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Triethylborane-Induced Hydrodehalogenation of Organic Halides by Tin Hydrides

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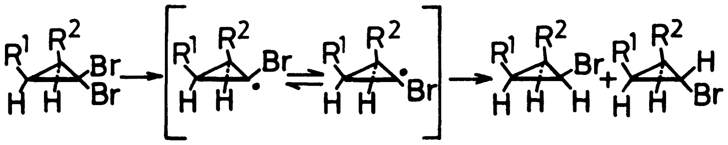
The reduction of organic halides with tributyltin hydride in the presence of a catalytic amount of triethylborane has been studied. (1) Alkyl iodides and alkyl bromides reacted easily with tin hydride at −78°C to give the corresponding hydrocarbons, while alkyl chlorides were sluggish to react and recovered unchanged. (2) The reduction of alkenyl halides such as 1-deuterio-1-iodo-1-dodecene and 1-iodo-1-triethylsilyl-1-dodecene proceeded nonstereospecifically. (3) The reduction of aryl halides with *n*-Bu_3SnH–Et_3B system was not so effective as the reduction of alkyl halides and alkenyl halides. Whereas aryl iodides were reduced at room temperature with *n*-Bu_3SnH, aryl bromides hardly reacted with *n*-Bu_3SnH even at 80 °C.

The free radical halogen abstraction from a C–Hal bond opens a broad variety of synthetic possibilities.[1,2] The simplest version is trapping of the outcoming radical by tin hydride, providing us with a facile route to replacement of halogen by hydrogen at the same carbon atom. The reactions are initiated by generation of tin radicals, which are produced mostly by radical initiators such as azobisisobutyronitrile (AIBN) or benzoyl peroxide. Recently we have found that Et_3B is an efficient radical initiator for generation of tin radicals from tin hydrides and applied this methodology to a couple of organic syntheses.[3] We would now like to report on a more detailed study on the reduction of organic halides with R_3SnH in the presence of Et_3B under mild reaction conditions.

Reduction of Alkyl Halides. A number of organic halides were reduced with *n*-Bu_3SnH–Et_3B system and the results are summarized in Table 1. Treatment of a solution of 1-bromododecane and tributyltin hydride in toluene with a catalytic amount of Et_3B (hexane solution, 10 mol%) gave dodecane quantitatively. It is worth noting that the reaction proceeded at low temperature such as −78 °C. Without Et_3B, 1-bromododecane was recovered quantitatively after treatment with *n*-Bu_3SnH in toluene at −78 °C for 3 h. Secondary bromoalkane and tertiary bromides were also easily reduced. The reactivity of the halides depends on the nature of the halogen. Iodides and bromides reacted easily with tin hydride in the presence of Et_3B, while chlorides were sluggish to react and were recovered practically unchanged. Heating a benzene solution of 1-chlorododecane with *n*-Bu_3SnH or Ph_3SnH in the presence of a catalytic amount of Et_3B at 70 °C for 5 h resulted in a recovery of the starting 1-chlorododecane quantitatively. Taking advantage of the difference in reactivity between bromide and chloride, it was possible to reduce one halogen in the presence of the other (Run 10).

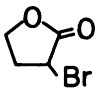
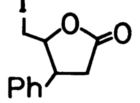
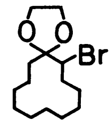
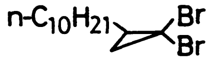
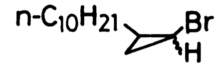
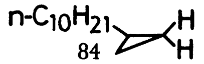
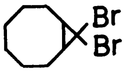
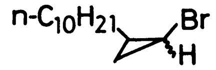
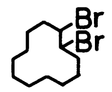
Reduction of halides containing other functional groups such as ether, hydroxyl, or carbonyl proved that these functionalities could be present in the molecule without perturbing the course of reduction, although the nature of the functional group slightly influences the development of the reaction. For example, *β*-bromopropiophenone (Run 7) and ethylene acetal (Run 13) were reduced slowly at −78 °C. The reaction mixture was allowed to come to room temperature and then stirred for several hours to complete the reduction. 11-Bromo-1-undecanol could not be reduced at low temperature because of its low solubility in toluene and the reaction was perpformed at 0 °C.

