Carbonyl propargylation or allenylation by 3-haloprop-1-yne with tin(II) halides and tetrabutylammonium halides

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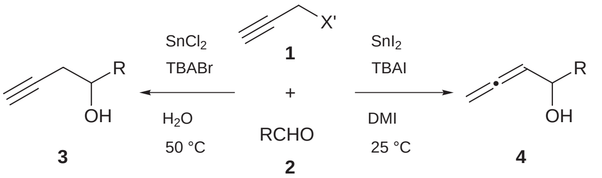
3-Bromoprop-1-yne causes carbonyl propargylation with tin(II) chloride and tetrabutylammonium bromide in water to produce 1-substituted but-3-yn-1-ols, while 3-chloroprop-1-yne causes carbonyl allenylation with tin(II) iodide and tetrabutylammonium iodide in 1,3-dimethylimidazolidin-2-one to produce 1-substituted buta-2,3-dien-1-ols.

Carbonyl propargylation or allenylation by 3-haloprop-1-yne with tin(II) chloride is one of the most convenient methods for introduction of propargyl (prop-2-ynyl) or allenyl functions.[1–3] The propargylation or allenylation is promoted by NaI or LiI; it has been presumed that the actual starting material, which reacts with tin(II) chloride, is 3-iodoprop-1-yne derived from the *in situ* reaction 3-bromoprop-1-yne with NaI or LiI.[1,3] We have found that carbonyl allylation by allylic acetates, allylic bromides, allylic chlorides and vinyl epoxides with rin(II) halide can be promoted by tetrabutylammonium bromide (TBABr).[4–8] A lack of reaction with TBABr might suggest that LiI is required to form the intermediate 3-iodoprop-1-yne.[3] Tetrabutylammonium halide (TBAX‴) probably reacts with tin(II) halide (SnX''_2) to form tetrabutylammonium trihalostannate, which is more nucleophilic than SnX''_2. We thus envisioned that TBAX‴ would promote carbonyl propargylation or allenylation by 3-haloprop-1-yne with SnX''_2.[9,10] We here report that using different halogens in SnX''_2 and TBAX‴ affects the selectivity between carbonyl propargylation and allenylation by 3-haloprop-1-yne; carbonyl propargylation occurs with $SnCl_2$ and TBABr, while carbonyl allenylation occurs with SnI_2 and TBAI.

The reaction of 3-haloprop-1-yne **1** and benzaldehyde (**2**, R = Ph) with SnX''_2 and TBAX‴ was investigated under various conditions. The results are summarized in Table 1. The reaction of 3-bromoprop-1-yne (**1**, X′ = Br) with $SnCl_2$ and TBABr at 50 °C in water led to carbonyl propargylation to produce 1-phenylbut-3-yn-1-ol (**3**, R = Ph) (entry 7, Method A), while the reaction of 3-chloroprop-1-yne (**1**, X′ = Cl) with SnI_2 and TBAI at 25 °C in 1,3-dimethylimidazolidin-2-one (DMI) led to carbonyl allenylation to produce 1-phenylbuta-2,3-dien-1-ol (**4**, R = Ph) (entry 13, Method B) [eqn. (1)]. TBAX‴ accelerated the carbonyl propargylation or allenylation; > 0.1 equiv. of TBAX‴ was required (entries 5–8). In the propargylation the use of $SnCl_2$ and TBABr (or TBACl) is superior to other combinations of reagents, while SnI_2–TBAI is the best combination of reagents for the allenylation. 3-Chloroprop-1-yne (**1**, X′ = Cl) did not react under the same conditions as those of the propargylation with **1** (X′ = Br). Water is a more effective solvent in the propargylation than some organic polar solvents, such as DMI and THF, in which both organic substrates and $SnCl_2$ are soluble (entries 1, 2 and 8). The by-product produced during the propargylation, 4-phenylbut-3-en-2-one (**5**, R = Ph), was probably formed by the hydration of allenylated product **4** (R = Ph).[3] The reaction of **1** (X′ = Cl) and **2** (R = Ph) with SnI_2–TBAI did not occur in water, and proceeded with lower selectivity for the allenylation in DMI–water (entry 14). Thus, water is unsuitable for the allenylation, in which DMI is a better solvent than DMF or THF (entries 11–13).



