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Reactivity of bismuth(III) halides towards alcohols. A tentative to mechanistic investigation

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Abstract—The reactivity of bismuth(III) halides (BiX_3; X=Cl, Br and I) towards a series of alcohols has been investigated. Three different reactions have been studied, namely: halogenation, dehydration and etherification. The behaviour of these bismuth derivatives was found to depend on the nature of the halide bonded to the bismuth atom. Their reactivities can be interpreted on the basis of the Hard and Soft Acids and Bases (HSAB) principle. A mechanism is proposed which involves the formation of a complex of the alcohol with Bi(III). © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Over the past few years an increasing number of papers have described the use of bismuth(III) salts as catalysts.[1] A few recent reports deal with the catalytic activity of Lewis acids derived from Bi(III).[1] This new interest to bismuth salts is understandable. Bismuth and its derivatives are regarded as the least toxic of the heavy elements[2] and they have been widely used in traditional medicine.[3]

In our continuing effort to develop bismuth salts as reagent for organic reactions, our laboratory recently reported the use of bismuth(III) halides in reactions such as the chlorination of alcohols[4] with $BiCl_3$, a convenient halogen exchange reaction[5] and an efficient benzylation reaction of alcohols.[6]

We present here a study of the activity of bismuth(III) halides for the halogenation of alcohols.

2. Results and discussion

2.1. Reactivity of $BiCl_3$

Initially, we started this study by comparing the reactivity of $BiCl_3$ in the chlorination of various primary, secondary, tertiary and benzylic alcohols. In the presence of $BiCl_3$, aliphatic alcohols yielded a mixture of the corresponding chlorides (70%) and alkenes (30%) while benzylic alcohols gave a mixture of chlorides (30%) and symmetrical ethers (70%).[4] In order to understand better the role played by $BiCl_3$ in this reaction and to suggest a mechanism, we have completed our investigations of this study by extending it towards a large series of aliphatic, cyclic, benzylic and allylic alcohols.[4] We have used CCl_4 as solvent to facilitate the ^1H NMR analysis of the reaction medium. Reactions were GC monitored and products were identified by comparison with authentic samples.

The present paper describes a mechanistic study of this chlorination reaction.

The results concerning primary, secondary and tertiary alcohols are presented in Table 1 and those for benzylic and allylic alcohols in Table 2.

Examination of Tables 1 and 2 showed that:

1. Primary alcohols did not react with $BiCl_3$. They were recovered unchanged after three days at reflux. This result, that we had already noted earlier,[4] agrees with that previously reported in the chlorination of alcohols by the $Me_3SiCl/BiCl_3$ system.[7]
2. Secondary alcohols gave alkenes (30%) together with the chlorides (70%) as proved by a constant alkene/chloride ratio during the reaction. At room temperature the reaction was slower but the alkene/chloride ratio remained unchanged.
3. Roughly the same ratios chloride and alkene were obtained from pentan-3-ol, hexan-2-ol, octan-2-ol and octan-3-ol. However, in these cases, several isomeric chlorides and alkenes were formed which would suggest a reaction through a carbocation pathway.
4. Tertiary alcohols appear to be the most reactive substrates towards $BiCl_3$ yielding exclusively the corresponding chlorides.

Keywords: bismuth; alcohols; chlorination; dehydration; etherification.

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Table 1. Chlorination of primary, secondary and tertiary alcohols by $BiCl_3$ (1 equiv.) in CCl_4

