Synthesis of homoallylic (but-3-enylic) alcohols from aldehydes with allylic chlorides, tin(II) chloride and potassium iodide in water

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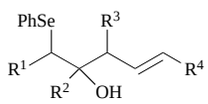
Homoallylic (but-3-enylic) alcohols have been prepared in good yields by reductive allylation of aldehydes in water with various allylic chlorides in the presence of tin(II) chloride and potassium iodide. The Barbier type reaction with prop-2-ynyl chloride is also achieved under the same conditions.

In a study concerning the reactivity of α-hydroxy-γ,δ-unsaturated phenyl selenides **1**, we were interested in the reductive allylations of α-phenylselanyl aldehydes and ketones with allylic organometallic reagents.



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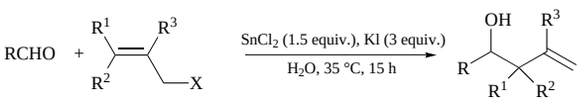
The use of allylic Grignard reagents led to partial deselenenylation of the substrates. We thus turned our attention to reactions using other allylmetals[1] and observed that hydroxy selenides **1** can be prepared through a Barbier type reaction involving an allyl halide and a metal (Zn, Sn or In) in water. We have also noted that the formation of homoallylic (but-3-enylic) alcohols was activated by addition of potassium or sodium iodide.[2] Reactions in water are of great interest and many papers have recently been devoted to the reductive allylation of carbonyl compounds in aqueous media.[3] Tin-mediated allylation can be improved by sonication.[4] With zinc, saturated aqueous NH_4Cl solution is generally used.[1] Whatever the solvent, the formation of homoallylic alcohols can be rationalized in terms of a cyclic six-membered ring transition state which explains the C–C bond formation from the γ-carbon of the allylic moiety. It has been shown that the reaction must occur in solution, and not through an electron transfer on the metal surface.[5]

Barbier-type allylation of aldehydes was also achieved in DMF in the presence of tin(II) chloride dihydrate, sodium iodide, allyl iodide[6] or various allylic chlorides.[7a] In THF, the formation of the organotin reagent can be catalysed by copper(I) halides or cyanide instead of sodium iodide.[7b] $SnCl_2$-Mediated allylation of aldehydes was carried out in water–solvent systems by heating without any further activation.[8] In a THF–H_2O mixture, γ-*syn*-allylation of aldehydes was observed using (*E*)-1-bromobut-2-ene in the presence of tin(II) iodide and tetrabutylammonium bromide or iodide.[9]

In this paper, we describe our results concerning the synthesis of homoallyl alcohols by reaction of aldehydes **2**–**9** with an allyltin reagent formed in water from tin(II) chloride, potassium iodide and allylic chloride **10** or bromide **10f**, according to Scheme 1.

The experimental conditions given in Scheme 1 have been optimized from the reaction between benzaldehyde and the allyltin reagent **19** (or **20**) (Scheme 2). The allyltin was formed from reaction between an allyl halide and SnX_2 (X = Cl or Br) in water containing potassium iodide at either 20 or 35 °C. Without KI, the reaction between benzaldehyde, $SnCl_2$ (1.5 equiv.) and allyl iodide (1.5 equiv.) at 35 °C was very slow (20% of allylation after 15 min, 60% after 30 min). The reaction



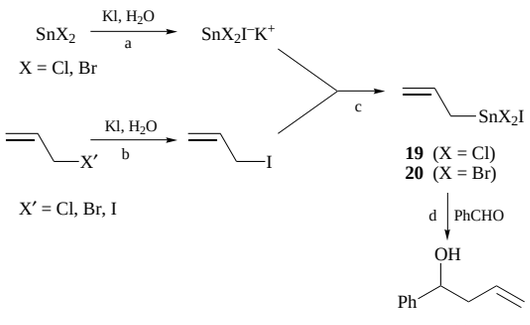
2, **11** R = Ph
3, **12** R = C_5H_{11}
4, **13** R = PrCHMe
5, **14** R = PhCHMe
6, **15** R = (*E*)-PrCH=CH
7, **16** R = Me_2C=CH-$(CH_2)_2$CHMeCH_2
8, **17** R = $MeCO(CH_2)_4$
9, **18** R = $PhCO(CH_2)_4$

