78–74° (7 mm). Nmr analysis showed the first fraction to contain 76% anisole, 17% **7**, and 7% **2**, while the second fraction contained 51% **7**, 18% **2**, 11% **1**, and 10% anisole. Anisole was identified by comparison with the nmr spectrum of an authentic sample and by conversion into its sulfonamide derivative: mp (isolated) 109–110.5°; mp (authentic) 111.5–112° (lit.[20] mp 111°); mmp 111–112.5° (no depression); ir spectra of sulfonamides matched perfectly.

Registry No.—**1**, 150-78-7; **2**, 39000-58-3; **3**, 104-93-8; **4**, 20023-36-3; **5**, 5396-38-3; **6**, 22566-53-6; **7**, 39000-61-8; **8**, 99-97-8; **9**, 589-92-4; **10**, 5259-65-4; **11**, 1012-72-2; **12**, 39000-62-9; **13**, 1087-02-1; **14**, 39000-63-0; **15**, 5009-02-9; **16**, 39000-65-2; **17**, 100-18-5; **18**, 39000-66-3; **19**, 106-42-3; **20**, 2808-79-9; **21**, 581-40-8; **23**, 39000-67-4; 1-methoxy-4-*tert*-butyl-1,3-cyclohexadiene, 37720-49-3; lithium, 7439-93-2.

Acknowledgment.—We are grateful to Dr. J. A. Moore, Dr. S. S. Kulp, Dr. H. Omura, L. A. Conley, and D. Viola for many services rendered during the course of the work.

Synthesis of *tert*-Carboxylic Acids from Olefins and Carbon Monoxide by Copper(I) Carbonyl Catalyst

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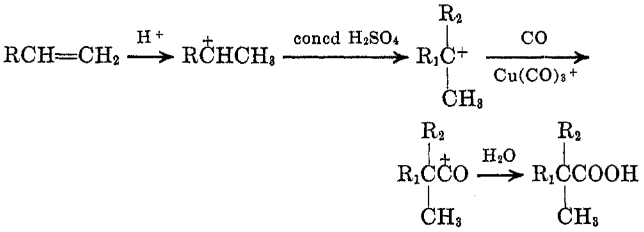
The new carbonylation reaction was proposed using Cu(I) carbonyl catalyst in concentrated H_2SO_4. In concentrated H_2SO_4 containing Cu(I) compound, olefins react with carbon monoxide at room temperature and atmospheric pressure to produce *tert*-carboxylic acids in high yields. Neither primary nor secondary carboxylic acids were found. The catalyst was prepared in concentrated H_2SO_4 from Cu(I) compounds and carbon monoxide. The amount of the Cu(I) compound sufficient for carrying out these carbonylation was as small as 0.2 mol/l. It is assumed that unstable Cu(I) tricarbonyl [$Cu(CO)_3^+$] is transiently formed in concentrated H_2SO_4. The yields of the *tert*-carboxylic acids are as follows: *tert*-C_7 acid, 72% from 1-hexene; *tert*-C_8 acid, 82% from 1-heptene; *tert*-C_9 acid, 94% from 1-octene; and *tert*-C_{11} acid, 97% from 1-decene. Reaction optimum temperature was 20–50° for the monoolefins. The yield and reaction rate decreased with the decrease of H_2SO_4 concentration. At the H_2SO_4 concentrations less than 80%, no carboxylic acids were obtained.

Much work has been published concerning the carbonylation of olefin with carbon monoxide. Reppe[1] and others[2] reported the reaction catalyzed by metal carbonyls, and mixtures of *n*-carboxylic acid and *sec*-carboxylic acid were obtained. This reaction proceeds at high temperature and high pressure. On the other hand, Koch[3] and others[4,5] obtained branched carboxylic acids by the carbonylation of olefins in strong acid such as H_2SO_4, HF, H_3PO_4, or $BF_3 \cdot H_2O$. However, metal catalysts were not used in Koch type reaction. All these reactions need high carbon monoxide pressures.

