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THE SELECTIVE AMINATION OF CARBONYL COMPOUNDS USING IRON PENTACARBONYL

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There are numerous methods available for the reductive amination of aldehydes or ketones with amines, but many of them normally require drastic reaction conditions and yields are often low.1,2)

In this communication, we wish to report the facile and selective amination of aldehydes or ketones using iron pentacarbonyl. A wide variety carbonyl groups are converted into secondary amines by this reaction. The principal advantages of this method over the previous ones are that the operation is simple, the reaction proceeds smoothly under mild conditions, applicable to low boiling carbonyl compounds, and the yields of the corresponding amines are exellent.

In the general procedure, to an alcoholic solution of 11 mmol of an aldehyde or a ketone and 11 mmol of an amine were added a 33 ml of 1N alcoholic potassium hydroxide solution and 1.5 ml (11 mmol) of iron pentacarbonyl [conditions which generate the hydridotetracarbonylferrate anion].3) The mixture was stirred for 5-10 hr at room temperature under one atmosphere of carbon monoxide which was absorbed slowly during the reaction. Yields of the products were determined by isolation or by glpc analyses using internal standards. Some representative reductive aminations are listed in Table 1.

Table 1. Reductive aminations of carbonyl compounds

Exp. No.	Compound	Amine	Product	Yield (%)
1	Benzaldehyde	Aniline	N-Benzylaniline	98
2	n-Butyraldehyde	Aniline	N-n-Butylaniline	100
3	Formaldehyde	Aniline	N-Methylaniline	91
4	n-Butyraldehyde	n-Butylamine	Di-n-butylamine	89
5	Acetone	Isopropylamine	Diisopropylamine	93
6	Cyclohexanone	Cyclohexylamine	Dicyclohexylamine	100
7*	Benzaldehyde	Aniline	N-Benzylaniline	79
8*	n-Butyraldehyde	n-Butylamine	Di-n-butylamine	60

*The reaction was conducted under argon atmosphere

The reaction also proceeded under argon atmosphere, but the yields of the products were lower (Exp. No. 7 and 8).

When the ferrate reacted with excess mixture of benzaldehyde and aniline under carbon monoxide, 2.6 mol/mol-$KHFe(CO)_4$ of N-benzylaniline was obtained at maximum with an absorption of carbon monoxide.

In the reductive amination of carbonyl compounds with amines, compounds of a type of Schiff bases are generally regarded as intermediates. The reduction of N-benzylideneaniline with the ferrate also smoothly proceeded under the similar condition to give 3.0 mol/mol-$KHFe(CO)_4$ of N-benzylaniline.

Other applications of this reaction are currently explored in our laboratory.

References

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