August, 1991] © 1991 *The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, **64**, *2593—2595 (1991)* 2593

Palladium Catalyzed Stereoselective Hydrodehalogenation of Alkenyl Halides with Tributyltin Hydride

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(Received April 10, 1991)

Synopsis. The reduction of alkenyl halides with tributyltin hydride in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium has been studied. Alkenyl iodides reacted easily with tributyltin hydride at 25 °C to give the corresponding hydrocarbons stereoselectively. However, the reaction of alkenyl bromides were sluggish at 25 °C and needed heating at 75 °C to complete.

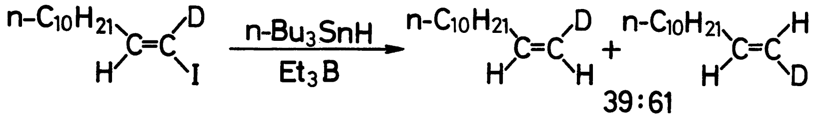
Triethylborane-induced hydrodehalogenation of alkeny halides with tributyltin hydride proceeded non-stereoselectively. For instance, the reduction of (*E*)-1-deuterio-1-iodo-1-dodecene (**1**) or (*Z*)-1-deuterio-1-iodo-1-dodecene with Et_3B–*n*-Bu_3SnH gave a similar isomeric mixture of (*Z*)-1-deuterio-1-dodecene (**2**) and (*E*)-isomer **3** (**2**:**3**=39:61, Scheme 1).[1] Here we report that the reduction of alkenyl iodides with tributyltin hydride in the presence of palladium catalyst proceeds effectively to give the corresponding alkenes with high stereoselectivity.[2]

A number of alkenyl iodides and bromides were reduced with *n*-Bu_3SnH in the presence of $Pd(PPh_3)_4$ catalyst and the results are summarized in Table 1. Whereas (*E*)-1-iodo-1-dodecene reacted easily with *n*-Bu_3SnH at 25 °C to give 1-dodecene in 92% yield after 3 h, (*E*)-1-bromo-1-dodecene was recovered unchanged after treatment with *n*-Bu_3SnH-$Pd(PPh_3)_4$ at 25 °C for 5 h. Heating a benzene solution of (*E*)-1-bromo-1-dodecene, *n*-Bu_3SnH, and $Pd(PPh_3)_4$ at 75 °C for 5 h gave 1-dodecene in 37% yield. The reduction of alkenyl iodides essentially proceeded stereoselectively except for the case of (*E*)-1-deuterio-1-iodo-1-dodecene (**1**). Treatment of **1** (1.0 mmol) with *n*-Bu_3SnH (1.3 mmol) in the presence of $Pd(PPh_3)_4$ (2 mol%) catalyst gave a mixture of (*Z*)-1-deuterio-1-dodecene (**2**) and (*E*)-isomer **3** (**2**:**3**=79:21) in 93% yield. The contamination of (*Z*)-isomer **2** by (*E*)-isomer **3** was attributed to the successive isomerization of (*Z*)-isomer **2**, which was a primary product, by the action of excess *n*-Bu_3SnH under the reaction conditions. In fact, a partial isomerization was observed upon treatment of (*Z*)-1-deuterio-1-dodecene (**2**) with a catalytic amount of *n*-Bu_3SnH and $Pd(PPh_3)_4$. Stirring a benzene solution of **2** (1.0 mmol), *n*-Bu_3SnH (0.2 mmol), and $Pd(PPh_3)_4$ (2 mol%) at 25 °C for 2 h gave a mixture of (*Z*)- and (*E*)-1-deuterio-1-dodecene (**2**:**3**=73:27). The contamination of (*Z*)-isomer **2** by (*E*)-isomer **3** was suppressed by slow addition of an equimolar amount of *n*-Bu_3SnH (1.0 mmol per 1.0 mmol of **1**) to a benzene solution of **1** and Pd catalyst with syringe drive over 1 h (Scheme 2).

