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THE REACTION OF CARBOXYLIC ALKYLCARBONIC ANHYDRIDES WITH DISODIUM TETRACARBONYLFERRATE. A NOVEL METHOD CONVERTING CARBOXYLIC ACIDS TO ALDEHYDES.

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Reactions between alkyl or acyl halides and metal carbonyl anions, such as $NaCo(CO)_4$, and $NaMn(CO)_5$, and $Na_2Fe(CO)_4$ are well known to give alkyl or acylmetal carbonyl complexes.[1] Little attention, however, has been paid to the reactions of metal carbonyl anions with other acid derivatives. The previous work in our laboratory has demonstrated that carboxylic anhydrides readily react with disodium tetracarbonylferrate to give acyliron carbonyl complexes from which aldehydes or aldehydic acids are easily derived in excellent yield.[2]

In this communication, we wish to report that carboxylic ethylcarbonic anhydrides, one of mixed anhydrides from carboxylic acid and carbonic acid, also react readily with disodium tetracarbonylferrate to give the corresponding aldehydes after quenching the reaction mixture with acetic acid.

Carboxylic acids are easily converted into carboxylic alkylcarbonic anhydrides by treatment of the acids with chloroformates in presence of triethylamine.[3]

The reaction of benzoic ethylcarbonic anhydride illustrates a typical procedure. To disodium tetracarbonylferrate (5.5 mmol) solution in THF was added 5.5 mmol of benzoic ethylcarbonic anhydride at room temperature under argon. The mixture was stirred for 20 minutes and then treated with acetic acid. Yield of products was determined by glpc analysis using internal standards

TABLE 1. The reaction of carboxylic ethylcarbonic anhydrides with $Na_2Fe(CO)_4$

No.	R^1-COOCOOC$_2$H$_5$ (R^1)	Product	Yield(%)
1	C_6H_5-	C_6H_5CHO	41
2	*p*-$CH_3C_6H_4$-	*p*-$CH_3C_6H_4CHO$	76
3	*p*-$CH_3OC_6H_4$-	*p*-$CH_3OC_6H_4CHO$	42
4	*o*-$CH_3OC_6H_4$-	*o*-$CH_3OC_6H_4CHO$	81
5	*n*-$CH_3(CH_2)_8CH_2$-	*n*-$CH_3(CH_2)_8CH_2CHO$	67
6	*n*-$CH_3(CH_2)_6CH_2$-	*n*-$CH_3(CH_2)_6CH_2CHO$	51

The results of typical reactions are shown in Table 1.

Both aromatic and aliphatic carboxylic ethylcarbonic anhydride have a great reactivity to disodium tetracarbonylferrate and are readily converted to the corresponding aldehydes via acyliron carbonyl complexes. IR Spectra of the reaction mixture had bands characteristic of an acyl-Fe group.[4] This method appears to be useful for synthesis of aldehydes in two steps from carboxylic acids. The preparation of carboxylic alkylcarbonic anhydrides and the reaction with disodium tetracarbonylferrate proceed rapidly and selectively under mild conditions.

Further studies on the utility of the present reaction are in progress.

Scheme 1.

$$R^1\text{-}\underset{\underset{O}{\|}}{C}\text{-O-}\underset{\underset{O}{\|}}{C}\text{-O-}C_2H_5 \xrightarrow{Na_2Fe(CO)_4} R^1\text{-}\underset{\underset{O}{\|}}{C}\text{-Fe(CO)}_4 \xrightarrow{H^+} R^1\text{-CHO}$$

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