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One-pot sequential deoximation and allylation reactions of aldoximes in aqueous solution

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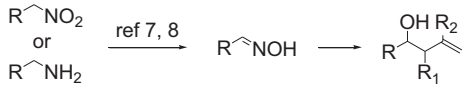
ABSTRACT

A simple procedure has been developed for conducting tin-mediated deoximation and allylation reactions of aldoximes in water to form homoallylic alcohols. Employing the new conditions, various homoallylic alcohols were produced in good to excellent yields.

1. Introduction

As a consequence of the fact that it is readily available and environmentally benign, water has received considerable attention recently as a solvent of choice for chemical reactions.[1] In particular, metal-mediated C–C bond forming reactions occurring in aqueous media have been intensively investigated.[2] Oximes are often used in organic synthesis as protected forms of carbonyl compounds[3] or as carbonyl derivatives for purification and characterization purposes.[4] Aqueous Barbier conditions have recently been devised for metal-mediated allylation reactions of oximes. However, owing to the poor electrophilicity of oximes, only activated oximes participate in metal-mediated C=N bond allylation reactions in aqueous media.[5,6] In light of these limitations, one-pot sequential deoximation and allylation reactions in water have not been reported.

Oximes can be prepared from noncarbonyl compounds, such as nitroalkanes[7] or primary amines.[8] In this regard, we have carried out studies aimed at developing sequential deoximation and allylation reactions of oximes in water. At the outset, we were cognizant of the fact that regeneration of carbonyl compounds from oximes classically involves the use of acid promoted hydrolysis or related processes.[9] In addition, in an earlier effort we demonstrated that enol ethers serve as good substrates in tin-mediated allylation reactions in water.[10] In the investigation described below, we have devised a procedure for carrying out aqueous, one-pot sequential deoximation and allylation reactions of oximes that efficiently generate homoallylic alcohols. This one-pot deoximation and allylation procedure that converts oximes to homoallylic alcohols can serve as an alternative method for the synthesis of homoallylic alcohols from nitroalkanes or primary amines via oximes (Scheme 1).



Scheme 1. An alternative method for the synthesis of homoallylic alcohols from nitroalkanes or primary amines via oximes.

2. Results and discussion

In a previous study,[10] we observed that formation of the allylstannane intermediate by reaction of allyl bromide with tin in water simultaneously creates sufficiently acidic conditions that enable hydrolysis of enol ethers. We believed that the acidic conditions that accompany generation of this intermediate in water would be sufficient to promote deoximation reactions of oximes. In order to probe this proposal, an investigation of tin-mediated one-pot deoximation and allylation reactions of benzaldoxime with allyl bromide was initiated. The results of this effort, in which various precursors of in situ generated allylstannane were used, are presented in Table 1. The observations show that formation of the

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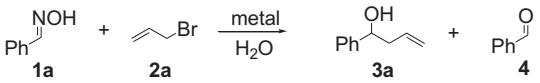
Table 1
Tin-mediated deoximation and allylation reactions of benzaldoxime in water[a]



Entry	Metal/additive (equiv)	Time (h)	**3a** Yield (%)	**1a**/**3a**/**4**
1	Sn (2.0)	26	62	15:85:0
2[b]	Sn (2.0)/HBr	24	95	0:100:0
3	$SnCl_2$ (2.0)	26	NA[c]	54:41:5
4	$SnCl_2$ (1.8)/KI (1.8)	20	94	0:100:0
5	$SnCl_2$ (2.0)/KI (2.0)/$CuCl_2$ (1.0)	27	NA[c]	13:87:0
6	$TiCl_3$ (1.0)	10	NA[c]	70:0:30
7	$SnCl_2$ (2.0)/$TiCl_3$ (1.0)	10	NA[c]	0:23:77
8	$SnCl_2$ (2.0)/KI (2.0)/$TiCl_3$ (1.0)	10	91	0:100:0
9	Sn (2.0)/$TiCl_3$ (1.0)	5	93	0:100:0

[a] Conditions: **1a** (1.0 mmol), allyl bromide **2a** (2.0 mmol), and indicated metal in water (2.0 mL) at rt.
[b] Conditions: **1a** (1.0 mmol), allyl bromide (2.0 mmol), tin powder (2.0 mmol), and HBr (0.2 mL) in water (1.8 mL) at rt.
[c] Not isolated.

allylstannane intermediate in water by reaction of allyl bromide with tin appears to promote the formation of conditions needed to deoximate benzaldoxime (Table 1, entry 1). The overall rate of this process was found to be accelerated when aqueous HBr was present in the aqueous solution (Table 1, entry 2).[11] In addition, the allylstannane intermediate generated from $SnCl_2$ was not as effective as that generated from tin (Table 1, entry 1 vs entry 3). Gratifyingly, this $SnCl_2$-mediated one-pot deoximation and allylation reactions of benzaldoxime was boosted with an additive KI (Table 1, entry 4).[10]