Recently we found that Cu(I) carbonyl was easily formed from Cu(I) compounds and carbon monoxide in concentrated H_2SO_4.[6] Cu(I) carbonyl has high catalytic activity in the carbonylation of alcohols to carboxylic acids at room temperature and atmospheric pressure.[7]

$$ROH \xrightarrow{H_2SO_4} R'^+ \xrightarrow[Cu(CO)_3^+]{CO} R'CO^+ \xrightarrow{H_2O} t\text{-}R'COOH$$

This paper describes the synthesis of *tert*-carboxylic acids, from olefins and carbon monoxide, catalyzed by Cu(I) carbonyl in concentrated H_2SO_4. From various types of olefins, *tert*-carboxylic acids are generally formed by the isomerization of the intermediate carbonium ion in concentrated H_2SO_4. The reactions using Cu(I) carbonyl catalyst provide new examples of the wide-ranging synthetic utility for carbonylation reactions.



$$RCH{=}CH_2 \xrightarrow{H^+} R\overset{+}{C}HCH_3 \xrightarrow{\text{concd } H_2SO_4} R_1\underset{CH_3}{\overset{R_2}{C^+}} \xrightarrow[Cu(CO)_3^+]{CO} R_1\underset{CH_3}{\overset{R_2}{\overset{+}{C}}}CO \xrightarrow{H_2O} R_1\underset{CH_3}{\overset{R_2}{C}}COOH$$

$R_1 = CH_3, C_2H_5, n\text{-}C_3H_7, n\text{-}C_4H_9, n\text{-}C_5H_{11}, n\text{-}C_6H_{13}, n\text{-}C_7H_{15}$

$R_2 = CH_3, C_2H_5, n\text{-}C_3H_7, n\text{-}C_4H_9$

Results and Discussion

The results of *tert*-carboxylic acid synthesis catalyzed by Cu(I) carbonyl from olefin and carbon monoxide are shown in Table I. Various kinds of olefins (terminal or internal olefins) gave *tert*-carboxylic acids in concentrated H_2SO_4. This is due to the isomerization of the carbonium ion intermediate prior to the carbonylation. Primary or secondary carboxylic acids were not found.

Cuprous oxide and cuprous sulfate were used as the Cu(I) compounds. The effect of the amount of cuprous oxide is illustrated in Figure 1. Without cuprous oxide, the rate of reaction was very slow, and the yield of carboxylic acid was less than 10%. When cuprous oxide was added in concentrated H_2SO_4, the rate of reaction increased considerably. The reaction was almost complete in 1–2 hr, and *tert*-carboxylic acids were obtained in high yields. On the other hand, Cu(II) compounds do not exhibit any catalytic activity.

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[1] W. Reppe and H. Kröper, *Justus Liebigs Ann. Chem.*, **582**, 38 (1953).

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[3] H. Koch, *Brennst. Chem.*, **36**, 321 (1955).

[4] K. E. Möller, *ibid.*, **45**, 129 (1964); Y. T. Eidus, K. V. Puzitskii, and S. D. Pirozhkov, *Neftekhimiya*, **8** (3), 343 (1968).

[5] S. Pawlenko, U. S. Patent 3,349,107 (1967); *Chem. Abstr.*, **68**, pc21540v (1967).

[6] Y. Souma and H. Sano, *Nihon Kagaku Zasshi*, **91**, 625 (1970).

[7] Y. Souma and H. Sano, *Kogyo Kagaku Zasshi*, **73**, 2723 (1970).

TABLE I

tert-CARBOXYLIC ACIDS DERIVED FROM OLEFINS AND CARBON MONOXIDE[a]

Olefin	Registry no.	Cu compd	Products	Registry no.	Yield, %
1-Hexene	592-41-6	Cu_2O	2,2-Dimethylpentanoic acid	1185-39-3	45
			2-Methyl-2-ethylbutanoic acid	19889-37-3	27
			2,2-Dimethylbutanoic acid	595-37-9	3
			2,2-Dimethylpropanoic acid		1
			Higher acids		4
Cyclohexene	110-83-8	Cu_2O	1-Methylcyclopentanecarboxylic acid	5217-05-0	63
1-Heptene	592-76-7	Cu_2O	2,2-Dimethylhexanoic acid	813-72-9	57
			2-Methyl-2-ethylpentanoic acid	5343-52-2	25
1-Octene	111-66-0	Cu_2O	2,2-Dimethylheptanoic acid	14250-73-8	54
			2-Methyl-2-ethylhexanoic acid	1185-29-1	27
			2-Methyl-2-propylpentanoic acid	31113-56-1	13
1-Octene		$CuSO_4$ + Cu powder	2,2-Dimethylheptanoic acid		48
			2-Methyl-2-ethylhexanoic acid		25
			2-Methyl-2-propylpentanoic acid		10
1-Octene		Cu powder[b]	2,2-Dimethylheptanoic acid		45
			2-Methyl-2-ethylhexanoic acid		23
			2-Methyl-2-propylpentanoic acid		8
2-Octene	111-67-1	Cu_2O	2,2-Dimethylheptanoic acid		36
			2-Methyl-2-ethylhexanoic acid		30
			2-Methyl-2-propylpentanoic acid		15
1-Decene	872-05-9	Cu_2O	2,2-Dimethylnonanoic acid	14250-75-0	49
			2-Methyl-2-ethyloctanoic acid	31199-56-1	24
			2-Methyl-2-propylheptanoic acid	39037-67-7	18
			2-Methyl-2-butylhexanoic acid		6
1,5-Hexadiene[c]	592-42-7	Cu_2O	α-Ethyl-γ-valerolactone	19639-00-0	30
1,5-Cyclooctadiene[c]	111-78-4	Cu_2O	Bicyclo[3.3.0]octanecarboxylic acid	32789-48-3	15

