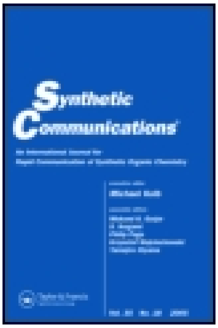

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TANDEM REDUCTION STUDIES OF BROMO COMPOUNDS USING TETRABUTYLAMMONIUM BOROHYDRIDE

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Abstract : Tetrabutylammonium borohydride can be used for multifunctional transformations through tandem reductions of halo compounds in THF.

The reduction of alkyl halides is generally effected by reagents such as $LiAlH_4$[1], $NaBH_4$ in diglyme[2], sodium cyanoborohydride[3], lithium-9-9-di-n-butyl-9-borabicyclo[3,3,1] nonane[4] etc. Generally BH_4^- reduction of alkyl halides result in the inactivation of the BH_4^- reagent by forming $B_2H_7^-$. Also the reagent is wasted during such conversions.

$$RX + 2BH_4^- \longrightarrow RH + B_2H_7^- + X^-$$

For better utilization of the reagent , a tandem reduction /hydroboration of other groups would be useful. Accordingly, tetrabutylammonium borohydride was prepared[5] as reported in the literature and its reactivity towards alkyl halides and

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aryl halides were examined. While alkyl halides are readily reduced , aromatic halides were not at all reduced by tetrabutylammonium borohydride. The borane species liberated during the reduction of alkyl halides can be used to perform the reduction of other functionalities present in the substrate. In order to achieve this sort of combined transformation, the reaction of tetrabutylammonium borohydride with various bifunctional substrates was studied. Interestingly, although the ester group is inert towards tetrabutylammonium borohydride in THF the reduction of bromoesters by tetrabutylammonium borohydride in THF gave the corresponding alcohol in good yield. For example,

$$\mathrm{BrCH_2(CH_2)_nCOOR} \xrightarrow{n\text{-}\mathrm{Bu_4NBH_4,THF}} \mathrm{CH_3(CH_2)_nCH_2OH}$$

Bromine at the terminal position as well as internally is easily reduced. Thus dibromoesters were reduced to the corresponding saturated alcohols in THF.

$$\mathrm{CH_3(CH_2)_nCH(Br)CH(Br)(CH_2)_nCOOR} \xrightarrow[\mathrm{THF}]{n\text{-}\mathrm{Bu_4NBH_4}} \mathrm{CH_3(CH_2)_nOH}$$

Even chloro amides were reduced to the corresponding amines by tetrabutylammonium borohydride in THF involving the reduction of both the chlorine and amide functional group.

$$\mathrm{RNHCOCH_2Cl} \xrightarrow{n\text{-}\mathrm{Bu_4NBH_4,THF}} \mathrm{RNHCH_2CH_3}$$

Bromo compounds with unsaturation undergo simultaneous hydroboration along with the reduction of halogen by tetrabutylammonium borohydride . Thus undecenyl bromide gave undecanol after the oxidative work up indicating the reduction of halogen followed by the hydroboration of the double bond.

$$H_2C{=}(CH_2)_8CH_2Br \xrightarrow[\text{(ii)}H_2O_2/NaOH]{\text{(i)}n\text{-}Bu_4NBH_4, C_6H_6} HO(CH_2)_9CH_3$$

Interestingly, bromo alkynes on reduction with tetrabutylammonium borohydride undergoes dihydroboration and on oxidation with H_2O_2 in basic medium gave the saturated alcohols in good yields.

$$HC{\equiv}CCH_2(CH_2)_nCH_2Br \xrightarrow[\text{(ii)}H_2O_2/NaOH]{\text{(i)}n\text{-}Bu_4NBH_4, C_6H_6} HOCH_2(CH_2)_nCH_3$$

Thus, the reagent offers good scope where multifunctional transformations are required. Also, it has the advantage over BMS or BH_3/THF in the reduction of substrates leading to the formation of amines.

Experimental Section:

Typical procedure for the reduction of halo compounds.

(1) Saturated alkyl halides: 5mmol of dodecyl bromide is stirred with 5mmol of tetrabutylammonium borohydride in THF at room temperature for 5 minutes under N_2 atm. The reaction is quenched with dil. sulphuric acid. THF is removed using rotary evaporator and the resulting mixture is extracted with choloform to yield dodecane.

(2) Unsaturated alkyl halides: 5mmol of undecenyl bromide is refluxed with 5mmol of tetrabutylammonium borohydride in benzene for 3h under N_2 atm. the reaction is quenched with dil. sulphuric acid. The pH is made slightly alkaline and the oxidative work up (OH^-/H_2O_2) of the reaction mixture yielded the saturatued alkanol, undecanol.

(3) Halo esters: 5mmol of the methyl-11-bromoundecanoate is refluxed with 5

Table :Reduction of bromo compounds with Tetrabutylammonium borohydride

Substrate	Reaction condition	Product	Yield[a] (%)
Benzyl bromide[b]	RT, THF, 5 min	Toluene	90
Benzylchloride[b]	RT, THF , 5 min	Toluene	90
Dodecylbromide[b]	RT, THF , 5 min	Dodecane	89
methyl -11-bromo undecanoate[b]	Δ, THF, 2h	Undecanol[6a]	92
methyl -10,11-di Bromo undecanoate[c]	Δ, THF, 2h	Undecanol[6a]	92
Dibromo methyl oleate[c]	Δ, THF, 2h	Octadecanol[6b]	91
α-Chloroacetanilide[b]	RT, THF, 5h	N-Ethylaniline	89
4-Nitro-α-Chloroacetanilide[b]	RT, THF, 5h	*p*-Nitro- N-Ethylaniline[6c]	90
Undecenyl bromide[b]	Δ, Benzene, 3h	Undecanol[6a]	85
1-Bromobutyne[b]	Δ, THF, 3h	Butanol	87
1-Bromopentyne [b]	Δ, THF, 3h	Pentanol	88

a= isolated yield; b = [substrate] : [BH_4^-] = 5 : 5 ; c = [substrate] : [BH_4^-] = 5 : 10

mmol of the tetrabutylammonium borohydride (10mmol for the dibromo esters) in dry THF for 2h under N_2 atm. The reaction is quenched with dil. sulphuric acid. THF is removed using a rotary evaporator and the resulting mixture is extracted with chloroform to yield undecanol.

(4) Chloro amides: 5mmol of chloroacetanilide is stirred with 5mmol of tetrabutylammonium borohydride in THF for 5h under N_2 atm. The reaction is quenched with dil.sulphuric acid. THF is removed using rotary evaporator and the resulting mixture is extracted with chloroform to yield N-ethylaniline.

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6 PMR data (6a) δ0.8(3H,t), δ1.1 - 1.5 (18H, broad), δ3.4(3H,t) ; (6b) δ0.9(3H,t), δ1.2 - 1.6 (32H, broad), δ3.5(3H,t) ; (6c) δ0.9(3H,t), δ3.4(2H,q), δ7.2(2H,d), δ7.8(2H,d).

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