The reduction of oximes to form imines, using trivalent titanium reductant has been described.[12] Thus, we envisaged that imines formed in this manner would be susceptible to rapid hydrolysis to produce aldehydes, which would readily react with the allyltin intermediate (Table 1, entry 1 vs 9 and entry 3 vs 7). The intervention and effect of this reduction process are seen by comparing the rates of reactions promoted by using $SnCl_2$/KI/$TiCl_3$ versus Sn/$TiCl_3$ (Table 1, entry 8 vs 9). In addition, it has been reported that regeneration of carbonyl compounds from oximes can be induced by cupric chloride under hydrolytic conditions.[9] However, the observations (Table 1, entry 4 vs 5) show that the $SnCl_2$/KI-mediated deoximation and allylation reaction of benzaldoxime is retarded by the presence of cupric chloride. As can be seen by viewing the combined results displayed in Table 1, Sn/$TiCl_3$ serves as a superior reagent combination for carrying out one-pot sequential deoximation and allylation reactions of benzaldoxime in water.

By using the conditions described above, the aldoxime substrate scope of the deoximation and allylation reaction with allyl bromide was probed (Table 2).[11] As can be seen by viewing the results displayed in Table 2, the yields of these processes, starting with both aromatic (Table 2, entries 1–10) and long chain aliphatic (Table 2, entries 11 and 12) oximes, are good to excellent. Interestingly, the presence of a free phenol group, that is, present in **1i** and the presence of a free hydroxy group, that is, present in **1l** do not alter the efficiency of the reaction (Table 2, entries 9 and 12).

Deoximation and allylation reactions of benzaldoxime with other allylic halides were explored next (Table 3). These processes give rise to various homoallylic alcohols in good to excellent yields. Interestingly, lactone formation occurred when the allylic bromide **2b** was employed in the Sn/$TiCl_3$-mediated allylation reaction of aliphatic aldoxime (Table 3, entry 7). However, the corresponding homoallylic alcohol was formed exclusively in the Sn/$TiCl_3$-mediated deoximation and allylation reaction of benzaldoxime with **2b** (Table 3, entry 2). In addition, 2-halohomoallylic alcohols are generated in excellent yields in reactions of the halogenated allylic bromides **2c** and **2d** (Table 3, entries 3, 4, 8, and 9). Finally, the γ-addition product **3p** is formed predominantly with a high level of diastereoselectivity in the reaction of benzaldoxime with crotyl bromide (Table 3, entry 5). It is worth noting that a moderate level of diastereoselectivity in the γ-addition product **3p** prepared from the Sn-mediated allylation reaction of benzaldehyde and crotyl halide has been reported.[10c,13] Moreover, the γ-addition product **3p** is formed predominantly with a moderate level of diastereoselectivity in the Sn/$TiCl_3$-mediated allylation reaction of benzaldehyde with crotyl bromide (83% yield, *syn*/*anti*=1.48:1).

3. Conclusion

In summary, the study described above has led to a one-pot deoximation and allylation reaction of aldoximes in water. The reaction is simple, mild, and inexpensive. In addition, this process serves as an alternative method for the synthesis of homoallylic alcohols from aldoximes.

4. Experimental section

4.1. General

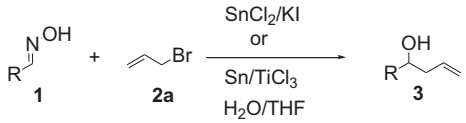
All commercially available chemicals were used without further purification. Oximes **1a**–**l** were prepared according to the reported procedures.[14] Iodoallylic bromides **2d** was prepared from reported procedure.[10] TLC analyses were run on a glass plate (Silica-gel 60 F_{254}) and were visualized using UV or a solution of phosphomolybdic acid in ethanol (5 wt %) or *p*-anisaldehyde stain. Flash chromatography was performed using silica-gel (70–230 mesh). ^1H and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer. Chemical shifts are reported relative to $CHCl_3$ [δ_H 7.24, δ_C (central line) 77.0]. Mass spectra and high-resolution mass spectra were recorded under electron spray interface (ESI) conditions.

