

THIOL-ACTIVATED SODIUM BOROHYDRIDE REDUCTION OF CARBOXYLATE ESTER

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Sodium borohydride itself cannot reduce carboxylate esters to corresponding alcohols, but modification studies of it have shown the stimulation of its reducing power and some of the modified reagents can reduce carboxylate esters.¹ Recently, Lalancette et al have shown that sulfurated sodium borohydride has stronger reducing power than sodium borohydride itself but cannot reduce carboxylate esters.² In this paper, we would like to describe that sodium borohydride under the coexistence of ethanedithiol reduced carboxylate esters to corresponding alcohols.

As shown in the table, benzoate esters were almost quantitatively reduced to corresponding benzyl alcohols by sodium borohydride mixing with ethanedithiol for 20 hr refluxing in dry tetrahydrofuran. But the reaction with ethylmercaptan or thiophenol instead of with ethanedithiol gave only few per cent of the reaction product under the same conditions. The substituent electronic effect was hardly found under the reaction conditions described here. Only in the cases of p-amino- and p-hydroxy-benzoates, there were no reaction products. It might be explained that p-amino or p-hydroxy group inhibits this reaction, since in the presence of cyclohexylamine methyl benzoate could not be reduced by this reducing system. Aliphatic carboxylate esters were also reduced by this reducing system as shown in the table. When an α,β -unsaturated ester was examined, methyl cinnamate was reduced to 3-phenylpropanol as like as the sodium borohydride reduction of α,β -unsaturated ketones to saturated alcohols.³

REFERENCES

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Table. Thiol-activated sodium borohydride reduction of carboxylate ester

Ester (mmole)	Thiol (mmole)	NaBH ₄ (mmole)	Product (% yield) ^a
Methyl benzoate (1.25)	ethanedithiol (5.0)	3.75	benzyl alcohol (100)
Methyl benzoate (2.5)	thiophenol (15.0)	7.5	benzyl alcohol (4)
Methyl benzoate (2.5)	ethylmercaptan (10.0)	7.5	benzyl alcohol (5)
Ethyl benzoate (2.5)	ethanedithiol (10.0)	7.5	benzyl alcohol (98)
Methyl benzoate (2.5)	ethanedithiol (10.0)	7.5 ^b	no reaction product
Methyl p-cyanobenzoate (2.5)	ethanedithiol (10.0)	7.5	p-cyanobenzyl alcohol (100)
Methyl p-toluate (2.5)	ethanedithiol (10.0)	7.5	p-toluylicarbinol (97)
Methyl p-anisate (2.5)	ethanedithiol (10.0)	7.5	p-anisylcarbinol (81)
Ethyl p-aminobenzoate (2.5)	ethanedithiol (10.0)	7.5	no reaction product
Ethyl p-hydroxybenzoate (2.5)	ethanedithiol (10.0)	7.5	no reaction product
Methyl n-caprate (2.5)	ethanedithiol (10.0)	7.5	n-decyl alcohol (100)
Methyl palmitate (2.5)	ethanedithiol (10.0)	7.5	cetyl alcohol (100)
Methyl cinnamate (2.5)	ethanedithiol (10.0)	7.5	3-phenylpropanol (100)

^a Yields were estimated by GLC. ^b With 20 mmoles of cyclohexylamine.