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Carbonylation of Saturated Hydrocarbons Catalyzed by Copper(I) Carbonyls in FSO_3H-Sb_5F

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Synopsis. Saturated hydrocarbons react with carbon monoxide in the presence of copper(I) carbonyl catalysts in FSO_3H-SbF_5. Tertiary-carboxylic acid and secondary-carboxylic acid were obtained in high yields at -2 to $+2$ °C and at 1 atm of carbon monoxide. For the isomerization process of intermediate carbonium ions, the cleavage of the C-C bond was recognized, and stable *t*-butyl cations were formed.

Several results on carbonylation catalyzed by copper(I) carbonyl ions have been described in previous papers.[1-5] The copper(I) carbonyl ions play an important role enriching the carbon monoxide concentration in strong acid solutions, and promotes the carbonylation rate to give tertiary-carboxylic acid in a high yield.

Olah has investigated the formation of alkyl cations from alkanes *via* hydride abstraction in FSO_3H–SbF_5, and presented the following equation.[6,7]

$$R_3CH \xrightarrow{FSO_3H\text{-}SbF_5} R_3C^+SbF_5FSO_3^- + H_2$$

Olah has reported that the alkyl cations rearranged to tertiary carbonium ions, and furthermore, stable *t*-butyl cations were formed from hydrocarbons of C_5—C_{16} by the cleavage of the C–C bond.

Paatz has studied the carbonylation of saturated hydrocarbons in HF–SbF_5 solutions, and obtained carboxylic acids and ketones.[8] However, the conversion of saturated hydrocarbons to carbonyl compounds was less than 30%, due to the low solubility of carbon monoxide in strong acids. Suzuki has also studied the carbonylation of 2,2,4-trimethylpentane and alcohol in HF–SbF_5 and obtained carboxylic acid.[9,10]

In this paper, the carbonylation of saturated hydrocarbons catalyzed by copper(I) carbonyl ions to give secondary-carboxylic acids and tertiary-carboxylic acids in high yields is described.

Table 1. The amount of carbon monoxide absorbed by Cu^+ in FSO_3H-SbF_5[a)]

Temp °C	Absorbed CO *n* in $Cu(CO)_n^+$
-45	4.0
-30	4.0
-20	4.0
-10	3.95
0	3.80
10	3.60
20	3.50
30	3.35

a) The amount of absorbed carbon monoxide was measured using 0.858 g of Cu_2O, 20 ml of FSO_3H and 10 ml of SbF_5.

Results and Discussion

Cuprous oxide absorbs carbon monoxide in FSO_3H–SbF_5 solutions to form a homogeneous catalyst solution containing copper(I) carbonyl ions. The amount of absorbed carbon monoxide increases when the temperature is lowered, as is shown in Table 1. In FSO_3H–SbF_5 solutions, $Cu(CO)_4^+$ exists in a mixture in equilibrium with $Cu(CO)^+$. The $\nu_{C=O}$ absorptions of $Cu(CO)_4^+$ and $Cu(CO)^+$ in FSO_3H–SbF_5 solutions were observed at 2183 and 2152 cm^{-1} respectively on the other hand, that of gaseous carbon monoxide occured at 2143 cm^{-1}.[11,12] The $\nu_{C=O}$ absorptions for $Cu(CO)_4^+$ and $Cu(CO)^+$ increased more than that for gaseous carbon monoxide. This indicates that the C–O bonding order becomes higher when the carbon monoxide coordinates to the cuprous ion.

Table 2. Carbonylation of saturated hydrocarbons[a)]

Substrate	Product	Yield %
Methylcyclopentane	1-Methylcyclopentanecarboxylic acid	45
	Cyclohexanecarboxylic acid	40
Methylcyclohexane	1-Methylcyclohexanecarboxylic acid	5
	Mixture of methylcyclohexanecarboxylic acid and ethylcyclopentanecarboxylic acid	90
Cyclohexane	Cyclohexanecarboxylic acid	45
Hexane	2,2-Dimethylpentanoic acid	55
	2-Methyl-2-ethylbutanoic acid	35
	2,2-Dimethylbutanoic acid	11
	2,2-Dimethylpropionic acid	17
	Cyclohexanecarboxylic acid	25
2-Methylpentane	2,2-Dimethylpentanoic acid	45
	2-Methyl-2-ethylbutanoic acid	30
2-Methylbutane	2,2-Dimethylbutanoic acid	20
	Mixture of 2,3-dimethylbutanoic acid and 4-methylpentanoic acid	40
Octane	2,2-Dimethylpropionic acid	195
Decane	2,2-Dimethylpropionic acid	102
	2,2-Dimethylbutanoic acid	20
	Mixture of 2-pentanecarboxylic acid and 3-pentanecarboxylic acid	30
	2,2-Dimethylpentanoic acid	30
	2-Methyl-2-ethylbutanoic acid	10

