COMMUNICATION

Stereoselective synthesis of enol acetates by the reaction of alkenylboronates with (diacetoxyiodo)benzene and sodium iodide

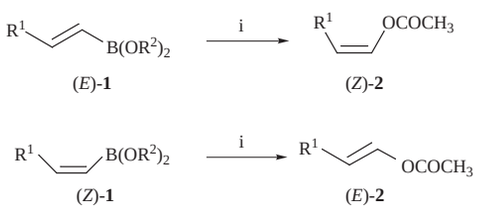
Miki Murata, Kaname Satoh, Shinji Watanabe and Yuzuru Masuda *

Department of Materials Science, Kitami Institute of Technology, Kitami 090-8507, Japan

Stereochemically pure (*E*)- and (*Z*)-alk-1-en-1-yl acetates have been easily prepared by acetoxylation of the (*Z*)- and (*E*)-alk-1-en-1-ylboronic acids or their esters, respectively, with (diacetoxyiodo)benzene and sodium iodide, in reasonable yields.

Although many useful synthetic reactions using organoboron compounds have been reported,[1] these do not include a procedure for synthesis of the corresponding alkenyl acetates from alkenylboron compounds. However there have been several reports of useful synthetic reactions in which enol esters served as intermediates for carbon–carbon or carbon–heteroatom bond formations.[2,3] Enol esters can be prepared from carbonyl compounds[4] or alkynes,[5] but there are many difficulties in the synthesis of stereodefined enol esters of aldehydes especially of the (*E*)-isomers.†

Previously, we reported a synthesis of alkyl acetates by acetoxylation of trialkylboranes with (diacetoxyiodo)benzene or lead(IV) acetate.[6a] We have now considered the analogous formation of alkenyl acetates *via* alkenylboron compounds.‡ Thus, we here describe a stereoselective conversion of alk-1-en-1-ylboronic esters **1** to alk-1-en-1-yl acetate **2** by the treatment with (diacetoxyiodo)benzene in the presence of sodium iodide (Scheme 1).



1a $R^1 = C_6H_{13}$
1b $R^1 = Bu$
1c $R^1 = MeCO(CH_2)_2$
1d $R^1 = NC(CH_2)_2$
1e $R^1 = Bu^t$
1f $R^1 = Ph$ $\quad R^2 = H$ or Pr^i

Scheme 1 *Reagents and conditions*: i, $PhI(OCOCH_3)_2$, NaI, DMF, room temp.

And then, since respective (*E*)- and (*Z*)-1-alk-1-en-1-ylboronic esters can be readily prepared regio- and stereo-selectively by the hydroboration reaction of alk-1-ynes or 1-haloalk-1-ynes,[1] their acetoxylation would allow for the formation of geometrically pure (*E*)- or (*Z*)-enol acetates **2**.

† It has been reported that the anti-Markovnikov addition of carboxylic acids to alkynes afforded (*Z*)-alk-1-en-1-yl esters,[5c] though the addition of acetic acid to hex-1-yne gave the corresponding enol acetate in only low yield.

‡ The authors have found the following reactions in the presence of $PhI(OAc)_2$ or $Pb(OAc)_4$.[6b,c]

$$(E)\text{-RCH=CHB}(C_6H_{11})_2 \longrightarrow (E)\text{-RCH=CHC}_6H_{11}$$

$$R_3B + HC{\equiv}CR' \longrightarrow RC{\equiv}CR' + (Z)\text{-RCH=CR'(OAc)}$$

Table 1 Synthesis of enol acetates (Scheme 1)

Entry	1-Alkenyboronic esters	$(OR^2)_2$	Product	Yield (%)[a]
1	(*E*)-**1a**	$(OH)_2$	(*Z*)-**2a**	93 (85)
2	(*E*)-**1a**	$(OPr^i)_2$	(*Z*)-**2a**	97
3	(*E*)-**1b**	$(OH)_2$	(*Z*)-**2b**	(77)
4	(*E*)-**1c**	$(OPr^i)_2$	(*Z*)-**2c**	(82)
5	(*E*)-**1d**	$(OPr^i)_2$	(*Z*)-**2d**	(85)
6	(*E*)-**1e**	$(OH)_2$	(*Z*)-**2e**	(71)
7	(*E*)-**1f**	$(OH)_2$	(*Z*)-**2f**	62[b]
8	(*Z*)-**1b**	$(OPr^i)_2$	(*E*)-**2b**	(70)
9	(*Z*)-**1e**	$(OPr^i)_2$	(*E*)-**2e**	(72)

[a] GC and/or isolated (in parentheses) yields are based on **1** used. [b] A 17% yield of (*E*)-β-iodostyrene was also produced.

Although simple treatment of alkenylboronic acids or esters (instead of alkenylborane)[6] with (diacetoxyiodo)benzene (IBA) did not give alk-1-enyl acetates as expected, it was found that a modified procedure with addition of sodium iodide and DMF as solvent was a remarkably efficient method of acetoxylation affording alk-1-enyl acetates. For instance, the treatment of (*E*)-oct-1-en-1-ylboronic acid **1a** with $PhI(OAc)_2$ (1.1 equiv.) in the presence of NaI (1.1 equiv.) and DMF at room temperature produced (*Z*)-oct-1-en-1-yl acetate **2a** in 93% yield (GC) (isolated, 85%) and in >99% isomeric purity, but such reaction in the absence of NaI afforded no detectable amount of **2a**. Lead(IV) acetate also acted in the same manner as IBA to provide (*Z*)-**2a** in 77% yield. The results obtained with representative **1** are summarized in Table 1. The reactions proceeded stereospecifically under mild conditions, and consequently for all compounds **1** studied no regio- or stereo-isomers of **2** were formed.

