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CARBOXYLATION REACTION OF DIISOBUTENE AND 1-OCTENE WITH CARBON MONOXIDE USING A Cu(I)CARBONYL BF_3-H_2O CATALYST SYSTEM

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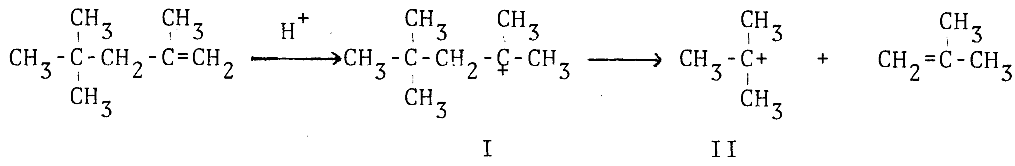
The carboxylation of diisobutene and 1-octene with carbon monoxide using Cu(I)carbonyl as catalyst in BF_3-H_2O takes place smoothly at room temperature to produce tertiary carboxylic acids in high yields. The present procedure is superior to that using the same catalyst in concentrated H_2SO_4, both from a point of view of high yield of carboxylic acids and ready separation of such acids from the catalyst layer.

Recently, a new interesting carboxylation procedure of olefins$^{1)}$ and alcohols$^{2)}$ with Cu(I)carbonyl catalyst in concentrated sulfuric acid has been reported by Souma et al. This procedure gives tertiary carboxylic acids in high yields under mild conditions. However, in order to isolate acids thus obtained, it is necessary to add a large amount of water. Consequently, the catalyst is not used repeatedly.

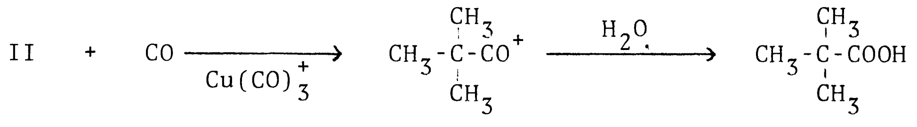
During the course of our studies on organic synthesis using strong Brönsted acid systems such as BF_3-H_3PO_4, BF_3-H_2O and HF-H_2O, it was found that Cu(I)carbonyl catalyst in BF_3-H_2O exerts a strong activity on the carboxylation of olefins, and that most of the carboxylic acids thus produced are readily separated from the catalyst layer. We wish to report here on the carboxylation reaction of diisobutene and 1-octene using a Cu(I)carbonyl-BF_3-H_2O system.

The reaction was carried out by essentially the same procedure as reported by Souma et al.$^{1)}$ The reaction conditions are described in Table 1. After the completion of the reaction, the reaction mixture was separated into two layers, namely the upper organic layer and lower catalyst layer, and both layers were analyzed respectively by glpc.

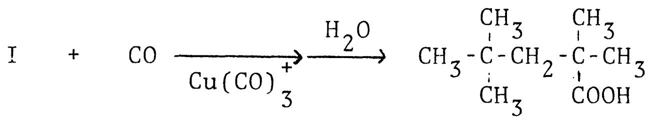
Since diisobutene is known to be cleaved to tert-butyl carbonium ion and isobutene in a strong acidic solution$^{3)}$ (eq. 1), the carboxylation should be considered to proceed through the reaction path shown in eqs. 2 and 3, as pointed out by Souma et al.$^{1,2)}$ The carboxylic acids thus obtained were composed of α,α-dimethylpropionic acid and C_9-acids, together with small amounts of C_{6-8} and other acids. In the case of 1-octene, no cleavage of the C-C bonds took place, and most of carboxylation products were C_9 acids (eq. 4). This reaction is accompanied by double bond isomerizations and isomerizations of the carbon skeleton with migration of alkyl groups, which occur through carbonium ions as well seen in Koch reaction.



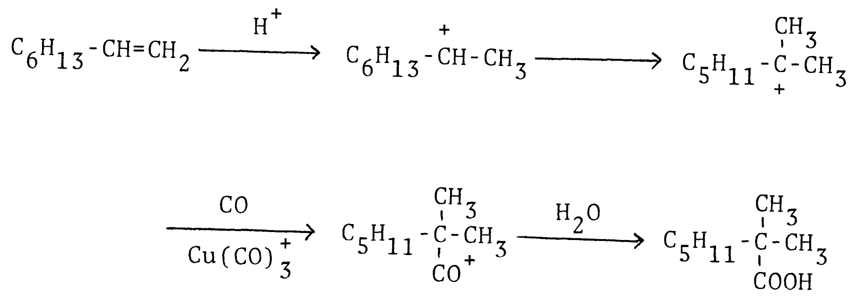
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{C}=CH_2 \xrightarrow{H^+} \underset{I}{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{+}{\overset{CH_3}{C}}-CH_3} \longrightarrow \underset{II}{CH_3-\underset{CH_3}{\overset{CH_3}{C}}+} + CH_2=\overset{CH_3}{C}-CH_3 \tag{1}$$