For **10**–**18**
a $R^1 = R^2 = R^3 = H$
b $R^1 = R^2 = H$, $R^3 = Me$
c $R^1 = R^2 = H$, $R^3 = Cl$
d $R^1 = Me$, $R^2 = R^3 = H$
e $R^1 = Ph$, $R^2 = R^3 = H$
f $R^1 = COOMe$, $R^2 = R^3 = H$
g $R^1 = R^2 = Me$, $R^3 = H$

Scheme 1

reached completion only after 45 min, compared to 100% allylation observed with KI (1.5 equiv.) in less than 20 min. As already observed in an organic solvent,[7a] the presence of iodide ions speeds up the reaction. A kinetic study of the reaction has shown that 100% of allylation occurred after 2 h when allyl bromide (1.5 equiv.) and $SnCl_2$ (1.5 equiv.) were used in the presence of KI (1.5 equiv.) at 35 °C. With allyl chloride, 50% allylation was observed after 4 h under the same conditions. Adding $SnBr_2$ (1.5 equiv.) in the place of $SnCl_2$ (1.5 equiv.), gave 60% allylation with allyl chloride (1.5 equiv.) over the same time period. Using allyl bromide (1.5 equiv.), $SnCl_2$ (1.5 equiv.) and KI (1.5 equiv.) led to complete reaction at 35 °C within 2 h.

Scheme 2 summarizes the synthesis of the homoallylic alco-



Scheme 2

hol **11a**. In water, $SnCl_2$ reacts with KI to form a red–orange solution of $KSnCl_2I$.[10] The $SnCl_2$ is prone to partial hydrolysis, imparting an acidic pH (*ca.* 1) to the solution, but this is a minor reaction, as formation of $KSnCl_2I$ occurs rapidly. Sodium iodide can be used instead of the potassium salt. After introduction of allyl iodide, the solution faded in colour immediately and the allyltin reagent **19** was formed. The

Table 1 Synthesis of homoallylic alcohols **11**–**18** in water

Entry	Comp.	R	R^1	R^2	R^3	Yield (%)
1	**11a**	Ph	H	H	H	92
2	**11b**	Ph	H	H	Me	74
3	**11c**	Ph	H	H	Cl	82
4	**11d**[a]	Ph	Me	H	H	79[b]
5	**11e**[c]	Ph	Ph	H	H	80[d]
6	**11g**	Ph	Me	Me	H	75
7	**12a**	C_5H_{11}	H	H	H	90
8	**12b**	C_5H_{11}	H	H	Me	71
9	**12c**	C_5H_{11}	H	H	Cl	74
10	**12e**[e]	C_5H_{11}	Ph	H	H	57
11	**12f**[e]	C_5H_{11}	COOMe	H	H	45
12	**12g**	C_5H_{11}	Me	Me	H	68
13	**13a**[f]	PrCHMe	H	H	H	67
14	**14a**[g]	PhCHMe	H	H	H	78
15	**15a**	(*E*)-PrCH=CH	H	H	H	53[h]
16	**16a**[i]	$Me_2C{=}CH(CH_2)_2CHMeCH_2$	H	H	H	40
17	**17a**	$MeCO(CH_2)_4$	H	H	H	79
18	**18a**	$PhCO(CH_2)_4$	H	H	H	76

[a] *syn*:*anti* = 62:38. [b] 65:35 mixture of **11d** and **21** (*E*:*Z* = 43:57). [c] *syn*:*anti* = 1:99. [d] 57:43 mixture of **11e** and **22**. [e] The stereochemistry cannot be assigned. [f] 60:40 mixture of diastereoisomers not assigned. [g] *syn*:*anti* = 43:57. [h] Isolated from a 70:30 mixture of **15a** and **23**.

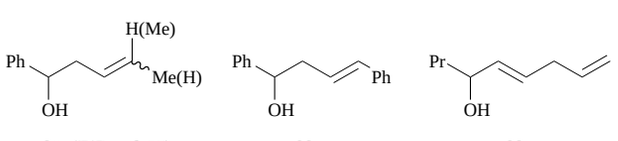
homoallyl alcohol **11a** was subsequently obtained in 95% yield after addition of benzaldehyde and stirring for a few minutes. At room temperature, we observed a slower allylation rate. The hydrolysis of the allyltin reagent is then an important limiting factor. When benzaldehyde was added 30 min after allyl iodide, the conversion reached only 78% at 35 °C.