As well as (*E*)-1-iodo-1-dodecene, trisubstituted alkenyl iodide such as (*E*)-1-iodo-1-trimethylsilyl-1-dodecene and (*E*)-6-iodo-6-dodecene were easily reduced with *n*-Bu_3SnH-$Pd(PPh_3)_4$ system (Entries 4, 6, 8, and 9 in Table 1). However, (*Z*)-alkenyl iodides such as (*Z*)-1-iodo-1-dodecene and (*Z*)-6-iodo-6-dodecene reacted more slowly than the corresponding (*E*)-iodides because of its steric hindrance. The reaction of (*Z*)-1-iodo-1-dodecene or (*Z*)-6-iodo-6-dodecene took 5 h at 25 °C or 75 °C to complete (Entries 2 or 7 in Table 1).

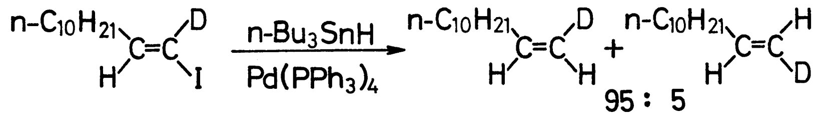
The method was successfully applied to the reduction of aryl iodides[3] as shown below (Scheme 3). The reduction of 1-iodonaphthalene with *n*-Bu_3SnH in the presence of Pd catalyst proceeded easily at 25 °C. In contrast, the reaction of 1-bromonaphthalene was sluggish at 25 °C. Heating a benzene solution of 1-bromonaphthalene at 75 °C for 5 h gave naphthalene in 72% yield along with recovered 1-bromonaphthalene (11%). Treatment of 1-iodo-2-(3-methyl-3-butenyl)benzene (**4**) with *n*-Bu_3SnH–$Pd(PPh_3)_4$ gave (3-methyl-3-butenyl)benzene (**5**) in 73% yield. The result showed sharp contrast to the radical reduction of **4** with Et_3B–*n*-Bu_3SnH system. The latter system gave a mixture of 1,1-dimethylindan (18%), 2-methyl-1,2,3,4-tetrahydronaphthalene (33%) and **5** (6%).[1]

We assume the following reaction mechanism: (1)



1 **2** **3**

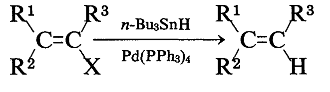
Scheme 1.



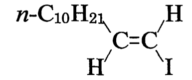
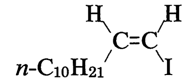
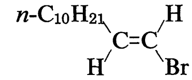
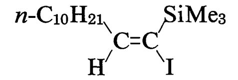
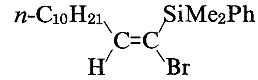
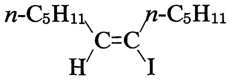
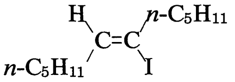
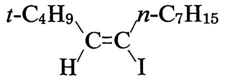
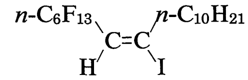
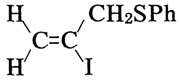
1 **2** **3**

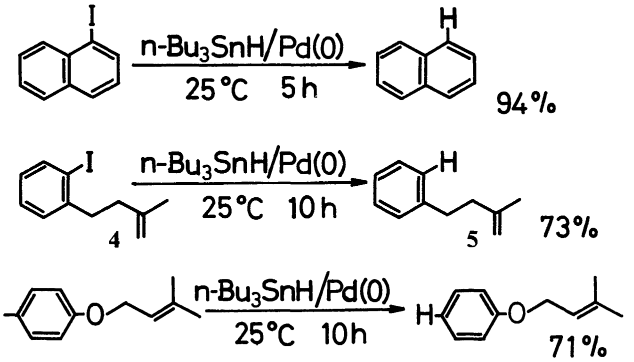
Scheme 2.