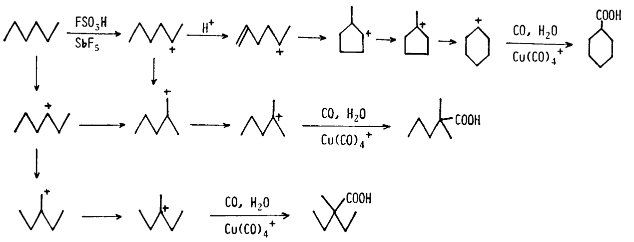
a) The reaction was carried out using 20 ml of FSO_3H, 10 ml of SbF_5, 0.858 g of Cu_2O and 30 mmol of saturated hydrocarbons at -2 to 2 °C for 2 h at 1 atm of CO.

In addition, ^{13}C NMR chemical shifts of $Cu(CO)_4^+$, $Cu(CO)^+$, and CO were observed at 171.1, 169.2, and 181.5 ppm, respectively.[12] The absorptions of $Cu(CO)_4^+$ and $Cu(CO)^+$ were chemically shifted to fields higher than that of gaseous carbon monoxide.

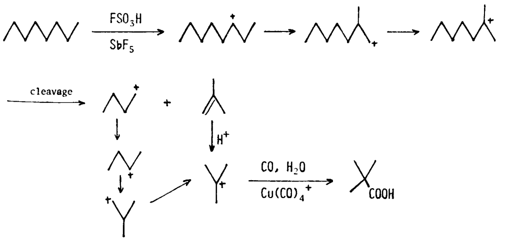
The significance of employing the copper(I) carbonyl catalysts in carbonylation reactions in FSO_3H–SbF_5 is the promotion of the rate of carbonylation, and at the same time, the increase in the yield of carbonylated products. The results are shown in Table 2. The reaction proceeded rapidly for temperatures −2 to 2 °C. Olah has stated that hydride abstraction tends to proceed in the order: primary hydrogen<secondary hydrogen<tertiary hydrogen.[7] The same tendency was observed for the carbonylation listed in Table 2.

Methylcyclopentane gave methylcyclopentanecarboxylic acid and cyclohexanecarboxylic acid.

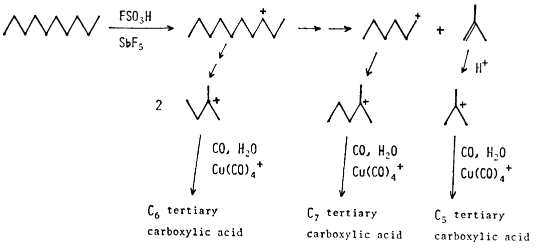
From hexane, C_5 and C_6 carboxylic acids such as 2,2-dimethylpropionic acid and 2,2-dimethylbutanoic acid were obtained together with C_7 carboxylic acids. This may be due to the formation of tertiary-butyl cations and tertiary pentyl cations by the β-scission of C_6 tertiary carbonium ions.



Octane gave only C_5 tertiary carboxylic acid, *i.e.*, 2,2-dimethylpropionic acid. It means that two *t*-butyl cations were formed by the cleavage of a C–C bond of octane.



Decane gave 2,2-dimethylpropionic acid as the main product, and at the same time, C_6 tertiary and C_7 tertiary carboxylic acids were obtained. A complicated cleavage of C–C bond appears to occur.



Experimental

The products were separated by preparative GLPC and analyzed by ^1H NMR, ^{13}C NMR, and IR spectroscopy, as described in a previous paper.[1] FSO_3H and SbF_5 were obtained from the Cationic Co.

Preparation of Copper(I) Carbonyl Catalysts. In a 300 ml three-necked flask equipped with a thermometer and a carbon monoxide gas burette, 0.858 g of Cu_2O was placed. The apparatus was evacuated using a rotary pump, and carbon monoxide was introduced from the gas burette. The mixture was stirred vigorously after 20 ml of FSO_3H and 10 ml of SbF_5 had been added. A colorless copper(I) carbonyl solution was formed by the absorption of carbon monoxide by Cu_2O.

Carbonylation of Saturated Hydrocarbons. From a syringe, 30 mmol of saturated hydrocarbons were added dropwise to the catalyst solution at −2 to 2 °C. Immediately carbon monoxide was absorbed. After the reaction was completed, the mixture was poured over ice. The mixture was shaken with hexane, and the total yield of carboxylic acids was determined by titrating the hexane extract with a 1/10 M NaOH ethanol solution. Each product was identified using authetic samples.[1]

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