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Synthesis of (*E*)-Alkenyl Iodides via (*E*)-[2′-(Tributyltin)alkenyl]dialkylboranes with Iodine

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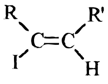
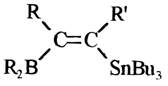
Introduction

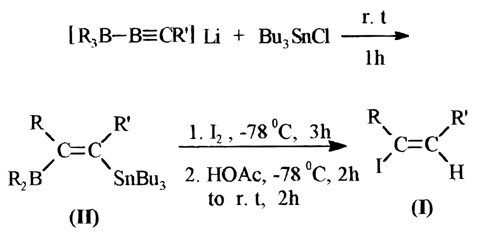
Alkenyl iodides, which are important starting materials in organic synthesis, are usually prepared by sequential reactions of alkynes, i.e., hydrometalations of various metal hydrides to alkynes followed by demetalations with iodine.[1] The hydrometalations of alkynes is convenient to prepare 1-iodo-1-alkenes in anti-Markovnikov fashion, but internal alkenyl iodides are scarcely obtained by these methods.[1c,2] For this purpose, the haloboration of *B*-bromo- or *B*-Iodo-9-borabicyclo[3.3.1]nonane (BBN) has been developed,[3] but only terminal alkynes can be haloborated by *B*-bromo or *B*-iodo-9-BBN; therefore, only 2-bromo- or 2-iodo-1-alkenes can be prepared by this method. Other methods, such as the stereoselective synthesis of internal alkenyl iodides by the hydroiodinations of alkynes via in situ generation of HI or its equivalent have also been reported.[4,5] But those methods could give satisfactory results only when the alkynes used are terminal or symmetric internal alkynes. In the case of unsymmetric internal alkynes, those reactions would give a mixture of two isomers owning to the low regioselectivity of the reaction. Thus, those methods are also not suitable for preparing the internal alkenyl iodides **I** with two different alkyl groups ($R \neq R'$, $R' \neq H$) on the carbon−carbon bond.


(I)


(II)

(*E*)-[2′-(Tributyltin)alkenyl]dialkylboranes **II**, which can be easily prepared by the reaction of lithium trialkylalkynylborates with tributyltin chloride,[6] are versatile synthetic intermediates. Wrackmeyer et al.[7,8] investigated the formation and transformation of the intermediates **II** containing two heteroatoms. The intermediates **II** can also react with [(methylthio)methyl]lithium−TMEDA to give 1,2-migrating products.[6] Recently, we found that the reaction of the intermediates **II** with ethyl (dimethylsufuranylidene)acetate, after protonation, afforded (*E*)-β,γ-unsaturated esters stereospecifically.[9] So we were interested in development of the application of the intermediates'**(II)** chemistry to organic synthesis. Herein, we wish to report the result of the reaction of the intermediates **II** with iodine at low temperature, followed by protonation, giving internal (*E*)-iodoalkenes in good overall yields.

Scheme 1



Results and Discussions

K. Wang et al. reported that the intermediates **II** reacted with iodine in refluxing THF to give internal alkynes, and the reaction presumably proceeded through the replacement of the tri-*n*-butyltin substituent with iodine followed by the elimination of *B*-iodo-9-BBN.[10] However, in most reactions of the intermediates **II**, the dialkylboron group takes priority in the reaction with reagents,[6,11,12] and alkenylboranes can also react with iodine under some conditions.[1a,13] Thus, in order to see the situation in which the iodination reaction occurred and if iodoalkenes could be obtained, we restudied the reaction of the intermediates **II** with iodine.

The repeated reactions of intermediates **II** with iodine in refluxing THF gave the same result as that of K. Wang. However, when the reaction was carried out and subsequently protonated with acetic acid at −78 °C, internal alkenyl iodides were obtained in good yields. Various intermediates **II** with different groups were synthesized, and their reactions with iodine by the above-mentioned procedure were carried out (as shown in Scheme 1). The results are summarized in Table 1.

