Selective Acetalization of Aldehydes with Trialkoxystibine using Allyl Bromide†

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Trialkoxystibine has been found to be an effective reagent for selective acetalization of aldehydes with the aid of allyl bromide.

In continuation of our studies on the reactivity of tertiary stibines,[1] we have found a new aldehyde-selective acetalization method which should be applicable to acid-sensitive or protic solvent-sensitive aldehydes. To our knowledge, although acetalization has been performed by many methods,[2] the use of organometallic compounds has scarcely been reported.

Usually, acetalization is accomplished with alcohols or orthoformic esters in an acidic medium by means of various catalysts, such as protic acids or Lewis acids ($FeCl_3$, NH_4NO_3, BF_3, $ZnCl_2$, rare earth metal chlorides[3]) and, as recently reported, alumina.[4] We now wish to communicate a novel and chemoselective acetalization method for aldehydes with trialkoxystibine with the aid of allyl bromide (equation 1).

$$R^1CHO + Sb(OR^2)_3 \xrightarrow{H_2C=CHCH_2Br} R^1CH(OR^2)_2 + \text{`}R^2O\text{–}\underset{\displaystyle X}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{Sb}}}}\text{–}CH_2CH{=}CH_2\text{'} \quad (1)$$

R^1 = alkyl, aryl; R^2 = Et, Pr^i

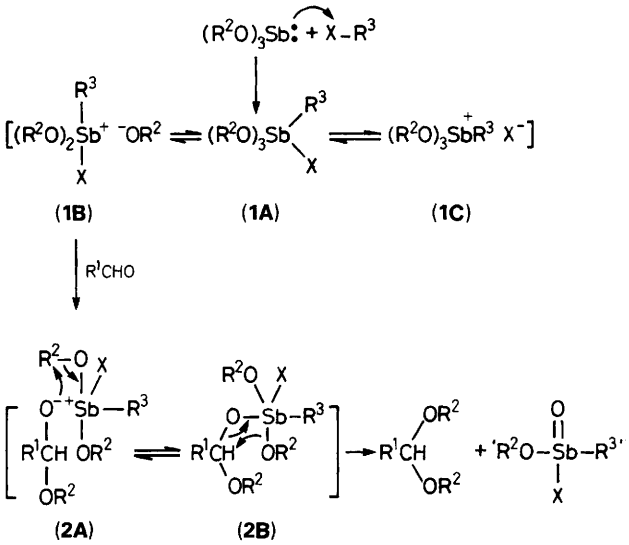
Table 1 gives the results of acetalization of aldehydes with trialkoxystibines mediated by allyl bromide. When triethoxystibine or tri-isopropoxystibine was used, reactions afforded

† This paper is the 78th report on the studies of the synthetic application of the elemento-organic compounds of Groups 15 and 16.

Table 1. Formation of acetals.[a]

Entry	R^1	R^2[in $Sb(OR^2)_3$]	*t*/h	Yield/%[b]
1	Ph	Et	2	97
2	*p*-ClC_6H_4	Et	2	98
3	*p*-$NO_2C_6H_4$	Et	2	98
4	Furyl	Et	2	97
5	n-C_8H_{17}	Et	2	97
6	$Me_2C{=}CH(CH_2)_2CMe{=}CHMe$	Et	4	95
7	*p*-$MeOC_6H_4$	Et	6	88
8	PhCH=CH	Et	4	85
9	Ph	Pr^i	4	99
10	*p*-$NO_2C_6H_4$	Pr^i	4	98
11	*p*-ClC_6H_4	Pr^i	4	99
12	*p*-$MeOC_6H_4$	Pr^i	6	92
13	n-C_6H_{13}	Pr^i	4	90
14	$Me_2C{=}CH(CH_2)_2CMe{=}CHMe$	Pr^i	6	93

[a] Reactions were carried out with an aldehyde (2 mmol), allyl bromide (2.2 mmol), and $Sb(OR^2)_3$ (2.2 mmol) at 80 °C. [b] Isolated yields based on the aldehyde.



Scheme 1

corresponding diethyl acetals or di-isopropyl acetals in good yields.

Various aliphatic, aromatic, and heterocyclic aldehydes can be converted to acetals by our method. Aliphatic or aromatic aldehydes with electron-withdrawing groups react faster than aromatic aldehydes with electron-repelling groups.

This method is chemoselective for aldehydes, ketones being less reactive than aldehydes. For example, only a 25% conversion to acetal was achieved with *p*-nitroacetophenone, even after heating at 100 °C for 16 h. Excellent chemoselectivity was observed with an equimolar mixture of benzaldehyde and acetophenone (equation 2).

$$\begin{matrix}\text{PhCHO}\\ \text{PhCOMe}\end{matrix} + Sb(OEt)_3 \xrightarrow[80\,^\circ\text{C, 16 h}]{BrCH_2CH{=}CH_2} \underset{96\%}{PhCH(OEt)_2} + \underset{0\%}{PhC(Me)(OEt)_2} \quad (2)$$

Several halides, such as allyl bromide, crotyl chloride, benzyl bromide, prop-2-ynyl bromide, ethyl bromoacetate, methyl iodide, and iodine, are able to promote the reaction. Allyl bromide appears to give the best results. In the absence of halides, reaction of *p*-chlorobenzaldehyde with triethoxystibine at 120 °C for 12 h afforded acetals only in 30% yield. The reaction proceeded well with equimolar amounts of trialkoxystibine and aldehyde. Evidently two alkoxy groups of the reagent are used for acetalization. A possible reaction mechanism is suggested in Scheme 1. Oxidative addition of halide to trialkoxystibine occurs first to form an unstable pentavalent antimony intermediate (**1**) as in the case of trialkyl stibines.[1c] Compound (**1**) could be in the covalent form (**1A**), ion-pair form (**1B**), or salt form (**1C**). Because the Sb–O bond is weaker than the Sb–C bond, the alkoxy anion produced from thermal decomposition of (**1B**) attacks the carbonyl group of the aldehyde to form intermediate (**2**) which also exists in two forms (**2A** or **B**). Eventually (**2**) gives rise to the corresponding acetal as shown in Scheme 1.

The above-mentioned reactions can be carried out either without solvent, or in tetrahydrofuran, light petroleum, *etc.* Trialkoxystibines were easily prepared from sodium alkoxide with $SbCl_3$.[5] The reaction proceeded conveniently in high yields. This procedure constitutes a new method for selective protection of aldehyde groups, especially suitable to acid-sensitive or protic solvent-sensitive compounds.

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