[a] In most cases 0.2 mol of olefin, 0.02 mol of Cu compound, and 105 ml of 98% H_2SO_4 were used, the reaction temperature was approximately 30°, and the reaction time varied from 1 to 2 hr. The pressure of carbon monoxide was 1 atm. [b] The amount of Cu powder was 0.04 mol. [c] The temperature was 5–10°.

However, the equimolar mixture of a Cu(II) compound and copper powder in concentrated H_2SO_4 showed similar catalytic activity to that of Cu(I) compounds in H_2SO_4.

$$Cu^{2+} + Cu^0 \xrightarrow{\text{concd } H_2SO_4} 2Cu^+$$

Copper powder in concentrated H_2SO_4 also exhibits catalytic activity; probably it is due to the formation of Cu_2SO_4 by the oxidation with concentrated H_2SO_4. The presence of Cl^-, Br^-, I^-, NO_3^-, and CN^- inhibits the catalytic activity. These ions prevent the formation of Cu(I) tricarbonyl. The optimum reaction temperature was 20–50° for monoolefins, and 5–10° for dienes. Above 55°, side reactions such as polymerization predominate. The olefin was slowly added into the Cu(I) carbonyl suspension. When the rate of the addition of olefin was too fast, polymerization occurred in competition with the carbonylation reaction.

The influence of the concentration of H_2SO_4 was examined. The results were shown in Figure 2. At H_2SO_4 concentrations above 80%, the rate of reaction increased. No carbonylation occurred at an H_2SO_4 concentration less than 80%. The effect of the H_2SO_4 concentration upon the carbonylation is parallel to its effect upon the formation of unstable Cu(I) tricarbonyl ion $Cu(CO)_3^+$ in H_2SO_4 solution.[6] Cu(I) monocarbonyl ion $Cu(CO)^+$ is formed at H_2SO_4 concentrations less than 80%, whereas Cu(I) tricarbonyl ion, which acts as the carbonylation catalyst, is formed at H_2SO_4 concentrations above 80%. These carbonyl ions exist as an equilibrium mixture.[8]

$$Cu^+ \xrightarrow{CO} Cu(CO)^+ \xrightarrow[\text{concd } H_2SO_4]{CO} Cu(CO)_3^+$$

$$Cu(CO)_3^+ \rightleftharpoons Cu(CO)^+ + 2CO$$

$Cu(CO)_3^+$ is very unstable and easily releases CO. In the presence of CO acceptors such as carbonium ions, carbon monoxide is liberated from Cu(I) tricarbonyl ion and transferred to the CO acceptor immediately. Carbon monoxide is continuously absorbed by Cu^+ in the solution from the gas phase and kept at high concentrations as a form of $Cu(CO)^+$ or $Cu(CO)_3^+$. In the reaction system Cu^+ acts as "CO carrier" from the gas phase to reaction species in the solution.

The structures of the products were convincingly determined by nmr, ir, and mass spectra as well as elemental analysis. In most cases the products were

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(8) The CO absorptions by Cu_2O were studied in various H_2SO_4 concentrations. At the H_2SO_4 concentrations less than 80%, the mole ratio of CO/Cu^+ was 1.0. However, CO/Cu^+ gradually increased with the increase of H_2SO_4 concentrations. CO/Cu^+ was 1.05 (85%), 1.20 (90%), 1.33 (95%), 1.50 (100%) at 20°. Moreover, at elevated CO pressures until 18 atm, the absorption of CO by Cu_2O was studied in concentrated H_2SO_4. The mole ratio of CO/Cu^+ reached 3 at −10° (CO 7 atm). CO/Cu^+ are shown as follows, in 100% H_2SO_4.

CO, atm	−10°	0°	20°
1	2.2	1.8	1.5
7	3.0	2.8	2.2
10	3.0	3.0	2.3
18	3.0	3.0	2.6

Thus the equilibrium of $Cu(CO)^+$ and $Cu(CO)_3^+$ was concluded (see ref 6).