Monodehalogenation of alkyl-substituted *gem*-dibromocyclopropanes with *n*-Bu_3SnH–Et_3B proceeded easily at −78 °C to provide stereoisomeric mixtures of monobromocyclopropanes. The isomeric ratios were almost the same as those obtained by reported ordinary procedure (without Et_3B).[4] The formation of *endo*- or *cis*-bromocyclopropanes as major products is explained as follows: (1) Tin radical attacks bromine to give a radical, (2) the intermediate radical equilibrates faster than hydrogen is transferred, (3) finally the less hindered approach of tin hydride provide endo or cis isomer selectively (Scheme 1). Reduction of monobromocyclopropanes to cyclopropanes did not proceed at −78 °C and it took prolonged reaction time (10 h) at



Scheme 1.

Table 1. Reduction of Alkyl Halides with n-Bu_3SnH-Et_3B

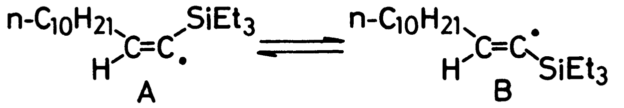
Run	Substrate	Reaction conditions		Procedure	Yield of alkane
		Temp	Time		
		°C	h		%
1	1-Iodododecane	−78	0.5	A	95
2	2-Iodododecane	−78	0.5	A	90
3	1-Bromododecane	−78	0.5	A	100
4	2-Bromododecane	−78	0.5	A	98
5	1-Bromoadamantane	−78	0.5	A	75
6	$BrCH_2CH_2CH_2OTHP$	−78	0.5	B	77
7	$PhCOCH_2CH_2Br$	25	10	B	87
8	$HOCH_2(CH_2)_9CH_2Br$	0	0.5	B	94
9	$MeOOC(CH_2)_9CH_2Br$	−78	0.5	B	95
10	$Cl(CH_2)_3COO(CH_2)_3Br$	−78	0.5	B	87
11		−78	0.5	B	90
12		−78	0.5	B	87
13		−78, 1; 20, 3		A	80
14		−78	1.0	A	 92(67/33)[a]
		20	15[b]	A	 84
15		−78	1.0	A	Monobromide 80(82/18)[c]
16		20	11	A	83
17	$CH_3(CH_2)_9CHBrCH_2Br$	−78	0.5	A	1-Dodecene 99
18		−78	0.5	A	Cyclododecene 96

a) Isomeric ratio (cis/trans). b) 2.2 mol of n-Bu_3SnH was employed. c) Isomeric ratio (endo/exo).

room temperature to complete the reaction. Treatment of dibromocyclopropanes with 2.2 mol of tin hydride at room temperature for 15 h afforded cyclopropanes directly in high yields.

β-Elimination has been achieved by treatment of *vic*-dibromoalkanes with n-Bu_3SnH-Et_3B system. *meso*-1,2-Dibromocyclododecane gave a mixture of *trans*- and *cis*-cyclododecene in an 1 : 1 ratio (Run 18).

