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BARBIER-GRIGNARD-TYPE ALLYLATION OF ALDEHYDES WITH METALLIC ANTIMONY

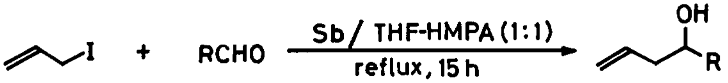
Yasuo BUTSUGAN,* Hirokazu ITO, and Shuki ARAKI
Department of Applied Chemistry, Nagoya Institute of
Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan

Abstract. Metallic-antimony-induced allylation of aldehydes by allylic halides and phosphates gave high yields of the corresponding homoallylic alcohols, regioselectively. α,β-Unsaturated aldehydes afforded only 1,2-addition products.

There has been increasing interest in the use of heteroatom elements in synthetic organic chemistry. However, relatively little attention has been paid for the synthetic utility of organoantimony compounds and metallic antimony itself.$^{1)}$ Here we describe the first example of Barbier-Grignard-type allylation of aldehydes using metallic antimony, which gives high yields of the corresponding homoallylic alcohols in a regio-specific manner.$^{2)}$

Refluxing a mixture of allyl iodide (2.4 mmol), benzaldehyde (2.0 mmol), and antimony powder (2.4 mmol) in THF-HMPA (1:1, 4 ml) for 15 h under argon gave 1-phenyl-3-buten-1-ol in 77% yield. Same reaction in THF (reflux) or in DMF (80 °C) gave lower yields (36 and 42%, respectively) of the product. Table 1 summarizes the results for other aromatic and aliphatic aldehydes. α,β-Unsaturated aldehydes afforded 1,2-addition products selectively.

Table 1. Sb-induced allylation of aldehydes$^{a)}$



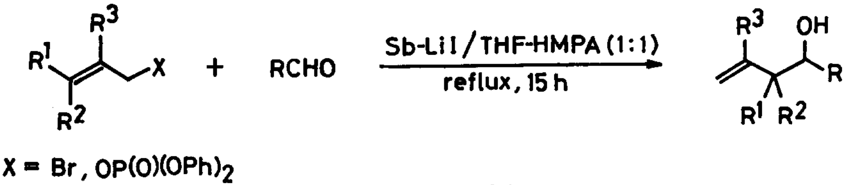
Aldehyde	Yield/%$^{b)}$
PhCHO	77
p-MeOC$_6$H$_4$CHO	59
p-ClC$_6$H$_4$CHO	100
Me(CH$_2$)$_6$CHO	80
	91
	55

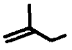
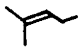
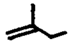
a) Allyl iodide : aldehyde : Sb = 1.2 : 1 : 1.2

b) Isolated yield; satisfactory spectral data (^{1}H-NMR, IR, and MS) were obtained for all the products.

Allylic bromides and phosphates are less reactive than allylic iodides, consequently giving poor yields of the coupling products (Table 2). However, this disadvantage could be overcome by the addition of lithium iodide. Thus,

Table 2. Sb-induced allylation with allylic bromides and phosphates in the presence of lithium iodide[a)]



Allylic compd	Aldehyde	Yield/%[b)]
 Br	$Me(CH_2)_6CHO$	84 (45)
"	$p\text{-}MeOC_6H_4CHO$	(44)
 Br	$Me(CH_2)_6CHO$	(32)
 Br	PhCHO	(27)[c)]
 Br	$Me(CH_2)_6CHO$	(46)
Ph  Br	"	(65)
 OP[d)]	"	83 (0)
"	PhCHO	93
 OP[d)]	"	76[e)]
 OP[d)]	$Me(CH_2)_6CHO$	86

a) Allylic compound : aldehyde : Sb : LiI = 1.2 : 1 : 1.2 : 1.2.

b) Isolated yield; the figures in parentheses indicate the yields in the absence of LiI.

c) Erythro : threo = 67 : 33.

d) OP = $OP(O)(OPh)_2$

e) Erythro : threo = 65 : 35.

as shown in Table 2, high yields of the adducts were attained when the reactions were carried out in the presence of one equivalent of lithium iodide.

The present antimony-induced allylation is highly regio-specific; giving the products coupled only at the γ-position of the allylic system. Furthermore, the reaction is chemoselective; ketones reacted very sluggishly (2-octanone, for example, reacted with allyl iodide to give only 17% of the adduct after 90 h's reflux) and ester and cyano groups remained unaffected.

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