Partial Reduction of 1-Acyl-3-methylimidazole-2-thiones to Aldehydes by Tri-n-butyltin Hydride

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In order to generate acyl radicals,[1] we have had an occasion to study the reaction of 1-acyl-3-methylimidazole-2-thiones with tri-n-butyltin hydride in refluxing toluene in the presence of azobisisobutyronitrile (AIBN) as a radical initiator. The reaction seemed to be initially very promising, yielding the corresponding aldehydes in high yields. However, we found that the reaction took place even without adding AIBN, indicative of non-radical nature of the present reaction.

1-Acyl-3-methylimidazole-2-thiones can be easily prepared from carboxylic acids, triphenylphosphine and bis-1-methyl-2-imidazole disulfide or acid chlorides and 2-mercapto-1-methylimidazole in the presence of triethylamine.[2] In the present study the latter method was used to prepare 1-acyl-3-methylimidazole-2-thiones due to the simplicity and high yields. Several 1-acyl-3-methylimidazole-2-thiones were chemoselectively reduced to the corresponding aldehydes with tri-n-butyltin hydride in refluxing toluene. The reaction was clean and completed within 2 h. Furthermore, the present reaction proceeded at room temperature, although it required 48 h for the completion. As shown in Table 1, the yields of aldehydes were excellent with both aliphatic and aromatic derivatives. 1-Acyl-3-methylimidazole-2-thiones with other reducible functional groups such as ketone, nitro and olefinic groups were selectively reduced to the corresponding aldehydes without attacking such functional groups. Furthermore, the aldehyde was not reduced to the alcohol under the present condition. When an equimolar mixture of 1-decanoyl-3-methylimidazole-2-thione and n-nonyl aldehyde was reacted with 1 equiv of tri-n-butyltin hydride, only n-decyl aldehyde was obtained along with unreacted n-nonyl aldehyde. The partial reduction of carboxylic acids to aldehydes via 3-acylthiazolidine-2-thiones, S-2-pyridyl thioates, and 1-acylimidazoles with tri-n-butyltin hydride was briefly investigated and no reaction occurred to an observable extent under the similar reaction conditions. Although we don't fully understand the mechanism of the present reaction, it is believed that the similarity might be realized with the reaction of acid chlorides with tri-n-butyltin hydride in which non-radical mechanism has been proposed.[3]

In conclusion, the present method is mechanistically interesting and offers several advantages of the mildness, high yield and functional groups selectivity. Although there are several methods to bring about such conversions,[4] we consider the present method as a usuful addition to therm.

Table 1. Reaction of 1-acyl-3-methylimidazole-2-thiones (RCOX) with $n\text{-}Bu_3SnH$[a]

1-acyl-3-methylimidazole-2-thiones (RCOX)[b]	Yield (RCHO), %
$CH_3(CH_2)_{16}$(87)	82
$CH_3(CH_2)_8$(92)	80
$CH_3(CH)_8$(92)	93[c]
$c\text{-}C_6H_{11}$(86)	94[c]
$CH_2=CH\text{-}(CH_2)_8$(91)	70
C_6H_5(93)	99[c]
$p\text{-}CH_3\text{-}CO\text{-}C_6H_4$(85)	85
$p\text{-}NO_2\text{-}C_6H_4$(80)	80

[a] The reaction was carried out with 1.1 equiv of $n\text{-}Bu_3SnH$ in refluxing toluene for 2 h. [b] The numbers in parentheses indicate isolated yields of 1-acyl-3-methylimidazole-2-thiones from acid chlorides [c] The yields were determined by GLC using an internal standard.

Experimental

A typical procedure for the preparation of 1-acyl-3-methylimidazole-2-thiones. To a stirred solution of 2-mercapto-1-methylimidazole (240 mg, 2.1 mmol) and triethylamine (334 ul, 2.4 mmol) in dichloromethane (7 m*l*) at 0 °C was added decanoyl chloride (400 mg, 2.1 mmol). After being stirred at room temperature for 2 h, the reaction mixture was diluted with dichloromethane (40 m*l*) and washed with cold 5% HCl, cold 5% $NaHCO_3$, and brine, dried and evaporated to dryness to give 1-decanoyl-3-methyl imidazole-2-thione (492 mg, 92%). The crude product was used without purification for further reaction. ^1H-NMR ($CDCl_3$) δ0.85-1.95(m, 17H), 3.47(s, 3H), 3.49(t, 2H, J = 7Hz), 6.61(d, 1H, J = 3Hz), 7.34(d, 1H, J = 3Hz). IR(KBr) 1740 cm^{-1}.

A typical procedure for the reaction of 1-acyl-3-methylimidazole-2-thione with tri-n-butyltin hydride. To a solution of 1-decanoyl-3-methylimidazole-2-thione (204 mg, 0.77 mmol) in toluene (3 m*l*) was added tri-n-butyltin hydride (248 mg, 0.852 mmol) and the solution was refluxed for 2 h. The reaction mixture was diluted with dichloromethane (40 m*l*), washed with water and brine, dried and evaporated to dryness. The crude product was subjected to silica gel column chromatography using ethyl acetate and hexane (1:10) as an eluent to yield decyl aldehyde (94 mg, 80%).

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