Reduction of Alkenyl Halides. The reduction of alkenyl iodides and bromides was also examined in the presence of a catalytic amount of Et_3B. Whereas iodides reacted easily with tin hydrides at −78 °C, bromides reacted slowly compared with iodides and it took 10 h to complete the reduction at room temperature. The effectiveness of Et_3B catalyst was confirmed by the fact that treatment of a solution of (*E*)-1-bromo-1-dodecene with n-Bu_3SnH in the absence of Et_3B at room temperature for 15 h resulted in quantitative recovery of (*E*)-1-bromo-1-dodecene. The typical results are summarized in Table 2. Treatment of (*E*)-1-deuterio-1-iodo-1-dodecene or (*Z*)-isomer with n-Bu_3SnH-Et_3B at −78 ° resulted in a formation of similar isomeric mixtures of (*E*)- and (*Z*)-1-deuterio-1-dodecene (*E*:*Z*=61 : 39—63 : 37). Thus, the reduction proceeded nonstereospecifically. Same stereochemical results were obtained with n-Bu_3SnH-AIBN system. The reaction of (*E*)- or (*Z*)-1-deuterio-1-iodo-1-dodecene with n-Bu_3SnH in the presence of AIBN at 50 °C provided similar isomeric mixtures of (*E*)- and (*Z*)-1-deuterio-1-dodecene (*E*:*Z*=60:40). The reduction of alkenyl halides having silyl group on the same carbon bearing iodine also followed non-stereospecific course (Runs 6 and 7). (*E*)-1-Iodo-1-triethylsilyl-1-dodecene (**1**) gave a mixture of (*Z*)-1-triethylsilyl-1-dodecene and (*E*)-isomer (*Z*:*E*=56:44) and (*Z*)-isomer **2** afforded a *Z*:*E*=57:43 mixture upon treatment with *n*-Bu_3SnH–Et_3B at −78 °C.[5] The results have been explained by fast equilibration of two configurations of the alkenyl radical before hydrogen transfer (Scheme 2).



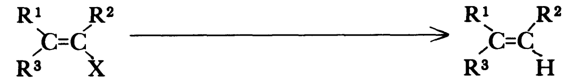
Scheme 2.

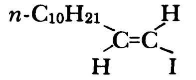
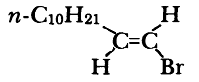
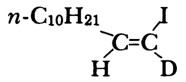
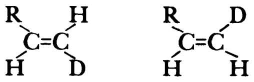
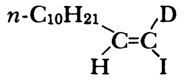
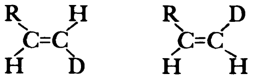
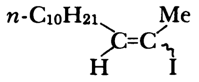
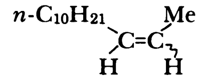
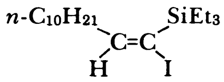
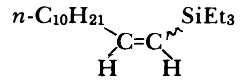
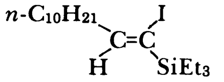
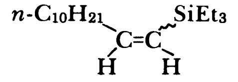
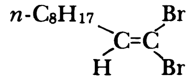
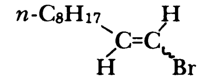
gem-Dibromoalkene provided monobromoalkene. For instance, reduction of 1,1-dibromo-1-dodecene gave an 1:1 mixture of 1-bromo-1-dodecene.

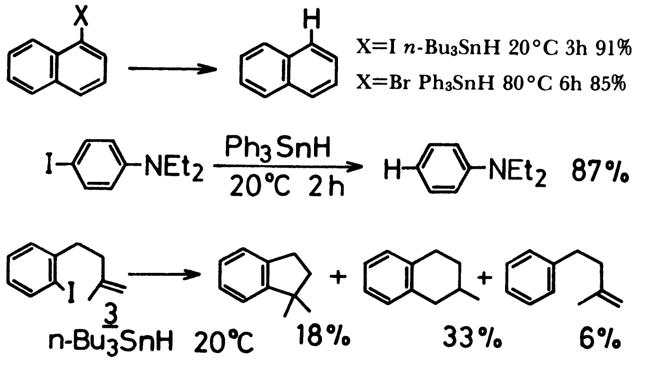
Reduction of Aryl Halides. The reduction of aryl iodides and bromides proceeded slowly with *n*-Bu_3SnH–Et_3B system.[6] 1-Iodonaphthalene reacted at room temperature, while 1-bromonaphthalene were inert. Aryl bromides were reduced at 80 °C, however, when more reactive Ph_3SnH was employed. The reaction was successively applied to the cyclization reaction. For instance, a mixture of five-membered ring and six-membered ring products was obtained upon treatment of aryl iodide **3** with *n*-Bu_3SnH–Et_3B (Scheme 3).