The reaction of **IIf** generated from $HC{\equiv}CCH_2OMe$ was chosen to determine the iodination situation. **IIf** reacted with iodine at low temperature to give **If**. The ^1H NMR spectrum of **If** showed a doublet peak (not a singlet) of the ethylene protons of the methoxymethylene group at 3.94 ppm ($J = 6.75$ Hz, 2H) and the triplet peak of the alkenyl proton at 5.31 ppm ($J = 6.75$ Hz, 1H). This fact apparently suggested that the iodination of **IIf** at low temperature took place at the carbon−boron bond rather than the carbon-tin bond. In the ^1H NMR spectra of all the iodoalkenes, the clean triplet peak of the vinyl proton appeared, and a strong NOE effect between the methylene protons of methoxymethylene group and the methylene protons (2.03 ppm) attached to the double bond in the NOESY spectrum of **If** appeared. The NOE effect between the vinyl proton (5.31 ppm) and methylene protons (2.03 ppm) was not observed. These facts indicated that the products **I** were single (*E*)-isomers.

If the iodination reaction was carried out at −78 °C for 3 h and then the reaction mixture was allowed to rise

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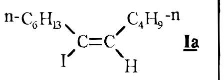
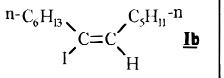
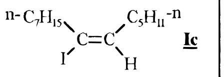
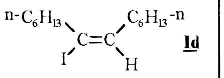
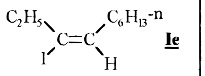
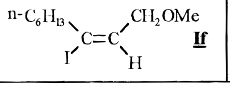
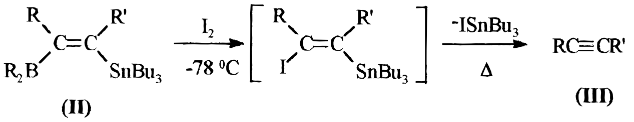
Table 1. Synthesis of Internal (*E*)-Alkenyl Iodides via (*E*)-[2′-(Tributyltin)alkenyl] dialkylboranes II with Iodine

entry	intermediate(II)		product^a	yield^b
	R	R'	(I)	(%)
1	n-C_6H_{13}	n-C_4H_9	 **Ia**	70
2	n-C_6H_{13}	n-C_5H_{11}	 **Ib**	68
3	n-C_7H_{15}	n-C_5H_{11}	 **Ic**	71
4	n-C_6H_{13}	n-C_6H_{13}	 **Id**	70
5	C_2H_5	n-C_6H_{13}	 **Ie**	74
6	n-C_6H_{13}	CH_2OMe	 **If**	41

^{a}All products were identified by ^{1}H NMR, IR, MS and elemental analysis. ^{b}Isolated yield.

Scheme 2



to room temperature, subsequent hydrolysis by acetic acid gave a mixture containing mainly internal alkyne with a small amount of internal alkenyl iodide. If the reaction mixture was stirred at −78 °C for 3 h and then was allowed to reflux for 1 h, only internal alkyne was obtained. These facts suggested that the iodination reaction occurred at the carbon−boron bond rather than the carbon−tin bond at least at low temperature and the elimination of tributyltin iodide at high temperature giving alkyne could take place (Scheme 2). The reaction procedure for iodination of intermediates **II** and subsequent protonation at low temperature could stereospecifically afford internal (*E*)-iodoalkenes in good yields. The reaction might be useful in organic synthesis.

Experimental Section

Tetrahydrofuran and hexane were freshly distilled from sodium metal and benzophenone under argon atmosphere. Reagents were purchased from Aldrich and used without further purification. All reactions were carried out under argon. (*E*)-[2′-(Tributyltin)alkenyl]dialkylboranes **II** were prepared from lithium trialkylalkynylborates and tributyltin chloride in a literature procedure.[6]

Typical Procedure for the Synthesis of Alkenyl Iodides. (*E*)-6-Iodo-5-dodecene (Table 1, **Ia**). To the solution of alkenyl intermediate II (R = n-C_6H_{13}, R′ = n-C_4H_9) (generated from 2.5 mmol of the starting material BH_3·THF) in THF was added iodine (2.5 mmol) in 10 mL of THF dropwise at −78 °C. After stirring for an additional 3 h, HOAc (2 mL) was added and the temperature was maintained at −78 °C for an additional 2 h and then raised to room temperature over 2 h. The mixture was neutralized with aqueous NaOH solution, and aqueous $Na_2S_2O_3$ solution was added to remove an excess of iodine. Half-saturated potassium fluoride solution was then added and the solution vigorously stirred. The resulting white precipitate of tributyltin fluoride was removed by filtration. The filtrate was extracted with ether. The combined organic layer was washed with brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel, eluting with petroleum ether, to afford 522 mg (71%) of **Ia**: ^{1}H NMR ($CDCl_3$, TMS) δ 0.89 (m, 6H), 1.27 (m, 12H), 1.80−2.26 (m, 4H), 5.28 (t, J = 6.8 Hz, 1H); IR 2970, 2910, 1470, 720 cm^{-1}; MS *m/z* (relative intensity) 294 (M$^+$, 9.47), 252 (2.96), 168 (5.43), 125 (14.40), 111 (31.69), 55 (100). Anal. Calcd for $C_{12}H_{23}I$: C, 48.98; H, 7.82; I, 43.20. Found: C, 48.71; H, 7.60; I, 43.57.