(1)

Table 1 Propargylation and allenylation of **2** (R = Ph) with SnX''_2 and TBAX‴ [a]

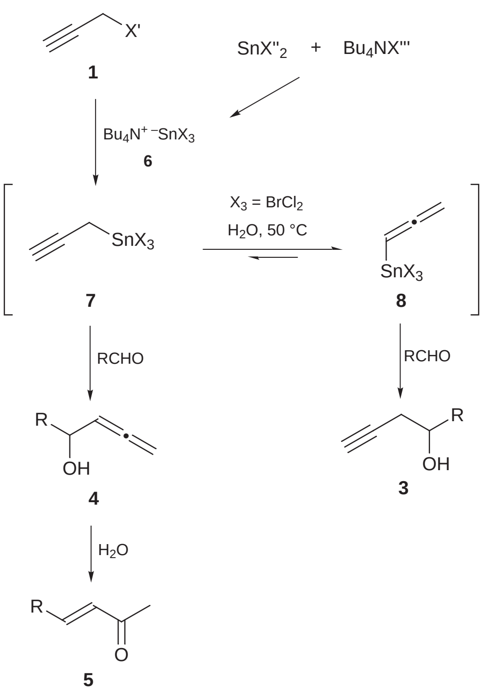
Entry	X′	X″	TBA X‴ (mmol)	Solvent	t/h	Yield (%) **3** + **4**[b]	**5**[c]
1	Br	Cl	Br (1)	DMI	24	25 (100:0)	4
2	Br	Cl	Br (1)	THF	10	60 (100:0)	9
3	Br	Cl	Br (1)	THF–H_2O[d]	8	70 (100:0)	8
4	Br	Cl	Br (1)	CH_2Cl_2–H_2O[d]	8	58 (100:0)	12
5	Br	Cl	—	H_2O	24	17 (100:0)	0
6	Br	Cl	Br (0.1)	H_2O	8	61 (100:0)	13
7[e]	Br	Cl	Br (0.3)	H_2O	8	70 (100:0)	9
8	Br	Cl	Br (1)	H_2O	7	72 (100:0)	10
9[f]	Br	Cl	Br (1)	H_2O	70	44 (100:0)	9
10	Br	Br	Br (1)	H_2O	10	58 (100:0)	15
11[f,g]	Cl	I	I (0.1)	THF	70	91 (31:69)	0
12[f,g]	Cl	I	I (0.1)	DMF	28	91 (19:81)	0
13[f,g,h]	Cl	I	I (0.1)	DMI	23	78 (4:96)	0
14[f,g]	Cl	I	I (0.1)	DMI–H_2O[d]	47	57 (33:67)	11

[a] The reaction of 3-haloprop-1-yne (1.5 mmol) and benzaldehyde (1.0 mmol) was carried out with SnX''_2 (1.5 mmol) and TBA in solvent (3 ml) at 50 °C. [b] Yields of a mixture of **3** (R = Ph) and **4** (R = Ph). The ratio in parentheses was determined by ^1H NMR analysis (JEOL GX-270 or Λ–500). [c] Isolated yields of **5** (R = Ph). [d] Organic solvent–H_2O = 1:1. [e] Method A. [f] The reaction was carried out at 25 °C. [g] NaI (1.5 mmol) was added. [h] Method B.