As already shown in DMF, the reactivity of the allyl halide, in the presence of $SnCl_2$, lies in the order I > Br > Cl. The reaction occurred faster when $SnBr_2$ was used instead of $SnCl_2$. This result clearly indicates that the reactivity of such reagents in water decreases with the electronegativity of X. The reactive species could be the cation $CH_2{=}CHCH_2SnX_2^+$ (aq.) and not the molecular organotin $CH_2{=}CHCH_2SnX_2I$ as proposed for trialkyltin chlorides Bu_2RSnCl.[11]

For practical and financial reasons, it is preferable to use tin(II) chloride and allylic chlorides which, in addition, allow easier structural variations. The corresponding allylic iodides are formed in water by nucleophilic substitution when potassium iodide is present. This transformation (reaction b, Scheme 2) is actually the slower step of the process, as in organic solvents.[7a] We have checked that the allylation of benzaldehyde increases when the aqueous solution of allyl chloride and potassium iodide is stirred for four hours before introduction of tin(II) chloride and aldehyde. The reaction is also accelerated when the concentration of KI is increased. In these conditions, at least two equivalents of KI are needed to achieve the best yields.

Table 1 presents the results obtained for the reductive allylation of benzaldehyde and hexanal, with $SnCl_2$ (1.5 equiv.), KI (3 equiv.) and an allylic chloride (1.5 equiv.) in water at 35 °C, according to Scheme 1. We have also observed that addition of ammonium chloride accelerates the reductive allylation when substituted or functionalized allylic chlorides are used. The reaction was then extended to α-substituted aldehydes **4**, **5**, (*E*)-hex-2-enal **6**, citronellal **7** and δ-oxo aldehydes **8** and **9**.

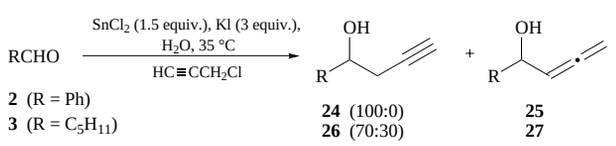
The reaction of benzaldehyde with but-2-enyl chloride gave a 65:35 mixture of 2-methyl-1-phenylbut-3-en-1-ol **11d** (*syn*:*anti* = 62:38)[12] and 1-phenylpent-3-en-1-ol **21** (*E*:*Z* = 43:57) (Table 1, entry 4). The acidic medium seems to be responsible for the formation of the homoallylic alcohol **21** which was not formed when an allylzinc reagent was used in the presence of NH_4Cl.[13] Alcohol **21** remains a minor product when the allylation is conducted with indium in water.[2] 1,4-Diphenylbut-3-en-1-ol **22** was formed as well as the expected 1,2-diphenylbut-3-en-1-ol **11e** (**11e**:**22** = 57:43) (entry 5).



21 (*E*/*Z* = 43:57) **22** **23**

With methyl 4-bromobut-2-enoate and hexanal (entry 11), a diastereoisomeric mixture of methyl 3-hydroxy-2-vinyloctanoate **12f** was isolated in fair yield. Good results were obtained with various aliphatic aldehydes and allyl chloride (entries 13, 14 and 15) except in the case of citronellal when a modest 40% yield was observed (entry 16). We have verified that the acidic conditions were responsible for the partial isomerisation of the homoallylic alcohol **15a** into nona-5,8-dien-4-ol **23** (**15**:**23** = 70:30) in the reaction of (*E*)-hex-2-enal **6** with allyl chloride (entry 15).