Table 1. Reduction of Alkenyl Halides with n-Bu_3SnH-$Pd(PPh_3)_4$



$$\begin{matrix} R^1 & & R^3 \\ & C=C & \\ R^2 & & X \end{matrix} \xrightarrow[Pd(PPh_3)_4]{n\text{-}Bu_3SnH} \begin{matrix} R^1 & & R^3 \\ & C=C & \\ R^2 & & H \end{matrix}$$

Entry	Alkenyl halide	Reaction condition		Product yield/% (Z:E)
		Temp/°C	Time/h	
1	 $\begin{matrix} n\text{-}C_{10}H_{21} & & H \\ & C=C & \\ H & & I \end{matrix}$	25	3	92
2	 $\begin{matrix} H & & H \\ & C=C & \\ n\text{-}C_{10}H_{21} & & I \end{matrix}$	25	5	82
3	 $\begin{matrix} n\text{-}C_{10}H_{21} & & H \\ & C=C & \\ H & & Br \end{matrix}$	75	5	37
4	 $\begin{matrix} n\text{-}C_{10}H_{21} & & SiMe_3 \\ & C=C & \\ H & & I \end{matrix}$	25	3	67 (95:5)
5	 $\begin{matrix} n\text{-}C_{10}H_{21} & & SiMe_2Ph \\ & C=C & \\ H & & Br \end{matrix}$	75	5	35 (5:95)
6	 $\begin{matrix} n\text{-}C_5H_{11} & & n\text{-}C_5H_{11} \\ & C=C & \\ H & & I \end{matrix}$	25	1	89 (94:6)
7	 $\begin{matrix} H & & n\text{-}C_5H_{11} \\ & C=C & \\ n\text{-}C_5H_{11} & & I \end{matrix}$	75	5	90 (0:100)
8	 $\begin{matrix} t\text{-}C_4H_9 & & n\text{-}C_7H_{15} \\ & C=C & \\ H & & I \end{matrix}$	25	3	71 (100:0)
9	 $\begin{matrix} n\text{-}C_6F_{13} & & n\text{-}C_{10}H_{21} \\ & C=C & \\ H & & I \end{matrix}$	25	3	97 (100:0)
10	 $\begin{matrix} H & & CH_2SPh \\ & C=C & \\ H & & I \end{matrix}$	25	1	82



Scheme 3.

Oxidative addition of alkenyl iodides to palladium, (2) reaction of the resulting alkenylpalladium iodides with tributyltin hydride to provide alkenylpalladium hydrides,[4] and (3) reductive elimination from the palladium compounds to give the corresponding alkenes and regenerate the palladium(0) complex.

Experimental

Distillation of the products was performed by use of Kugelrohr (Büchi) and boiling points are indicated by an air-bath temperature without correction. ^1H NMR and ^{13}C NMR spectra were taken on a Varian XL-200 spectrometer and $CDCl_3$ was used as solvent unless otherwise noted. Chemical shifts are given in δ with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. The analyses were carried out at the Elemental Analysis Center of Kyoto University. Purification of products was performed by silica-gel (Wakogel C-100) column chromatography.

Preparation of Alkenyl Iodides. (E)-1-Iodo-1-dodecene and (E)-1-bromo-1-dodecene were prepared following the reported procedure.[5] (E)-1-Deuterio-1-iodo-1-dodecene was prepared by hydroalumination of 1-deuterio-1-dodecyne with i-Bu_2AlH followed by iodination.[1] (E)-1-Iodo-1-trimethylsilyl-1-dodecene and (E)-1-bromo-1-dimethylphenylsilyl-1-dodecene were prepared according to the literature.[6] (E)-6-Iodo-6-dodecene and (Z)-6-iodo-6-dodecene were prepared from 6-dodecyne following the reported procedure for the preparation of (E)-3-iodo-3-hexene[7] and (Z)-3-iodo-3-

hexene.[8] Hydroalumination of 2,2-dimethyl-3-undecyne with i-Bu$_2$AlH followed by iodination gave a mixture of (E)-2,2-dimethyl-4-iodo-3-undecene and (E)-2,2-dimethyl-3-iodo-3-undecene (2 : 1). The former was purified by preparative glpc (OV-1 2% on Chromosorb W 60—80 mesh, 2 m, 150 °C, t_r=6.72 min ((E)-2,2-dimethyl-4-iodo-3-undecene) and t_r=8.64 min ((E)-2,2-dimethyl-3-iodo-3-undecene). (E)-1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-8-iodo-7-octadecene was prepared by the reaction of 1-dodecyne with n-C$_6$F$_{13}$I in the presence of triethylborane.[9]

