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Hydroborations, Reductions and Reductive Iodinations Using BHI_2: $N(C_2H_5)_2Ph$ Complex

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Abstract: The BHI_2:$N(C_2H_5)_2Ph$ complex, prepared by the reaction of BH_3:$N(C_2H_5)_2Ph$ with I_2, is useful for hydroboration of alkenes, reduction of amides, iodination of alcohols, reductive iodination of carboxylic acids, aldehydes and ketones. Selective hydroboration of monosubstituted olefin over disubstituted olefinic moiety and terminal olefin over internal alkyne moiety have been achieved using this reagent. Carboxylic esters and nitriles are not affected by this reagent. Selective hydroboration of 1-alkenes and selective reductive iodination of cyclohexanone are achieved in the presence of ester and nitrile functional groups.

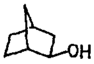
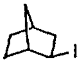
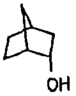
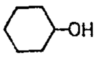
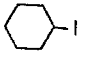
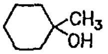
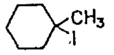
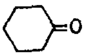
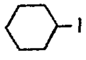
The haloboranes, XBH_2 and X_2BH have been proved to be useful reagents,[1-5] especially in selective hydroborations. These haloboranes have an advantage over monoalkyl and dialkyl boranes since oxidation of organoboranes obtained using the alkylborane agents give products derived from the alkyl moieties which might pose problems during work up. The reactivities of chloro and bromo borane-Lewis base complexes have been studied in some detail. Although the I_2BH:SMe_2 complex is readily available through the reaction of BH_3:SMe_2 with I_2,[6] the reactivities of this reagent have not been examined in detail. We wish to report that the diiodoborane-N,N-diethylaniline I_2BH:$N(C_2H_5)_2Ph$ (DIBA) complex readily available through the reaction of BH_3:$N(C_2H_5)_2Ph$ with I_2 is useful for hydroborations, iodination of alcohols, reduction of amides and reductive iodination of carbonyl compounds.[7]

Hydroboration-oxidation of 1-decene with the diiodoborane-N,N-diethylaniline (DIBA) complex in 12h at room temperature gives 1-decanol in 81% yield (entry no. 1, Table 1). The reaction with styrene gives 2-phenylethanol in 83% yield (entry no.2, Table 1). The ^1H NMR spectrum of the product indicates the absence of signals corresponding to 1-phenylethanol.

Hydroboration of 1-decyne for 12h followed by oxidation using $NaOAc/H_2O_2$ yields 1-decanal (50%) and 1-decanol (20%) (entry no.3, Table 1). The formation of 1-decanol indicates that a 1,1-dibora derivative is also formed in the hydroboration in addition to the alkenylborane.

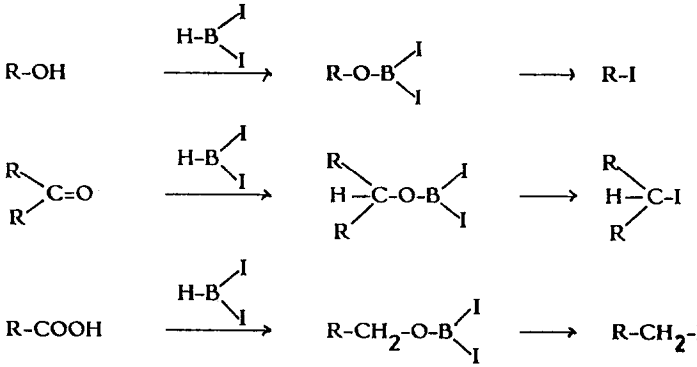
A representative tertiary amide is reduced to the corresponding amine in 81% yield (entry no.4, Table 1). However, a secondary amide gives poor results (entry no.5, Table 1). It was also observed that the methyl-1-decanoate and 1-octyl cyanide remained unreacted under the reaction conditions. The inertness of the nitrile group is interesting since BH_3:THF reacts with nitriles at room temperature.[9] The B_2H_6/I_2 system has been reported to give iodides from alcohols.[10] A similar reactivity pattern is expected for the BHI_2 complex and hence the reagent should be useful for iodination of alcohols and reductive iodination of carbonyl compounds (Scheme 1).