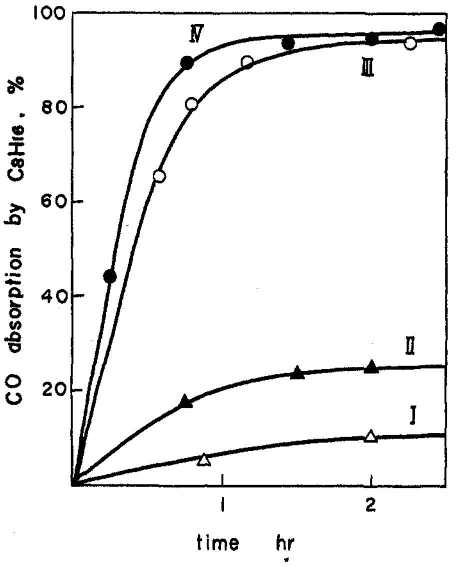
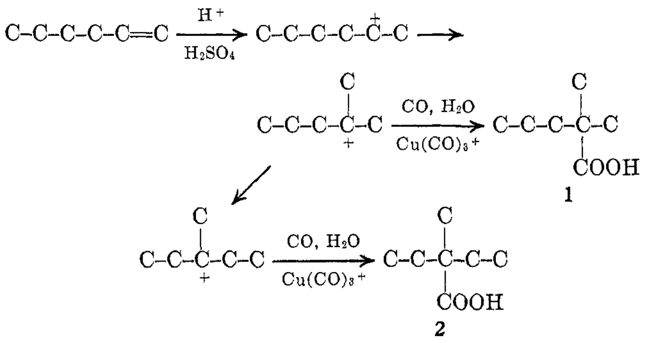


Figure 1.—Catalytic effect of Cu(I) compound. Cuprous oxide was used as Cu(I) compound [98% H_2SO_4 (2 mol) and 1-octene (0.2 mol) at 35°]: I ,Cu_2O (0 mmol); II, Cu_2O (1 mmol); III, Cu_2O (20 mmol); IV, Cu_2O (40 mmol).

mixtures of the isomers. When the mixtures of the isomers were separable by glpc, each isomer was isolated by preparative glpc and was subjected to structure analysis. When the separation of isomers was not easily performed by glpc, the mixture was analyzed by ^{13}C nmr.

1-Hexene reacts with carbon monoxide. 2,2-Dimethylpentanoic acid (1) and 2-methyl-2-ethylbutanoic acid (2) were obtained and separated by glpc. First,



1-hexene is protonated and the resulting carbonium ion rearranges to the *tert*-carbonium ion. The skeleton rearrangement take place subsequently, then the *tert*-carbonium ion reacts with carbon monoxide. Other acyclic olefins react with carbon monoxide similarly. 1-Heptene gives 2,2-dimethylhexanoic acid and 2-methyl-2-ethylpentanoic acid.

The products, obtained from 1-octene, 2-octene, and 1-decene, were not separated by glpc, but the structure and the ratio of each isomer of the mixture were convincingly determined by ^{13}C nmr. 1-Octene and 2-octene give 2,2-dimethylheptanoic acid, 2-methyl-2-ethylhexanoic acid, and 2-methyl-2-propylpentanoic acid. 1-Decene gives 2,2-dimethylnonanoic acid, 2-methyl-2-ethyloctanoic acid, 2-methyl-2-propylheptanoic acid, and 2-methyl-2-buthylhexanoic acid. Finally, the structures of all the products were determined by ^{13}C nmr. ^{13}C chemical shift assignments of each compound are shown in Chart I.

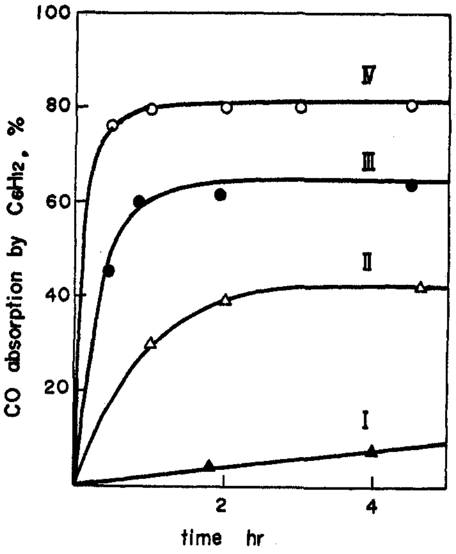
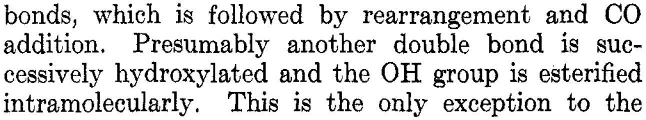


Figure 2.—The influence of H_2SO_4 concentration, with Cu_2O (20 mmol) and 1-hexene (200 mmol) at 30°: I, 85% H_2SO_4; II, 88% H_2SO_4; III, 92% H_2SO_4; IV, 98% H_2SO_4.

