ChemComm

Carbonyl propargylation by 1-substituted prop-2-ynyl mesylates and carbonyl allenylation by 3-substituted prop-2-ynyl mesylates with tin(II) iodide and tetrabutylammonium iodide

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Received (in Cambridge, UK) 14th August 2000, Accepted 5th September 2000
First published as an Advance Article on the web 28th September 2000

1-Substituted prop-2-ynyl mesylates cause propargylation of aldehydes with tin(II) iodide, tetrabutylammonium iodide and sodium iodide in 1,3-dimethylimidazolidin-2-one to produce 2-substituted but-3-yn-1-ols, while 3-substituted prop-2-ynyl mesylates cause allenylation of aldehydes under the same conditions as those of the propargylation by 1-substituted prop-2-ynyl mesylates to produce 2-substituted buta-2,3-dien-1-ols.

Table 1 Allenylation by prop-2-ynyl mesylate with SnI_2 and TBAI[a]

R^3	Time/h	Yield (%)[b] **2** + **3**	**2**:**3**[c]
C_6H_5	45	85	78:22
ClC_6H_4	48	80	75:25
$CH_3OC_6H_4$	70	74	78:22
$CH_3(CH_2)_5$	71	66	66:34
c-C_6H_{11}	72	68	81:19

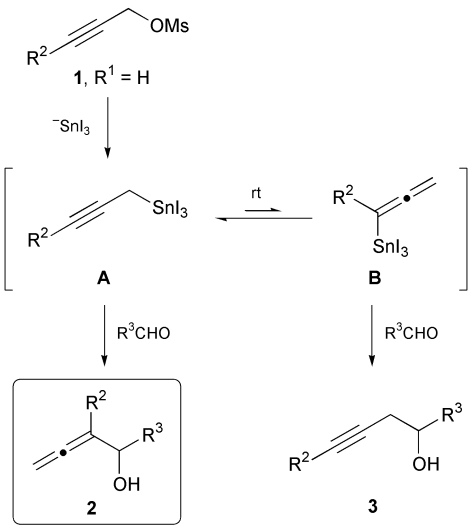
[a] The reaction of prop-2-ynyl mesylate (1.5 mmol) with aldehydes (1.0 mmol) was carried out using SnI_2 (1.5 mmol), TBAI (0.10 mmol) and NaI (1.5 mmol) in DMI (3 ml) at 10 °C. [b] Yields of a mixture of **2** and **3**. [c] The ratio was determined by ^{1}H NMR analysis (JEOL Λ-500).

Alkynes and allenes have formed an attractive chemistry for high reactivities with metal complexes or reagents.[1] Thus, the preparation of alkynes and allenes becomes an important theme. Barbier-type carbonyl propargylation or allenylation with propargylic halides is one of the most convenient methods for the introduction of propargyl or allenyl functions.[2–7] However, it is not easy to control selectivity between Barbier-type propargylation and allenylation with propargylic halides. We have established both selective propargylation and allenylation by 1-haloprop-2-yne with tin(II) halide and tetrabutylammonium halide (TBAX) through choice of reaction conditions: carbonyl propargylation occurs with 1-bromoprop-2-yne, $SnCl_2$ and TBABr at 50 °C in water, while carbonyl allenylation occurs with 1-chloroprop-2-yne, SnI_2 and TBAI at 25 °C in 1,3-dimethylimidazolidin-2-one (DMI).[8] ^{1}H NMR observations (JEOL Λ-500) have confirmed that prop-2-ynyltriiodotin (propargyltin), derived from 1-chloroprop-2-yne with SnI_2 and NaI at 25 °C in DMF-d_7, does not isomerize to propa-1,2-dienyltriiodotin (allenyltin) at 25 °C but does so at 50 °C.[8,9] We thus hoped that this kind of isomerization of propargyltin to allenyltin would be prohibited by the steric effect of a 3-substituent in 1-haloprop-2-ynes and be promoted by the steric effect of a 1-substituent in 1-haloprop-2-ynes.[10] We here

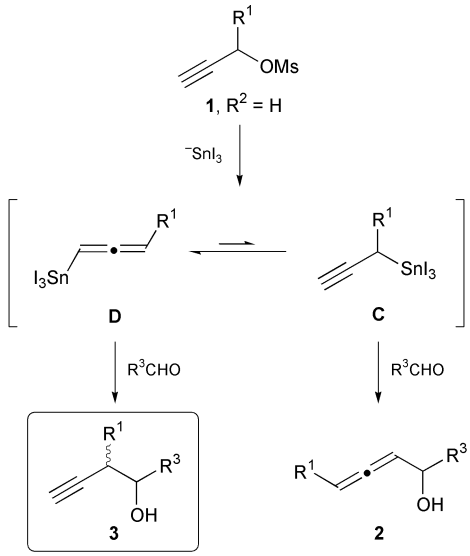
Table 2 Selective carbonyl propargylation or allenylation mediated by steric effects[a]