Table 2 Either propargylation or allenylation with SnX''_2 and TBAX‴

R	Method[a]	t/h	Yield (%) **3** + **4**[b]	**5**[c]
4-$MeO_2CC_6H_4$	A	7	75 (100:0)	14
4-$MeO_2CC_6H_4$	B	24	80 (17:83)	0
4-NCC_6H_4	A	16	77 (100:0)	4
4-NCC_6H_4	B	23	62 (2:98)	0
4-MeC_6H_4	A	20	70 (100:0)	4
4-MeC_6H_4	B	23	53 (7:93)	0
4-$MeOC_6H_4$	A	16	62 (100:0)	4
4-$MeOC_6H_4$	B	25	50 (5:95)	0
$Me(CH_2)_6$	A	12	63 (100:0)	0
$Me(CH_2)_6$	B	90[d]	50 (7:93)	0
c-C_6H_{11}	A	12	48 (100:0)	7
c-C_6H_{11}	B	88[d]	71 (20:80)	0

[a] Method A: Entry 7 in Table 1. Method B: Entry 13 in Table 1. [b] Yields of a mixture of **3** and **4**. The ratio in parentheses was determined by ^1H NMR analysis (JEOL GX-270 or Λ–500). [c] Isolated yields. [d] The reaction was carried out at 0 °C.



Scheme 1

The propargylation (Method A) and allenylation (Method B) of various aldehydes by 3-haloprop-1-yne **1** was carried out under the conditions which gave the best results for benzaldehyde, as summarized in Table 2. Aromatic aldehydes bearing an electron-donating or —withdrawing group and aliphatic aldehydes can be used to afford the corresponding 1-substituted but-3-yn-1-ols **3** using the $SnCl_2$–TBABr/water system or the corresponding 1-substituted buta-2,3-dien-1-ols **4** with the SnI_2–TBAI/DMI system in moderate yields.

A plausible mechanism was illustrated with Scheme 1. The difference between propargylation using the $SnCl_2$–TBABr/water system and allenylation using the SnI_2–TBAI/DMI system may be due to the Lewis acidity of the tin, reaction temperature and reaction medium. ^{1}H NMR (JEOL Λ–500) observation in [$^2H_7$]DMF at 25 °C revealed that prop-2-ynyltriiodotin (**7**, X = I) was first formed *via* the reaction of 3-chloroprop-1-yne (**1**, X′ = Cl) with SnI_2 and NaI. Prop-2-ynyltriiodotin (**7**, X = I) probably proceeded *via* γ-addition to the aldehyde (carbonyl allenylation), without isomerizing to propa-1,2-dienyltriiodotin (**8**, X = I), in dry polar solvents such as DMI and DMF to produce buta-2,3-dien-1-ols **4**.‡ In contrast, the isomerization of prop-2-ynylbromodichlorotin (**7**, X_3 = $BrCl_2$), derived from reaction of 3-bromoprop-1-yne (**1**, X′ = Br) with $SnCl_2$ and TBABr at the organic–aqueous interface, to propa-1,2-dienylbromodichlorotin (**8**, X_3 = $BrCl_2$) probably occurred more rapidly at 50 °C than carbonyl allenylation by **7** (X_3 = $BrCl_2$).§ The carbonyl propargylation by **8** (X_3 = $BrCl_2$) at 50 °C in water thus produced but-3-yn-1-ols **3**.¶

Notes and References

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‡ The carbonyl allenylation by **7** (X = I) seems to have proceeded *via* an acyclic antiperiplanar transition state, because of the weakly Lewis acidic tin in **7** (X = I). See ref. 7 and 8.

§ It was shown by ^{1}H NMR analysis (JEOL Λ–500) that prop-2-ynyltriiodotin (**7**, X = I), derived from 3-chloroprop-1-yne (**1**, X′ = Cl) *via* reaction with SnI_2 and NaI in [$^2H_7$]DMF, isomerized easily to propa-1,2-dienyltriiodotin (**8**, X = I) at 50 °C; J. A. Marshall, R. H. Yu and J. F. Perkins, *J. Org. Chem.*, 1995, **60**, 5550.

¶ The carbonyl propargylation by **8** (X_3 = $BrCl_2$), which has a strongly Lewis acidic tin, seems to have proceeded *via* a usual six-membered cyclic transition state.

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