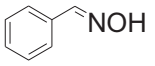
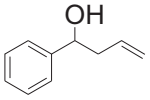
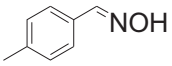
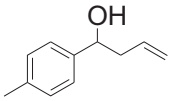
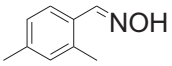
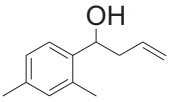
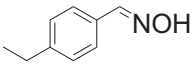
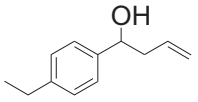
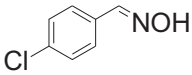
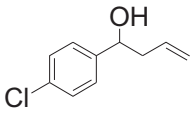
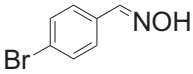
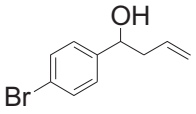
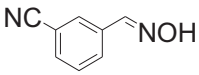
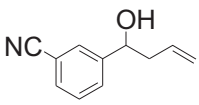
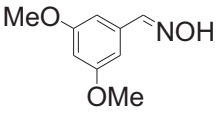
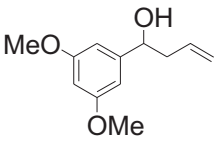
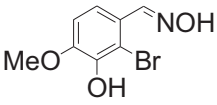
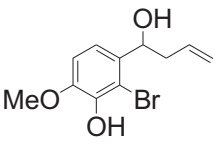
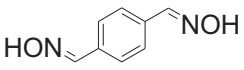
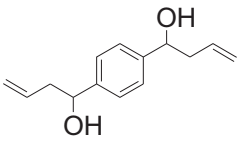
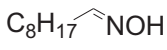
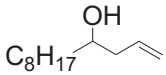
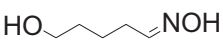
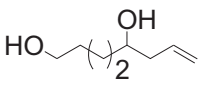
4.2. Synthesis

4.2.1. General procedure for allylation reactions of aldoximes in an aqueous solution to form homoallylic alcohols. $SnCl_2$/KI condition: A mixture of aldoxime **1** (1.0 mmol), an allylating agent (2.0 mmol), tin chloride dihydrate (1.8 mmol), and potassium iodide (1.8 mmol) in THF/H_2O (1/3, 2 mL) was stirred at ambient temperature. Reaction was monitored by TLC until no starting material was observed. The mixture was extracted with Et_2O or CH_2Cl_2 (3×5 mL). The combined organic layers were washed with 5% $Na_2S_2O_{3(aq)}$ (10 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was subjected to silica-gel chromatography to furnish the pure product **2** (Et_2O/hexanes (1:5)). *Sn/TiCl₃ condition*: A mixture of aldoxime **1** (1.0 mmol), an allylating agent (2.0 mmol), tin (1.5 mmol), and $TiCl_3$ (1.0 mmol, 20% in 3% hydrochloric acid) in THF/H_2O (1/3, 2 mL) was stirred at ambient temperature. Reaction was monitored by TLC until no starting material was observed. The mixture was extracted with Et_2O or CH_2Cl_2 (3×5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was subjected to silica-gel chromatography to furnish the pure product **2** (Et_2O/hexanes (1:5)).

*4.2.1.1. 1-Phenylbut-3-en-1-ol (**3a**).* Following the general procedure, the title compound was obtained (138 mg, 93%). Oil; TLC (Et_2O/hexanes (1:2)) R_f=0.35; ^1H NMR (300 MHz, $CDCl_3$) δ 2.05 (br s, 1H), 2.47–2.53 (m, 2H), 4.72 (dd, *J*=7.5, 5.4 Hz, 1H), 5.11–5.19 (m,

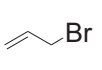
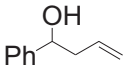
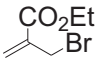
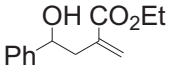
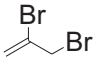
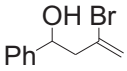
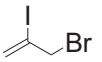
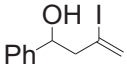
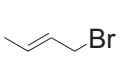
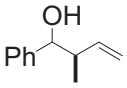
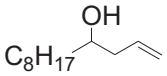
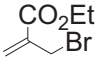
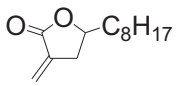
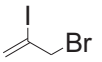
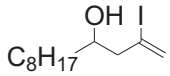
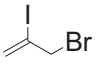
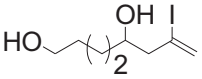
Table 2
Tin-mediated deoximation and allylation reactions of aldoximes[a]



Entry	Substrate		Product		Yield[a] (%)	Yield[b] (%)
1		**1a**		**3a**	94	93
2		**1b**		**3b**	97	NA[c]
3		**1c**		**3c**	95	NA[c]
4		**1d**		**3d**	92	NA[c]
5		**1e**		**3e**	96	94
6		**1f**		**3f**	94	93
7		**1g**		**3g**	86	88
8		**1h**		**3h**	96	91
9		**1i**		**3i**	66	92
10		**1j**		**3j**	80	83
11		**1k**		**3k**	81	91
12		**1l**		**3l**	NA[c]	91

[a] Conditions: oxime (1.0 mmol), allyl bromide (2.0 mmol), and $SnCl_2$ (1.8 mmol)/KI (1.8 mmol).
[b] Conditions: oxime (1.0 mmol), allyl bromide (2.0 mmol), and Sn (1.5 mmol)/$TiCl_3$ (1.0 mmol).
[c] Reaction was not performed.