In cyclohexene carbonylation proceeds after the rearrangement to methylcyclopentane carbonium ion. Compound 3 was shown to be 1-methylcyclopentane-

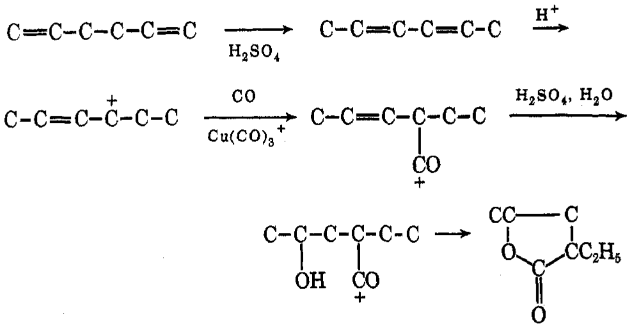


3

carboxylic acid by its characteristic ^1H nmr methyl signal at δ 1.28 (s).

1,5-Hexadiene gives the γ-valerolactone derivative. The reaction scheme is not simple. The first step of the reaction is the protonation of one of the double bonds, which is followed by rearrangement and CO addition. Presumably another double bond is successively hydroxylated and the OH group is esterified intramolecularly. This is the only exception to the formation of *tert*-carboxylic acids from olefins tested in our experiments.

Compound 4 was determined to be α-ethyl-γ-valerolactone from its characteristic ^1H nmr signals at δ 1.40

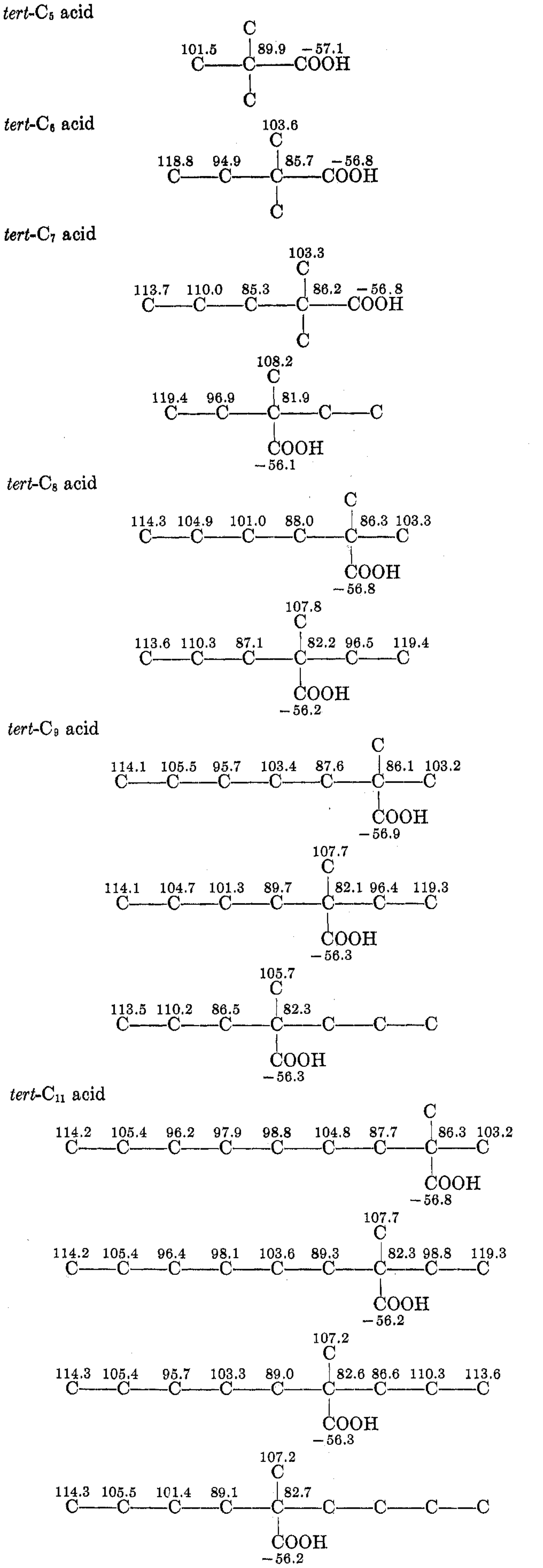


4

(d, CH_3CHO–), 1.00 (t, CH_3CH_2–), 2.05 (m, –CO-CHC_2H_5), and 4.50 (m, CH_3CHO–). Mass spectra showed *m/e* (rel intensity) 128 (10, M^+), 113 (12), 100 (62), 55 (100).