Table 1: Hydroborations, Reductions, and Reductive iodinations using $BHI_2{:}N(C_2H_5)_2Ph$ complex

Entry No.	Substrate	Reaction time	Product[d]	Yield (%)
1	$H_3C(CH_2)_7CH{=}CH_2$	12h[a]	$H_3C(CH_2)_8CH_2OH$	81
2	$PhCH{=}CH_2$	12h[a]	$PhCH_2CH_2OH$	83
3	$H_3C(CH_2)_7C{\equiv}CH$	12h[a]	$H_3C(CH_2)_8CHO$ +	50
			$H_3C(CH_2)_8CH_2OH$	20
4	$H_3C(CH_2)_8CON(CH_3)Ph$	12h[b]	$H_3C(CH_2)_8CH_2N(CH_3)Ph$	81
5	$PhNHCOCH_3$	12h[b]	$PhNHCH_2CH_3$	41
6	$H_3C(CH_2)_{14}CH_2OH$	12h[c]	$H_3C(CH_2)_{14}CH_2I$	84
7		6h[c]		82
8		6h[c]		69
9		12h[c]		86
10		1h[c]		89
11		11h[c]		75
12	$H_3C(CH_2)_5CHO$	11h[c]	$H_3C(CH_2)_5CH_2I$	82
13	$PhCH_2COOH$	11h[c]	$PhCH_2CH_2I$	66
14	$HOOC(CH_2)_8COOH$	11h[c]	$IH_2C(CH_2)_8CH_2I$	60

(a) The experiments were carried out using organic substrate (5 mM), amine-borane (5 mM) and iodine (5 mM). The organoborane was oxidised using $NaOH/H_2O_2$. (b) Amide (5 mM), amine-borane (10 mM) and iodine (10 mM) were used. (c) For entries 6-10, alcoholic substrates (10 mM); amine-borane (10 mM) and iodine (10 mM) were utilized. For entries 11, 12, the ketonic and aldehydic substrates (10 mM), amine-borane (10 mM) and iodine (10 mM) were utilized. For entry 13, the carboxylic acid substrate (10 mM), amine-borane (30 mM) and iodine (30 mM) were utilized. For entry 14, the carboxylic acid substrate (5 mM), amine-borane (30 mM) and iodine (30 mM) were utilized. For entry 6, the alcohol was added at 25°C in 1h and then stirred for 12h at 80°C. For entries 11-14, the substrates were added at 0°C, the contents were brought to 25°C in 1h and stirred for 11h at 25°C. (d) The products were isolated by column chromatography, silica gel using (hexane/ethyl acetate) as an eluent and identified by spectral data (IR, ^1H NMR and ^{13}C NMR) and comparison with data reported in the literature.

Scheme 1



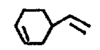
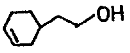
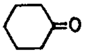
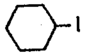
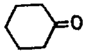
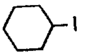
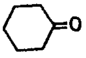
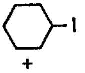
Reaction of BHI_2:amine complex with representative primary, secondary and tertiary alcohols gives the corresponding alkyl iodides in good yields (Table 1). Reductive iodination of cyclohexanone and 1-heptanal gives the corresponding iodides in reasonable yields (entry nos. 11 & 12, Table 1). Reductive iodination of carboxylic acids gives the corresponding primary alkyl iodides in 60-66% yields (entry nos. 13 & 14, Table 1).

