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The Facile Syntheses of Aldehydes and Aldehydic Acids from Carboxylic Acid Anhydrides Using Disodium Tetracarbonylferrate (−II)

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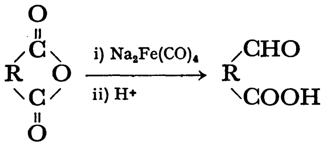
Disodium tetracarbonylferrate reacts readily with aliphatic and aromatic carboxylic acid anhydrides under mild conditions; the corresponding aldehydes are formed in high yields by quenching the reaction solution with acetic acid. Intermolecular anhydrides give aldehydes and acids, and intramolecular ones give aldehydic acids. The reaction mechanism *via* acylcarbonylferrates is assumed.

Disodium tetracarbonylferrate has been shown to be an inexpensive, versatile and selective reagent converting alkyl halides, tosylates, and acid halides into aldehydes, carboxylic acid derivatives, and ketones in high yields.[1–4] On the other hand, though aldehydes are known to be derived from various carboxylic acid derivatives such as acid chlorides, imide chlorides, thioesters, hydrazides, and nitriles,[5] there have been only a few reports describing the reduction of carboxylic acid anhydrides to aldehydes.[6,7] These reactions can be applied mainly to aliphatic acid anhydrides and are of no practical use because of the low yields of the products or of their prolonged reaction times. We now report the facile syntheses of aldehydes and aldehydic acids from carboxylic acid anhydrides in good yields using the ferrate. The preliminary report of this work was published elsewhere.[8]

Results and Discussion

Carboxylic acid anhydrides react readily with disodium tetracarbonylferrate [I] in dry tetrahydrofuran (THF) at room temperature under argon atmosphere to give reduced products, *i.e.* aldehydes or aldehydic acid, after quenching the reaction mixture with acetic acid. Intermolecular acid anhydrides give aldehydes and acids, and intramolecular ones give aldehydic acids in excellent yields.

$$(RCO)_2O \xrightarrow[\text{ii) }H^+]{\text{i) }Na_2Fe(CO)_4} RCHO + RCOOH$$



The reaction is completed in less than 20 minutes with a color change from pale yellow to dark red. The results of this reaction are shown in Table 1. This reaction can be applied to a wide variety of anhydrides, not only to aliphatic but also to aromatic ones; α,β-unsaturated carboxylic anhydrides such as maleic anhydride were not, however, reduced to the corresponding aldehydes.

TABLE 1. REDUCTION OF CARBOXYLIC ACID ANHYDRIDE USING DISODIUM TETRACARBONYLFERRATE

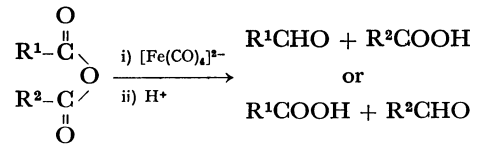
No.	Anhydride	Product	Yield (%)[a]
1	Propionic	Propionaldehyde	90[b]
2	*n*-Butyric	*n*-Butyraldehyde	61[b]
3	Isobutyric	Isobutyraldehyde	41[d]
4	*n*-Valeric	*n*-Valeraldehyde	67[b]
5	*n*-Caproic	*n*-Capronaldehyde	60[b]
6	Benzoic	Benzaldehyde	73[b]
7	*p*-Toluic	*p*-Tolualdehyde	75[b]
8	Succinic	Succinaldehydic acid	81[d]
9	Glutaric	Glutaraldehydic acid	60[c]
10	Phthalic	Phthalaldehydic acid	61[c]
11	Tetrachlorophthalic	Tetrachlorophthalaldehydic acid	83[c]
12	1,8-Naphthalic	1,8-Naphthaldehydic acid	75[c]

a) (mol of product/mol of anhydride) × 100. b) Yields were determined by glpc. c) Isolated yields. d) Isolated yields as 2,4-DNP.

The scheme of this reaction is reasonably considered as follows. One of the carbonyl groups of the anhydride is attacked nucleophilically by the ferrate to give an acyltetracarbonylferrate [II] and carboxylate, which are protonated to aldehyde and acid, as shown in Eq. (1), by quenching the reaction mixture with acetic acid. These reactions were monitored by infrared spectra. The absorption band at 1780 cm^{-1} due to the stretching vibration of the terminal carbonyls of the ferrate[9] disappeared as soon as anhydrides were added and two new bands at 1890 cm^{-1} and 1550—1600 cm^{-1} appeared. The former is attributed to the terminal carbonyls and the latter to the acyl group of [II].[10] In addition, the bands characteristic of carboxylates appeared. At this point the absorption bands of carbonyls of the anhydrides were not observed. These results support the scheme described above.

$$(RCO)_2O + [Fe(CO)_4]^{2-} \longrightarrow \underset{[II]}{[RCO\text{-}Fe(CO)_4]^-} + RCOO^- \longrightarrow RCHO + RCOOH \qquad (1)$$

In the reaction of mixed carboxylic anhydrides, two ways for the nucleophilic attack of the ferrate to the two carbonyl groups of the anhydride are possible and thus the formation of two different aldehydes can be expected (Eq. (2)).



$$\begin{matrix} R^1-\overset{\displaystyle O}{\overset{\|}{C}}\diagdown \\ O \\ R^2-\underset{\displaystyle O}{\underset{\|}{C}}\diagup \end{matrix} \xrightarrow[\text{ii) } H^+]{\text{i) } [Fe(CO)_4]^{2-}} \begin{matrix} R^1CHO + R^2COOH \\ \text{or} \\ R^1COOH + R^2CHO \end{matrix} \qquad (2)$$

Several mixed anhydrides were allowed to react with the ferrate and the structural effects of anhydrides in this reaction were investigated. To make the comparison of the effects easy, benzoic acid was employed as one of the acids used as components of the anhydride. The results obtained are listed in Table 2.

