

Sodium Acyloxyborohydride as New Reducing Agents. II.

Reduction of Nitriles to the corresponding Amines

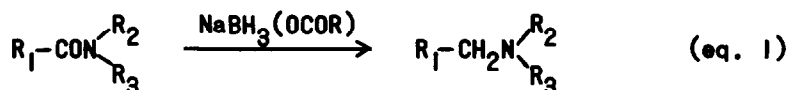
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Recently we reported that sodium acyloxyborohydride in refluxing tetrahydrofuran or dioxane reduced carboxamides to the corresponding amines in excellent yields (eq. 1) and the main reactive species in these reactions were not free diborane.¹⁾



The reduction of nitriles with complex hydrides [LiAlH_4 , $\text{LiAlH}_4\text{-AlCl}_3$ ²⁾, $\text{NaBH}_4\text{-AlCl}_3$ ³⁾, AlH_3 ⁴⁾, B_2H_6 ⁵⁾, $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OMe})_2$ ⁶⁾, $\text{NaBH}_4\text{-CoCl}_2$ ⁷⁾, etc.] to the corresponding amines is well known.

We have further examined the reducing characteristics of these versatile reagents, [$\text{NaBH}_3(\text{OCOR})$] and now wish to describe that sodium trifluoroacetoxyborohydride [$\text{NaBH}_3(\text{OCOCF}_3)$]⁸⁾ in tetrahydrofuran provides a convenient method for the reduction of both aliphatic and aromatic nitriles to the corresponding amines in high yields under mild conditions (eq. 2).



The results are summarized in the following Table in which four last entries are a few examples of selective reduction by this easily accessible reagent just as by diborane⁵⁾. (aromatic COOEt , NO_2 and Cl remained intact.) Further studies on this problem, now under way, certainly are necessarily to evaluate our metal-hydride complex as a useful reagent for selective reduction.

The following procedure for benzonitrile is representative. To a stirred

Table I

Reduction of Nitriles with Sodium Trifluoroacetoxyborohydride

Nitriles	Yield of amine HCl%	Nitriles	Yield of amine HCl%
benzonitrile	82.4	4-nitrophenylacetonitrile	71
diphenylacetonitrile	70	3-nitrobenzonitrile	75.8
phenylacetonitrile	70	p-chlorophenylacetonitrile	70
p-tolunitrile	78.3	methyl 4-cyanobenzoate	89.4

suspension of NaBH_4 (1.9g, 50 mmoles) in THF (30 ml) was added CF_3COOH (5.7g, 50 mmoles) in THF (5 ml) over a period of 10 minutes at 20° . To this solution of $\text{NaBH}_3(\text{OCOCF}_3)$ was added benzonitrile (1.03g, 50 mmoles) in THF (5 ml), and the mixture was stirred at room temperature for 4 hours. The excess reagent was cautiously decomposed with water below 10° and the resulting mixture was concentrated to dryness in vacuo and extracted with methylene chloride. The extract was washed with water and dried over Na_2SO_4 . The methylene chloride solution was treated with dry hydrogen chloride, evaporated in vacuo and the residue was crystallized from methanol-ether to give benzylamine hydrochloride (1.19g, 82.4%).

The work is being continued.

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- 8) The reduction of benzonitrile with $\text{NaBH}_3(\text{OCOCH}_3)$ gave poor yield of benzylamine.