Table 3
Tin-mediated deoximation and allylation reactions of aldoxime with various allylic bromides[a]

Entry	Substrate	Allylating agent	Product	Yield[a] (%)	Yield[b] (%)
1	**1a**	 **2a**	 **3a**	94	93
2	**1a**	 **2b**	 **3m**	80	95
3	**1a**	 **2c**	 **3n**	92	NA[c]
4	**1a**	 **2d**	 **3o**	91	90
5	**1a**	 **2e**	 **3p**	94 (3.7:1)[d]	88 (3.3:1)[d]
6	**1k**	**2a**	 **3k**	81	91
7	**1k**	 **2b**	 **3q**	NA[c]	82
8	**1k**	 **2d**	 **3r**	NA[c]	76
9	**1l**	 **2d**	 **3s**	NA[c]	81[e]

[a] Conditions: oxime (1.0 mmol), allylic bromide (2.0 mmol), and $SnCl_2$ (1.8 mmol)/KI (1.8 mmol) in water (2.0 mL) at rt.
[b] Conditions: oxime (1.0 mmol), allylic bromide (2.0 mmol), and Sn (2.0 mmol)/$TiCl_3$ (1.0 mmol) in water (2.0 mL) at rt.
[c] Reaction was not performed.
[d] Diastereomeric ratio=(*syn*/*anti*).
[e] The product was isolated as the corresponding acetate derivative.

2H), 5.70–5.84 (m, 1H), 7.25–7.35 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.8 (CH_2), 73.3 (CH), 118.5 (CH_2), 125.8 (CH ×2), 127.5 (CH), 128.4 (CH ×2), 134.4 (CH), 143.8 (C). These data are in agreement with those reported in the literature.[15]

*4.2.1.2. 1-p-Tolylbut-3-en-1-ol (**3b**).* Following the general procedure, the title compound was obtained (157 mg, 97%). Oil; TLC (Et_2O/hexanes (1:2)) R_f=0.30; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.03 (d, J=2.1 Hz, 1H), 2.33 (s, 3H), 2.50 (dd, J=6.9, 6.9 Hz, 2H), 4.69 (br t, J=6.9 Hz, 1H), 5.10–5.17 (m, 2H), 5.68–5.83 (m, 1H), 7.13–7.16 (d, J=8.1 Hz, 2H), 7.24 (d, J=8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0 (CH_3), 43.7 (CH_2), 73.1 (CH), 118.2 (CH_2), 125.7 (CH ×2), 129.1 (CH ×2), 134.6 (CH), 137.2 (C), 140.9 (C). These data are in agreement with those reported in the literature.[16]

*4.2.1.3. 1-(2,4-Dimethylphenyl)but-3-en-1-ol (**3c**).* Following the general procedure, the title compound was obtained (167 mg, 95%). Oil; TLC (Et_2O/hexanes (1:2)) R_f=0.45; IR (neat): 3377, 2925, 1632, 1446 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.10 (br s, 1H), 2.30 (s, 3H), 2.31 (s, 3H), 2.35–2.55 (m, 2H), 4.92 (q, J=4.8 Hz, 1H), 5.15–5.21 (m, 2H), 5.78–5.90 (m, 1H), 6.79 (m, 1H), 7.04 (d, J=7.8 Hz, 1H), 7.36 (d, J=7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.9 (CH_3), 20.9 (CH_3), 42.6 (CH_2), 69.5 (CH), 118.0 (CH_2), 125.1 (CH), 126.8 (CH), 131.0 (CH), 134.2 (C), 134.8 (CH), 136.7 (C), 138.9 (C); MS m/z (rel intensity) 176 (M^+, 1), 158 (11), 143 (22), 135 (100); HRMS $[M]^+$ for $C_{12}H_{16}O$: 176.1201, found 176.1194.

*4.2.1.4. 1-(4-Ethylphenyl)but-3-en-1-ol (**3d**).* Following the general procedure, the title compound was obtained (162 mg, 92%). Oil; TLC (Et_2O/hexanes (1:2)) R_f=0.38; IR (neat): 3387, 2968, 1435 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (t, J=7.8 Hz, 3H), 2.13 (d, J=3.0 Hz, 1H), 2.50 (dd, J=6.9, 6.9 Hz, 2H), 2.62 (q, J=7.8 Hz, 2H), 4.66–4.71 (m, 1H), 5.11–5.18 (m, 2H), 5.73–5.87 (m, 1H), 7.17 (d, J=8.1 Hz, 2H), 7.26 (d, J=8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.5 (CH_3), 28.5 (CH_2), 43.7 (CH_2), 73.2 (CH), 118.2 (CH_2), 125.8 (CH ×2), 127.8 (CH ×2), 134.6 (CH), 141.1 (C), 143.5 (C). These data are in agreement with those reported in the literature.[17]

*4.2.1.5. 1-(4-Chlorophenyl)but-3-en-1-ol (**3e**).* Following the general procedure, the title compound was obtained (172 mg, 94%). Oil; TLC (Et_2O/hexanes (1:2)) R_f=0.28; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.14 (d, J=2.7 Hz, 1H), 2.35–2.55 (m, 2H), 4.67–4.72 (m, 1H), 5.11–5.17 (m, 2H), 5.71–5.80 (m, 1H), 7.20–7.31 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.8 (CH_2), 72.5 (CH), 118.8 (CH_2), 127.2 (CH ×2), 128.5 (CH ×2), 133.1 (C), 133.9 (CH), 142.3 (C). These data are in agreement with those reported in the literature.[18]