The reaction of an aldehyde with prop-2-ynyl iodide in an aprotic solvent in the presence of $SnCl_2$ has been studied.[14] Reaction of prop-2-ynyl bromide and benzaldehyde led to a mixture of prop-2-ynylic alcohol **24** and allenyl alcohol **25** (31:69) when the allylation was conducted in DMF with KI activation.[7b] In THF, with CuBr catalysis, a 96:4 mixture of **24**:**25** was obtained.[7b] By contrast, following the conditions described above for the allylation, $SnCl_2$, KI, prop-2-ynyl chloride and benzaldehyde in water gave selectively the prop-2-ynylic alcohol **24** in 71% yield while reaction with hexanal led to a 70:30 mixture of non-1-yn-4-ol **26** and allenyl alcohol **27** in 78% overall yield (Scheme 3).



2 (R = Ph)
3 (R = C_5H_{11})

24 (100:0)
26 (70:30)

25
27

Scheme 3

In conclusion, we have shown that the reductive allylation of aromatic or aliphatic aldehydes can be achieved through a Barbier-type reaction using an allylic chloride and $SnCl_2$ with KI activation in water. The allyltin reagents are stable enough to provide the homoallylic alcohols **11**–**18** in good yields. The reaction can be applied to aliphatic aldehydes, conjugated enals and keto aldehydes. A large variety of allylic chlorides can be used. Under the same conditions, prop-2-ynyl chloride and benzaldehyde gave 1-phenylbut-3-yn-1-ol **24**. With hexanal a mixture of the prop-2-ynylic and allenic alcohols **26** and **27** was obtained.

Experimental

Nuclear magnetic resonance spectra were recorded on a Bruker AC 200 spectrometer. Chemical shifts are expressed in parts per million (ppm) downfield of tetramethylsilane (^{1}H spectra) and

referenced to the central peak of the deuteriated chloroform triplet (^{13}C spectra). *J* Values are given in Hz. The IR spectra were recorded on a Perkin Elmer FTIR 1600 and the data obtained from thin films. Microanalyses were carried out on a Carlo-Erba 1106 apparatus. The chromatographic separations were carried out on Acros Silica gel (0.200–0.500 mm). Solvents were purified prior to use and light petroleum refers to the fraction with bp 40–60 °C. All the allylic chlorides are commercial compounds.

Preparation of methyl 4-bromobut-2-enoate 10f[15]

A solution of methyl crotonate (1.0 g, 10 mmol) and *N*-bromosuccinimide (1.78 g, 10 mmol) in CCl_4 (14 ml), containing some crystals of benzoyl peroxide, was heated at reflux for 5 h. After cooling, the reaction mixture was filtered. The filtrate was dried, evaporated and the oily residue was distilled under reduced pressure to give the title compound (80%), bp 80 °C/20 mmHg.

Preparation of 6-oxoheptanal 8[16]

According to the literature method,[16] 1-methylcyclohexene (1.92 g, 20 mmol) dissolved in CH_2Cl_2 (75 ml) was treated with ozone at −78 °C with stirring in the presence of sodium hydrogen carbonate (2 g). After the appearance of a blue colour, a stream of nitrogen was introduced during 10 min and dimethyl sulfide (15 ml) was added at −78 °C. The stirring was continued for 3 h at room temperature and the organic solution was washed with water (4 × 100 ml), dried and evaporated. The aldehyde **8** was purified by distillation, bp 42 °C/0.01 mmHg, 42% yield; δ_H(200 MHz; $CDCl_3$) 1.40–1.65 (4H, m, 3-H, 4-H), 2.09 (3H, s, 7-H), 2.30–2.50 (4H, m, 2-H, 5-H), 9.71 (1H, t, *J* 1.7, 1-H).

Preparation of 6-oxo-6-phenylhexanal 9[17]

This aldehyde was prepared from 1-phenylcyclohexene according to the same procedure, bp 100 °C/0.05 mmHg, mp 33 °C, 48% yield; δ_H(200 MHz; $CDCl_3$) 1.60–1.80 (4H, m, 3-H, 4-H), 2.45 (2H, dt, *J* 1.6, 6.3, 2-H), 2.96 (2H, t, *J* 6.8, 5-H), 7.35–7.55 (3H, m, Ph), 7.9–8.0 (2H, m, Ph), 9.73 (1H, t, *J* 1.6, 1-H); δ_C(200 MHz; $CDCl_3$) 21.4, 23.3, 37.8, 43.4, 127.7, 128.3, 132.7, 136.7, 199.4, 202.0; ν_{max}/cm^{-1} 3062 (CH arom.), 2945 (CH aliph.), 1714 and 1678 (CO).