(E)-6-Iodo-6-dodecene: Bp 60—65 °C (bath temp, 1 Torr, 1 Torr=133.322 Pa); IR (neat) 2954, 2924, 2854, 1729, 1630, 1466, 1459, 1379, 1269, 1195, 1136, 1108, 727 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.89 (t, J=6.7 Hz, 3H), 0.90 (t, J=6.5 Hz, 3H), 1.20—1.69 (m, 12H), 2.02 (td, J=7.3, 7.2 Hz, 2H), 2.36 (t, J=7.3 Hz, 2H), 6.18 (t, J=7.6 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=14.01, 22.45, 22.52, 28.80, 28.87, 30.55, 30.84, 31.28, 38.37, 103.6, 141.4. Found: C, 48.85; H, 8.06%. Calcd for C$_{12}$H$_{23}$I: C, 48.99; H, 7.88%.

(Z)-6-Iodo-6-dodecene: Bp 60—65 °C (bath temp, 1 Torr); IR (neat) 2954, 2924, 2854, 1729, 1643, 1465, 1459, 1429, 1378, 1274, 1134, 726 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.90 (t, J=6.8 Hz, 6H), 1.20—1.69 (m, 12H), 2.10 (td, J=6.8, 6.7 Hz, 2H), 2.45 (t, J=7.6 Hz, 2H), 5.46 (t, J=6.7 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=14.04, 22.42, 22.55, 28.10, 29.03, 30.37, 31.35, 36.35, 45.09, 109.8, 134.8. Found: C, 48.88; H, 8.00%. Calcd for C$_{12}$H$_{23}$I: C, 48.99; H, 7.88%.

(E)-2,2-Dimethyl-4-iodo-3-undecene: Bp 75—80 °C (bath temp, 1 Torr); IR (neat) 2954, 2924, 2854, 1730, 1618, 1465, 1365, 1243, 1202, 1114 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.89 (t, J=7.0 Hz, 3H), 1.12 (s, 9H), 1.25—1.45 (m, 8H), 1.50—1.70 (m, 2H), 2.44 (t, J=7.6 Hz, 2H), 6.24 (s, 1H); ^{13}C NMR (CDCl$_3$) δ=14.10, 22.64, 23.74, 29.17, 30.32, 30.93, 31.78, 36.84, 40.52, 106.3, 150.7. Found: C, 50.84; H, 8.35%. Calcd for C$_{13}$H$_{25}$I: C, 50.66; H, 8.17%.

(E)-1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-8-iodo-7-octadecene: Bp 105—110 °C (bath temp, 1 Torr); IR (neat) 2926, 2854, 1636, 1466, 1365, 1240, 1204, 1146, 1067 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.88 (t, J=5.8 Hz, 3H), 1.15—1.40 (m, 14H), 1.40—1.70 (m, 2H), 2.63 (t, J=7.3 Hz, 2H), 6.32 (t, J=14.4 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=14.05, 22.71, 28.47, 29.34, 29.48, 29.59, 30.10, 31.94, 41.18, 123.1 (t, J=6.5 Hz), 126.5 (t, J=24.0 Hz). Found: C, 35.45; H, 3.87%. Calcd for C$_{18}$H$_{22}$F$_{13}$I: C, 35.31; H, 3.62%.

