

Tin-Catalyzed Formation of Alkyl Lactates from Trioses and

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- Summary**
1. Tin halides are excellent catalysts for the reaction of trioses (dihydroxyacetone and glyceraldehyde) with alcohols to give alkyl lactates.
 2. The estimated reaction mechanism involves the isomerization of dihydroxy-acetone to pyruvic aldehyde, which undergoes the further isomerization and the simultaneous addition of alcohol to give alkyl lactate.
 3. Tin halides can catalyze the both isomerizations while some other metal halides only the first resulting in the predominant formation of pyruvic aldehyde dimethylacetal.

1. What to do with glycerin?

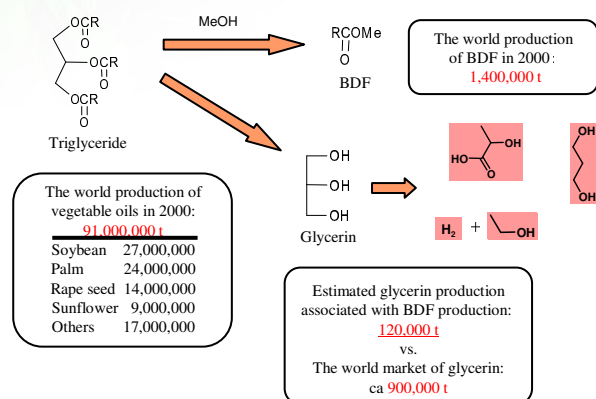
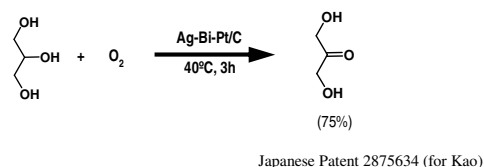


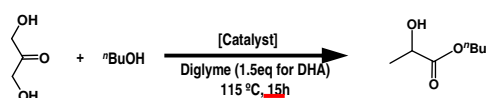
Table 1. Effect of Catalyst

Catalyst (10 mol%)	Yield (%)	
	(1)	(2)
CuCl ₂	trace	71
RhCl ₃ ·xH ₂ O	2	61
Zr-Cl ₄	13	58
Cr-Cl ₃ ·6H ₂ O	50	16
AlCl ₃ ·6H ₂ O	62	14
InCl ₃ ·4H ₂ O	67	7
SnCl ₂	89	2
SnCl ₄ ·5H ₂ O	82	9
SnBr ₂	83	8
SnI ₂	71	8
(acac) ₂ SnCl ₂	76	3

2. Catalytic Oxidation of glycerin to dihydroxyacetone



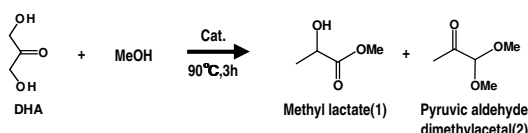
3. Reaction of dihydroxyacetone with *n*-butanol to butyl lactate



Catalyst	Yield (%)
ZrCl ₄ (3 mol%)	74
CrCl ₃ ·6H ₂ O (4 mol%)	82

European Patent 0460831A2 (for BP)

4. This Work



Pyruvic aldehyde dimethylacetal(2) is mainly formed with halides of Cu, Rh, Zr, while methyl lactate(1) becomes the main product when halides of Cr, Al, In, Sn are used as catalyst, among which tin halides exhibits excellent performances.

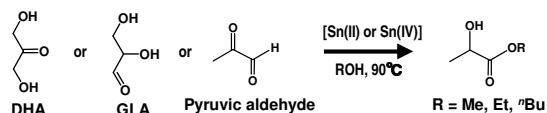


Table 2. Effect of Substrates

Substrate	Catalyst (10 mol%)	Time	Yield (%)		
			Me	Et	ⁿ Bu
DHA	SnCl ₂	2 h	84	78	84
	SnCl ₄ ·5H ₂ O	1 h	78	84	91
GLA	SnCl ₂	2.5 h	63	85	82
	SnCl ₄ ·5H ₂ O	8 h	85		
Pyruvic aldehyde	SnCl ₂	1 h	62	88	82
	SnCl ₂	3 h	81		
	SnCl ₂	3 h	88	74	78

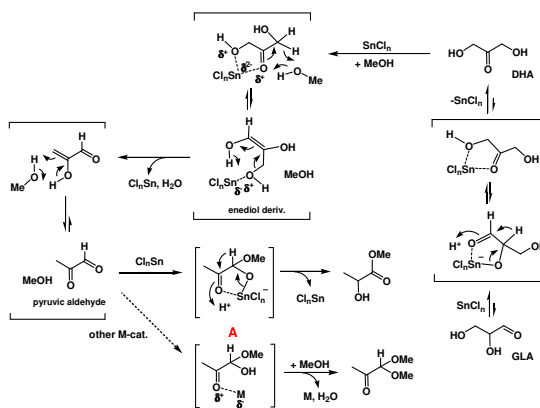


Fig. Estimated Overall Reaction Mechanism