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THE PARTIAL REDUCTION OF CARBOXYLIC ACIDS TO ALDEHYDES via 3-ACYLTHIAZOLIDINE-2-THIONES WITH DIISOBUTYLALUMINUM HYDRIDE

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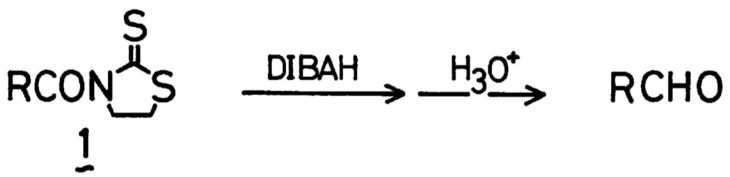
3-Acylthiazolidine-2-thiones (1), prepared from free carboxylic acids and thiazolidine-2-thione by using 2-chloro-1-methylpyridinium iodide in the presence of triethylamine, were reduced to the aldehydes with diisobutylaluminum hydride (DIBAH) in good yields even when excess amount of DIBAH was used.

Recently, there have been reported many methods for the partial reduction of carboxylic acid derivatives to aldehydes which is one of the most useful reactions in organic syntheses. For example, carboxylic esters were reduced to aldehydes with stoichiometric amount of various aluminum hydrides.[1] Also, the reduction of 1-acylimidazole[2] and N,N-dialkylcarboxamide[3a, b] were carried out by using lithium aluminum hydride,[2] di- and triethoxyaluminum hydride,[3a] and bis(dialkylamino)aluminum hydride.[3b] But in these reductions, the resulting aldehydes or their precursors were further reduced to alcohols and/or amines when excess amount of reducing agent was used.

We now wish to report the partial reduction of carboxylic acids to the corresponding aldehydes via 3-acylthiazolidine-2-thiones (1)[4] with DIBAH in toluene. In the present reduction, aldehydes were obtained in good yields even when the excess amount of reducing agent was employed.



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The following experiment provides a typical procedure for the reduction of 3-acylthiazolidine-2-thiones (1) to the aldehydes with DIBAH: Crystalline 3-(3-phenylpropionyl)thiazolidine-2-thione (252 mg, 1.0 mmol) was added in one portion to the vigorously stirred toluene (4 ml) solution of DIBAH (171 mg, 1.2 mmol) at -78°C under an argon atmosphere. The mixture was stirred for 15 min at this temperature and then at -45°C for 1.5 h. To the reaction mixture were successively added 2N-sulfuric acid (ca. 0.5 ml), petroleum ether (ca. 10 ml), and sodium chloride (ca. 1 g). Resulting crystalline mass was filtered off and washed with petroleum ether. The combined organic solution was dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was chromatographed by thin-layer chromatography on silica-gel to give the desired 3-phenylpropionaldehyde in 91% yield (122 mg).

The results of the partial reduction of various 3-acylthiazolidine-2-thiones (1) with DIBAH are summarized in the following Table.

Table. The Partial Reduction of 3-Acylthiazolidine-2-thione (1) with DIBAH[a)]

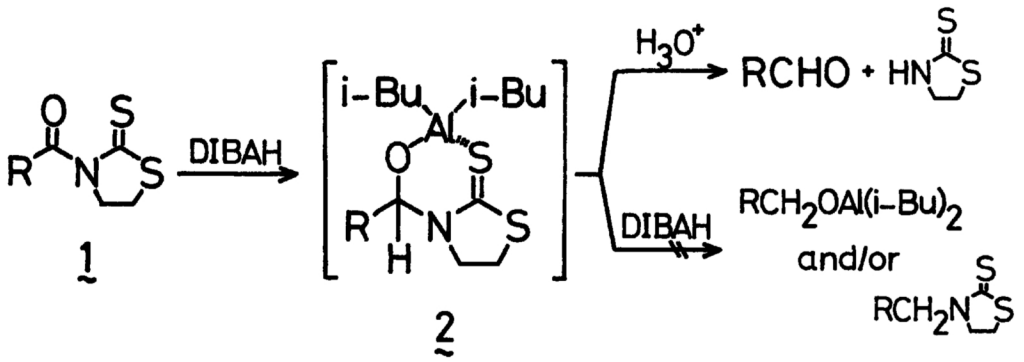
R	Molar Ratio DIBAH/1	Yield of Aldehyde[b)] (%)
$PhCH_2CH_2$	1.2	91(85)[c)]
	1.5	93
	2.1	90
	4.0	69
p-ClC_6H_4	1.2	84
$PhCH_2$	1.2	64
CH_3CH_2PhCH	1.2	(75)
$PhCH_2CH_2CH_2$	1.2	90
$CH_2=CH(CH_2)_7CH_2$	1.2	66(74)
$CH_3(CH_2)_{15}CH_2$	1.2	82
PhCH=CH	1.2	(74)