2-Iodo-3-phenylthio-1-propene. 3-Bromo-2-iodo-1-propene[10] (2.47 g, 10 mmol) was added to a methanol solution of sodium benzenethiolate, generated from benzenethiol (1.1 g, 10 mmol) and sodium (0.23 g, 10 mg-atom) in methanol under argon atmosphere. After stirring for 1.5 h, the resulting mixture was poured into water. Extractive workup followed by silica-gel column chromatography gave the title compound (1.5 g) in 65% yield: Bp 103—108 °C (bath temp, 1 Torr); IR (neat) 3056, 2954, 2924, 1728, 1619, 1609, 1583, 1480, 1439, 1400, 1273, 1226, 1191, 1088, 1025, 900, 737, 688 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=3.83 (s, 2H), 5.73 (bs, 1H), 6.57 (bs, 1H), 7.3—7.5 (m, 5H); ^{13}C NMR (CDCl$_3$) δ=48.96, 105.8, 127.0, 127.7, 128.9, 130.7, 134.6. Found: C, 39.01; H, 3.10%. Calcd for C$_9$H$_9$IS: C, 39.15; H, 3.29%.

General Procedure for the Reduction of Alkenyl Iodides and Aryl Iodides. The reduction of (E)-1-iodo-1-dodecene was representative. Tributyltin hydride (0.38 g, 1.3 mmol) was added dropwise by syringe drive over 20 min to a solution of (E)-1-iodo-1-dodecene (0.29 g, 1.0 mmol) and Pd(PPh$_3$)$_4$ (23 mg, 2 mol%) at 25 °C under argon atmosphere. After completion of the addition, stirring was continued for another 1 h. The resulting mixture was poured into water and extracted with ethyl acetate (20 ml×3). Combined organic layers were dried over Na$_2$SO$_4$ and concentrated in vacuo to give a colorless oil which was submitted to silica-gel column chromatography using hexane as eluant to give 1-dodecene (0.15 g) in 92% yield. In the case of the reduction of (Z)-iodoalkenes, an addition of benzene solution of n-Bu$_3$SnH was achieved over 2 h by syringe drive.

Isomerization of (Z)-1-Deuterio-1-dodecene. Tributyltin hydride (58 mg, 0.2 mmol) was added to a solution of (Z)-1-deuterio-1-dodecene (**2**, 0.17 g, 1.0 mmol) and Pd(PPh$_3$)$_4$ (23 mg, 2 mol%) at 25 °C under argon atmosphere. After stirring for 2 h, the reaction mixture was poured into water and extracted with ethyl acetate. The examination of the crude product by ^{1}H NMR showed that (Z)-isomer **2** was partially isomerized into (E)-isomer **3** (**2** : **3**=73 : 27).

(Z)-2,2-Dimethyl-3-undecene: Bp 88—90 °C (bath temp, 13 Torr); IR (neat) 2954, 2922, 1729, 1466, 1363, 1273 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.88 (t, J=6.7 Hz, 3H), 1.10 (s, 9H), 1.20—1.48 (m,10H), 2.11—2.21 (dt, J=7.0, 7.0 Hz, 2H), 5.15 (dt, J=12.0, 7.0 Hz, 1H), 5.31 (d, J=12.0 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=14.12, 22.67, 28.37, 29.26, 29.37, 30.32, 31.16, 31.86, 33.07, 129.1, 139.5. Found: C, 85.61; H, 14.54%. Calcd for C$_{13}$H$_{26}$: C, 85.63; H, 14.37%.

(Z)-1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-7-octadecene: Bp 85—90 °C (bath temp, 1 Torr); IR (neat) 2926, 2856, 1729, 1664, 1466, 1364, 1240, 1203, 1146, 1121, 1102, 1067, 842, 810, 766, 743, 733, 718, 703 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.88 (t, J=6.2 Hz, 3H), 1.20—1.60 (m, 16H), 2.20—2.46 (m, 2H), 5.38—5.68 (m, 1H), 6.05—6.28 (m, 1H); ^{13}C NMR (CDCl$_3$) δ=14.08, 22.69, 28.57, 29.05, 29.13, 29.34, 29.53, 31.90, 115.9 (t, J=23.4 Hz), 145.7 (t, J=5.9 Hz). Found: C, 44.74; H, 4.66%. Calcd for C$_{18}$H$_{23}$F$_{13}$: C, 44.45; H, 4.77%.

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