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BORON TRIFLUORIDE ETHERATE/HALIDE ION, A NOVEL REAGENT FOR THE CONVERSION OF ALLYL, BENZYL AND TERTIARY ALCOHOLS TO THE HALIDES

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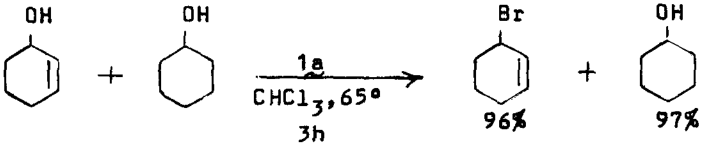
Summary : A combination of boron trifluoride etherate and halide ion is found to be an excellent reagent for the conversion of allyl, benzyl and tertiary alcohols to the halides.

The conversion of alcohols to halides is a useful transformation in synthetic organic chemistry. Numerous methods have been devised in literature to achieve this goal[1]. Few recent ones include iodo-[2] and bromotrimethyl silanes[3], chlorotrimethyl silane/sodium iodide[4], and hexamethyl disilazane/iodine[5]. None of these reagents discriminate between various forms of alcohol functionalities and hence offer no use for the selective conversion of allyl, benzyl and tertiary alcohols to the halides. However, Olah et al[6] have recently reported that a combination of trichloromethyl silane/iodide ion is useful for the selective conversion of benzyl and tertiary alcohols to the iodides.

We have reported earlier that a combination of inexpensive boron trifluoride etherate and iodide ion is extremely useful for the mild and regioselective cleavage of various ether linkages[7]. We now report that a combination of boron trifluoride etherate and halide ion (X^-), **1**, (**1a**, X=Br; **1b**, X=I) is useful for the conversion of allyl, benzyl and tertiary alcohols to the corresponding halides. Tetraethyl ammonium bromide and iodide or more conveniently sodium bromide and iodide are used as the source of halide ions. In the former case the reaction medium is dichloromethane or chloroform (Method A) and in the latter case acetonitrile is the preferred solvent (Method B). The results of this study is summarised in Table I.

Thus, the reactions of allyl alcohols 2,3 and 4 and benzyl alcohols 5,6 and 7, with 1a or 1b (Method A or B) proceeded cleanly to yield the corresponding bromides (entries 1-7, Table I) and iodides (entries 10-12, Table I) in high yields. Where as the reaction of tertiary alcohols 8 and 9 with 1a or 1b (Method A) gave rise to the desired bromides and iodides (entries 8,9 and 13, Table I), the corresponding reaction via Method B lead to uncharacterised products. Also the reaction of allyl alcohol e.g. cinnamyl alcohol with 1a and 1b (Method A or B) is found to be susceptible to the reaction condition employed. At higher temperature the reaction led to polymeric products. However, with suitable manipulation of the reaction condition i.e. using 1.5 molar excess of the reagent the reaction can be brought to completion within 4-5 h at 25° to yield high yields of the desired halides (entries 2,10, Table I).

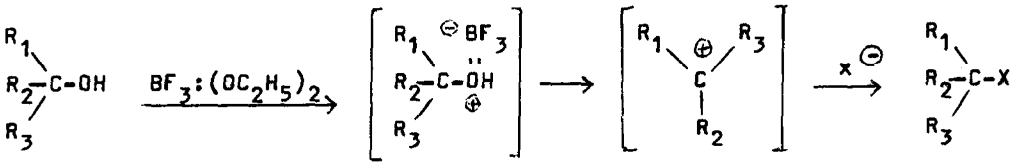
Primary and secondary alcohols, such as 1-octanol, 2-octanol and cyclohexanol are inert to 1 even under prolonged reaction condition (65°, 8-10 h). This permitted a selective conversion of Cyclohex-2-en-1-ol to the bromide in the presence of cyclohexanol (eqn. 1).



(1)

The earlier observation[8] that acetates are inert to the reagent 1 would also allow a selective conversion of allyl, benzyl and tertiary alcohol functions to the halides in presence of an acetate moiety.