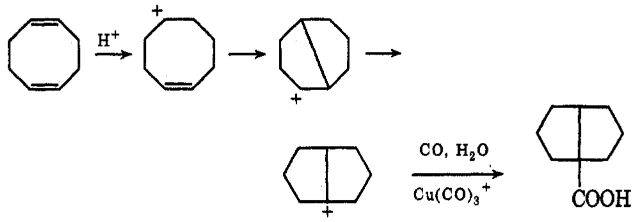
1,5-Cyclooctadiene gives bicyclo[3.3.0]octanecarboxylic acid. The scheme involving the transannular

CHART I.—^{13}C CHEMICAL SHIFTS OF *tert*-CARBOXYLIC ACIDS[a]



[a] In parts per million upfield from external benzene standard.

addition of the carbonium ion to the second double bond may be taken to explain the product. The typical ^{1}H nmr spectra of **5** appear at δ 2.70 (m, -CH-).



5

Mass spectra showed *m/e* (rel intensity) 154 (32, M+), 113 (93), 109 (75), 67 (100).

Experimental Section

The infrared spectra were taken on neat samples on a Hitachi EPI-S2. ^{1}H nmr spectra were taken on a JEOL PS-100 at 100 MHz in CCl_4 solvent. Chemical shifts are given in δ units (parts per million) downfield from internal tetramethylsilane. Completely proton-decoupled ^{13}C nmr spectra were obtained at 15.1 MHz on a JEOL PS-100 spectrometer equipped with the SD-HC heterospin decoupler and IS-100 field-frequency synchronous sweep system of the proton-irradiating frequency. Complete analysis and discussion of ^{13}C nmr were given elsewhere.[9] Mass spectra were measured on the Shimazu LKB-9000 gas chromatograph–mass spectrometer with 70 eV ionizing current. Glpc analysis was performed using a 3M FFAP column (10% on Chromosorb WAW). Elemental analyses were done on a Yanagimoto CHN MT-2.

Reagents.—1-Hexene, 1-heptene, 1-octene, 2-octene, 1-decene, cyclohexene, 1,5-hexadiene, and 1,5-cyclooctadiene were all commercial reagents and were purified by distillation.

Cu_2O, $CuSO_4$, Cu powder, carbon monoxide, and 98% H_2SO_4 were all commercial reagents, which were used without further purification.

Preparation of Cu(I) Carbonyl.—In a 1-l. three-necked flask equipped with a thermometer and a carbon monoxide gas buret were placed 2.86 g (0.02 mol) of Cu_2O and 105 ml (2 mol) of 98% H_2SO_4. The apparatus was evacuated by a diffusion pump to remove air, and then carbon monoxide was introduced from the gas buret. The mixture of Cu_2O and H_2SO_4 was stirred vigorously. Carbon monoxide was absorbed by cuprous ion in about 40 min. The ratio of CO/Cu^+ reached 1.35 at 30° (CO 1 atm).

Carbonylation of Olefin.—From a syringe, 24.8 ml (0.2 mol) of 1-hexene was added dropwise during 50 min to the Cu(I) carbonyl suspension. Carbon monoxide was soon absorbed and treated with olefin. CO absorption was finished in 1–2 hr, and the reaction mixture was poured over ice–water. The products were extracted by benzene. Excess alkali was added to the benzene extract. The water phase was acidified by H_2SO_4. Carboxylic acids were again extracted by benzene. The products of **1** and **2** were isolated by preparative glpc. The structures of products were determined by ir, nmr, and mass spectra as well as elemental analysis.

2,2-Dimethylbutanoic acid was obtained by the carbonylation of 1-hexene as a by-product: bp 163°; n^{25}_D 1.4205 [lit.[10] bp 96° (20 mm), n^{20}_D 1.4142]; d^{25}_4 0.9293; ir 2990, 1705 (C=O), 1260 1190 cm^{-1}; nmr δ 0.90 (t, 3, J = 7 Hz, $-CH_2CH_3$), 1.20 (s, 6, CH_3CCOOH), 1.62 (q, 2, J = 7 Hz, $-CH_2CH_3$), 10.9 (s, 1, COOH).

