Tetrahedron Letters,Vol.30,No.41,pp 5663-5664,1989
Printed in Great Britain

0040-4039/89 $3.00 + .00
Pergamon Press plc

A Simple Convenient Procedure for Iodination of Alcohols and Reductive Iodination of Carbonyl Compounds using N,N-Diethylaniline-Borane-I_2 system.

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Abstract: Alcohols, carboxylic acids and carbonyl compounds give the corresponding alkyl iodides in moderate to good yields on reaction with N,N-diethylaniline-borane complex and iodine.

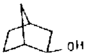
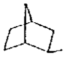
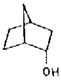
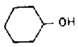
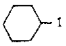
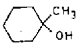
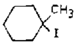
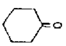
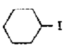
Several new methods of iodination of alcohols, which utilize phosphorous[1] and silyl derivatives[2] have appeared. Although vacuum line procedures for the iodination of alcohols utilizing B_2H_6 and I_2[3] or MBH_4 (M = Li, Na) and I_2[4,5] appeared, these methods did not receive much attention. In continuation of our efforts in the development of new synthetic methods based on amine-borane complexes,[6,7] generated using $I_2/NaBH_4/$amine system, we were looking for a simple method of iodination of alcohols and reductive iodination of carbonyl compounds. A recent report[8] on the reductive bromination of aromatic ketones using Br_2-trimethylamine:BH_3 complex prompted us to disclose our results on the application of N,N-diethylaniline:BH_3-I_2 system for iodination of alcohols and reductive iodination of representative ketone, aldehyde and carboxylic acids.

We have observed that alcohols (1 mole eq) are readily iodinated with the reagent prepared using N,N-diethylaniline:BH_3 (1 mole eq) and I_2 (1 mole eq) [Table]. Reductive iodination of cyclohexanone (1 mole eq) and heptanaldehyde (1 mole eq) with the reagent prepared using N,N-diethylaniline:BH_3 (1 mole eq) and I_2 (1 mole eq) give the corresponding alkyliodides in 75 and 82% yields [Table]. The carboxylic acids (1 mole eq) are converted into the corresponding alkyl iodides with N,N-diethylaniline:BH_3 (3 mole eq) and I_2 (3 mole eq) [Table].

The following is the representative procedure for the reductive iodination of cyclohexanone and n-heptanaldehyde. Borane-N,N-diethylaniline complex was prepared <u>in situ</u> by bubbling diborane, generated by dropwise addition of iodine (10 mM) in diglyme (10 ml) to $NaBH_4$ (20 mM) in diglyme (5 ml) at 25°C, into a solution of N,N-diethylaniline (10 mM) in dry benzene (60 ml) for 1h.[6] Iodine (10 mM) in benzene (20 ml) was added at 10°C in order to convert borane-amine complex into diiodoborane-amine complex. The contents were stirred for 2h at 25°C. The carbonyl compound (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 H_2O (15 ml) and the organic layer was separated. The aqueous layer was extracted with ether (50 ml). The combined organic extract was washed with saturated aq.NaCl solution and dried over $MgSO_4$. The solvent was removed and the iodocompound was isolated by column chromatography on silica gel using hexane as eluent. The results are summarized in the Table.

The formation of exo-2-norbornyl iodide from both exo-2-norborneol and endo-2-norborneol indicates that the reactions in these cases go through a common intermediate, i.e. the 2-norbornyl cation,[9] and the reactions may take a similar course with other substrates. The reductive iodination of carbonyl compounds and carboxylic acids would also go through the intermediacy of alkoxyboron compounds since these substrates would readily undergo reduction by the boron hydride species present in the medium. Infra-red spectrum of a mixture of N,N-diethylaniline:BH_3 (1 mole eq) and I_2 (1/2 mole eq) in benzene shows B-H absorptions at 2400, 2450 cm^{-1} corresponding to the presence of IBH_2-amine complex.[10,11] The spectrum of the amine-borane (1 mole eq) and I_2 (1 mole eq) reagent used in the present transformations shows B-H absorption at 2500 cm^{-1} corresponding to the presence of I_2BH-amine complex.[12] In conclusion, the N,N-diethylaniline :BH_3 and I_2 system constitutes a simple, mild reagent for iodination of alcohols and reductive iodination of carbonyl compounds.

Table: Iodination and Reductive Iodination using N,N-diethylaniline:BH_3 and I_2 reagent system

Entry No.	Substrate[a]	Reaction conditions		Product[d]		Yield (%)
		Time	temp.			
1	$H_3C\text{-}(CH_2)_{14}\text{-}CH_2\text{-}OH$	12h[b]	80°C	$H_3C\text{-}(CH_2)_{14}\text{-}CH_2\text{-}I$	[1]	84
2		6h	25°C		[2]	82
3		6h	25°C		[2]	69
4		12h	25°C		[3]	86
5		1h	25°C		[4]	89
6		11h[c]	25°C		[3]	75
7	$H_3C\text{-}(CH_2)_5\text{-}CHO$	11h[c]	25°C	$H_3C\text{-}(CH_2)_5\text{-}CH_2I$	[5]	82
8.	$Ph\text{-}CH_2CO_2H$	11h[c]	25°C	$Ph\text{-}CH_2CH_2\text{-}I$	[6]	66
9	$HO_2C\text{-}(CH_2)_8\text{-}CO_2H$	11h[c]	25°C	$I\text{-}H_2C\text{-}(CH_2)_8\text{-}CH_2\text{-}I$	[7]	60

a) For entries 1-5, alcoholic substrates (10 mM), amine-borane (10 mM) and I_2 (10 mM) were utilized. For entries 6,7, the ketonic and aldehydic substrates (10 mM), amine-borane (10 mM) and I_2 (10 mM) were utilized. For entries 8,9, the carboxylic acid substrates (10 mM), amine-borane (30 mM) and I_2 (30 mM) were utilized. (b) The alcohol was added at 25°C, stirred for 1h and then stirred for 12h at 80°C. (c) The substrate was added at 0°C, brought to 25°C in 1h and then stirred for 11h at 25°C. (d) Products were isolated by column chromatography (silica gel/hexane) and identified by spectral data (IR, ^1H NMR and ^{13}C NMR) and comparison with the data reported in the literature. The ^{13}C NMR data (δ in ppm/$CDCl_3$) are as follows: [1] 6.0, 14.0, 22.6, 28.6, 29.5, 29.7, 30.6, 31.9, 33.6 [2] 28.3, 28.6, 29.8, 36.2, 37.8, 45.0, 47.8 [3] 25.1, 27.5, 32.5, 39.5 [4] 24.8, 25.0, 38.9, 45.7, 58.9 [5] 6.8, 13.9, 22.5, 28.1, 30.4, 31.5, 33.5 [6] 6.1, 40.5, 127.2, 128.2, 129.0, 141.0 [7] 7.3, 28.4, 29.2, 30.4, 33.5.

Acknowledgement: This research work was supported by the DST (New Delhi). We are also grateful to the UGC (New Delhi) for providing some instruments through Special Assistance and COSIST programmes.

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(Received in UK 21 August 1989)