*4.2.1.6. 1-(4-Bromophenyl)but-3-en-1-ol (**3f**).* Following the general procedure, the title compound was obtained (211 mg, 93%). Oil; TLC (Et_2O/hexanes (1:2)) R_f=0.28; IR (neat): 3327, 2910, 1489, 1412 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.09 (d, J=3.0 Hz, 1H), 2.41–2.51 (m, 2H), 4.66–4.71 (m, 1H), 5.11–5.18 (m, 2H), 5.69–5.83 (m, 1H), 7.20 (d, J=7.8 Hz, 2H), 7.45 (d, J=7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.8 (CH_2), 72.5 (CH), 118.9 (CH_2), 121.2 (C), 127.5 (CH ×2), 131.5 (CH ×2), 133.9 (CH), 142.8 (C). These data are in agreement with those reported in the literature.[18]

*4.2.1.7. 3-(1-Hydroxybut-3-enyl)benzonitrile (**3g**).* Following the general procedure, the title compound was obtained (152 mg, 88%). Oil; TLC (Et_2O/hexanes (1:2)) R_f=0.10; ^1H NMR (300 MHz, $CDCl_3$) δ 2.26 (d, J=2.7 Hz, 1H), 2.37–2.56 (m, 2H), 4.73–4.78 (m, 1H), 5.12–5.18 (m, 2H), 5.68–5.82 (m, 1H), 7.40–7.56 (m, 3H), 7.58 (d, J=1.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.8 (CH_2), 72.1 (CH), 112.4 (C), 118.8 (C), 119.5 (CH_2), 129.1 (CH), 129.4 (CH), 130.3 (CH), 131.1 (CH), 133.3 (CH), 145.3 (C). These data are in agreement with those reported in the literature.[19]

*4.2.1.8. 1-(3,5-Dimethoxyphenyl)but-3-en-1-ol (**3h**).* Following the general procedure, the title compound was obtained (190 mg, 91%). Oil; TLC (Et_2O/hexanes (1:2)) R_f=0.18; IR (neat): 3400, 3080, 2930, 1607 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.14 (d, J=2.7 Hz, 1H), 2.44–2.52 (m, 2H), 3.77 (s, 6H), 4.64 (t, J=7.2 Hz, 1H), 5.10–5.18 (m, 2H), 5.72–5.86 (m, 1H), 6.35 (d, J=2.4 Hz, 1H), 6.49 (d, J=2.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.6 (CH_2), 55.3 (CH_3 ×2), 73.3 (CH), 99.4 (CH), 103.7 (CH ×2), 118.3 (CH_2), 134.4 (CH), 146.5 (C), 160.8 (C ×2). These data are in agreement with those reported in the literature.[20]

*4.2.1.9. 2-Bromo-3-(1-hydroxybut-3-enyl)-6-methoxyphenol (**3i**).* Following the general procedure, the title compound was obtained (251 mg, 92%). Oil; TLC (Et_2O/hexanes (1:2)) R_f=0.18; IR (neat): 3456, 2937, 1609, 1488 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.28 (br s, 1H), 2.31–2.38 (m, 1H), 2.55–2.63 (m, 1H), 3.88 (s, 3H), 5.02–5.06 (m, 1H), 5.12–5.19 (m, 2H), 5.78–5.92 (m, 1H), 6.01 (br s, 1H), 6.83 (d, J=8.1 Hz, 1H), 7.04 (d, J=8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.1 (CH_2), 56.3 (CH_3), 71.5 (CH), 108.3 (C), 109.6 (CH), 117.6 (CH), 118.4 (CH_2), 134.4 (CH), 135.7 (C), 142.7 (C), 146.2 (C); MS m/z (rel intensity) 272 (M^+, 4), 257 (11), 255 (12), 231 (100); HRMS $[M]^+$ for $C_{11}H_{13}BrO_3$: 272.0048, found 272.0041.