In order to examine the chemoselectivities of this reagent system, we have carried out several experiments using bifunctional substrates or a mixture of two substrates. The results are summarized in Table 2. Hydroboration of 4-vinyl-1-cyclohexene for 12h followed by $NaOH/H_2O_2$ oxidation yields the corresponding cyclohexenyl ethanol (entry no.1, Table 2). This illustrates faster reaction of a terminal alkene over an internal cyclic olefinic moiety. The hydroboration of 1-allyldecyne (entry no.2, Table 2) followed by oxidation with $NaOAc/H_2O_2$ gives the corresponding alkynol in 61% yield. This is surprising since the reaction of a similar enyne with $HBBr_2:SMe_2$ complex leads to preferential hydroboration of the acetylenic moiety.[11] This difference in the reactivity is not understood. Nevertheless, the complementary result should be synthetically useful. It was observed that both olefin and tertiary amide groups are attacked by the reagent (entry no.3, Table 2). The ester group is spared when it is present along with olefin as indicated by entry no.5 in Table 2. Also, hydroboration of 1-decene is successfully carried out in the presence of a nitrile. This is interesting since both nitrile and olefinic moieties are attacked by reagents such as BH_3:THF.[9]

In order to examine whether reductive iodination of cyclohexanone can be carried out in the presence of other functional groups, we have carried out experiments using cyclohexanone along with 1-decene, octyl cyanide and methyl-1-decanoate in individual runs. The olefin also undergoes hydroboration along with reductive iodination of cyclohexanone (entry no.7, Table 2). However, the reductive iodination of cyclohexanone can be successfully carried out in the presence of carboxylic ester and nitrile groups (entry nos. 8 & 9, Table 2).

In conclusion, the $HBI_2:N(C_2H_5)_2Ph$ reagent is useful for hydroboration of alkenes, reduction of tertiary amides, iodination of alcohols, reductive iodination of carbonyl compounds with some interesting selectivities.

Table 2: Hydroborations, Reductions and Reductive iodinations of a mixture or bifunctional substrates

Entry No.	Substrate	Product	Yield (%)[a]
1			76[b]
2	$n\text{-}C_8H_{17}C\equiv CCH_2CH=CH_2$	$n\text{-}C_8H_{17}C\equiv C(CH_2)_2CH_2OH$	61[b]
3	$H_2C=CH(CH_2)_8CON(CH_3)Ph$	$HOH_2C(CH_2)_9CH_2N(CH_3)Ph$	72[c]
4	$H_3C(CH_2)_7CH=CH_2$ +	$H_3C(CH_2)_8CH_2OH$ +	78[d]
	$H_3C(CH_2)_8COOCH_3$	$H_3C(CH_2)_8COOH_3$	92
5	$H_2C=CH(CH_2)_8COOCH_3$	$HOH_2C(CH_2)_9COOCH_3$	80[b]
6	$H_3C(CH_2)_7CH=CH_2$ +	$H_3C(CH_2)_8CH_2OH$ +	77[d]
	$H_3C(CH_2)_7C\equiv N$	$H_3C(CH_2)_7C\equiv N$	93
7	$H_3C(CH_2)_7CH=CH_2$ +	$H_3C(CH_2)_8CH_2OH$ +	40[e]
			46
8	 +	 +	75[f]
	$H_3C(CH_2)_7C\equiv N$	$H_3C(CH_2)_7C\equiv N$	94
9	 +	 +	71[f]
	$H_3C(CH_2)_8COOCH_3$	$H_3C(CH_2)_8COOCH_3$	92