R^1	R^2	R^3	Time/h	Yield (%)[b] **2** + **3**	**2**:**3**[c]	**3** *syn*:*anti*[c]
H	CH_3	C_6H_5	48	58	~100:0	
H	CH_3	ClC_6H_4	47	65	~100:0	
H	CH_3	$CH_3C_6H_4$	55	52	~100:0	
H	CH_3	$C_6H_5CH{=}CH$	71	21[d]	94:6	
H	CH_3	$C_6H_5CH_2CH_2$	51	62	90:10	
H	CH_3	$CH_2{=}CH(CH_2)_8$	50	57	89:11	
H	CH_3	$CH_3(CH_2)_5$	67	65	90:10	
H	CH_3	c-C_6H_{11}	79	41	84:16	
H	C_6H_5	C_6H_5	71	81	~100:0	
H	C_6H_5	ClC_6H_4	63	84	~100:0	
H	C_6H_5	$CH_3C_6H_4$	90	76	~100:0	
H	C_6H_5	$C_6H_5CH_2CH_2$	79	56	90:10	
H	C_6H_5	$CH_2{=}CH(CH_2)_8$	75	32	98:2	
H	C_6H_5	$CH_3(CH_2)_5$	70	35	98:2	
H	C_6H_5	c-C_6H_{11}	71	48	93:7	
CH_3	H	C_6H_5	71	71	12:88	49:51
CH_3	H	ClC_6H_4	79	83	6:94	48:52
CH_3	H	$CH_3C_6H_4$	75	65	6:94	47:53
CH_3	H	2-Furyl	70	41	0:~100	50:50
CH_3	H	$C_6H_5CH{=}CH$	72	75	0:~100	47:53
CH_3	H	$C_6H_5CH_2CH_2$	70	66	1:99	19:81
CH_3	H	$CH_2{=}CH(CH_2)_8$	47	55	1:99	26:74
CH_3	H	$CH_3(CH_2)_5$	71	48	10:90	35:65
CH_3	H	c-C_6H_{11}	70	44	14:86	—[e]
Pr	H	C_6H_5	75	66	2:98	48:52
Pr	H	ClC_6H_4	72	85	1:99	50:50
Pr	H	$CH_3(CH_2)_5$	75	41	8:92	22:78

[a] The reaction of 1- or 3-substituted prop-2-ynyl mesylates (1.5 mmol) with aldehydes (1.0 mmol) was carried out using SnI_2 (2.0 mmol), TBAI (0.20 mmol) and NaI (2.0 mmol) in DMI (3 ml) at rt. [b] Yields of a mixture of **2** and **3**. [c] The ratios were determined by ^{1}H NMR analysis (JEOL Λ-500). For the ratio of *syn* to *anti*, see ref. 8. [d] The reaction was carried out in the presence of MS 4Å in THF. [e] The ratio was not confirmed.



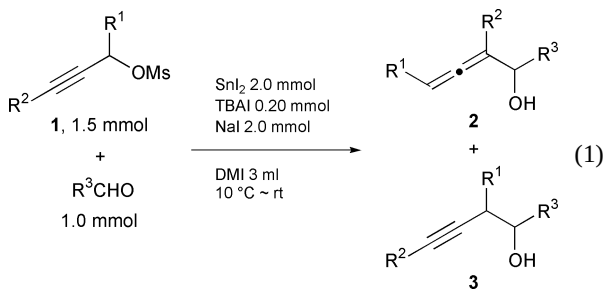
Scheme 1 Allenylation.



Scheme 2 Propargylation.

report on selective Barbier-type carbonyl propargylation and allenylation mediated by steric effects, using the 1- or 3-substituted prop-2-ynyl mesylates‡ as Barbier-type propargylating or allenylating reagents, rather than the more usual corresponding halides (1-haloprop-2-ynes), because the mesylates are superior to the halides for ease of preparation and the stability of propargylic substrates.[11]

The reaction of prop-2-ynyl mesylate (**1**; R^1, R^2 = H) with some aldehydes was carried out using SnI_2, TBAI and NaI under the same conditions as those reported for the carbonyl allenylation by 1-chloroprop-2-yne [eqn. (1)].[8] The results are



