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THE FACILE SYNTHESES OF ALDEHYDES AND ALDEHYDIC ACIDS FROM CARBOXYLIC ACID ANHYDRIDES USING DISODIUM TETRACARBONYLFERRATE

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Aldehydes are known to be derived from various carboxylic acid derivatives on hydrogenation. However, there has been only a few reports describing the selective hydrogenation of carboxylic acid anhydrides to aldehydes. These reactions can be applied only to aliphatic acid anhydrides and are synthetically of no practical use because of its low yields of the products[1] or of its prolonged reaction time.[2]

Here we report the facile syntheses of aldehydes and aldehydic acids from not only aliphatic but also aromatic carboxylic acid anhydrides in high yields using disodium tetracarbonylferrate. This is the first example that acid anhydrides react with an anionic metal carbonyl complex.

In the general procedure, to 11 mmol of disodium tetracarbonylferrate in tetrahydrofuran, 11 mmol of the anhydride was added with stirring at room temperature under argon. The reaction was monitored by means of infrared spectrum. Several minutes later, absorption bands characteristic of the anhydride disappeared and then the reaction mixture was treated with acetic acid or hydrochloric acid. Yields of the products were determined by isolation or by glpc analyses using internal standards.

The results of typical reactions are shown in Table 1.

Table 1. Reduction of acid anhydrides

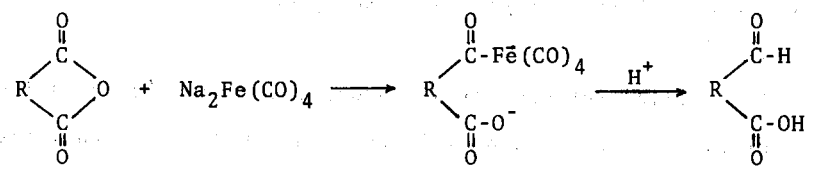
Acid anhydride	Product	Yield (%)*
Phthalic anhydride	Phthalaldehydic acid	61
Succinic anhydride	β-Formylpropionic acid	81
Benzoic anhydride	Benzaldehyde	73
Propionic anhydride	Propionaldehyde	90
Benzoic propionic anhydride	Benzaldehyde	34
	Propionaldehyde	27

*(mol of product/mol of acid anhydride) × 100

Intermolecular acid anhydrides gave aldehydes and acids, and intramolecular acid anhydrides gave aldehydic acids.

The principal advantage of this reaction is that the reaction is rapid under ambient conditions and gives excellent yields for a wide variety of acid anhydrides.

A plausible reaction scheme may be presented.



In this reaction, acylcarbonylferrates are assumed to be formed as an intermediate; infrared spectra of the reaction mixtures have bands characteristic of an acyl-Fe group and a carboxylate.[3,4]

References

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