

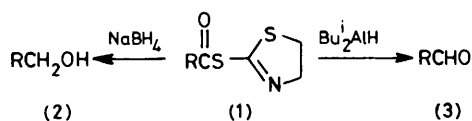
Efficiently Monitored Reduction of Carboxylic Acids into Alcohols or Aldehydes via 2-Thiazoline-2-thiol Esters by Sodium Borohydride or Di-isobutylaluminium Hydride

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Summary Carboxylic acids were converted into their 2-thiazoline-2-thiol esters (1), which were treated with sodium borohydride or di-isobutylaluminium hydride to give the alcohols (2) or the aldehydes (3) respectively, in good yields.

REDUCTION of carboxylic acids to alcohols with sodium borohydride through mixed carbonic-carboxylic acid anhydrides¹ and its application² have been reported. Direct diborane reduction of carboxylic acids into alcohols in quantitative yields has also been published.³ Also, reduction of alkyl carboxylates to aldehydes with di-isobutylaluminium hydride has attracted attention.⁴ We here report a new improved method for the reduction of carboxylic acids into alcohols or aldehydes, using 2-thiazoline-2-thiol esters (1). These esters are easily prepared by



condensation of carboxylic acids with 2-thiazoline-2-thiol through dehydration⁵ or by treatment of acid chlorides with thallium(I) 2-thiazoline-2-thiolate.⁶ The 2-thiazoline-2-thiolate anion is shown to be a very good leaving group.

Thus, treatment of the esters (1) with NaBH₄ (3 mol. equiv.) in aqueous tetrahydrofuran at room temperature gave the alcohols (2) in high yields, whereas treatment with Bu₂AlH (1.1 mol. equiv.) in hexane-dichloromethane (1:1) under argon or nitrogen at -20 to -50 °C gave the aldehydes (3) in satisfactory yields (Table).† In both cases,

TABLE. Reduction of 2-thiazoline-2-thiol esters with NaBH₄ or Bu₂AlH.

R	(2) ^a	(3) ^{a,b}
Ph	92	93
[CH ₂] ₁₄ Me	99	79
[CH ₂] ₈ Me	98	72
[CH ₂] ₄ Me	96	54
CH=CHPh (<i>trans</i>)	92	64
[CH ₂] ₇ CO ₂ Me	73	

^a % Isolated yield. ^b Identity confirmed by 2,4-dinitrophenylhydrazine derivative.

the end point of the reduction can be easily judged by the disappearance of the original yellow colour of the 2-thiazoline-2-thiol esters.

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† Satisfactory elemental analyses, and mass, ¹H n.m.r., and i.r. spectral data have been obtained for all new compounds.

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