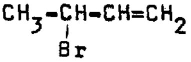
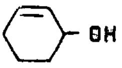
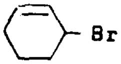
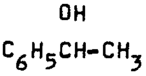
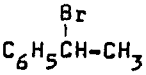
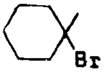
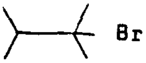
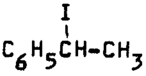
The above results, therefore, suggest that allyl, benzyl and tertiary alcohols react *via* corresponding carbocation species to the halides (eqn. 2).



(2)

This is further supported by the reaction of R-(+)-1-phenyl-1-ethanol ($[\alpha]_D^{25}$ + 26.1°, 50% e.e.[9]) with 1a in chloroform which yielded R-(+)-1-phenyl-1-bromoethane ($[\alpha]_D^{25}$ + 3.46°, 2%[10] e.e.), indicating almost complete racemisation.

TABLE I : CONVERSION OF ALLYL, BENZYL AND TERTIARY ALCOHOLS TO HALIDES[a]

Entry	Substrate		Reagent[b]	Time (h)	Product	Method (Yield %)[d]
1.	$C_6H_5CH{=}CHCH_2OH$	2	1a	5	$C_6H_5CH{=}CHCH_2Br$	A[f](78)
2.	-do-		1a[e]	5	-do-	B (79)
3.	$CH_3CH{=}CHCH_2OH$	3	1a	4	$CH_3CH{=}CH{-}CH_2Br$ (9.1) +  $CH_3{-}\underset{Br}{CH}{-}CH{=}CH_2$ (0.9)	A (65)
4		4	1a	8		A (81)
5.	$C_6H_5CH_2OH$	5	1a	4	$C_6H_5CH_2Br$	A (79);B(76)
6.	(m)-PhO-$C_6H_4CH_2OH$	6	1a	10	(m)-PhO-$C_6H_4CH_2Br$	A (70)[h]
7.	 $C_6H_5\overset{OH}{CH}{-}CH_3$	7	1a	3	 $C_6H_5\overset{Br}{CH}{-}CH_3$	A (74);B(70)
8.		8	1a	3		A[f](60)
9.		9	1a	3		A[f](78)
10.	2		1b[e]	4	$C_6H_5CH{=}CH{-}CH_2I$	A(70)[g];B(64)[g]
11.	5		1b	4	$C_6H_5CH_2I$	A(68); B(70)
12.	7		1b	2.5	 $C_6H_5\overset{I}{CH}{-}CH_3$	A(79)[h];B(76)[h]
13.	8		1b	5		A[f](65)[h]

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[a] All reactions were carried out in 20 mmolar scale; [b] The reactions were carried out with 50% excess of the reagent in refluxing chloroform (Method A) or acetonitrile (Method B) unless otherwise stated; [c] All products gave satisfactory IR and NMR characteristics; [d] Yield of the isolated product by distillation; [e] With 1.5 molar excess of the reagent at 25°; [f] Refluxing dichloromethane; [g] m.p. 56-57°; [h] Isolated as oil. Distillation is associated with decomposition.

General Procedure

Method A : A mixture of alcohols (20 mmol), tetraethyl ammonium bromide or iodide (30 mmol) and freshly distilled boron trifluoride etherate (30 mmol) in CH_2Cl_2 or $CHCl_3$ (30 ml) was refluxed for specified time. The reaction mixture was cooled, and saturated $NaHCO_3$ solution (20 ml) was added. The organic layer was separated and the aqueous layer extracted once with CH_2Cl_2 or $CHCl_3$ (20 ml). The combined organic layer was washed once each with 10% aqueous sodium thiosulfate and saturated brine solution and dried over anhydrous sodium sulphate. Removal of solvent yielded the crude product which was further distilled (entries 1-5, 7-9 and 11), recrystallized (entry 10) or purified by chromatography over short silica gel column using hexane as eluent (entries 6, 12 and 13).

Method B : A mixture of alcohol (20 mmol), sodium bromide or iodide (30 mmol) and boron trifluoride etherate (30 mmol) in acetonitrile (50 ml) was refluxed or stirred at 25° for specified time. After the usual work up, the product was isolated as before.

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