$$II + CO \xrightarrow[Cu(CO)_3^+]{} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CO^+ \xrightarrow{H_2O} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-COOH \tag{2}$$



$$I + CO \xrightarrow[Cu(CO)_3^+]{} \xrightarrow{H_2O} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{COOH}{\overset{CH_3}{C}}-CH_3 \tag{3}$$



$$C_6H_{13}-CH=CH_2 \xrightarrow{H^+} C_6H_{13}-\overset{+}{C}H-CH_3 \longrightarrow C_5H_{11}-\underset{+}{\overset{CH_3}{C}}-CH_3$$

$$\xrightarrow[Cu(CO)_3^+]{CO} C_5H_{11}-\underset{CO^+}{\overset{CH_3}{C}}-CH_3 \xrightarrow{H_2O} C_5H_{11}-\underset{COOH}{\overset{CH_3}{C}}-CH_3 \tag{4}$$

The experimental results obtained by using Cu(I)carbonyl catalyst in the presence of BF_3-H_2O with a molar ratio of 0.9 and various organic solvents are summarized in Table 1. The results obtained with Cu(I)carbonyl catalyst in concentrated H_2SO_4 without a solvent, and with cyclohexane and chlorobenzene as a co-solvent are listed in Table 2.

From these experimental results, we wish to emphasize that the present procedure is superior to that using the same catalyst in concentrated H_2SO_4, not only in yield of carboxylic acids but also in its ready separation of such acids from the catalyst layer without an addition of a large amount of water. In addition, the catalyst in BF_3-H_2O was found to be able to use repeatedly by separation of the upper organic layer in which most of the carboxylic acids produced are contained.

In order to examine recycling use of the catalyst, the following reaction was carried out. After the completion of the first reaction under the same conditions described in Table 1, the upper organic layer was separated, and water was added into the lower catalyst layer to keep a molar ratio of BF_3/H_2O. Then an organic solvent and an olefin were supplied, and the mixture was subjected again to the reaction.

Table 1. Carboxylation of Diisobutene and 1-Octene Using a $Cu(CO)_3^+$-BF_3-H_2O Catalyst System in Various Solvents$^{a)}$

olefin	Solvent	Total yield of acids %	Product distribution %		Acid distribution %			
			in cat. layer	in org. layer	$C_5^{b)}$	C_{6-8}	C_9	other
Diisobutene	None	77	37	63	32	13	36	19
Diisobutene	Cyclohexane	82	63	37	41	14	35	10
Diisobutene	Chlorobenzene	80	15	85	44	11	36	9
1-Octene	Cyclohexane	80	trace	99	trace	-	99	-

a) In most cases, 2g of Cu_2O, 34g of BF_3-H_2O with a molar ratio of 0.9, 50ml of organic solvent, and 0.1 mole of olefin were used. The reaction was carried out at 30°C for about 30min. The pressure of carbon monoxide was 1 atm.

b) α,α-dimthylpropionic acid.

Table 2. Carboxylation of Diisobutene Using $Cu(CO)_3^+$-H_2SO_4 Catalyst System$^{a)}$

Solvent	Total yield of acids, %	Product distribution, %	
		in catalyst layer (lower)	in organic layer (upper)
None	40	98	2
Cyclohexane	40	93	7
Chlorobenzene	39	71	29
Chlorobenzene$^{b)}$	28	18	82

a) The reaction was carried out by using 40g of 98%-H_2SO_4 under the same conditions in Table 1.

b) Using 40g of 90%-H_2SO_4.

The amount of Cu^+ in organic layer was analysed as Cu^{++}, after oxidation with air, by the usual atomic absorption spectroscopic method. The representative results obtained by the reaction with 1-octene were summarized in Table 3. As shown in the Table, it was found that the catalyst is used repeatedly without any deterioration of activity and the amount of cupper ion in organic layer was negligible. In the case of diisobutene in cyclohexane, the accumulation of carboxylic acids in the catalyst layer was observed with successive employments of the catalyst. However, this tendency was remarkably decreased when a catalyst with a BF_3/H_2O ratio of 0.7 or lower was used.

Consequently, the present procedure seems to have a great advantage in practical preparation of carboxylic acids by carboxylation of olefins with carbon monoxides.

Table 3. Repeated Use Experiment of the Catalyst in Carboxylation of 1-Octene[a)]

No. of repeated exp.	Yield of acids, %		Cu^{++} ion found in organic layer
	in org. layer	in catalyst layer	
1	73	-	trace
2	69	-	trace
3	72	-	trace
4	67	-	trace
5	65	0.8	trace

a) The reaction was carried out in cyclohexane under the same conditions described in Table 1.

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