The Et_3B-induced reaction has following characteristics compared to ordinary reaction. (1) Tributyltin radical or triphenyltin radical can be generated at low

Table 2. Reduction of Alkenyl Halides with *n*-Bu_3SnH–Et_3B


$R^1R^3C{=}CR^2X \longrightarrow R^1R^3C{=}CR^2H$

Run	Substrate	Reaction conditions Temp/°C	 Time/h	Yield of alkene/%
1	 $n\text{-}C_{10}H_{21}(H)C{=}C(H)(I)$	20	0.5	1-Dodecene 77
2	 $n\text{-}C_{10}H_{21}(H)C{=}C(H)(Br)$	20	12	1-Dodecene 98
3	 $n\text{-}C_{10}H_{21}(H)C{=}C(I)(D)$	−78, 2;	20, 0.5	 $R(H)C{=}C(H)(D)$ $R(H)C{=}C(D)(H)$ 83 (63:37)
4	 $n\text{-}C_{10}H_{21}(H)C{=}C(D)(I)$	−78, 2;	20, 0.5	 $R(H)C{=}C(H)(D)$ $R(H)C{=}C(D)(H)$ 87 (61:39)
5	 $n\text{-}C_{10}H_{21}(H)C{=}C(Me)(I)$	−78	0.5	 $n\text{-}C_{10}H_{21}(H)C{=}C(Me)(H)$ 84
6	 $n\text{-}C_{10}H_{21}(H)C{=}C(SiEt_3)(I)$ **1**	−78	0.5	 $n\text{-}C_{10}H_{21}(H)C{=}C(SiEt_3)(H)$ 95 (*Z*/*E*=56/44)
7	 $n\text{-}C_{10}H_{21}(H)C{=}C(I)(SiEt_3)$ **2**	−78	0.5	 $n\text{-}C_{10}H_{21}(H)C{=}C(SiEt_3)(H)$ 98 (*Z*/*E*=57/43)
8	 $n\text{-}C_8H_{17}(H)C{=}C(Br)(Br)$	−78	0.5	 $n\text{-}C_8H_{17}(H)C{=}C(H)(Br)$ 80 (*Z*/*E*=1:1)



Scheme 3. Triethylborane-catalyzed reduction of aryl halides.

temperature such as −78 °C and thereby the reduction of organic halides (iodides and bromides) proceeds at lower temperature than that with n-Bu_3SnH–AIBN (or dialkyl peroxide) system. The mildness of the reaction will offer promising possibilities for selective reduction. (2) The reduction of organic halides with n-Bu_3SnH–Et_3B system takes place easily to give the corresponding hydrocarbons in comparable yields to previously reported procedure.

Triethylborane proved to be an effective radical initiator in the presence of trace amount of oxygen. Other role of Et_3B, however, is not clear. We are studying on this point from the intrinsic mechanistic interest.

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, $CDCl_3$ was used as solvent unless otherwise noted, chemical shifts being given in δ with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. The analyses were carried out by the staff at the Elemental Analyses Center of Kyoto University. Purification of products was performed by silica gel (Wakogel C-100) column chromatography.

Tributyltin Hydride and Triphenyltin Hydride. These compounds were prepared according to the reported procedure.[7]

Preparation of Alkyl Halides. Commercially available organic halides such as 1-bromododecane, 2-bromododecane, 1-iodododecane, 1-bromoadamantane, and α-bromo-γ-butyrolactone were used without further purification. Methyl 11-bromo undecanoate,[8] β-bromopropiophenone,[9] and 4,5-dihydro-5-iodomethyl-4-phenyl-2(3*H*)-furanone[10] were prepared according to the literature. *gem*-Dibromocyclopropanes were generated following the literature.[4] *vic*-Dibromides were prepared by treatment of 1-dodecene and *trans*-cyclododecene with bromine in ether.