*4.2.1.10. 1,1′-(1,4-Phenylene)dibut-3-en-1-ol (**3j**).* Following the general procedure, the title compound was obtained (181 mg, 83%). Oil; TLC (Et_2O/hexanes (1:2)) R_f=0.10; IR (neat): 3366, 2910, 1643, 1421 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.30 (br s, 2H), 2.44–2.49 (m, 4H), 4.68 (q, J=7.2 Hz, 2H), 5.09–5.15 (m, 4H), 5.69–5.83 (m, 2H), 7.29 (br s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.7 (CH_2 ×2), 73.0 (CH ×2), 118.3 (CH_2 ×2), 125.8 (CH ×4), 134.4 (CH ×2), 143.1 (C ×2). These data are in agreement with those reported in the literature.[21]

*4.2.1.11. Dodec-1-en-4-ol (**3k**).* Following the general procedure, the title compound was obtained (168 mg, 91%). Oil; TLC (Et_2O/hexanes (1:2)) R_f=0.38; ^1H NMR (300 MHz, $CDCl_3$) δ 0.85 (t, J=6.9 Hz, 3H), 1.15–1.50 (m, 14H), 1.70 (t, J=3.6 Hz, 1H), 2.05–2.15 (m, 1H), 2.22–2.30 (m, 1H), 3.61 (br s, 1H), 5.07–5.11 (m, 2H), 5.73–5.87 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0 (CH_3), 22.6 (CH_2), 25.6 (CH_2), 29.2 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 31.8 (CH_2), 36.8 (CH_2), 41.9 (CH_2), 70.7 (CH), 117.9 (CH_2), 134.9 (CH). These data are in agreement with those reported in the literature.[22]

*4.2.1.12. Oct-7-ene-1,5-diol (**3l**).* Following the general procedure, the title compound was obtained (131 mg, 91%). Oil; TLC (EtOAc/hexanes (1:2)) R_f=0.08; ^1H NMR (300 MHz, $CDCl_3$) δ 1.41–1.63 (m, 6H), 1.70–1.90 (m, 2H), 2.08–2.32 (m, 2H), 3.63 (t, J=6.0 Hz, 3H), 5.10 (d, J=12.6 Hz, 2H), 5.73–5.87 (m, 1H). These data are in agreement with those reported in the literature.[10]

*4.2.1.13. Ethyl 4-hydroxy-2-methylene-4-phenylbutanoate (**3m**).* Following the general procedure, the title compound was obtained (209 mg, 95%). Oil; TLC (Et_2O/hexanes (1:2)) R_f=0.20; ^1H NMR (300 MHz, $CDCl_3$) δ 1.29 (t, J=7.2 Hz, 3H), 2.61–2.80 (m, 3H), 4.19 (q, J=7.2 Hz, 2H), 4.86 (dd, J=8.4, 3.9 Hz, 1H), 5.70 (d, J=1.5 Hz, 1H), 6.21 (d, J=1.5 Hz, 1H), 7.24–7.36 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1 (CH_3), 42.5 (CH_2), 61.0 (CH_2), 73.1 (CH), 125.7 (CH ×2), 127.4 (CH), 128.1 (CH_2), 128.3 (CH ×2), 137.1 (C), 143.9 (C), 167.7 (C). These data are in agreement with those reported in the literature.[23]

*4.2.1.14. 3-Bromo-1-phenylbut-3-en-1-ol (**3n**).* Following the general procedure, the title compound was obtained (209 mg, 92%). Oil; TLC (Et_2O/hexanes (1:2)) R_f=0.30; IR (neat): 3389, 3040, 2914, 1628 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.33 (br s, 1H), 2.69–2.86 (m, 2H), 4.98–5.02 (m, 1H), 5.10 (d, J=1.8 Hz, 1H), 5.65 (d, J=1.8 Hz, 1H), 7.24–7.38 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 51.2 (CH_2), 71.5 (CH), 119.9 (CH_2), 125.7 (CH ×2), 127.8 (CH), 128.5 (CH ×2), 130.0 (C), 142.8 (C). These data are in agreement with those reported in the literature.[18]

*4.2.1.15. 3-Iodo-1-phenylbut-3-en-1-ol (**3o**).* Following the general procedure, the title compound was obtained (247 mg, 90%). Oil; TLC (Et_2O/hexanes (1:2)) R_f=0.48; IR (neat): 3378, 3031, 2899, 1615 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.22 (d, J=3.0 Hz, 1H), 2.73 (d, J=6.9 Hz, 2H), 4.92–4.97 (m, 1H), 5.82 (d, J=1.2 Hz, 1H), 6.12 (d, J=1.2 Hz, 1H), 7.24–7.38 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 54.7 (CH_2), 72.3 (CH), 106.9 (C), 125.9 (CH ×2), 127.8 (CH), 128.5 (CH ×2), 127.9 (CH_2), 142.6 (C); MS m/z (rel intensity) 274 (M^+, 2), 127 (7), 107 (100), 79 (62); HRMS $[M]^+$ for $C_{10}H_{11}IO$: 273.9855, found 273.9862.