Anal. Calcd for $C_6H_{12}O_2$: C, 62.04; H, 10.41. Found: C, 61.75; H, 10.31.

***tert*-C$_7$ carboxylic acids** were obtained by the carbonylation of 1-hexene. The products were the mixtures of 2,2-dimethylpentanoic acid (**1**) and 2-methyl-2-ethylbutanoic acid (**2**): bp 194°; n^{25}_D 1.4248 [lit.[10] bp 110–114° (20 mm), n^{20}_D 1.4208–1.4242]; d^{25}_4 0.9207; ir of separated **1** 2980, 1710 (C=O), 1480, 1240, 1190 cm^{-1}; ir of separated **2** 2990, 1708 (C=O), 1470, 1260, 1185 cm^{-1}; ^{1}H nmr of separated **1** δ 0.92 (t, 3, J = 7 Hz, CH_3CH_2-), 1.18 (s, 6, CH_3C-), 1.49 (m, 4, $-CH_2-$), 11.03 (br s,

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[9] J. Iyoda, Y. Souma, and H. Sano, *Bull. Gov. Ind. Res. Inst., Osaka*, **23**, 197 (1972).

[10] H. Koch and W. Haff, *Justus Liebigs Ann. Chem.*, **618**, 251 (1958).

1, COOH); ^{1}H nmr of separated 2 δ 0.90 (t, 6, J = 7 Hz, CH_3CH_2–), 1.12 (s, 3, CH_3C–), 1.55 (m, 4, CH_3CH_2–), 10.9 (br, s, 1, COOH).

Anal. Calcd for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.34; H, 11.05.

***tert*-C$_8$ carboxylic acids** were obtained by the carbonylation of 1-heptene. The products were the mixtures of 2,2-dimethylhexanoic acid (A) and 2-methyl-2-ethylpentanoic acid (B): bp 214°; n^{25}D 1.4310; $d^{25}{}_4$ 0.9154; ir 2950, 1700 (C=O), 1470, 1280, 1180 cm^{-1}; ^{1}H nmr of separated A δ 0.95 (t, 3, J = 6 Hz, CH_3CH_2–), 1.20 (s, 6, CH_3C–), 1.36 (m, 6, –CH_2–), 11.5 (br, s, 1, COOH); ^{1}H nmr of separated B δ 0.92 (t, 6, J = 7 Hz, CH_3CH_2–), 1.13 (s, 3, CH_3C–), 1.44 (m, 6, –CH_2–), 11.40 (br s, 1, COOH).

Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.19; H, 11.11.

***tert*-C$_9$ carboxylic acids** were obtained by the carbonylation of 1-octene and 2-octene. The products were the mixtures of 2,2-dimethylheptanoic acid, 2-methyl-2-ethylhexanoic acid, and 2-methyl-2-propylpentanoic acid with the ratio of 4:2:1: bp 132–133° (15 mm); n^{25}D 1.4291; $d^{25}{}_4$ 0.9037; ir 2950, 1705 (C=O), 1470, 1205 cm^{-1}; ^{1}H nmr δ 1.12, 1.19 (s, CH_3CCOOH), 10.9 (br, 2, –COOH).

Anal. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.47. Found: C, 67.93; H, 11.78.

***tert*-C$_{11}$ carboxylic acids** were obtained by the carbonylation of 1-decene. The products were the mixtures of 2,2-dimethylnonanoic acid, 2-methyl-2-ethyloctanoic acid, 2-methyl-2-propylheptanoic acid, and 2-butylhexanoic acid with the ratio of 8:4:3:1: bp 142–143° (7 mm); n^{25}D 1.4368 [lit.[10] bp 139–148.5° (20 mm), n^{20}D 1.4363]; $d^{25}{}_4$ 0.8976; ir 2950, 1700 (C=O), 1470, 1260 cm^{-1}; ^{1}H nmr δ 1.12, 1.18 (s, CH_3CCOOH), 9.80 (br, s, –COOH).

Anal. Calcd for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90. Found: C, 71.01; H, 12.22.

1-Methylcyclopentanecarboxylic acid was obtained by the carbonylation of cyclohexene: ir 2980, 1705 (C=O), 1460, 1280, 1200 cm^{-1}; ^{1}H nmr δ 1.28 (s, 3, CH_3C–), 1.70 (m, 6, –CH_2–), 2.16 (m, 2, –HCHCCOOH), 11.78 (br, s, –COOH).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 66.02; H, 9.57.

