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CARBOXYLATION OF ACTIVE METHYLENE COMPOUNDS WITH CARBON DIOXIDE IN THE PRESENCE OF FERRIC ALKOXIDE

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Active methylene compounds such as cyclohexanone and acetophenone are carboxylated by the reaction with carbon dioxide in the presence of ferric ethoxide under mild conditions to give β-ketoacids.

Recently the reaction between transition metal compounds and carbon dioxide has attracted much attention because of the possibility of the transition metal as catalysts for the catalytic fixation of carbon dioxide. Only a few examples, however, of the catalytic fixation of carbon dioxide have been known. On the other hand, it has been reported that the carboxylation of active methylene compounds with carbon dioxide proceeds stoichiometrically by the use of carboxylation agents such as $NaNH_2$, NaOPh,$^{1)}$ $Mg(OMe)_2$,$^{2)}$ and basic nitrogen compounds,$^{3)}$ though the use of transition metal compounds has not been reported.

As the first step of the investigation of the catalytic fixation of carbon dioxide, we have studied on the carboxylation of active methylene compounds with carbon dioxide in the presence of transition metal compounds, and have found that ketones which contain a methylene group near the carbonyl group react with carbon dioxide in the presence of ferric ethoxide to give β-ketoacids.

A typical experiment was carried out as follows: A 100-ml glass autoclave was charged with 4.0 g of ferric ethoxide and 10 ml of dimethylformamide. Carbon dioxide was injected to a pressure of 5 atm at room temperature, and agitation was commenced. After half an hour 2.0 g of cyclohexanone was added, and the temperature was raised to 80°C. During the reaction, the pressure of CO_2 was held at 5 atm. After two hours the reaction mixtures were cooled and poured in 50 ml of cold water. Unchanged cyclohexanone and by-products were removed by shaking with ether. The resulting aqueous layer was cooled to 0°C, acidified with dilute sulfuric acid, and then extracted with four 30-ml portions of ether. The extracts were combined and dried over magnesium sulfate for one hour at 0°C. After evaporation of ether *in vacuo* at room temperature, 0.9 g of crude crystals of cyclohexanone-2-carboxylic acid was obtained. Recrystallyzation from *n*-pentane-ether gave 0.7 g of pure product, mp 78-79°C (lit.[4] 78-80°C).

Table 1 Carboxylation of Ketones with Carbon Dioxide in the Presence of $Fe(OEt)_3$ (DMF 10 ml, CO_2 5 atm, reaction time 2 hr)

Ketone	g	$Fe(OEt)_3$[a] g	React. temp. °C	Product[b]	g	Yield %[c]
Cyclohexanone	2.0	4.0	80	Cyclohexanone-2-carboxylic acid	0.9	31
"	5.0	4.0	80	"	1.4	48
"	2.0	4.0	room temp.	"	0.1>	
Acetophenone	2.4	4.0	80	Benzoylacetic acid[d]	0.2	7

a) Ferric methoxide was also effective for the carboxylation of ketones.

b) The products were identified by comparisons of IR spectrum and melting point with those of the respective authentic samples.

c) Yield is expressed in mole per cent based on the amount of ketone employed.

d) Benzoylacetic acid was extracted from reaction mixtures by shaking with an aqueous solution of sodium carbonate, mp 97-99°C (lit.[2] 98-100°C).

Hidai et al. have reported that alkoxides of transition metals, such as Fe, Ti, Nb, and Zr, absorb carbon dioxide; to account for this result they have supposed the formation of $M(OR)_{n-1}O\overset{O}{\overset{\|}{C}}OR$.[5] In the carboxylation reactions we have investigated, it is considered that $Fe(OEt)_2O\overset{O}{\overset{\|}{C}}OEt$ is formed initially from the reaction of CO_2 with $Fe(OEt)_3$ and then reacts with ketones to give β-ketoacids.

REFERENCES

1) For recent reviews, see M. Kobayashi and S. Inoue, Kagaku, 28, 942 (1973).

2) M. Stiles, J. Amer. Chem. Soc., 81, 2598 (1959).

3) E. Haruki, M. Arakawa, N. Matsumura, Y. Otsuji, and E. Imoto, Chem. Lett., 429 (1974) and references cited therein.

4) R.P. Linstead and A.B. Wang, J. Chem. Soc., 807 (1937).

5) M. Hidai, T. Hikita, and Y. Uchida, Chem. Lett., 521 (1972).

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