A Simple Method for the Conversion of Adamantyl, Benzyl and Benzyhydryl Alcohols to Their Corresponding Bromides and Chlorides and the Transhalogenation of Adamantyl, Benzyl, Benzhydryl and Tertiary Alkyl Bromides and Chlorides

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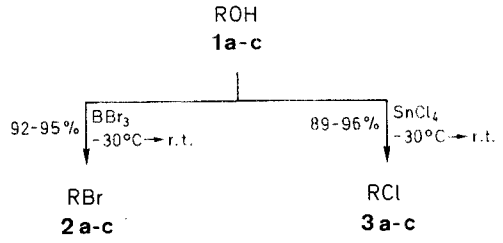
Adamantyl, benzyl, and benzhydryl alcohols have been converted to their corresponding bromides and chlorides in the absence of a solvent, rapidly and in high yield using boron tribromide and tin(IV) chloride, respectively. Additionally the above bromides and chlorides can be interconverted by a transhalogenation process using the same reagents in the absence of solvent.

The conversion of alcohols to halides is an important transformation in synthetic organic chemistry and numerous methods have been reported to achieve this goal.[1-3] Most recently reagents reported for the conversion of an alcohol to the corresponding halide include: iodo-[4] and bromotrimethyl silane,[5] chlorotrimethylsilane/sodium iodide,[6,7] hexamethyldisilane/iodide ion,[8] trichloromethylsilane/iodide ion,[9] and halide ion/boron trifluoride etherate.[10,11] The conversion of aliphatic alcohols to the corresponding bromides using boron tribromide has also been reported.[12] We now wish to report the utility of boron tribromide and tin(IV) chloride for the rapid and high yield formation of adamantyl, benzyl and benzhydryl alcohols **1a–c** to their corresponding halides **2a–c** and **3a–c** in the absence of a solvent (Scheme **A**) (Table 1).



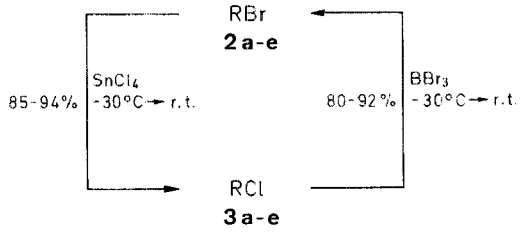
Scheme **A**

The reactions of adamantyl, benzyl and benzhydryl alcohols with either boron tribromide or tin(IV) chloride proceed cleanly in the absence of solvent to give the corresponding bromides and chlorides, respectively, in high yield (89–95%). It is significant that even though 1-adamantyl alcohol is a bridgehead alcohol, its reactions with either boron tribromide or tin(IV) chloride proceed readily in the absence of solvent without any complications. An attempt was made to replace boron tribromide with boron trichloride in hexane solution in the reaction of 1-adamantyl alcohol; however, no reaction occurred even after 24 hours.

We would also like to report a simple, rapid and high yield method for the conversion of adamantyl, benzyl, benzhydryl and tertiary alkyl chlorides to bromides using boron tribromide and the corresponding bromides to chlorides using tin(IV) chloride in the absence of solvent. Several methods[17], are known for the conversion of alkyl chlorides to the corresponding bromides and for the conversion of alkyl bromides to the corresponding iodides; however, only a few examples are known for the conversion of alkyl bromides to the corresponding chlorides.[18]

The conversion of an alkyl chloride to the corresponding bromide can take place at high temperatures (80–150°C) by using a reagent like silver difluorochloroacetate[19] and carrying out the reaction for 16–140 hours. It has been reported[20] that halogen exchange at the bridgehead position of polycyclic compounds can occur by using a catalytic amount of aluminum tribromide, which is generated *in situ* from aluminum and bromine in halogenated solvents. In this method, the solvent is used as the halogen source. For example, in preparing an alkyl chloride from the corresponding alkyl bromide, chloroform is used as the source of chlorine, regardless of the bromine contained in the catalytic amount of aluminum tribromide (Lewis acid). More recently, a method has been reported[21] for the transhalogenation of geminal bromonitroalkanes to the corresponding chloro compounds using thioalkoxide and *N*-chlorosuccimimide as the chlorine source.

The transhalogenation of benzyl and benzhydryl halides **2a,b,d** and **3a,b,d**, typical tertiary alkyl halides **2e** and **3e** and adamantyl halides **2c** and **3c** has been carried out as shown in Scheme **B**.



Scheme **B**

Table 2 shows that benzyl and benzhydryl chlorides can be converted to the corresponding bromides in 89–92% yield by reaction with boron tribromide and that benzyl and benzhydryl bromides can be converted to the corresponding chlorides by reaction with tin(IV) chloride in 91–94% yield. The conditions for both reactions involve addition of the reactants, in the absence of solvent, for a period of 15–60 minutes. Similar conversions are achieved under comparable conditions for the reactions of *tert*-butyl halides and adamantyl halides. When 1-adamantyl bromide was added to stannic chloride at −30°C and the resulting mixture allowed to warm to room temperature, an 88% yield of 1-adamantyl chloride was obtained after purification. In comparison with other methods,[19,20] the present method is more convenient, relatively faster, and solvent and high temperatures are not required. On the other hand, when 1-adamantyl chloride was added to boron bromide at −30°C and the reaction mixture allowed to warm to room temperature over a 30 minute period, 1-adamantyl bromide was obtained in 91% yield.