(a) Products were isolated by column chromatography (silica gel, hexane/ethyl acetate) and identified by spectral data (IR, ^1H and ^{13}C NMR) and comparison with the data reported in the literature. (b) The experiments were carried out using amine-borane (5 mM), I_2 (5 mM) and organic substrates (5 mM). The organoborane was oxidised using $NaOH/H_2O_2$. (c) Amide (5 mM), amine-borane (15 mM) and I_2 (15 mM) were used. The organoborane was oxidised using $NaOH/H_2O_2$. (d) Amine-borane (5 mM), I_2 (5 mM) and 1-decene (5 mM), methyl-1-decanoate (5 mM) or octyl cyanide (5 mM) were used. The organoborane was oxidised using $NaOH/H_2O_2$. (e) To the reagent prepared from amine-borane (5 mM) and I_2 (5 mM), a mixture of 1-decene (5 mM) and cyclohexanone (5 mM) was added at 0°C. The contents were brought to 25°C in 1h and then stirred for 11h. The organoborane was oxidised using $NaOH/H_2O_2$. (f) To the reagent prepared from amine-borane (5 mM) and I_2 (5 mM), a mixture of cyclohexanone (5 mM) and 1-methyldecanoate (5 mM) or octylcyanide (5 mM) was added at 0°C. The contents were brought to 25°C in 1h and then stirred for 11h.

EXPERIMENTAL SECTION

General: Benzene distilled freshly over benzophenone-sodium was used as solvent for all experiments. Infrared spectra were recorded on a Perkin-Elmer spectrometer 1310 with polystyrene as reference. NMR spectra were recorded on a JEOL-FX-100 spectrometer in deuterated chloroform using tetramethylsilane as internal standard. The chemical shifts (δ) are expressed in ppm downfield from the signal for internal Me_4Si. TLC plates coated with silica gel were used with hexane/ethyl acetate mixture as eluent and spots were developed in iodine. For column chromatographic purification under gravity, column grade silica gel (100-200 mesh size) was employed. N-methyl-N-phenyldecanamide and N-methyl-N-phenylundecenamide were prepared using the corresponding acids and N-methylaniline.[12] Trideca-4-yn-1-ene was prepared using 1-decyne and allyl bromide following a reported procedure.[13]

Hydroboration of 4-vinyl-1-cyclohexene: Borane-N,N-diethylaniline complex was prepared in situ by bubbling diborane, generated by dropwise addition of iodine (I_2) (1.27 g, 5 mM) in diglyme (10 ml) to $NaBH_4$ (0.4 g, 10 mM) in diglyme (5 ml) at 25°C, into a solution of N,N-diethylaniline (0.745 g, 5 mM) in dry benzene (50 ml) for 1h.[14] Iodine (1.27 g, 5 mM) in benzene (20 ml) was added at 10°C in order to convert borane-amine complex into diiodoborane-amine complex.[7] The contents were stirred for 2h at 25°C. The 4-vinyl-1-cyclohexene (0.540 g, 5 mM) was added to this reagent at 25°C, stirred for 12h. The reaction was quenched with water (5 ml) and oxidised using NaOH (3N, 10 ml)/H_2O_2 (30%, 10 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic layer was washed with 3N HCl (20 ml), water, brine and dried over anhydrous $MgSO_4$. On evaporation of solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/90:10), 2-(4-cyclohexenyl)ethanol[15] (0.48 g, 76%) was isolated. IR(neat): ν_{max} 3275, 3050, 1040, 920, 650 cm^{-1}. ^1H NMR (δ ppm/ $CDCl_3$): 5.60 (s, 2H); 3.64(t, 2H); 2.20-1.20(m, 10H). ^{13}C NMR(δ ppm, $CDCl_3$): 126.8, 126.1, 60.1, 39.0, 31.4, 29.7, 28.6, 24.7.

