\mathbf{CH_3}$), 1.20—1.95 (m, $-\mathbf{CH_2}-$), 12.5

(br. s, -COOH). Found: C, 62.28; H, 9.75%. Calcd for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63%.

C_{13} t-Dicarboxylic Acids (a mixture of 2,2,8,8-tetramethylnonanedioic acid and 2-ethyl-2,7,7-trimethyloctanedioic acid) were obtained from 1,10-undecadiene. Mp 132—134°C. IR(KBr): 2970, 1680 (C=O), 1400, 1250, 1193, 920 cm^{-1}. NMR (CCl_4) δ 0.84 (t, J=7Hz, CH_3-CH_2-), 1.04 (s, $CH_3\text{-}\overset{|}{\underset{|}{C}}\text{-}$), 1.14 (s, $CH_3\text{-}\overset{|}{\underset{|}{C}}\text{-}CH_3$), 1.26—1.88 (m, -$CH_2$-), 11.2 (br. s, -COOH). Found: C, 64.29; H, 10.38%. Calcd for $C_{13}H_{24}O_4$: C, 63.91; H, 9.90%.

C_{14} t-Dicarboxylic Acids (a mixture of 2,2,9,9-tetramethyldecanedioic acid and 2-ethyl-2,8,8-trimethylnonanedioic acid) were obtained from 1,12-dodecanediol. Mp 114—118°C. IR(KBr): 2970, 1680 (C=O), 1460, 1250, 1180, 920 cm^{-1}. NMR (CCl_4) δ 0.86 (t, J=7Hz, CH_3-CH_2-), 1.08, 1.14 (s, $CH_3\text{-}\overset{|}{\underset{|}{C}}\text{-}$), 1.20—1.80 (m, -$CH_2$-), 12.2 (br. s, -COOH). Found: C, 65.47; H, 10.57%. Calcd for $C_{14}H_{26}O_4$: C, 65.09; H, 10.14%.

2-Ethyl-4-pentanolide, *2,2-Dimethylheptanoic Acid*, *2-Methyl-2-ethylhexanoic Acid* and *1,4-Dimethylcyclohexanecarboxylic Acid* were identified using authentic samples obtained by the carbonylation of 1,5-hexadiene, 1-octene and 1,4-dimethylcyclohexane, respectively.[1,3]

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