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Synthetic applications of BI_3:$N(C_2H_5)_2Ph$ complex

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Abstract

Reaction of I_2(1.5 mole eq.) with $BH_3.N(C_2H_5)_2Ph$ (1 eq.) in benzene at room temperature gives $BI_3.N(C_2H_5)_2Ph$ reagent. The BI_3 reagent prepared in this way on reaction with CH_3COOH gives HI which is useful for hydroiodination of alkenes and alkynes to obtain alkyl and alkenyl iodides in 74 to 84% yields. The BI_3 reagent is also useful for cleavage of N-carbamates to secondary amines. Application of this reagent for cleavage of ethers, esters and sulphonates is also described

Key words: Iodoborane, alkyl and alkenyl iodide synthesis, cleavage of carbamates, ethers, esters and sulphonates.

1. Introduction

The BF_3:OEt_2 is the most readily accessible boron halide reagent and has been widely utilized as an acid[1] BCl_3 and BBr_3 reagents are also commercially available and are useful in several applications[2]. In many reactions utilizing BCl_3 and BBr_3 reagents, the halogen moiety participate in the reaction to give halogenated products (for example cleavage of ethers by BBr_3). Although the BI_3 reagent should also be useful for such applications, utilization of this reagent has not been studied in detail. We wish to report the results of a detailed investigation of the synthesis of BI_3:$N(C_2H_5)_2Ph$ in benzene and utilization of this reagent in organic synthesis.

2. Results and discussion

2.1. Synthesis of BI_3:$N(C_2H_5)_2Ph$

It has been found that various iodoborane-N, N-diethylaniline complexes can be prepared through the reaction of H_3B:$N(C_2H_5)_2Ph$ with appropriate amounts of I_2.

The iodoborane complexes prepared in this way exhibited spectral properties reported for similar haloborane derivatives[3,4]. Whereas the IR spectrum of the BH_2I complex showed a doublet absorption at 2400, 2450 cm^{-1}, the BHI_2 appeared as a singlet at 2500 cm^{-1}. The BI_3 reagent does not exhibit the >B–H absorption in this region as expected.

* For correspondence.

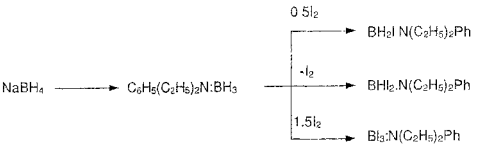
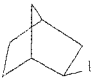


Table I

Hydroiodination using BI_3:N,N-diethylaniline and acetic acid system

Entry no [a]	*Substrate*	*Product* [b]	*Yield(%)*
1	$H_3C(CH_2)_7CH{=}CH_2$	$H_3C(CH_2)_7\underset{\displaystyle I}{CH}{-}CH_3$	82
2	$H_3C(CH_2)_{13}CH{=}CH_2$	$H_3C(CH_2)_{13}\underset{\displaystyle I}{CH}{-}CH_3$	83
3	$H_2C{=}CH(CH_2)_6COOH$	$H_3C{-}\underset{\displaystyle I}{CH}(CH_2)_6COOH$	76
4	$H_2C{=}CH(CH_2)_6COOCH_3$	$H_3C{-}\underset{\displaystyle I}{CH}(CH_2)_6COOCH_3$	80
5			74
6			82
7	$HC{\equiv}C(CH_2)_7CH_3$	$H_2C{=}\underset{\displaystyle I}{C}(CH_2)_7CH_3$	84
8	$HC{\equiv}C(CH_2)_6CH_3$	$H_2C{=}\underset{\displaystyle I}{C}(CH_2)_6CH_3$	84

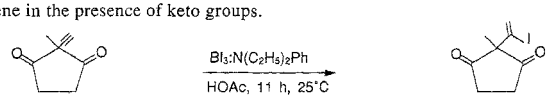
(a) For entries 1–5, 7 and 8 the unsaturated hydrocarbons (10 mmol), triiodoborane–amine complex (5 mmol) and acetic acid (15 mmol) were utilized. For entry 6, the unsaturated hydrocarbon (30 mmol) triiodoborane- amine complex (5 mmol) and acetic acid (15 mmol) were utilized. After workup the product was separated from the starting diene by fractional distillation under reduced pressure (0.5 mm/80°C). Optimum results were obtained when 10 mmol of alkenes and alkynes are utilized for 5 mmol of BI_3 amine complex and the yields are based on the ratio of reagents utilized.

(b) 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.

