

Selective Reduction of Aromatic Aldehyde in The Presence of Aromatic
Ketone by NaBH_4 and SnCl_2 in THF[#]

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Aromatic aldehydes were more selectively reduced to the corresponding alcohols than the related ketones by a reducing system consisting of NaBH_4 and SnCl_2 in THF in a common flask.

The selective reduction of carbonyl group occurring with other functional groups¹⁾ is important in organic synthesis. It is difficult to reduce aldehydes selectively in the presence of ketones, while such useful and important reductions have been obtained by some procedures: with tetraalkylammonium borohydride,²⁾ triacetoxyborohydride,³⁾ tributyltin hydride on silica gel,⁴⁾ 9-borabicyclo[3,3,1]nonane pyridine,⁵⁾ and sodium borohydride and thiol⁶⁾ etc. While, in the course of the research to reduce organic compounds by sodium borohydride and metal salts, the authors have found a novel selective reduction procedure of aldehyde in the presence of ketones by sodium borohydride and SnCl_2 in THF. A typical procedure is as follows: A mixture of acetophenone(0.5 g, 4.2 mmol), benzaldehyde(0.5 g, 4.7 mmol), NaBH_4 (0.2 g, 5.2 mmol), SnCl_2 (2.5 g, 13.2 mmol), and THF(30 ml) in a common flask was heated under reflux for 1.5 h. After the reaction, the mixture was consecutively treated with HCl and NaOH. Then, the resultant neutralized mixture was heated and filtered during hot. The filtrate was analyzed by TLC, GLC, and NMR. Only 8.0% of 1-phenylethanol(92.0% of acetophenone intact) and 96.8% of benzyl alcohol(3.2% of benzaldehyde intact) were detected.

The results of the reduction of aromatic aldehyde in the presence of aromatic ketones in a common flask by a reducing system consisting of sodium borohydride and tin(II) chloride in THF are shown in Table 1. Generally, aldehydes are more readi-

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This paper is dedicated to the late Professor Ryoza Goto, Kyoto University.

ly reduced than ketones by alkali metal borohydride, aluminohydride and diborane, while the absolute rates of reduction are too fast to take advantage of the inherent relative rate difference between aldehyde and ketones.³⁾ Hence, selective reduction of aldehyde in the presence of ketones is ordinarily impracticable. While, as shown in Table 1, the aromatic aldehydes are more readily reduced to the corresponding alcohols than the aromatic ketones by the reducing system consisting of NaBH_4 and SnCl_2 in THF, in a common flask (Table 1).

Table 1. Selective reduction of aldehyde in the presence of^{a)} ketones by NaBH_4 and SnCl_2 in THF in a common flask

Substrate	mmol	Reduction product	Yield/%
Benzaldehyde +	4.7	benzaldehyde	3.2
Acetophenone	4.2	benzyl alcohol	96.8
		acetophenone	92.0
		1-phenylethanol	8.0
<i>o</i> -Tolualdehyde +	4.2	<i>o</i> -tolualdehyde	5.8
<i>p</i> -Methylacetophenone	3.6	<i>o</i> -methylbenzyl alcohol	94.2
		<i>p</i> -methylacetophenone	92.5
		1- <i>p</i> -methylphenylethanol	7.5
<i>p</i> -Tolualdehyde +	4.2	<i>p</i> -tolualdehyde	6.2
<i>p</i> -Chloroacetophenone	3.2	<i>p</i> -methylbenzyl alcohol	93.7
		<i>p</i> -chloroacetophenone	97.0
		1- <i>p</i> -chlorophenylethanol	3.0
<i>p</i> -Tolualdehyde +	4.2	<i>p</i> -tolualdehyde	5.6
<i>p</i> -Methylacetophenone	3.6	<i>p</i> -methylbenzyl alcohol	94.4
		<i>p</i> -methylacetophenone	93.0
		1- <i>p</i> -methylphenylethanol	7.0

a) A mixture of substrate, NaBH_4 (0.2 g, 5.2 mmol), and SnCl_2 (2.5 g, 13.2 mmol) in THF (30 ml) was heated under reflux for 1.5 h.

While in the absence of SnCl_2 in the above reducing system, the related ketones were reduced to the corresponding alcohols about 30-40% in quantity. The tetrahydrofuran and acetonitrile were the most suitable solvent, but in a protic solvent such as methanol and ethanol, the reducing system even in the presence of tin(II) chloride reduces a ketone to corresponding alcohol (50%).

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