Tetrahedron Letters,Vol.26,No.27,pp 3277-3278,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

Amination Of Organic Azides Using Tetracarbonylhydridoferrate, $HFe(CO)_4^-$ As A Highly Selective Reducing Agent

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Summary: Reductive amination of organic azides using tetracarbonylhydridoferrate(O) gave the corresponding amines in good to excellent yields at room temperature or -40°C under carbon monoxide atmosphere.

A selective general procedure for the reduction of organic azide to amine has long been of interests. Successful methods for synthesis of primary amines from organic azides have been carried out through catalytic hydrogenation[1] and lithium aluminium hydride.[2] More recently under phase tranfer catalysis sodium borohydride efficiently performs the reduction of organic azides[3]. Most procedures generally satisfactory results but have some limited applicabilities and require tedious conditions.

Recently, tetracarbonylhydridoferrate has been shown to be a convenient selective reagent for carbonylation and/or reduction of a variety of organic functional such as a nitro group,[4a] and olefinic bonds of conjugated diene, enamine, α,β -unsaturated carbonyl compound,[4b] alkyl halide,[4c] olefin oxide or N-alkylation of amines[4d] and ketones.

In this letter, we wish to report a simple and convenient method for the reductive amination of organic azide using tetracarbonylhydridoferrate as a reducing agent.

In the general procedure: To the ethanolic potassium tetracarbonylhydridoferrate(11 mmol) was dropwise added organic azide(11 mmol) for 5 - 10 min. And the mixture was stirred for 12 hr at room temperature under carbon monoxide. The reaction proceeded to evolve explosively nitrogen gas and then an absorption of carbon monoxide ceased in about 3 hr. The reaction mixture was oxidized to expose on air. The filtered reaction mixture was concentrated to about 5 ml on rotary evaporator and products were separated by vacuum distillation or recrystallization and analyzed by means of ir, nmr, glpc, m.p., b.p., and chemical analyses.

The results of typical reactions are shown in Table 1. The only isolated products obtained from organic azides were the corresponding primary amines, but the expected isocyanates were not obtained. On the other hand, benzoylazide gave ethylphenylcarbamate in a good yield at room temperature but gave benzamide quantitatively at -40°C under carbon monoxide.

$$R\text{-}N_3 \xrightarrow[KHFe(CO)_4,\ EtOH]{CO,\ r.t.} R\text{-}NH_2 + N_2, \quad RCON_3 \xrightarrow[KHFe(CO)_4,\ EtOH]{CO,\ -40^{\circ}C} RCONH_2 + N_2$$

Table 1. Amination of Organic Azides using Tetracarbonylhydridoferrate.

Exp. No.	Organic Azide($R\text{-}N_3$)	Product	Temp(°C)	Yield(%)[a]
1	Phenyl-	Aniline	r.t.	77
2	p-Chlorophenyl-	p-Chloroaniline	r.t.	100
3[b]	o-Chlorophenyl-	o-Chloroaniline	r.t.	78
4	p-Methylphenyl-	p-Toluidine	r.t.	84
5	p-Methoxyphenyl-	p-Anisidine	r.t.	85
6	n-Hexyl-	n-Hexylamine	r.t.	70
7	Benzoyl-	Benzamide	- 40°C	98

a) Isolated yield, 12hr. b) Reaction time, 24hr.

The principal advantage of this reaction is that the reaction is rapid under ambient conditions and gives in good to excellent yields for a wide variety of primary amines. In this reaction, an organic nitrene is assumed to be formed as an intermediate.

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(Received in Japan 5 March 1985)