

Reactions of Carbonyl Compounds with Benzyltrialkylstibonium Bromide mediated by Different Strong Bases†

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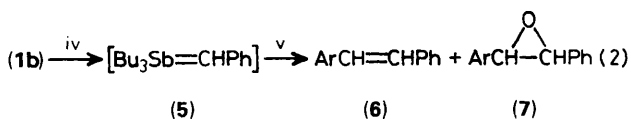
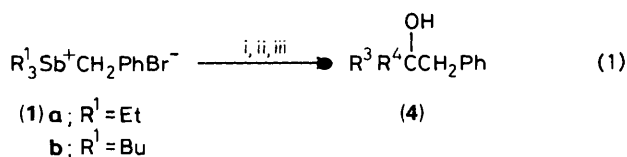
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Reactions of carbonyl compounds with benzyltrialkylstibonium bromide mediated by alkyl-lithium gave homobenzylic alcohols, while mediated by lithium di-isopropylamide (LDA) gave a mixture of an alkene and an epoxide

Few reports have appeared in the literature concerning the application of organoantimony in organic synthesis.¹ Among

† This paper is the 77th report on the studies of the application of organo compounds of Groups XV and XVI in organic synthesis.

the pathways reported for stibonium salts, Henry and Wittig claimed that the triphenylstibonium methyllide, prepared from Ph_3SbMeI with PhLi , reacted with benzophenone to form Ph_2CHCHO .² However, Doleshall *et al.* later reported a quite different result, indicating that the reaction of Ph_3SbMeX (X



Reagents and conditions: i, R²Li; ii, R³COR⁴; iii, H₂O; iv, LDA, tetrahydrofuran (THF), -78°C; v, ArCHO.

Table 1. Synthesis of homobenzylic alcohols.

| Entry | R ³ R ⁴ C=O | RLi | Yield ^a /% |
|-------|---|--------------------|-----------------------|
| 1 | PhCHO | Bu ⁿ Li | 92 |
| | | Bu ^t Li | 90 |
| | | PhLi | 90 |
| | | Bu ⁿ Li | 92 ^b |
| 2 | <i>p</i> -ClC ₆ H ₄ CHO | Bu ⁿ Li | 94 |
| 3 | PhCH=CHCHO | Bu ^t Li | 77 |
| 4 | <i>p</i> -MeC ₆ H ₄ CHO | PhLi | 82 |
| 5 | C ₆ H ₄ NCHO | PhLi | 86 |
| 6 | CH ₂ (CH ₂) ₄ C=O | Bu ⁿ Li | 35 |
| 7 | <i>p</i> -MeOC ₆ H ₄ CHO | Bu ⁿ Li | 74 |

^a Isolated yields. ^b (1a) was used. In other entries (1b) was used.

Table 2. Synthesis of (6) and (7).

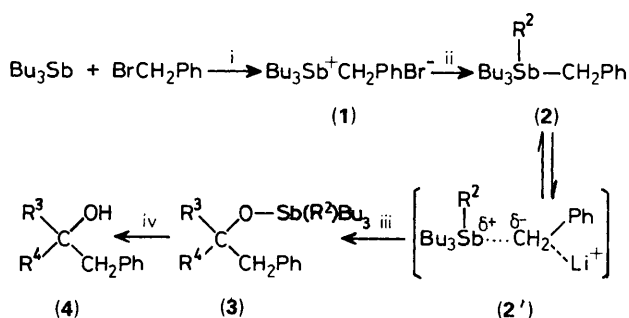
| Entry | Aldehyde | Yields ^a /% | |
|-------|---|------------------------|-----|
| | | (6) | (7) |
| 1 | <i>p</i> -ClC ₆ H ₄ CHO | 60 | 25 |
| 2 | PhCHO | 56 | 21 |
| 3 | <i>p</i> -MeC ₆ H ₄ CHO | 53 | 23 |

^a Isolated yields. The (*E*): (*Z*) ratios of the products have not been determined.

= I or BF₄) with PhLi followed by treating with benzophenone gave rise to Ph₄SbMe and the benzophenone remained unchanged.³ On the other hand, Wittig and Laib reported that Me₂Sb(CH₂Ph)₂Br reacted with PhLi affording Me₂SbCH(CH₂Ph)Ph, a product proposed from the rearrangement of stibonium ylide.⁴

We report another pathway for these compounds: a quaternary stibonium salt, benzyltributylstibonium bromide, after being treated with alkyl or phenyl lithium, reacted with carbonyl compounds to give alcohols (equation 1), instead of alkenes⁵ or epoxides,⁶ the products expected by analogy with the reactions of other heteroatom ylides. However, when (1b) was treated with lithium di-isopropylamide (LDA) and then allowed to react with aromatic aldehydes, we did obtain a mixture of an alkene and an epoxide (equation 2).

Benzyltrialkylstibonium bromide (1) was readily accessible by mixing a trialkyl stibine with benzyl bromide at room temperature. When Et₃Sb and Bu₃Sb were used, we isolated pure solids of Et₃Sb(CH₂Ph)Br (1a) and Bu₃Sb(CH₂Ph)Br (1b), respectively; confirmed by microanalyses, ¹H NMR and



Scheme 1. Reagents and conditions: i, room temp.; ii, R²Li; iii, R³COR⁴; iv, H₂O.

IR spectra. In a typical procedure, unpurified (1b) (2.2 mmol) was dissolved in THF and treated with an alkyl lithium or phenyl lithium (2.2 mmol in hexane) at -78°C. After half an hour, aldehyde (2 mmol) was added and the solution was allowed to reach room temperature with continuous stirring. After the usual work-up, silica gel chromatography gave the homobenzylic alcohols (4) in good yields. When RLi or PhLi was used, neither benzophenone nor acetophenone reacted under the same conditions. The results are depicted in Table 1.

Although some quaternary stibonium salts with an electron-withdrawing substituent condensed directly with carbonyl compounds when they were heated,⁷ the benzyltrialkylstibonium bromide did not react with carbonyl compounds in the absence of alkyl or phenyl lithium, even up to 150°C. This RLi promoted condensation of benzyltrialkylstibonium bromides with carbonyl compounds is novel. Various lithium reagents such as BuⁿLi, Bu^tLi, and PhLi could promote the reaction effectively. Instead of formation of a stibonium ylide, as in the case of phosphonium⁵ or arsonium⁶ analogues, a pentaorganostiborane (2) may be formed,⁸ as in the case of Ph₃SbMeX.³ Due to the weakness of Sb-C bond which was polarized in the presence of Li⁺, (2) underwent nucleophilic addition to carbonyl compounds as shown in Scheme 1. When LDA was used as a base, a quite different result was obtained, as shown in equation (2) and Table 2. Other quaternary stibonium salts such as allyltributylstibonium bromide, (3-ethoxycarbonyl-2-propenyl)tributylstibonium tetraphenylborate, etc., have the same character.

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