a) Reduction at -78°C for 15 min and then -50∼-40°C for 0.5-2 h otherwise indicated.

b) Isolated yield.

c) Numbers in parentheses denote the yield in the case of reverse addition (addition of DIBAH to 1) at -78°C and then stirring for 2 h at this temperature.

As shown in Table, the yields of aldehydes were good to high both in the cases of aliphatic and aromatic derivatives by just adding crystalline 3-acylthiazolidine-2-thiones (1) to DIBAH. Only in the case that 3-acylthiazolidine-2-thiones (1) were oily substances, the reverse addition (addition of DIBAH to 3-thiazolidine-2-thiones (1)) gave successful results. Moreover, even in the case of reduction of 3-(3-phenylpropionyl)thiazolidine-2-thione with excess amount of DIBAH, 3-phenylpropionaldehyde was obtained in good yield; 90% yield (2.1 equivalents of DIBAH) or 69% yield (4.0 equivalents). This result was rationalized by considering a key six-membered chelate intermediate (2), formed by the attack of DIBAH to the carbonyl moiety of 3-acylthiazolidine-2-thione (1). The gem-aminoalcohol structure of the resulting intermediate (2) might be inert toward further reduction under the reaction condition. Thus, aldehyde was isolated by quenching the intermediate (2) with dilute acid.



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It is noteworthy that various 3-acylthiazolidine-2-thiones (1), readily prepared from free carboxylic acids and thiazolidine-2-thione by using 2-chloro-1-methylpyridinium iodide[5] and triethylamine, were smoothly reduced with DIBAH under mild conditions to give the aldehydes in good yields.

Further selective reduction is now in progress.

REFERENCES AND NOTES

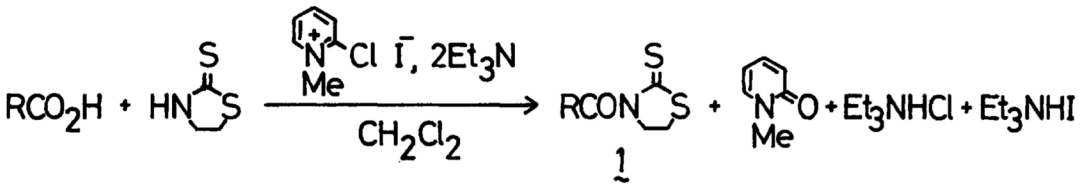
1) M. Muraki and T. Mukaiyama, Chem. Lett., 1975, 215 and references therein.

2) H. A. Staab and H. Brauenling, Justus Liebigs Ann. Chem., 654, 119 (1962).

3a) H. C. Brown and A. Tsukamoto, J. Am. Chem. Soc., 86, 1089 (1964);

b) M. Muraki and T. Mukaiyama, Chem. Lett., 1975, 875 and references therein.

4) 3-Acylthiazolidine-2-thiones (1) were easily prepared by simply adding two equivalents of triethylamine to the mixture of equimolar amounts of free carboxylic acid, thiazolidine-2-thione, and 2-chloro-1-methylpyridinium iodide[5] in dichloromethane at room temperature in good yields.



R=$PhCH_2$ 76%, R=$PhCH_2CH_2$ 80%, R=CH_3CH_2PhCH 75%

5) Recently new synthetic methods by using various onium salts of azaaromatics have been successfully investigated in our laboratory. For example; E. Bald, K. Saigo, and T. Mukaiyama, Chem. Lett., 1975, 1163; K. Saigo, M. Usui, K. Kikuchi, E. Shimada, and T. Mukaiyama, Bull. Chem. Soc. Jpn., 50, 1863 (1977); T. Mukaiyama, K. Narasaka, and K. Kikuchi, Chem. Lett., 1977, 441.

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