2.2. Hydroiodination of alkenes and alkynes using BI_3:$N(C_2H_5)_2Ph$ and CH_3COOH

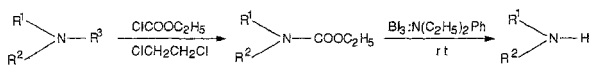
Reaction of BI_3:$N(C_2H_5)_2Ph$ complex with CH_3COOH gives hydroiodic acid. The reagent generated in this way readily undergoes addition with olefins to give alkyl iodides in moderate to good yields (Table I), under mild conditions. The reaction of 1-alkyne stops at the 2-iodoalkene stage (Table I). Reaction of 1,5-cyclooctadiene gives 5-iodocyclooctene in 82% yield. The conditions tolerate an ester group as illustrated by the conversion of methyl undecenoate to the corresponding iodide[5]

Shibasaki *et al*[6] reported that this reagent is useful for the conversion of an alkyne to iodoalkene in the presence of keto groups.



2.3. Cleavage of N-carbamates, ethers, esters and reduction of sulphonates

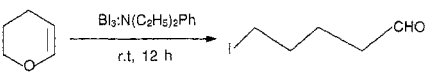
The N-carbamates of tertiary amines can be readily prepared from tertiary amines[7]. It has been observed that the BI_3:$N(C_2H_5)_2Ph$ complex cleaves such N-carbamates at room temperature (Scheme 1)[7]



SCHEME 1.

After workup the corresponding secondary amines are obtained in moderate to good yields (Table II). This method should serve as a good alternative to the existing methods of cleavage of N-carbamates[8–10]

We have also observed that the BI_3 reagent cleaves 3,4-dihydro-2H-pyran to 4-iodopentanal in 76% yield.



Recently, Kabalka *et al*[11] reported several applications of this readily accessible BI_3 reagent. The reagent is useful for the cleavage of ethers and geminal diacetates[11].

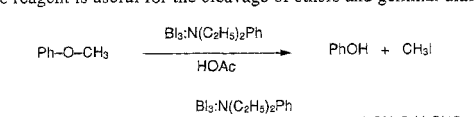
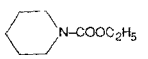
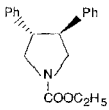
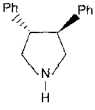
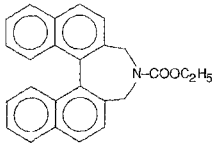
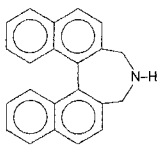


Table II
Cleavage of N-ethylcarbamates using $I_3B{:}N(C_2H_5)_2Ph$[a]

Sl no	*Substrate*[b]	*Product*[c]	*Yield (%)*[d]
1			78
2			87
3	$(PhCH_2)_2N{-}COOC_2H_5$	$(PhCH_2)_2NH$	85
4			85

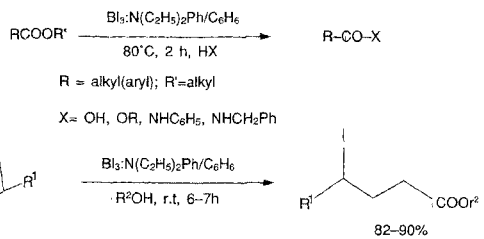
(a) All reactions were carried out using N-ethylcarbamate (5 mmol) and $I_3B{:}N(C_2H_5)_2Ph$(5 mmol) at 25°C for 8 h

(b) N-carbamates were obtained from the corresponding N-benzyl tertiary amines by refluxing tertiary amine (5 mmol) and ethyl chloroformate (6 mmol) in dichloroethane (20 ml).

(c) Products were identified by IR, ^1H NMR and ^{13}C NMR and physical constants data and comparison with the data reported in literature.

(d) Yields are of isolated and purified products

Certain esters[12] and lactones[13] have been cleaved with the BI_3 reagent to give useful products.



The BI_3 reagent is also useful for the conversion of sulphonic acid derivatives and sulphoxides to the corresponding disulphides and sulphides[14]

$$RSOOX \xrightarrow[22\text{–}95\%]{BI_3.N(C_2H_5)_2Ph/C_6H_6} RSSR$$

$$RSOR \xrightarrow[77\text{–}80\%]{BI_3\ N(C_2H_5)_2Ph/C_6H_6} RSR$$

Attempted iodoboration-oxidation of 1-decyne with this reagent, resulted in iodoaldehyde in low yield.

$$R\text{–}C{\equiv}C\text{–}H \xrightarrow[NaOAc/H_2O_2]{BI_3:N(C_2H_5)_2Ph} \underset{30\%}{\overset{I}{\underset{|}{}}R\text{–}CH\text{–}CHO}$$

3. Conclusions

The BI_3:$N(C_2H_5)_2Ph$ reagent can be readily prepared by the reaction of I_2 with the BH_3:$N(C_2H_5)_2Ph$ complex. The reagent prepared in this way has been used for hydroiodination of alkenes and alkynes, cleavage of N-carbamates and ethers, and iodoboration of 1-decyne. The synthetic utilities and ready accessibility of this reagent system should make the reagent attractive for applications in organic synthesis.