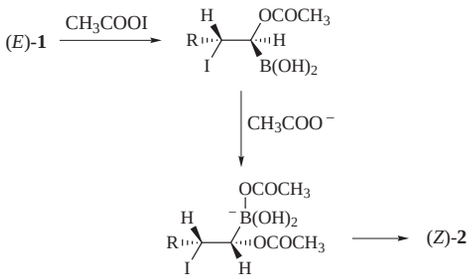
Following this, as was expected, (*E*)-alk-1-en-1-yl acetates (entries 8 and 9) could be also prepared by employing the corresponding (*Z*)-alk-1-en-1-ylboronic esters in a similar reaction to that described above.

The yields and the stereoselectivity of the products seemed not to depend on steric hindrance in **1** (entries 6 and 9). However, the reaction employing (*E*)-β-styrylboronic acid **1f** yielded significant amounts (17%) of (*E*)-β-iodostyrene as a by-product whose stereochemistry was consistent with that of **1f** (entry 7), along with the major (*Z*)-**2f** (62% yield), suggesting perhaps electronic effects.§ A mechanistic study was attempted.

Similar treatment of **1a** to that above with the known acetyl hypoiodite (CH_3COOI) formed *in situ* from (diacetoxyiodo)-benzene (1.1 equiv.) and iodine (0.55 equiv.)[7] gave only 44% yield of **2a**, but this was improved with the addition of sodium acetate (1.1 equiv) to provide **2a** in 89% yield. We suggest that this reaction proceeds *via* formation of acetyl hypoiodite and acetoxy anion from (diacetoxyiodo)benzene and sodium iodide.

§ Recently, it has been reported that a reaction of alk-1-en-1-ylboronic acids with (diacetoxyiodo)benzene in the presence of $BF_3{\cdot}Et_2O$ yielded alk-1-en-1-yl(phenyl)iodonium salts.[8] The present formation of (*E*)-1-iodoalk-1-ene as by-product may involve such boron–iodine exchange followed by a nucleophilic substitution with sodium iodide.[9]

Although our evidence for the reaction mechanism is still inconclusive,§ bearing in mind the inversion of starting geometry and a probable *in situ* formation of hypoiodite, this reaction is considered to proceed through *anti*-addition[7a,c] of the hypoiodite to the carbon–carbon double bond of alk-1-en-1-ylboronate followed by *anti*-deiodoboration[10] with the aid of acetoxy anion, as shown in Scheme 2.



Scheme 2

As discussed above, this reaction is not only interesting as a new approach to the synthesis of enol acetates but also useful to obtain geometrically pure (*E*)- or (*Z*)-alk-1-en-1-yl acetates respectively, and further investigations for mechanistic studies and synthetic applications are currently in progress in our laboratory.

Experimental

Typical procedure: preparation of (*Z*)-oct-1-en-1-yl acetate 2a

The flask was charged with (diacetoxyiodo)benzene (5.5 mmol), NaI (5.5 mmol), DMF (30 cm^3) and (*E*)-**1a** (0.78 g, 5.0 mmol) prepared by the method described in the literature [ref. 1(*a*), p. 64]. The reaction mixture was stirred at room temperature for 16 h. The product was extracted with diethyl ether, and the extract was washed with water and dried over $MgSO_4$. After removal of the solvent, the residue was purified by chromatography over silica gel to give (*Z*)-**2a** (0.73 g, 85%); ν_{max}(neat)/cm^{-1} 1759, 1672 and 751; $\delta_H(CDCl_3)$ 0.8–1.0 (m, 11H), 1.9–2.2 (m, 2H), 2.10 (s, 3H), 4.79 (q, 1H, *J* 6.5¶), 6.92 (d, 1H, *J* 6.5); $\delta_C(CDCl_3)$ 13.0, 19.6, 21.6, 23.4, 27.9, 28.2, 30.7, 113.2, 133.1, 167.0; *m*/*z* (EI) 170.1293 ($C_{10}H_{18}O_2$ requires 170.1307).

(*E*)-Hex-1-en-1-yl acetate 2b

Using (*Z*)-**1b** prepared by the method described in the literature,[11] a similar procedure to above afforded (*E*)-**2b** in 70% isolated yield; ν_{max}(neat)/cm^{-1} 1755, 1675 and 936; $\delta_H(CDCl_3)$ 0.7–1.4 (m, 7H), 1.9–2.2 (m, 2H), 2.07 (s, 3H), 5.41 (dt, 1H, *J* 12.5, 7.4), 7.06 (dt, 1H, *J* 12.5, 1.3); $\delta_C(CDCl_3)$ 13.7, 20.6, 22.0, 26.8, 31.6, 115.0, 135.4, 168.1; *m*/*z* (EI) 142.0995 ($C_8H_{14}O_2$ requires 142.0994).

¶ *J* Values are given in Hz.

Acknowledgements

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