Preparation of homoallylic alcohols (general procedure)

The aldehyde (2 mmol) was added to water (10 ml) containing potassium iodide (1.0 g, 6 mmol), stannous chloride dihydrate (0.677 g, 3 mmol) and allyl chloride **10** (3 mmol). The mixture faded in colour and saturated aqueous ammonium chloride (5 ml) was added when the allylic chlorides **10b**–**10g** were used. The stirring was continued for 15 h at 35 °C. Extraction with CH_2Cl_2 (3 × 30 ml) gave an organic phase which was washed with water, dried and concentrated. The oily residue was chromatographed on silica gel. Traces of the aldehydic substrate were first removed by eluting with light petroleum–CH_2Cl_2 (95:5) and then pure but-3-enylic alcohol was obtained by eluting with a 60:40 mixture of the same solvents. The following compounds were prepared by this method.

1-Phenylbut-3-en-1-ol 11a.[12] Oil, 92% yield.

3-Methyl-1-phenylbut-3-en-1-ol 11b.[18] Oil, 74% yield.

3-Chloro-1-phenylbut-3-en-1-ol 11c.[19] Oil, 82% yield.

2-Methyl-1-phenylbut-3-en-1-ol 11d and 1-phenylpent-3-en-1-ol 21.[20] Obtained as a mixture (**11d**:**21** = 65:35), 79% yield.

1,2-Diphenylbut-3-en-1-ol 11e.[21] Oil, 71% yield (*syn*:*anti* = 1:99).

2,2-Dimethyl-1-phenylbut-3-en-1-ol 11g.[12] Oil, 75% yield.

Non-1-en-4-ol 12a.[22] Oil, 90% yield.

2-Methylnon-1-en-4-ol 12b.[23] Oil, 71% yield.

2-Chlorononon-1-en-4-ol 12c.[24] Oil, 74% yield.

3-Phenylnon-1-en-4-ol 12e. Compound **12e** was obtained in 57% yield as a mixture of diastereoisomers which could not be distinguished following purification by silica gel chromatography [light petroleum–CH_2Cl_2 (80:20) as eluent]; δ_H(200 MHz; $CDCl_3$) 0.91 (3H, t, *J* 6.5, 9-H), 1.15–1.60 (8H, m, 5-H, 6-H, 7-H, 8-H), 2.08 (1H, m, O*H*), 3.29 (1H, dd, *J* 7.5, 8.5, 3-H), 3.70–3.90 (1H, m, 4-H), 5.10–5.30 (2H, m, 1-H), 6.00–6.30 (1H, m, 2-H), 7.15–7.45 (5H, m, Ph); δ_C(200 MHz; $CDCl_3$) 13.8, 22.3, 25.1, 31.5, 34.2, 57.0, 73.7, 117.3, 126.3, 127.3, 128.3, 138.1, 141.5; ν_{max}/cm^{-1} 3431 (OH), 3027 (CH arom.), 2954 (CH aliph.), 1640 (CH=CH_2) (Found: C, 82.36; H, 10.28. Calc. for $C_{15}H_{22}O$: C, 82.52; H, 10.16%).

Methyl 3-hydroxy-2-vinyloctanoate 12f. Compound **12f** was obtained in 45% yield as a mixture of diastereoisomers which could not be distinguished following Kugelrohr distillation. δ_H(200 MHz; $CDCl_3$) 0.84 (3H, t, *J* 6.4, 8-H), 1.15–1.50 (8H, m, 4-H, 5-H, 6-H, 7-H), 2.61 (1H, m, O*H*), 3.00–3.10 (1H, m, 2-H), 3.68 (3H, s, C*H*$_3$), 3.80–3.95 (1H, m, 3-H), 5.15–5.29 (2H, m, C*H*$_2$=CH), 5.65–6.0 (1H, m, CH$_2$=C*H*); δ_C(200 MHz; $CDCl_3$) 13.9, 22.4, 25.1, 31.6, 33.9, 51.9, 55.6, 71.3, 120.2, 131.6, 173.7; ν_{max}/cm^{-1} 3469 (OH), 3062 (CH alkene), 2960 (CH aliph.), 1734 (CO) (Found: C, 65.81; H, 9.92. Calc. for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07%).

