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An $SnCl_2$-Promoted α-Methylene-γ-butyrolactone Synthesis in an Aqueous Medium

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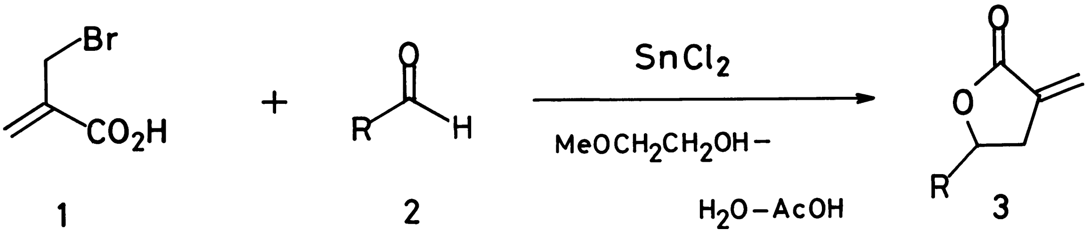
Reaction of α-bromomethylacrylic acid with aldehydes in an $SnCl_2$-$MeOCH_2CH_2OH$-H_2O system provides γ-substituted-α-methylene-γ-butyrolactones.

Preparation of α-methylene-γ-butyrolactone moiety which has potentially biological activity, has been a subject of extensive synthetic studies.[1)] Organometal-mediated 2-carboalkoxyallylation of aldehydes (chromium,[2)] zinc,[3)] nickel,[4)] and silicon[5)]) in a dry aprotic solvent has been recognized as one of the most straightforward approaches towards α-methylene-γ-butyrolactone synthesis. Meanwhile, Sn(II) halides have never been employed for carbon-carbon formation in an aqueous solvent presumably due to their less reactivities[6)] and the fast protonation of the corresponding stannanes although extensive studies in aprotic media have been developed by Mukaiyama.[7,8)] Here, we describe a facile one-pot lactonization in an $SnCl_2$-$MeOCH_2CH_2OH$-H_2O system as shown in Scheme 1.



Scheme 1.

A typical experimental procedure is as follows; A mixture of **1** (1.2 mmol), benzaldehyde (2.4 mmol), $SnCl_2$ (1.2 mmol) dissolved in $MeOCH_2CH_2OH$ (0.75 ml), H_2O (0.40 ml), AcOH (0.20 ml) and conc. HCl (0.01 ml) was stirred under argon atmosphere at 60-70 °C for 3 h, affording 3 (R=Ph 85%) after chromatography.

The result of the lactonization is listed in Table 1. Both aromatic and aliphatic aldehydes undergo smooth lactonization by the aid of $SnCl_2$ in aqueous medium. Crotonaldehyde gave 1,2-adduct. The oxidative addition of **1** to

$SnCl_2$ would produce 4 which would be stabilized by intramoleculer chelation of Sn(IV) with carboxyl group. In fact, $SnCl_2$ reacts with 1 faster than allyl bromide in the same conditions, and 4 does not react with ketones while diallyl dibromostannane does. Therefore, 4 reacts smoothly with benzaldehyde providing 3 (R=Ph) as a sole product in the presence of an equivalent amount of acetophenone.

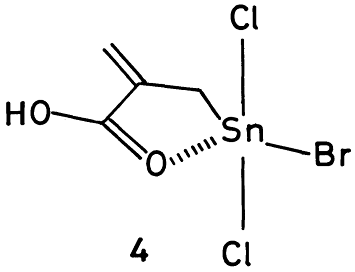

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Table 1.

Entry	Aldehyde	Yield of 3 (%)
1	PhCHO	85
2	p-MeC_6H_4CHO	78
3	p-ClC_6H_4CHO	85
4	Furfural	66
5	n-$C_6H_{13}CHO$	88
6	i-C_3H_7CHO	85
7	$PhCH_2CHO$	87
8	Crotonaldehyde	60
9	PhCH=CHCHO	51

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