(*E*)-7-Iodo-6-tridecene(Ib): yield 524 mg (68%); ^{1}H NMR δ 0.88 (m, 6H), 1.24 (m, 14H), 1.87−2.25 (m, 4H), 5.27 (t, J = 6.8 Hz, 1H); IR 2970, 2910, 1470, 720 cm^{-1}; MS *m/z* 308 (M$^+$, 37.29), 181 (3.36), 168 (5.98), 111 (27.20), 97 (40.36), 69 (100). Anal. Calcd for $C_{13}H_{25}I$: C, 50.65; H, 8.12; I, 41.23. Found: C, 50.92; H, 7.87; I, 41.25.

(*E*)-7-Iodo-6-tetradecene(Ic): yield 571 mg (71%); ^{1}H NMR δ 0.91 (m, 6H), 1.24 (m, 16H), 1.80−2.28 (m, 4H), 5.28 (t, J = 6.8 Hz, 1H); IR 2970, 2910, 1470, 720 cm^{-1}; MS *m/z* 322 (M$^+$, 17.32), 196 (20.20), 125 (22.19), 97 (61.70), 69 (100). Anal. Calcd for $C_{14}H_{27}I$: C, 52.17; H, 8.39; I, 39.44. Found: C, 52.08; H, 8.21; I, 39.72.

(*E*)-7-Iodo-7-tetradecene(Id): yield 563 mg (70%); ^{1}H NMR δ 0.89 (m, 6H), 1.28 (m, 16H), 1.80−2.26 (m, 4H), 5.27 (t, J = 6.8 Hz, 1H); IR 2970, 2910, 1470, 720 cm^{-1}; MS *m/z* 322 (M$^+$, 29.89), 196 (13.07), 111 (20.24), 83 (72.67), 69 (92.24), 55 (100). Anal. Calcd for $C_{14}H_{27}I$: C, 52.17; H, 8.39; I, 39.44. Found: C, 52.44; H, 8.43; I, 39.16.

(*E*)-3-Iodo-3-decene(Ie): yield 492 mg (74%); ^{1}H NMR δ 0.91 (m, 6H), 1.27 (m, 8H), 1.80−2.20 (m, 4H), 5.30 (t, J = 6.8 Hz, 1H); IR 2970, 2910, 1470, 720 cm^{-1}; MS *m/z* 266 (M$^+$, 11.47), 139 (2.99), 97 (35.63), 69 (64.71), 55 (100). Anal. Calcd for $C_{10}H_{19}I$: C, 45.11; H, 7.14; I, 47.74. Found: C, 45.50; H, 6.88; I, 47.62.

(*E*)-1-Methoxy-3-iodo-2-nonene(If): yield 289 mg (41%) [eluting with petroleum ether/ether (30/1 v/v)]; ^{1}H NMR δ 0.89 (t, J = 6.54 Hz, 3H), 1.28 (m, 8H), 2.03 (t, J = 7.13 Hz, 2H), 3.32 (s, 3H), 3.94 (d, J = 6.75 Hz, 2H), 5.31 (t, J = 6.75 Hz, 1H); IR 1100 (brs), 720 cm^{-1}; MS *m/z* 282 (M$^+$, 7.61), 207 (37.18), 155 (3.06), 137 (30.85), 109 (58.20), 95 (95.82), 81 (100). Anal. Calcd for $C_{10}H_{19}IO$: C, 42.55; H, 6.74; I, 45.04. Found: C, 42.23; H, 7.01; I, 44.85.

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