In the process of transhalogenation, the Lewis acid is acting as the source of added halogen. It is suggested that the Lewis acid first abstracts halogen from the starting alkyl halide to form the metal anion $SnCl_4Br^-$ or BBr_3Cl^- and the alkyl carbenium ion intermediate.[26] The halogen that originally existed in the Lewis acid then migrates to the carbenium ion to form the new alkyl halide (Scheme **C**).

Scheme **C**

Table 1. Conversion of Alcohols to their Corresponding Halides by Boron Tribromide and Tin(IV) Chloride

Substrate	ROH	Reagent	Reaction Time (min)	Product[a]	Yield[b] (%)	mp (°C) or bp (°C)/mbar	
						found	reported
1a	$PhCH_2OH$	BBr_3	30	**2a**	93	bp 94/25	198–199/1013[13]
1b	Ph_2CHOH	BBr_3	30	**2b**	95	mp 39	37–38[14]
1c	1-adamantyl-OH	BBr_3	60	**2c**	92	mp 118	118[15]
1a	$PhCH_2OH$	$SnCl_4$	60	**3a**	95	bp 177/1013	179/1013[16]
1b	Ph_2CHOH	$SnCl_4$	60	**3b**	96	–[c]	–[a]
1c	1-adamantyl-OH	$SnCl_4$	120	**3c**	89	mp 164–166	165[15]

[a] All products were characterized by mp or bp, and comparison of their spectral and GC data with authentic samples.
[b] Yield of isolated product.
[c] Product purified by column chromatography (SiO_2, hexane/ether, 95 : 5) and identified.

Table 2. Transhalogenation of Benzyl-, Benzhydryl-, Adamantyl- and Tertiary Alkyl Halides Using Tin(IV) Chloride and Boron Tribromide

Substrate	RX (X = Br, Cl)	Reagent	Reaction Time (min)	Product[a]	Yield[b] (%)	mp (°C) or bp (°C)/mbar	
						found	reported
2a	$PhCH_2Br$	$SnCl_4$	60	**3a**	91	bp 177/1013	179/1013[16]
2b	Ph_2CHBr	$SnCl_4$	45	**3b**	94	–[c]	–[a]
2c	1-adamantyl-Br	$SnCl_4$	60	**3c**	86	mp 164–166	165[15]
2d	$PhCH(CH_3)Br$	$SnCl_4$	60	**3d**	93	bp 83/24	81–82/21[24]
2e	$t\text{-}C_4H_9Br$	$SnCl_4$	180	**3e**	85	bp 51/1013	51/1013[25]
3a	$PhCH_2Cl$	BBr_3	15	**2a**	89	bp 94/33	198–199[13]
3b	Ph_2CHCl	BBr_3	15	**2b**	92	mp 39	37–38[14]
3c	1-adamantyl-Cl	BBr_3	30	**3c**	86	mp 118	118[15]
3d	$PhCH(CH_3)Cl$	BBr_3	15	**3d**	90	bp 84/17	85/17[22]
3e	$t\text{-}C_4H_9Cl$	BBr_3	120	**3e**	80	bp 73/1013	73/1013[23]

[a] All products were characterized by mp or bp, and comparison of their spectral and GC data with authentic samples.
[b] Yield of isolated product.
[c] Product purified by column chromatography (SiO_2, *n*-hexane/ether, 95 : 5) and identified.

One requirement for the success of this method is that R^+ should be a stable carbonium ion like benzyl, benzyhdryl or tertiary alkyl. When the secondary alkyl halide bromocyclohexane was allowed to react with tin(IV) chloride, the resulting reaction was very slow. Even at 60°C, after seven hours, chlorocyclohexane was obtained in only 9% yield in addition to 2% cyclohexene. Moreover, primary alkyl halides did not result in transhalogenation under similar conditions.

In conclusion, this method is excellent for the rapid and high yield conversion of 1-adamantyl, benzyl, and benzhydryl alcohols to their corresponding bromides on reaction with boron tribromide and conversion to their corresponding chlorides on reaction with stannic chloride as well as for transhalogenation of adamantyl, benzyl, benzyhdryl and tertiary alkyl halides.

1-Adamantyl Chloride (3c); Typical Procedure:
1-Adamantyl alcohol (**1c**; 1.5 g, 10 mmol) is added to $SnCl_4$ (7.8 g, 30 mmol) at −30°C over a 5 min period. The mixture is then allowed to warm to room temperature over a 2 h period. The mixture is then carefully poured into ice water (30 mL) and extracted with ether (3 × 20 mL). The combined ether extract is dried ($MgSO_4$) and evaporated. The residue is recrystallized from hexane to give 1-adamantyl chloride (**3c**); yield: 1.52 gr (89%); mp 118°C.

Diphenylbromomethane (2b). Typical Procedure:
Diphenylchloromethane (**3b**; 1 g, 5 mmol) is added to BBr_3 (3.7 g, 15 mmol) at −30°C over a 5 min period. The mixture is then allowed to warm to room temperature for 15 min. The mixture is carefully poured into ice water (20 mL) and extracted with ether (3 × 15 mL). The combined ether extract is dried ($MgSO_4$) and evaporated. The residue is recrystallized from hexane to give diphenylbromomethane; yield: 1.13 gr (92%); mp 30°C.

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