3,3-Dimethylnon-1-en-4-ol 12g.[25] Oil, 68% yield.

5-Methyloct-1-en-4-ol 13a.[26] Oil, 67% yield. 60:40 Mixture of diastereoisomers which have not been separated.

2-Phenylhex-5-en-3-ol 14a.[27] Oil, 78% yield.

Nona-1,5-dien-4-ol 15a.[28] Oil. Isolated in 53% yield after chromatographic separation from its regioisomer **23** on silica gel, eluting with a mixture of light petroleum–CH_2Cl_2 (50:50); δ_H(200 MHz; $CDCl_3$) 0.86 (3H, t, *J* 7.3, 9-H), 1.36 (2H, m, *J* 7.3, 8-H), 1.82 (1H, m, O*H*), 1.97 (2H, q, *J* 7.2, 7-H), 2.20–2.30 (2H, m, 3-H), 4.08 (1H, q, *J* 6.2, 4-H), 4.95–5.15 (2H, m, 1-H), 5.35–5.85 (3H m, 2-H, 5-H, 6-H).

Nona-5,8-dien-4-ol 23. Compound **23** was isolated as an impure oil containing small amounts of alcohol **15a**; δ_H(200 MHz; $CDCl_3$) 0.88 (3H, t, *J* 7.2, 1-H), 1.20–1.55 (4H, m, 2-H, 3-H), 1.60 (1H, m, O*H*), 2.75 (2H, dt, *J* 10, 6.4, 7-H), 4.06 (1H, m, 4-H), 4.95–5.05 (2H, m, 9-H), 5.40–5.50 (1H, m, 5-H), 5.55–5.65 (1H, m, 6-H), 5.70–5.85 (1H, m, 8-H).

6,10-Dimethylundeca-1,9-dien-4-ol 16a.[29] Oil, 40% yield (Kugelrohr distillation). 50:50 Mixture of diastereoisomers.

7-Hydroxydec-9-en-2-one 17a.[30] Oil, 79% yield.

6-Hydroxy-1-phenylnon-8-en-1-one 18a.[31] Oil, 71% yield.

1-Phenylbut-3-yn-1-ol 24.[32] This oily compound was prepared in 71% yield using benzaldehyde and prop-2-ynyl chloride according to the general procedure used for the synthesis of but-3-enylic alcohols; δ_H(200 MHz; $CDCl_3$) 2.05 (1H, t, *J* 2.6, 4-H), 2.59 (1H, d, *J* 2.7, O*H*), 2.63 (2H, dd, *J* 2.6, 6.3, 2-H), 4.83 (1H, dt, *J* 2.7, 6.3, 1-H), 7.20–7.45 (5H, m, Ph); δ_C(200 MHz; $CDCl_3$) 29.0, 70.7, 72.1, 125.6, 127.7, 128.2, 129.9, 142.3; ν_{max}/cm^{-1} 3620 (OH), 3330 (HC≡), 3080 (CH arom.), 2930 (CH aliph.).

Non-1-yn-4-ol 26[33] **and nona-1,2-dien-4-ol 27.**[34] The two alcohols **26** and **27** were obtained as a 70:30 mixture (78% yield). **26**: δ_H(200 MHz; $CDCl_3$) 0.83 (3H, t, *J* 6.5, 9-H), 1.15–1.55 (8H, m, 5-H, 6-H, 7-H, 8-H), 2.00 (1H, t, *J* 2.6, 1-H), 2.25 (1H, m, O*H*), 2.15–2.45 (2H, m, 3-H), 3.60–3.75 (1H, m, 4-H); **27**: δ_H(200 MHz; $CDCl_3$) 0.83 (3H, t, *J* 6.5, 9-H), 1.15–1.55 (8H, m, 5-H, 6-H, 7-H, 8-H), 2.25 (1H, m, O*H*), 4.05–4.15 (1H, m, 4-H), 4.78 (2H, m, 1-H), 5.15 (1H, q, *J* 6.7, 3-H).

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