CHEMISTRY LETTERS, pp. 1527-1528, 1981. © The Chemical Society of Japan 1981

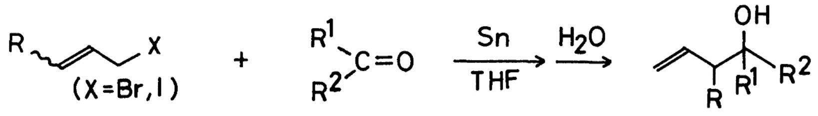
AN EFFICIENT SYNTHESIS OF HOMOALLYL ALCOHOLS BY THE REACTION OF ALLYL HALIDES WITH CARBONYL COMPOUNDS IN THE PRESENCE OF METALLIC TIN

Teruaki MUKAIYAMA and Taira HARADA
Department of Chemistry, Faculty of Science,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

In the presence of metallic tin, allyl halides were found to react smoothly with carbonyl compounds under mild conditions to give the corresponding homoallyl alcohols in good yields.

Recently, much attention has been focussed on the stereoselective allylation of carbonyl compound since the β-alkylalkanol unit thus formed is characteristic unit of numerous macrolides and polyether antibiotics.1) In a series of our studies on the C-C bond forming reaction utilizing stannous halide, we have already reported that allyltin dihaloiodide, formed through oxidative addition of allyl iodide to stannous halide, reacts with carbonyl compounds to give the corresponding homoallyl alcohols in high yields, however, the reaction is limited only to allyl iodides as allyl components.2)

In continuation of these studies, we now wish to report that, by the employment of metallic tin, not only allyl iodide but allyl bromide 1 reacts with carbonyl compounds 2 under mild conditions to give the corresponding homoallyl alcohols 3 in good yields. The overall scheme is shown in next equation.



1 2 3

Oxidative metallations of organic halide with metallic tin were reported in the literature indicating that the metallations were generally carried out at a high temperature in the presence of a catalyst.3) However, the organotin compounds thus formed were not utilized in C-C bond forming reaction. Consequently, the reaction outlined in the above equation does constitute the first example of the Grignard type reaction just using metallic tin.

Now it was found that (i) a wide variety of carbonyl compounds reacted smoothly to afford the corresponding homoallyl alcohols in good yields, (ii) the reaction was carried out simply by stirring a mixture of allyl halide, carbonyl compound and metallic tin in THF under essentially neutral conditions, (iii) the Wurtz type coupling product was not formed, and (iv) both allyl iodide and allyl bromide could be used as allylating agents.

The following experimental procedure is typical. A suspension of metallic tin[4] (131 mg, 1.1 mmol), allyl iodide (168 mg, 1.0 mmol) and benzaldehyde (85 mg, 0.8 mmol) in 3 ml of THF was stirred for 0.5 hr at room temperature. The reaction was quenched by the addition of water and the mixture was concentrated under reduced pressure in order to remove most of THF, and the organic materials were extracted with ether. The ethereal layer was sequentially washed with water and sat. NaCl aq, and dried over $MgSO_4$. 1-Phenyl-3-buten-1-ol (97 mg, 82% yield) was isolated by preparative TLC (silica gel). All products were characterized by ir and nmr spectra. The results are listed in Table 1.

Table 1 Reaction of Allyl Halides with Carbonyl Compounds in the Presence of Metallic Tin in THF at Room Temperature

Allyl Halide	Carbonyl Compound	Time(hr)	Yield of 3(%)[a]
$CH_2=CHCH_2I$	PhCHO	0.5	82
$CH_2=CHCH_2I$	$PhCH_2CH_2CHO$	0.5	87
$CH_2=CHCH_2I$	PhCH=CHCHO	0.5	79
$CH_2=CHCH_2I$	$p\text{-}ClC_6H_4CHO$	0.5	88
$CH_2=CHCH_2I$	PhCH(Me)CHO	0.5	76
$CH_2=CHCH_2I$	$PhCH_2CH_2COCH_3$	overnight	50[b]
$CH_2=CHCH_2Br$	PhCHO	overnight	82
$CH_3CH=CHCH_2Br$	PhCHO	overnight	76[c]

a) Yields were based on carbonyl compounds. All compounds gave satisfactory spectral date (NMR and IR). b) 30% of 4-phenyl-2-butanone was recovered. c) Threo: erythro ratio (59:41) of 2-methyl-1-phenyl-3-buten-1-ol was evaluated from NMR spectrum.

Although the reaction mechanism is not yet clear, we assumed that diallyltin dihalide is initially formed through the oxidative addition of two equivalents of allyl halide to a metallic tin and then the diallyltin dihalide reacts with carbonyl compounds with concomitant rearrangement in the allylic part. Actually, when the diallyltin dibromide, prepared separately by the method of K. Sisido et. al[5], was allowed to react with carbonyl compounds, the corresponding homoallyl alcohols were obtained in good yields (see Table 2).

Table 2 Reaction of Diallyltin Dibromide with Carbonyl Compounds in THF[a]

Carbonyl Compound	Time,	Temp(°)	Yield of 3(%)
PhCHO	10 min	-78	84
$PhCH_2CH_2CHO$	10 min	-78	88
PhCH=CHCHO	5 min	-78	87
PhCH(Me)CHO	5 min	-78	89
$PhCH_2CH_2COCH_3$	overnight	r.t.	75

a) All reactions were carried out with 0.5 mmol of diallyltin dibromide and 1.0 mmol of carbonyl compound in 3 ml of THF.

References
1) S. Masamune, G. S. Bates and J. W. Corcoran, Angew. Chem., Int. Ed. Engl., 16, 585 (1977). 2) T. Mukaiyama, T. Harada and S. Shoda, Chem. Lett., 1980, 1507.
3) For example, see K. Sisido, Y. Takeda, and Z. Kinugawa, J. Am. Chem. Soc., 83, 538 (1961). 4) Commercially available tin powder was used after treatment as described in ref. 3. 5) K. Sisido and Y. Takeda, J. Org. Chem., 26, 2301 (1961).

(Received August 26, 1981)