Hydroboration of trideca-4-yn-1-ene: I_2BH-N,N-diethylaniline complex (5 mM) was prepared in situ as above.[7,14] The trideca-4-yn-1-ene (0.90 g, 5 mM) was added to this reagent at 25°C, stirred for 12h. The reaction was quenched with water (5 ml) and oxidised using NaOH (3N, 10 ml)/H_2O_2 (30%, 10 ml). The organic layer was separated and aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with 3N HCl (20 ml), water, brine and dried over anhydrous $MgSO_4$. On evaporation of solvent and purification by chromatography on silica gel colum (hexane:ethyl acetate/90:10), trideca-4-yn-1-ol (0.60 g, 61%) was isolated. IR(neat): ν_{max} 3300, 1500, 1125 cm^{-1}. ^1H NMR(δ ppm, $CDCl_3$): 3.76-3.60(t, 2H); 2.32-2.00(m, 4H); 1.84-1.12(m, 15H); 0.92-0.72(t, 3H). ^{13}C NMR(δ ppm/$CDCl_3$): 80.8, 79.2, 61.6, 31.7, 29.4, 29.0, 28.5, 18.5, 15.2, 13.9. MS:m/z 195(M-1,5), 178(10), 153(10), 121(20), 107(30), 97(100), 93(50), 79(70), 67(30). Anal. calcd. for $C_{13}H_{24}O$:C, 79.53; H, 12.32. Found: C, 79.45; H, 12.33.

Reduction and hydroboration of N-methyl-N-phenylundecenamide: I_2BH-N,N-diethylaniline complex (15 mM) was prepared in situ as above.[7,14] The N-methyl-N-phenylundecenamide (1.30 g, 5 mM) was added to this reagent at 25°C, stirred for 12h. The reaction was quenched with water (5 ml) and oxidised using NaOH (3N, 10 ml)/H_2O_2 (30%, 10 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with water, brine and dried over anhydrous $MgSO_4$. On evaporation of solvent and purification by chromatography on silica gel (hexane:ethyl acetate/90:10) N-methyl-N-phenylundecanol (1.00 g, 81%) was isolated. IR(neat) ν_{max}: 3300, 3025, 1600, 740, 680 cm^{-1}. ^1H NMR(δ ppm/$CDCl_3$): 7.24-6.48(m, 5H); 3.68-3.48(t, 2H); 3.32-3.08(t, 2H); 2.88(s, 3H); 1.68-1.04(m, 19H). ^{13}C NMR(δ ppm, $CDCl_3$): 149.1, 128.8, 115.7, 111.9, 62.0, 52.3, 37.2, 32.4, 29.3, 26.9, 26.3, 25.5. MS:m/z 277(M, 20), 172(10), 142(10), 120(100), 107(40), 77(30). Anal. Calcd. for $C_{18}H_{31}NO$: N, 5.04; C, 77.92; H, 11.26. Found: N, 4.95; C, 77.75; H, 11.28.

Iodination of endo-norborneol: I_2BH-N,N-diethylaniline complex (10 mM) was prepared in situ as above.[7,14] The endo-norborneol (1.10 g, 10 mM) was added to this reagent at 25°C, stirred for 6h. The reaction was quenched with water (10 ml) and the organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with 3N HCl (20 ml), water, brine and dried over anhydrous $MgSO_4$. On evaporation of solvent and purification by chromatography on silica gel column (hexane), exo-norbornyl iodide[16] (1.54 g, 69%) was isolated. IR (neat) ν_{max}: 2950, 1440, 740 cm^{-1}. ^1H NMR(δ ppm, $CDCl_3$): 4.00-3.80 (m, 1H); 2.60-1.00(m, 10H). ^{13}C NMR(δ ppm, $CDCl_3$): 47.8, 45.0, 37.8, 36.2, 29.8, 28.6, 28.3. The ^{13}C NMR data are identical with the data reported in the literature.[17]

Reductive iodination of n-heptanaldehyde: I_2BH-N,N-diethylaniline complex (10 mM) was prepared in in situ as above.[7,14] n-Heptanaldehyde (1.14 g, 10 mM) was added to this reagent at 0°C and in 1h it was brought to 25°C. The contents were stirred further for 11h at 25°C. The reaction mixture was quenched with water (10 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with dil.HCl (3N, 20 ml), H_2O, brine and dried over anhydrous $MgSO_4$. On evaporation of solvent and purification by chromatography on silica gel column (hexane), n-heptyl iodide[18] (1.88 g, 82%) was isolated. IR(neat) ν_{max}: 2950, 1480, 720 cm^{-1}. ^1H NMR(δ ppm, $CDCl_3$): 3.28-3.00(t, 2H); 2.00-1.08(m, 10H); 0.88(t, 3H). ^{13}C NMR(δ ppm, $CDCl_3$): 33.5, 31.5, 30.4, 28.1, 22.5, 13.9, 6.8.