4. Experimental

4.1. Synthesis of BI_3:$N(C_2H_5)_2Ph$

Borane-N, N-diethylaniline complex was prepared *in situ* by bubbling diborane, generated by dropwise addition of iodine (10 mmol) in diglyme (25 ml) to $NaBH_4$ (20 mmol) in diglyme (5 ml) at 25°C, into a solution of N, N-diethylaniline (5 mmol) in dry benzene (60 ml) for 1 h[15]. Iodine (7.5 mmol) in benzene (20 ml) was added at 10°C and then stirred for 2 h at room temperature to convert the borane–aniline complex into triiodoborane aniline complex.

4.2. Hydroiodination of 1-decene using BI_3:$N(C_2H_5)_2Ph$ and acetic acid system

BI_3:$N(C_2H_5)_2Ph$ complex (5 mmol) was prepared *in situ* as above. Acetic acid (0.9 g, 15 mmol) was added to this reagent at 10°C. The 1-decene (1.4 g, 10 mmol) was added under nitrogen and the contents were stirred for 12 h, at 25°C. The reaction was quenched with water (10 ml) and the organic layer was separated and the aqueous layer was extracted with ether (2 × 20 ml). The combined organic extract was washed with dil.HCl (3N, 20 ml), water, brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent and purification by column chromatography on silica gel (hexane), 2-iododecane (2.19 g, 82%) was isolated. IR(neat)υ_{max}: 2950, 1460, 720 cm^{-1}. ^1H NMR(100MHz, $CDCl_3$): δppm 0.8–0.96(t, 3H),

1.08–1.52(m, 14H), 1.8–2.0 (d, 3H), 4.0–4.2 (m, 1H). ^{1}C NMR (25MHz, $CDCl_3$) : δppm 14.1, 22.6, 28.8, 28.9, 29.2, 29.4, 29.7, 29.8, 31.8, 42.9.

4.3. Cleavage of 3,4-dihydro-2H-pyran using BI_3:N(C_2H_5)$_2$ Ph

BI_3:N(C_2H_5)$_2$ Ph complex (10 mmol) was prepared *in situ* as above. 3,4-Dihydro-2H-pyran (10 mmol, 0.84 g) was added under nitrogen and the contents were stirred for 12 h at 25°C. The reaction was quenched with water (10 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 × 20 ml). The combined organic extract was washed with dil. HCl (3N, 20 ml), sodium thiosulphate solution (20 ml), water, brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent and purification by chromatography on silica gel column (hexane:ethyl acetate/95:5), 4-iodo-1-pentanal (1.61 g, 76%) was isolated. IR(neat)υ_{max}:2950, 2750, 1720, 740 cm^{-1}. ^{13}C NMR (25MHz, $CDCl_3$)·δppm 8.0, 24.0, 33.8, 43.7, 203.0.

4.4. Cleavage of N-ethylcarbamate of 3,4-diphenylpyrrolidine

BI_3:N(C_2H_5)$_2$Ph complex (5 mmol) was prepared *in situ* as above. The N-ethylcarbamate of 3,4-diphenylpyrrolidine (1.47 g, 5 mmol) in benzene (20 ml) was added slowly during 15 min under nitrogen atmosphere and the mixture was stirred further for 8 h. The reaction was quenched with water and neutralized using 3N NaOH solution. The organic layer was separated and washed with NaOH solution (3N, 3 × 10 ml), brine and dried over anhydrous $MgSO_4$. Evaporation of the solvent afforded crude product which was separated from N, N-diethylaniline by column chromatography on alumina (neutral) using hexane:ethyl acetate/80:20). Yield: 0.95 g (80%). IR(neat)υ_{max}: 3345, 1600cm^{-1}. ^{1}H NMR(100MHz, $CDCl_3$):δppm 2.3 (s, 1H), 2.8–3.4 (m, 6H), 6.9(m, 10H). $[\alpha]_D^{20}$ = + 222°(Cl, $CHCl_3$), lit.[16] $[\alpha]_D^{20}$ = –226°($CHCl_3$).

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