*4.2.1.16. 2-Methyl-1-phenylbut-3-en-1-ol (**3p**, anti/syn: 1:3.7).* Following the general procedure, the title compound was obtained (152 mg, 94%). Oil; TLC (Et_2O/hexanes (1:2)) R_f=0.40; IR (neat): 3412, 2926, 1634, 1447 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.85 (d, J=6.9 Hz, 0.6H), 0.99 (d, J=6.9 Hz, 2.4H), 1.98 (d, J=3.3 Hz, 0.8H), 2.20 (d, J=3.3 Hz, 0.2H), 2.40–2.60 (m, 1H), 4.30–4.40 (m, 0.2H), 4.58–4.61 (m, 0.8H), 5.00–5.07 (m, 1.6H), 5.10–5.20 (m, 0.4H), 5.69–5.80 (m, 1H), 7.23–7.35 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 16.5, 44.6, 46.3, 77.4, 77.8, 115.5, 116.8, 126.5, 126.8, 127.3, 127.6, 128.0, 128.2, 140.3, 140.6, 152.5. These data are in agreement with those reported in the literature.[24]

*4.2.1.17. 3-Methylene-5-octyldihydrofuran-2(3H)-one (**3q**).* Following the general procedure, the title compound was obtained (172 mg, 82%). Oil; TLC (Et_2O/hexanes (1:2)) R_f=0.55; ^1H NMR (300 MHz, $CDCl_3$) δ 0.80 (t, J=6.0 Hz, 3H), 1.37–1.72 (m, 14H), 2.51–2.59 (m, 1H), 2.98–3.06 (m, 1H), 4.46–4.51 (m, 1H), 5.59 (d, J=2.4 Hz, 1H), 6.19 (d, J=2.4 Hz, 1H). These data are in agreement with those reported in the literature.[25]

*4.2.1.18. 2-Iodododec-1-en-4-ol (**3r**).* Following the general procedure, the title compound was obtained (220 mg, 71%). Oil; TLC (Et_2O/hexanes (1:2)) R_f=0.68; IR (neat): 2928, 2856, 1739, 1233 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.85 (t, J=6.6 Hz, 3H), 1.25–1.50 (m, 14H), 1.73 (br s, 1H), 2.36–2.56 (m, 2H), 3.75–3.86 (m, 1H), 5.81 (d, J=1.2 Hz, 1H), 6.13 (q, J=1.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1 (CH_3), 22.6 (CH_2), 25.6 (CH_2), 29.2 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 31.8 (CH_2), 36.1 (CH_2), 52.9 (CH_2), 69.8 (CH), 107.9 (C), 128.5 (CH_2); MS m/z (rel intensity) 310 (M^+, 1), 168 (34), 143 (48), 69 (100); HRMS $[M]^+$ for $C_{12}H_{23}IO$: 310.0794, found 310.0797.

*4.2.1.19. 7-Iodooct-7-ene-1,5-diyl diacetate (**3s**).* Following the general procedure, the crude diol was then treated with Ac_2O (2 mmol) and pyridine (2 mmol) in Et_2O (5 mL) at rt overnight to give the title compound (287 mg, 81%). An oil; TLC (EtOAc/hexanes (1:4)) R_f=0.47; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.28–1.39 (m, 2H), 1.52–1.65 (m, 4H), 1.99 (s, 6H), 2.53 (dd, J=14.7, 5.4 Hz, 1H), 2.66 (dd, J=14.7, 7.5 Hz, 1H), 4.00 (t, J=6.6 Hz, 2H), 5.03–5.11 (m, 1H), 5.74 (s, 1H), 6.04 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.9 (CH_3), 21.0 (CH_3), 21.5 (CH_2), 28.2 (CH_2), 32.8 (CH_2), 49.4 (CH_2), 64.0 (CH_2), 71.9 (CH), 104.9 (C), 128.3 (CH_2), 170.3 (C), 171.0 (C). These data are in agreement with those reported in the literature.[10]

Acknowledgements

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Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2012.01.074.