(1)

summarized in Table 1. Prop-2-ynyl mesylate (**1**; R^1, R^2 = H) proved to be as available as 1-chloroprop-2-yne for the selective carbonyl allenylation with SnI_2 and TBAI. Thus, we investigated whether the 1- or 3-substituents of prop-2-ynyl mesylates affect the selectivity between propargylation and allenylation under the same conditions as those of prop-2-ynyl mesylate (**1**; R^1, R^2 = H) [eqn. (1)]. The results are summarized in Table 2. 3-Substituted prop-2-ynyl mesylates (**1**; R^1 = H, R^2 = CH_3 and R^1 = H, R^2 = C_6H_5) caused the same allenylation of various aldehydes as that of **1** (R^1, R^2 = H). In particular, with aromatic aldehydes, only allenyl carbinols **2** were obtained. The reaction of cinnamaldehyde in DMI afforded 1-phenylhexa-1,3-dien-5-one derivatives that were probably formed by the hydration of the corresponding allenyl carbinols **2** (R^2 = CH_3, C_6H_5) followed by dehydration.[4,8] 1-Substituted prop-2-ynyl mesylate (**1**; R^1 = CH_3, R^2 = H and R^1 = Pr, R^2 = H) caused the preferential propargylation of various aldehydes. The selectivity for this propargylation was enhanced by the use of THF–H_2O (1 : 1) as a solvent instead of DMI: R^1 = CH_3, R^2 = H, R^3 = C_6H_5; rt, 72 h; 92%, **2** : **3** = 0 : ~100, *syn*:*anti* = 46:54.

A plausible mechanism for the allenylation is illustrated in Scheme 1. 3-Substituent R^2 (CH_3 or C_6H_5), being bulkier than H, probably prohibits propargyltin intermediate **A** from isomerizing to allenyltin intermediate **B**. Thus allenyl carbinols **2** are produced more selectively than in the allenylation by prop-2-ynyl mesylate (**1**; R^1, R^2 = H), *via* nucleophilic addition of the propargyltin **A** at the γ-position.[8] A plausible mechanism for the propargylation is illustrated in Scheme 2. 1-Substituent R^1 (CH_3 or Pr) probably promotes the isomerization of the initially prepared propargyltin **C** to allenyltin **D**, even at room temperature, or mediates a direct preparation of allenyltin **D**.§ The allenyltin **D** then undergoes nucleophilic addition to aldehydes at the γ-position to afford homopropargyl alcohols **3**.

Notes and references

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‡ The 1- or 3-substituted prop-2-ynyl mesylates were prepared from 1- or 3-substituted prop-2-yn-1-ols and methanesulfonyl chloride with triethylamine in ether on an ice-bath. 1-Phenylprop-2-ynyl mesylate was not prepared under the conditions described above: see I. S. Aidhen and R. Braslau, *Synth. Commun.*, 1994, **24**, 789.

§ It was shown by ^{1}H NMR analysis (JEOL Λ-500) that the reaction of 1-methylprop-2-ynyl mesylate with SnI_2 and NaI in DMF-d_7 produced 3-methylprop-1,2-dienyltriiodotin **D** (R^1 = CH_3) at 25 °C; δ 1.73 (dd, J = 7.2, 2.6 Hz, 3H), 5.21 (quintet, J = 6.7 Hz, 1H), 6.09 (dq, J = 5.6, 2.6 Hz, 1H).

1 *Modern Acetylene Chemistry*, ed. P. J. Stang and F. Diederich, VCH, Weinheim, 1995; H. Yamamoto, in *Comprehensive Organic Synthesis*, ed. I. Fleming and B. M. Trost, Pergamon Press, Oxford, 1991, vol. 2, p. 81; H. F. Schuster and G. M. Coppola, *Allenes in Organic Synthesis*, Wiley, New York, 1984.
2 T. Mukaiyama and T. Harada, *Chem. Lett.*, 1981, 621.
3 G. P. Boldrini, E. Tagliavini, C. Trombini and A. Umani-Ronchi, *J. Chem. Soc., Chem. Commun.*, 1986, 685.
4 M. Iyoda, Y. Kanao, M. Nishizaki and M. Oda, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 3380.
5 A. Kundu, S. Prabhakar, M. Vairamani and S. Roy, *Organometallics*, 1999, **18**, 2782.
6 H. Tanaka, T. Hamatani, S. Yamashita and S. Torii, *Chem. Lett.*, 1986, 1461.
7 K. Belyk, M. J. Rozema and P. Knochel, *J. Org. Chem.*, 1992, **57**, 4074.
8 Y. Masuyama, A. Ito, M. Fukuzawa, K. Terada and Y. Kurusu, *Chem. Commun.*, 1998, 2025.
9 J. A. Marshall, R. H. Yu and J. F. Perkins, *J. Org. Chem.*, 1995, **60**, 5550.
10 For selective formation of propargylmetals and allenylmetals utilizing steric effects, see: J. Nokami, T. Tamaoka, T. Koguchi and R. Okawara, *Chem. Lett.*, 1984, 1939; L.-J. Zhang, Y.-Z. Huang and Z.-H. Huang, *Tetrahedron Lett.*, 1991, **32**, 6579; S. Kobayashi and K. Nishio, *J. Am. Chem. Soc.*, 1995, **117**, 6392.
11 For selective propargylation by propargylic mesylates with Et_2Zn or InI in the presence of Pd^{II} catalysts, see: J. A. Marshall and N. D. Adams, *J. Org. Chem.*, 1999, **64**, 5201; J. A. Marshall and C. M. Grant, *J. Org. Chem.*, 1999, **64**, 8214.