Reductive iodination of sebacic acid: I_2BH-N,N-diethylaniline complex (30 mM) was prepared in situ as above.[7,14] Sebacic acid (1.00 g, 5 mM) was added to this reagent at 0°C and in 1h it was brought to 25°C. The contents were stirred for 11h at 25°C. The reaction was quenched with water (10 ml) and the organic layer was separated. The aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with dil.HCl (3N, 20 ml), H_2O, brine and dried over anhydrous $MgSO_4$. On evaporation of solvent and purification by chromatography on silica gel column (hexane), 1,10-diiododecane[19] (1.18 g, 60%) was isolated. IR(neat) ν_{max}: 2950, 1480, 720 cm^{-1}. ^1H NMR(δ ppm, $CDCl_3$): 3.28-3.04(t, 4H); 2.00-1.16(m, 16H). ^{13}C NMR(δ ppm, $CDCl_3$): 33.5, 30.4, 29.2, 28.4, 7.3.

Hydroboration of methyl undecenoate: I_2BH-N,N-diethylaniline complex (5 mM) was prepared in situ as above.[7,14] Methyl undecenoate (0.99 g, 5 mM) was added to this reagent at 25°C and stirred for 12h. The reaction was quenched with water (5 ml) and oxidised using NaOH (3N, 10 ml)/H_2O_2 (30%, 10 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with HCl(3N, 20 ml), water, brine and dried over anhydrous $MgSO_4$. On evaporation of solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/90:10), methyl-11-hydroxyundecanoate[20] (0.80 g, 80%) was isolated. IR(neat) ν_{max}: 3300, 2900, 1720, 1440, 1160, 1040 cm^{-1}. ^1H NMR(δ ppm, $CDCl_3$): 3.64-3.36(m, 5H); 2.32-2.04(t, 2H); 1.76(s, 1H); 1.64-1.00(m, 18H). ^{13}C NMR(δ ppm, $CDCl_3$): 174.4, 62.4, 51.3, 33.9, 32.5, 29.3, 29.0, 25.6, 24.8.

Reaction of 1:1 mixture of 1-decene and octyl cyanide with HBI_2:$N(C_2H_5)_2Ph$ complex: I_2BH-N,N-diethylaniline complex (5 mM) was prepared in situ as above.[7,14] 1-Decene (0.70 g, 5 mM) and octyl cyanide (0.69 g, 5 mM) were added to this reagent at 25°C, stirred for 12h. The reaction was quenched with water (5 ml) and oxidised using NaOH (3N, 10 ml)/H_2O_2 (30%, 10 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with water, brine and dried over anhydrous $MgSO_4$. On evaporation of solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/ 90:10), 1-decanol (0.62 g, 77%) was isolated and octyl cyanide (0.65 g, 93%) was recovered.

Reaction of 1:1 mixture of 1-decene and cyclohexanone with HBI_2:$N(C_2H_5)_2Ph$ complex: I_2BH-N,N-diethylaniline complex (5 mM) was prepared in situ as above.[7,14] 1-Decene (0.70 g, 5 mM) and cyclohexanone (0.49 g, 5 mM) were added to this reagent at 10°C and in 1h it was brought to 25°C. The contents were stirred further for 11h at 25°C. The reaction was quenched with water (5 ml) and oxidised using NaOH (3N, 10 ml)/H_2O_2 (30%, 10 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 x 20 ml). The combined organic extract was washed with HCl (3N, 20 ml), water, brine and dried over anhydrous $MgSO_4$. On evaporation of solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/90:10), 1-decanol (0.32 g, 40%) and cyclohexyliodide (0.46 g, 46%) were isolated.

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