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AN EFFICIENT METHOD FOR THE PREPARATION OF HOMOALLYLIC ALCOHOL DERIVATIVES BY THE REACTION OF ALLYL IODIDE WITH CARBONYL COMPOUNDS IN THE PRESENCE OF STANNOUS HALIDE

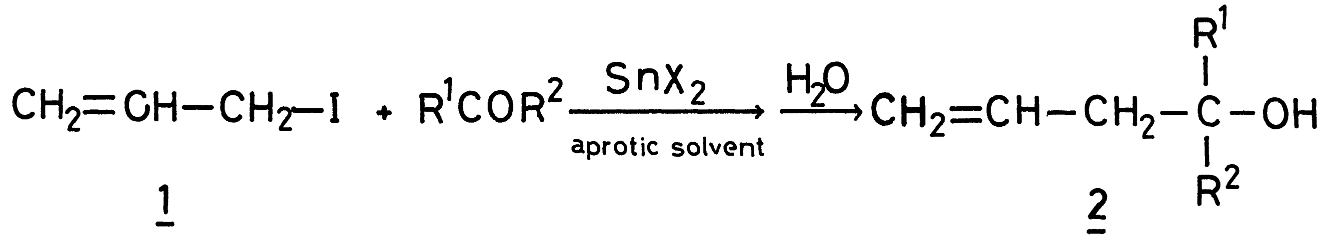
Teruaki MUKAIYAMA, Taira HARADA, and Shin-ichiro SHODA
Department of Chemistry, Faculty of Science
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

Allyl iodide reacts in situ under mild conditions with stannous halide to form allyltin dihaloiodide, which in turn reacts with carbonyl compounds in an aprotic solvent to give the corresponding homoallylic alcohol derivatives in good yields.

The addition of allylorganometallics to carbonyl compounds is one of the most important methods for the formation of homoallylic alcohol derivatives.1) In general, the formation of an allylic Grignard reagent, a typical allylorganometallic, is carried out by use of large excess of magnesium metal and by keeping the concentration of unreacted halide very low in order to avoid an undesired coupling reaction of the reagent with unreacted allyl halide.2)

On the other hand, Lewis acid mediated and non-catalyzed insertion reaction of carbonyl group into the Sn-C bond of allyltin compounds giving homoallylic alcohol derivatives have been of interest, but the former of these methods suffers the disadvantage in that an excess of Lewis acid, such as $BF_3 \cdot OEt_2$, is required.3) The latter is limited to a polarized carbonyl attached to electronwithdrawing group4) or required high reaction temperature.5)

In the course of our studies on the formation of C-C bond utilizing stannous halide, we found that carbonyl compounds in general, and aldehydes in particular are subjected to allylic attack by allyltin dihaloiodide, formed in situ from allyl iodide 1 and the stannous halide6), to give homoallylic alcohol derivatives 2 in good yields under mild conditions without using additives as Lewis acid.



$$CH_2{=}CH{-}CH_2{-}I \;+\; R^1COR^2 \xrightarrow[\text{aprotic solvent}]{SnX_2} \xrightarrow{H_2O} CH_2{=}CH{-}CH_2{-}\overset{R^1}{\underset{R^2}{C}}{-}OH$$

$\underline{1}$ $\underline{2}$

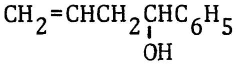
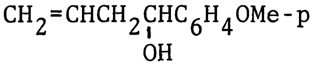
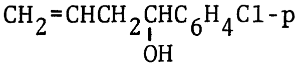
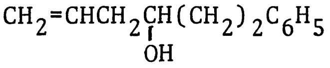
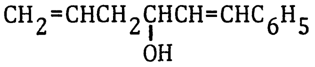
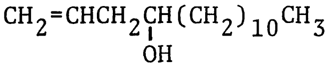
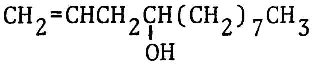
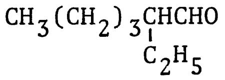
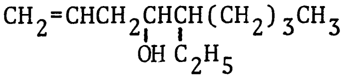
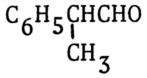
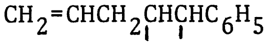
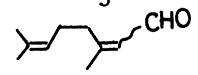
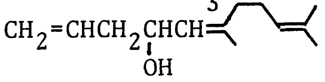
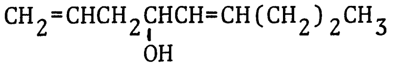
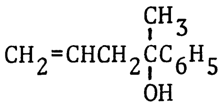
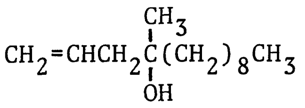
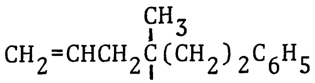
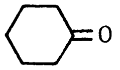
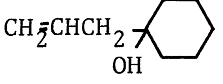
When our work is just in progress, G. Tagliavini et. al., 7) have reported the addition of allyltin dichlorobromide, formed by reaction of allyl bromide and stannous chloride, toward carbonyl compounds with view to obtaining the physical and chemical properties of allyltin dichlorobromide and allylbutyltin halides. They obtained a heavy brown slush by the reaction of allyltin dichlorobromide with benzaldehyde, whilst 30% yield of allyldimethylcarbinol with acetone.

The present work is independently undertaken to develop an efficient method for the preparation of homoallylic alcohol derivatives by the reaction of allyl iodide with carbonyl compounds in the presence of stannous halide utilizing the reducing property of divalent tin. Expectedly, it was made clear that (1) a wide variety of aliphatic and aromatic carbonyl compounds can enter the reaction smoothly without using additives as Lewis acid to afford the corresponding homoallylic alcohols in good yield, (2) the reaction is carried out simply by stirring a mixture of allyl iodide, carbonyl compound and stannous halide in an aprotic solvent under essentially neutral conditions and (3) the Wurtz type coupling products derived from the allyl iodide were not formed.