Table 2. Reaction of mixed anhydrides with disodium tetracarbonylferrate in THF[a)]

No.	$R^1\underset{\displaystyle O}{\underset{\|}{C}}-O-\underset{\displaystyle O}{\underset{\|}{C}}R^2$ R^1	R^2	Ratio[b)] R^1CHO	R^2CHO
13	CH_3	C_6H_5	64	36
14	CH_3CH_2	C_6H_5	44	56
15	$(CH_3)_2CH$	C_6H_5	30	70
16	$CH_3(CH_2)_6$	C_6H_5	31	69
17	*p*-$CH_3C_6H_4$	C_6H_5	48	52
18	*m*-$CH_3C_6H_4$	C_6H_5	43	57
19	*p*-$CH_3OC_6H_4$	C_6H_5	32	68
20	*p*-ClC_6H_4	C_6H_5	55	45
21	*o*-$CH_3C_6H_4$	C_6H_5	21	79
22	*o*-ClC_6H_4	C_6H_5	18	82
23	*o*-$CH_3OC_6H_4$	C_6H_5	61	39
24	*o*-$CH_3OC_6H_4$	*p*-$CH_3C_6H_4$	61	39
25	*o*-$CH_3OC_6H_4$	*p*-ClC_6H_4	59	41

a) At 25 °C for 20 min. b) Total yields of aldehydes are 60—80% in all cases.

In the reaction of benzoic aliphatic carboxylic anhydride (Exps. 13—16), the proportion of aliphatic aldehydes to benzaldehyde decreases as the alkyl groups become bulky, showing that the nucleophilic attack of the ferrate appears to be sterically affected.

In the series of benzoic substituted benzoic anhydrides (Exps. 17—23), different substituents such as Cl–, CH_3–, and CH_3O– have different effects on the reaction and distribution of the products. When the substituents are located at *meta* and *para* positions, the distribution of aldehydes is affected by their electron donating-withdrawing property: that is, an electron withdrawing group, Cl–, seems to favor the formation of substituted benzaldehyde but electron-donating groups, CH_3– and CH_3O–, are unfavorable for such formation. This shows that the nucleophilic attack is affected by the electron density on the carbon of carbonyl group of the anhydrides. In the cases in which the substituents are located at an *ortho* position, the Cl– and CH_3– groups have steric hindrance effects and disturb considerably the formation of substituted benzaldehydes. But the CH_3O– group has no such effects but on the contrary promotes the formation of *o*-anisaldehyde (Exps. 23—25). The effect of *o*-CH_3O–, quite different from that of *o*-Cl and *o*-CH_3, may be due to some interaction between the methoxy group and ion-paired disodium tetracarbonylferrate.[11)]

Experimental

The carboxylic acid anhydrides shown in Table 1 were all commercial products except for *p*-toluic anhydride. The other anhydrides were prepared in the usual manner from sodium carboxylates and acid chlorides in THF or in benzene. Disodium tetracarbonylferrate, $Na_2Fe(CO)_4$, was prepared according to the method described in the literature.[2)] Iron pentacarbonyl was a commercial product and used without further purification.

General Procedure for the Reaction of Intermolecular Carboxylic Anhydrides with $Na_2Fe(CO)_4$. To 11 mmol of disodium tetracarbonylferrate in THF (50 ml), 11 mmol of acid anhydride in THF (10 ml) was added with stirring at room temperature under argon atmosphere. Twenty minutes later, the reaction mixture was treated with glacial acetic acid (1.2 ml) and stirred for an additional five minutes. Then it was poured into 50 ml of water and extracted with 20 ml of pentane and 20 ml of ethyl ether, and the organic extract was submitted to glpc analysis. The aldehydes were identified by comparison of the retention time of glpc with those of authentic samples and yields were determined using internal standards.

General Procedure for the Reaction of Intramolecular Carboxylic Anhydrides with $Na_2Fe(CO)_4$. In 60 ml of THF, 11 mmol of disodium tetracarbonylferrate and carboxylic acid anhydride was allowed to react according to the above procedure. After quenching with 1.2 ml of glacial acetic acid, the reaction solvent was distilled off under a reduced pressure, and the residue was extracted with 0.5 M NaOH aqueous solution (50 ml) and filtered. The filtrate was acidified and extracted with three portions of ether (70 ml). After drying over sodium sulfate, the organic layer was evaporated and the residue was purified by recrystallization or converted into 2,4-dinitrophenylhydrazone. The products were identified by NMR, IR, elemental analyses, and by comparison with literature data or with authentic samples.

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