α-Ethyl-γ-valerolactone was obtained by the carbonylation of 1,5-hexadiene: ir 2950, 1760 (C=O), 1460, 1175 cm^{-1}; ^{1}H nmr δ 1.00 (t, 3, J = 7 Hz, CH_3CH_2–), 1.40 (d, 3, J = 7 Hz, CH_3-CH–), 1.70 (m, 2, –CH_2–), 2.05 (m, 1, –CHC_2H_5), 2.50 (m, 2, –CH_2–), 4.50 (m, 1, –CHO–); mass spectrum (70 eV) *m/e* (rel intensity) 128 (10, M$^+$), 113 (12), 100 (62), 56 (90), 55 (100), 41 (88).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 65.15; H, 9.42.

Bicyclo[3.3.0]octanecarboxylic acid was obtained by the carbonylation of 1,5-cyclooctadiene: ^{1}H nmr δ 2.70 (m, 1, –CH–), 1.00–2.30 (m, 12, –CH_2–), 10.8 (br, s, –COOH); mass spectrum (70 eV) *m/e* (rel intensity) 154 (32, M$^+$), 126 (73), 113 (93), 109 (75), 67 (100).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.24; H, 8.76.

Registry No.—Carbon monoxide, 630-08-0; Cu_2O, 1317-39-1; H_2SO_4, 7664-93-9.

Steric Effects in the Cupric Ion Oxidation of α-Ketols[1]

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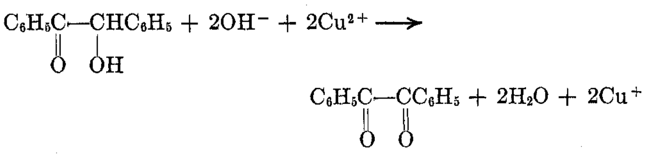
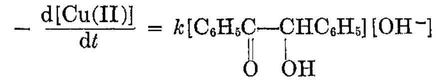
The kinetics of the oxidation of a series of α-ketols by copper(II) in buffered aqueous pyridine have been studied spectrophotometrically. At concentrations of cupric ion greater than 0.025 *M* the reaction exhibits first-order dependence with respect to copper(II), which is typical of a mechanism involving a rate-determining enolization of a copper(II)–ketol complex. The following order of reactivities was observed: α-hydroxyacetophenone > 2-hydroxycyclohexanone = benzoin > 4,4′-dimethoxybenzoin > 3-hydroxy-2-butanol > 2-hydroxycyclopentanone > 4-hydroxy-3-hexanone > 4-hydroxy-2,5-dimethyl-3-hexanone ≫ 4-hydroxy-2,2,5,5-tetramethyl-3-hexanone. In the cases of benzoin, 4,4′-dimethoxybenzoin, and 2-hydroxycyclopentanone large negative entropies of activation and large deviations from first-order kinetics were observed. These kinetic results are interpreted in terms of an intermediate copper(II)–ketol complex possessing a chelate structure.

Although the copper(II) oxidation of reducing sugars in alkaline aqueous media has been known for a very long time,[2] it has only been more recently that the mechanism of the reaction has been investigated.[3–7] The reaction is quite general for primary and secondary alcohols which possess an α-carbonyl group and is synthetically useful for the oxidation of acyloins to the corresponding diketones.[8] Weissberger, Schwarze, and Mainz[3] found that the oxidation of benzoin to benzil by ethanolic Fehling's solution was first order with respect to both the concentration of ketol and hydroxide ion, but was zero order with respect to copper(II) as shown by eq 1. In addition, it was found that the rates of



$$\underset{\substack{\| \\ O}}{C_6H_5C}\!-\!\underset{\substack{| \\ OH}}{CHC_6H_5} + 2OH^- + 2Cu^{2+} \longrightarrow \underset{\substack{\| \\ O}}{C_6H_5C}\!-\!\underset{\substack{\| \\ O}}{CC_6H_5} + 2H_2O + 2Cu^+$$



$$-\frac{d[Cu(II)]}{dt} = k[\underset{\substack{\| \\ O}}{C_6H_5C}\!-\!\underset{\substack{| \\ OH}}{CHC_6H_5}][OH^-] \qquad (1)$$

autoxidation and racemization of benzoin, under identical conditions, obeyed the same rate law and proceeded at the same rate as the copper(II) oxidation.[9] Kinetic behavior of this type is indicative of an initial rate-determining enolization. Marshall and Waters[6] observed a similar behavior when they investigated the oxidation of acetoin and benzoin with Benedict's solution.

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