The following experimental procedure is typical. A suspension of stannous fluoride8) (182 mg, 1.1 mmol), allyl iodide $\underline{1}$ (168 mg, 1.0 mmol) and benzaldehyde (85 mg, 0.8 mmol) in 3 ml of 1,3-Dimethyl-2-imidazolidinone9) (=DMI) was stirred for 1 hr at room temperature. Water was added to the reaction mixture which was subsequently extracted with ether. The organic layer was washed with water, dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The residue was subjected to preparative TLC(silica gel) yielding allylphenylcarbinol (104 mg) in 88% yield. All products were characterized by ir and nmr spectra. The results are listed in Table. The yields listed in the Table are those after isolation and are based on the starting carbonyl compound.

At the present stage, the reaction mechanism is not yet made clear, however, allyltin dihaloiodide, formed through oxidative addition of allyl iodide to stannous halide, reacts with carbonyl compounds with concomitant rearrangement in the allylic part. Related work is in progress.

Table Reaction of Allyl Iodide with Carbonyl Compounds in the Presence of Stannous Fluoride in DMI

Carbonyl Compounds	Ratio a)	Conditions		Homoallylic Alcohols b)	(Yield, %)
		temp(°C),	time(hr)		
C_6H_5CHO	1.2	r.t	1.0	 $CH_2{=}CHCH_2\underset{OH}{C}HC_6H_5$	(88)
$p\text{-}MeOC_6H_4CHO$	1.2	r.t	0.3	 $CH_2{=}CHCH_2\underset{OH}{C}HC_6H_4OMe\text{-}p$	(93)
$p\text{-}ClC_6H_4CHO$	1.2	r.t	1.0	 $CH_2{=}CHCH_2\underset{OH}{C}HC_6H_4Cl\text{-}p$	(96)
$C_6H_5(CH_2)_2CHO$	1.2	r.t	0.5	 $CH_2{=}CHCH_2\underset{OH}{C}H(CH_2)_2C_6H_5$	(90)
$C_6H_5CH{=}CHCHO$	1.2	r.t	0.7	 $CH_2{=}CHCH_2\underset{OH}{C}HCH{=}CHC_6H_5$	(91)
$CH_3(CH_2)_{10}CHO$	1.2	r.t	0.5	 $CH_2{=}CHCH_2\underset{OH}{C}H(CH_2)_{10}CH_3$	(82)
$CH_3(CH_2)_7CHO$	1.2	r.t	0.5	 $CH_2{=}CHCH_2\underset{OH}{C}H(CH_2)_7CH_3$	(80)
 $CH_3(CH_2)_3\underset{C_2H_5}{C}HCHO$	1.2	r.t	0.9	 $CH_2{=}CHCH_2\underset{OH}{C}H\underset{C_2H_5}{C}H(CH_2)_3CH_3$	(82)
 $C_6H_5\underset{CH_3}{C}HCHO$	1.2	r.t	1.0	 $CH_2{=}CHCH_2\underset{OH}{C}H\underset{CH_3}{C}HC_6H_5$	(89)
	1.2	r.t	0.7		(91)
$CH_3(CH_2)_2CH{=}CHCHO$	1.2	r.t	0.6	 $CH_2{=}CHCH_2\underset{OH}{C}HCH{=}CH(CH_2)_2CH_3$	(73)
$C_6H_5COCH_3$	2.0	50	15	 $CH_2{=}CHCH_2\overset{CH_3}{\underset{OH}{C}}C_6H_5$	(50) (35) c)
$CH_3(CH_2)_8COCH_3$	2.0	50	14	 $CH_2{=}CHCH_2\overset{CH_3}{\underset{OH}{C}}(CH_2)_8CH_3$	(59) (24) c)
$C_6H_5(CH_2)_2COCH_3$	2.0	50	14	 $CH_2{=}CHCH_2\overset{CH_3}{\underset{OH}{C}}(CH_2)_2C_6H_5$	(61) (23) c)
	2.0	r.t	10		(73)

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a) Molar ratio of allyl iodide to carbonyl compound.

b) All the products gave satisfactory NMR and IR spectra.

c) Recovered ketone (%).

References and Notes

1) G. Courtois and L. Miginiac, J. Organomet. Chem., 69, 1 (1974).
2) W. G. Young, Chem. Rev., 56, 753 (1956).
3) H. Yatagai, Y. Yamamoto and K. Maruyama, J. Am. Chem. Soc., 102, 4548 (1980) and references cited therein.
4) E. W. Abel and R. H. Rowley, J. Organomet. Chem., 84, 199 (1975).
5) K. König and W. P. Neumann, Tetrahedron Lett., 1967, 495.
6) For an oxidative addition reaction of divalent tin to alkyl halide, see P. F. R. Ewings and P. G. Harrison, Inorg. Chim. Acta., 18, 165 (1976) and references cited therein.
7) A. Gambaro, V. Peruzzo, G. Plazzogna and G. Tagliavini, J. Organomet, Chem., 197, 45 (1980).
8) When stannous chloride and stannous bromide are employed in place of stannous fluoride in the reaction of allyl iodide with benzaldehyde, the yields of allylphenylcarbinol are 84% and 80%, respectively. Commercially available stannous fluoride (94% purity) was throughly dried before use by heating in vacuo at ca. 130°C for an hour.
9) Of several aprotic solvents screened, the highest yield was obtained when DMI was used.

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