3-Bromopropyl 4-Chlorobutyrate. A solution of 4-chlorobutyryl chloride (1.4 g, 10 mmol) in ether (10 ml) was added dropwise to a solution of 3-bromo-1-propanol (1.39 g, 10 mmol) and pyridine (1.6 g, 20 mmol) in ether (10 ml) at 0 °C under an argon atmosphere. The resulting mixture was stirred for 15 min at 0 °C, then for 2 h at room temperature. The mixture was diluted with ethyl acetate (20 ml) and poured into 1 M HCl (1 M=1 mol dm^{-3}) solution. Organic layer was separated and washed with 1 M HCl (2×20 ml) and brine (2×20 ml). Concentration of the dried (Na_2SO_4) organic layer gave a crude oil which was purified by silica-gel column chromatography followed by distillation to provide the title compound (1.8 g) in 74% yield. Bp 120 °C (bath temp, 2 Torr, 1 Torr=133.322 Pa); IR (neat) 2960, 1733, 1442, 1421, 1391, 1364, 1298, 1174, 1146, 1090, 1050, 1009, 785, 650 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.00—2.26 (m, 4H), 2.53 (t, J=7.3 Hz, 2H), 3.48 (t, J=6.5 Hz, 2H), 3.62 (t, J=6.3 Hz, 2H), 4.21 (t, J=6.1 Hz, 2H). Found: C, 34.68; H, 5.05%. Calcd for $C_7H_{12}O_2ClBr$: C, 34.52; H, 4.97%.

Preparation of Alkenyl Halides. (*E*)-1-Iodo-1-dodecene or (*E*)-1-bromo-1-dodecene were prepared by hydroalumination followed by treatment with iodine or bromine.[11]

(*E*)-1-Deuterio-1-iodo-1-dodecene. The compound was generated by hydroalumination of 1-deuterio-1-dodecyne followed by iodination. ^1H NMR ($CDCl_3$) δ=0.80—1.00 (m, 3H), 1.20—1.50 (m, 16H), 2.00—2.15 (m, 2H), 6.53 (tm, J=7.5 Hz, 1H).

(*Z*)-1-Deuterio-1-iodo-1-dodecene. Hydroalumination of 1-trimethylsilyl-1-dodecyne in hexane–ether (1:1) followed by the addition of D_2O gave (*Z*)-1-deuterio-1-trimethylsilyl-1-dodecene.[12] Iododesilylation[13] of alkenylsilane gave the title compound. ^1H NMR ($CDCl_3$) δ=0.75—0.95 (m, 3H), 1.10—1.50 (m, 16H), 2.00—2.20 (m, 2H), 6.18 (t, J=7.0 Hz, 1H).

2-Iodo-2-tridecene. The compound was prepared by iododesilylation according to the reported procedure.[13] A solution of iodine (0.25 g, 1.0 mmol) in dichloromethane (5.0 ml) was added to a solution of (*Z*)-2-trimethylsilyl-2-tridecene generated from 1-trimethylsilyl-1-dodecyne (0.25 g, 1.0 mmol)[14] in dichloromethane (5.0 ml) at 25 °C and the resulting mixture was stirred for 1 h. Work-up followed by purification by TLC (silica gel) gave 2-iodo-2-tridecene (0.20 g) in 65% yield as an isomeric mixture (*E*:*Z*=4:6). ^1H NMR ($CDCl_3$) δ=0.75—0.95 (m, 3H), 1.20—1.50 (m, 16H), 2.00 (m, 2H), 2.33 (s, 1.8H), 2.45 (s, 1.2H), 5.38 (tq, J=6.8, 1.5 Hz, 0.4H), 6.15 (tq, J=7.5, 1.7 Hz, 0.6H).

