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REACTION OF VINYLOXYTIN. A NEW METHOD FOR THE PREPARATION OF β-HYDROXYALKANOATE

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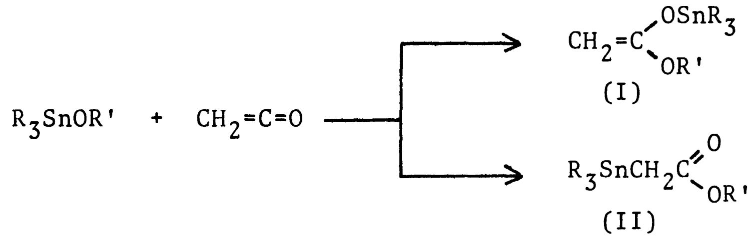
It was suggested that vinyloxytin was produced by passing gaseous ketene into a methylene chloride solution of tin alkoxide at low temperature. The vinyloxytin thus formed further reacted with various carbonyl compounds at low temperature in the presence of strong Lewis acid such as $TiCl_4$ or $AlCl_3$ to give the corresponding β-hydroxyalkanoates.

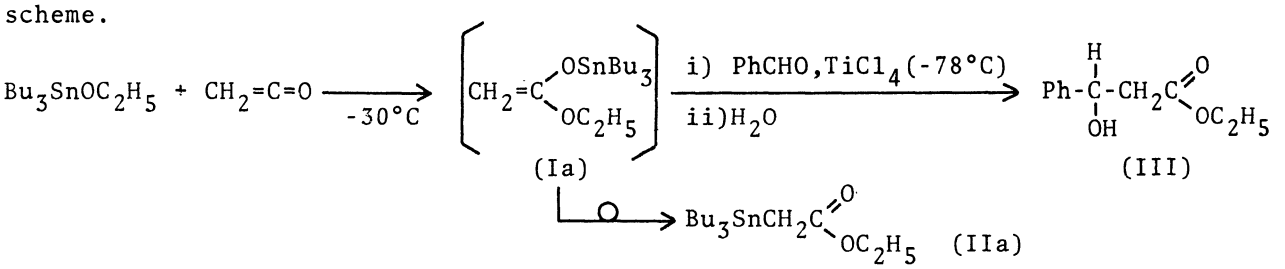
We recently reported that vinyloxyborane, formed from thioboronite and ketene, reacted with various carbonyl compounds to give the corresponding β-hydroxyalkanethioates in excellent yields.$^{1)}$ As a part of this study, the reaction of tin alkoxide with ketene was examined with the consideration that vinyloxytin, which was expected to have the same reactivity toward carbonyl compounds as well as vinyloxyborane, would be formed at low temperature.

Lutsenko et al. reported$^{2)}$ that only II was isolated in practice by the reaction of tin alkoxide with ketene though there can be considered possible formation of two products (I) and (II). On the other hand, Noltes et al. reported$^{3)}$ that



triethyl(ethoxycarbonylmethyl)tin (IIb) reacted with carbonyl compounds such as Cl_3CCHO to afford the corresponding β-hydroxyalkanoates at room temperature, but the same reaction with benzaldehyde took place only when they were heated for 8 hr at 50-60°C in the presence of $ZnCl_2$ as a catalyst.

It was found by the present experiment that the reaction of tri-n-butyl(ethoxycarbonylmethyl)tin (IIa) (bp 150-152°C/0.6 mmHg) with benzaldehyde in CH_2Cl_2 in the presence of $TiCl_4$ at the temperatures ranging from -78°C to room temperature did not proceed to afford an expected product of β-hydroxyalkanoate. Contrary to the above results, β-hydroxyalkanoate was obtained in good yield when gaseous ketene was passed into a solution of tri-n-butyltin ethoxide at -30°C, followed by the addition of benzaldehyde and $TiCl_4$ at -78°C. However, β-hydroxyalkanoate was not obtained when the same reaction was carried out by the addition of benzaldehyde and $TiCl_4$ at -78°C after the reaction mixture of tin alkoxide and ketene was allowed to stand at 0°C for several hours. From these results, it was assumed that the reaction proceeded, at low temperature, through an initial formation of active intermediate, vinyloxytin, which in turn reacted with carbonyl compound to give β-hydroxyalkanoate. Whereas, only IIa, unreactive toward carbonyl compounds, resulted at about 0°C by the rearrangement of tri-n-butylstannyl group as shown in the following scheme.



(Ia) (III) (IIa)

A typical experimental procedure is shown in the following; gaseous ketene was passed into a solution of tri-n-butyltin ethoxide (0.429 g, 1.28 mM) in CH_2Cl_2 (5 ml) at -30°C under argon for 1.5 hr. Then benzaldehyde (0.113 g, 1.07 mM) in CH_2Cl_2 (3 ml) was added to the reaction mixture at -78°C, followed by dropwise addition of $TiCl_4$ (0.14 ml, 1.28 mM). After stirring for a few minutes, the reaction mixture was poured into a large amounts of phosphate buffer (pH 7.0), and the mixture was extracted with ether and dried over anhydrous sodium sulfate. After removal of the solvent, tri-n-butyltin fluoride was precipitated by the addition of 16 ml of KF saturated methanol solution. The mixture was concentrated in vacuo to remove methanol and the residue was extracted with ether and precipitate was separated by filtration. The filtrate was washed with water and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was chromatographed over silica gel to obtain 0.145 g (70%) ethyl β-hydroxyhydrocinnamate (III). The results are listed in Table.

Table. Yields of β-hydroxyalkanoates[a)]

Carbonyl compound	Yield[c)] %
PhCHO	70
$PhCH_2CH_2CHO$	49
PhCH=CHCHO	34
$PhCOCH_3$	59[b)]
Ph_2CO	17[b)]

a) The alkanoates were confirmed by IR and PMR spectra.
b) Dehydration products.
c) In the absence of $TiCl_4$, β-hydroxyalkanoate was not obtained.

It was also found that β-hydroxyalkanoate was obtained in 54% yield by the reaction of Ia, which was obtained from tri-n-butyltin ethoxide and ketene at -30°C, with β-phenylpropionaldehyde in ether when $AlCl_3$ was used in place of $TiCl_4$ in the above experiment.

1) K. Inomata, M. Muraki, and T. Mukaiyama, Bull. Chem. Soc. Japan., 46, 1807 (1973).
2) I. F. Lutsenko and S. V. Ponomarev, Zh. Obsch. Khim., 31, 2025 (1961): Chem. Abstr., 55, 27024d (1961).
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