References and notes

1. (a) Li, C. J. *Chem. Rev.* **2005**, *105*, 3095; (b) Lindström, U. M. *Chem. Rev.* **2002**, *102*, 2751; (c) Chan, T. H.; Issac, B. M. *Pure Appl. Chem.* **1996**, *68*, 919; (d) Li, C. J. *Tetrahedron* **1996**, *52*, 5643; (e) Li, C. J.; Chan, T. H. *Organic Reactions in Aqueous Media*; John Wiley: New York, NY, 1997; (f) Paquette, L. A. In *Green Chemistry: Frontiers in Benign Chemical Synthesis and Processing*; Anastas, P., Williamson, T., Eds.; Oxford University: New York, NY, 1998.
2. Li, C. J. Metal-Mediated C–C Bond Formations in Aqueous Media In *Organic Reactions in Water Principles, Strategies and Applications*; Lindström, U. M., Ed.; Blackwell: Ames, IA, 2007.
3. Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 3rd ed.; John Wiley: New York, NY, 1999.
4. Shriner, R. L.; Fuson, R. C.; Curtin, D. Y.; Morrill, T. C. *The Systematic Identification of Organic Compounds*, 6th ed.; John Wiley: New York, NY, 1980.
5. Wolan, A.; Joachimczak, A.; Budny, M.; Kozakiewicz, A. *Tetrahedron Lett.* **2011**, *52*, 1195.
6. (a) Hanessian, S.; Yang, R.-Y. *Tetrahedron Lett.* **1996**, *37*, 5273; (b) Ritson, D. J.; Cox, R. J.; Berge, J. *Org. Biomol. Chem.* **2004**, *2*, 1921.
7. (a) Wang, K.; Qian, X.; Cui, J. *Tetrahedron* **2009**, *65*, 10377; (b) Domingo, L. R.; Picher, M. T.; Arroyo, P.; Sez, J. A. *J. Org. Chem.* **2006**, *71*, 9319; (c) Czekelius, C.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 612; (d) Kabalka, G. W.; Pace, R. D.; Wadgaonkar, P. P. *Synth. Commun.* **1990**, *20*, 2453; (e) Baran, J.; Mayr, H. *J. Org. Chem.* **1989**, *54*, 5012; (f) Barton, D. H. R.; Beaton, J. M. *J. Am. Chem. Soc.* **1961**, *83*, 4083; (g) Barton, D. H. R.; Beaton, J. M.; Geller, L. E.; Pechet, M. M. *J. Am. Chem. Soc.* **1961**, *83*, 4076.
8. Suzuki, K.; Watanabe, T.; Murahashi, S.-I. *Angew. Chem., Int. Ed.* **2008**, *47*, 2079.
9. Quan, N.; Shi, X.-X.; Nie, L.-D.; Dong, J.; Zhu, R.-H. *Synlett* **2011**, 1028.
10. Lin, M.-H.; Hung, S.-F.; Lin, L.-Z.; Tsai, W.-S.; Chuang, T.-H. *Org. Lett.* **2011**, *13*, 332 For other related $SnCl_2$/KI-mediated allylation reactions: (a) Gremyachinskiy, D. E.; Smith, L. L.; Gross, P. H.; Samoshin, V. V. *Green Chem.* **2002**, *4*, 317; (b) Samoshin, V. V.; Gremyachinskiy, D. E.; Smith, L. L.; Bliznets, I. V.; Gross, P. H. *Tetrahedron Lett.* **2002**, *43*, 6329; (c) Houllemare, D.; Outurquin, F.; Paulmier, C. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1629.
11. The Sn/HBr reaction condition was not pursued further because its high acidity that might alter the functional group compatibility of the process.
12. (a) Lee, S. Y.; Lee, B. S.; Lee, C.-W.; Oh, D. Y. *J. Org. Chem.* **2000**, *65*, 256; (b) Timms, G. H.; Wildsmith, E. *Tetrahedron Lett.* **1971**, *2*, 195.
13. (a) Zhou, Y.; Zha, Z.; Zhang, Y.; Wang, Z. *ARKIVOC* **2008**, *11*, 142; (b) Guimaraes, R. L.; Lima, D. J. P.; Barros, M. E. S. B.; Cavalcanti, L. N.; Hallwass, F.; Navarro, M.; Bieber, L. W.; Malvestiti, I. *Molecules* **2007**, *12*, 2089; (c) Tan, K.-T.; Chng, S.-S.; Cheng, H.-S.; Loh, T.-P. *J. Am. Chem. Soc.* **2003**, *125*, 2958; (d) Li, X.-R.; Loh, T.-P. *Tetrahedron: Asymmetry* **1996**, *7*, 1535.
14. Ramón, R. S.; Bosson, J.; Díez-González, S.; Marion, N.; Nolan, S. P. *J. Org. Chem.* **2010**, *75*, 1197.
15. Li, S.; Wang, J.-X.; Wen, X.; Ma, X. *Tetrahedron* **2011**, *67*, 849.
16. Vasylyev, M.; Alper, H. *J. Org. Chem.* **2010**, *75*, 2710.
17. Yoo, J.; Oh, K. E.; Keum, G.; Kang, S. B.; Kim, Y. *Polyhedron* **2000**, *19*, 549.
18. Mandai, T.; Nokami, J.; Yano, T.; Yoshinaga, Y.; Otera, J. *J. Org. Chem.* **1984**, *49*, 172.
19. Hixson, S. S.; Franke, L. A.; Gere, J. A.; Xing, Y.-D. *J. Am. Chem. Soc.* **1988**, *110*, 3601.
20. Brimble, M. A.; Bryant, C. J. *Org. Biomol. Chem.* **2007**, *5*, 2858.
21. Chen, C.-T.; Chao, S.-D. *J. Org. Chem.* **1999**, *64*, 1090.
22. Li, G.-L.; Zhao, G. *J. Org. Chem.* **2005**, *70*, 4272.
23. Selander, N.; Kipke, A.; Sebelius, S.; Szabo, K. J. *J. Am. Chem. Soc.* **2007**, *129*, 13723.
24. Hoffmann, R. W.; Zeiss, H.-J. *J. Org. Chem.* **1981**, *46*, 1309.
25. Fristad, W. E.; Peterson, J. R.; Ernst, A. B. *J. Org. Chem.* **1985**, *50*, 3143.