(*E*)-1-Iodo-1-triethylsilyl-1-dodecene and (*Z*)-1-Iodo-1-triethylsilyl-1-dodecene. These compounds were prepared from 1-triethylsilyl-1-dodecyne following the reported procedure.[12]

1,1-Dibromo-1-decene. The title compound was prepared from decanal, carbon tetrabromide, and triphenylphosphine.[15]

General Procedure for the Reduction of Alkyl Halides. (a) Procedure A: The hydrodehalogenation of 1-bromododecane is representative of procedure A. A dry 30-ml flask was equipped with septum inlet, a stirring bar, and three-way stop cock. One end of stop cock was connected to a balloon which was filled with argon. The inner atmosphere of the apparatus was replaced by argon. The flask was charged with a solution of 1-bromododecane (0.25 g, 1.0 mmol) in toluene (4.0 ml) and cooled to −78 °C with an Dry Ice–methanol bath. A solution of tributyltin hydride (0.33 g, 1.1 mmol) in toluene (4.0 ml) and a hexane solution of Et_3B (1.0 M, 0.1 ml, 0.1 mmol) was added successively. The solution was stirred for 30 min at −78 °C. The disappearance of the starting material was confirmed by thin layer chromatographic assay. The resulting mixture was transferred into 100 ml round-bottomed flask using 25 ml of methanol. The solvent was evaporated as an azeotropic mixture to afford a crude oil which was submitted to silica-gel column chromatography (hexane as an eluant) to give dodecane (0.17 g) quantitatively. **(b) Procedure B:** The procedure was used for the reduction of the compounds which have polar functional groups such as hydroxyl or carbonyl in the molecule. The reduction of 11-bromo-1-undecanol to 1-undecanol is representative. A solution of tributyltin hydride (0.33 g, 1.0 mmol) in toluene (4.0 ml) was added to a solution of 11-bromo-1-undecanol (0.25 g, 1.0 mmol) in toluene (4.0 ml) at 0 °C. Et_3B (1.0 M hexane solution, 0.1 ml, 0.1 mmol) was added and the resulting mixture was stirred at 0 °C for 30 min. The reaction mixture was diluted with EtOAc (20 ml) and saturated aqueous potassium fluoride (2 ml) and anhydrous potassium fluoride (1.0 g) were added to remove tributyltin bromide.[16] The mixture was stirred for another 30 min and the precipitated tributyltin fluoride was removed by filtration and washed with ethyl acetate. Combined filtrates were washed with brine and dried over anhydrous sodium sulfate and concentrated in vacuo. The residual oil was purified by silica-gel column chromatography (hexane/ethyl acetate=5/1 as an eluant) to give 1-undecanol (0.16 g) in 94% yield.

General Procedure for the Reduction of Alkenyl Halides. The reactions were performed following the procedure A described for the reduction of alkyl halides. A solution of tributyltin hydride (0.33 g, 1.1 mmol) in toluene (4.0 ml) and Et_3B (1.0 M hexane solution, 0.1 ml, 0.1 mmol) were added successively to a solution of 1,1-dibromo-1-decene (0.30 g, 1.0 mmol) in toluene (4.0 ml) at −78 °C and the resulting mixture was stirred at −78 °C for 30 min. Concentration followed by purification by silica-gel column chromatography gave 1-bromo-1-decene (0.18 g) in 80% yield as an isomeric mixture (E/Z=1/1).

Reduction of Aryl Halide 3 with *n*-Bu_3SnH-Et_3B. A solution of *n*-Bu_3SnH (0.35 g, 1.2 mmol) in benzene (2.0 ml) was added dropwise over 2 h by syringe pump to a solution of aryl iodide **3** (0.24 g, 1.0 mmol) and Et_3B (1.0 M hexane solution, 0.1 ml, 0.1 mmol) in benzene (10 ml) at 20 °C. The resulting mixture was stirred more than 1 h after the completion of the addition. Work-up followed by purification by preparative TLC on silica gel gave a mixture of 1,1-dimethylindan (18%), 2-methyl-1,2,3,4-tetrahydronaphthalene (33%), and (3-methyl-3-butenyl)benzene (6%), whose spectra were identical with those of authentic samples.[17,18]

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