Alcohols (1 equiv.)	T (°C)	Reaction times	Conversion (%)	Products
Hexan-1-ol	Reflux	3 days	0	–
2-Ethylhexan-1-ol	Reflux	3 days	0	–
2-Methylhexan-1-ol	Reflux	3 days	0	–
Octan-1-ol	Reflux	3 days	0	–
2-Methylpropan-1-ol	Reflux	3 days	0	–
Cyclohexanol	Reflux	1 h	100	70% Chlorocyclohexane+30% cyclohexene
Cyclopentanol	Reflux	1 h 30	100	70% Chlorocyclopentane+30% cyclopentene
Butan-2-ol	Reflux	45 min	100	70% 2-Chlorobutane+30% but-2-ene
Pentan-3-ol	Reflux	2 h	100	41% 3-Chloropentane+29% 2-chloropentane+30% pent-2-ene
Hexan-2-ol	Reflux	1 h 30 min	100	46.5% 2-Chlorohexane+26% 3-chlorohexane+27.5% hex-2-ene
Octan-2-ol	Reflux	12 h	100	41% 2-Chlorooctane+19% 3-chlorooctane+5.5% 4-chlorooctane+12.5% oct-2-ene+12.5% oct-3-ene+6% oct-4-ene+3.5% oct-1-ene
Octan-3-ol	Reflux	12 h	100	14.5% 2-Chlorooctane+28% 3-chlorooctane+9.5% 4-chlorooctane+13% 2-octene+15% 3-octene+13% 4-octene+7% 1-octene
2-Methylpropan-2-ol	25°C	5 min	100	100% 2-Chloro-2-methylpropane
2-Methylbutan-2-ol	25°C	5 min	100	100% 2-Chloro-2-methylbutane
1-Methylcyclohexanol	25°C	5 min	100	100% 1-Chloro-1-methylcyclohexane

Table 2. Chlorination of benzylic and allylic alcohols by $BiCl_3$ (1 equiv.) in CCl_4

Alcohols (1 equiv.)	T (°C)	Reaction times	Conversion (%)	Products
Benzyl alcohol	25°C	30 min	100	30% Benzyl chloride+70% benzyl ether
	Reflux	5 min		100% Benzyl chloride
1-Phenylethanol	25°C	30 min	100	30% 1-Chloro-1-phenylethane+70% bis(1-phenylethyl)ether
	Reflux	5 min		100% 1-Chloro-1-phenylethane
2-Phenylpropany2-ol	25°C	30 min	100	30% 2-Chloro-2-phenylpropane+70% bis(2-phenylpropyl)ether
	Reflux	5 min		100% 2-Chloro-2-phenylpropane
Prop-2-en-1-ol	25°C	7 h	100	70% 1-Chloroprop-2-ene+30% bis(prop-2-enyl)ether
	Reflux	15 min		100% 1-Chloroprop-2-ene
But-2-en-1-ol	25°C	1 h	100	60% 1-Chlorobut-2-ene 25% 2-Chlorobut-3-ene 15% (But-2-enyl)(1-methylprop-2-enyl)ether
	Reflux	5 min	100	70% 1-Chlorobut-2-ene+30% 2-chlorobut-3-ene
But-3-en-2-ol	25°C	1 h 30	100	60% 1-chlorobut-2-ene+20% 2-chlorobut-3-ene 20% (But-2-enyl)(1-methylprop-2-enyl)ether
	Reflux	5 min	100	75% 1-Chlorobut-2-ene+25% 2-chlorobut-3-ene

5. With benzylic alcohols, and in agreement with previous work,[4] at room temperature, the corresponding chlorides were formed in 30% yield only; the main product was the symmetrical ether. We have observed that ethers and chlorides were obtained concurrently. However, when the reaction is conducted in refluxing CCl_4, the ether was not formed and the chloride was obtained with excellent yields (97%).
6. As benzylic alcohols, allylic alcohols have led at room temperature to a mixture of chloride and ether, the chloride being predominant in that case. At reflux, only the chloride was obtained. Also we have observed that allylic alcohols are subject to an allylic rearrangement induced by $BiCl_3$, to give mixtures of isomers. Thus both angelic alcohol (but-3-en-2-ol) and crotyl alcohol (but-2-enol) predominantly led to crotyl chloride (1-chloro-but-2-ene) together with the same unsymmetrical ether containing both crotylic and angelic groups.

We then have studied the chlorination of a series of cyclic alcohols possessing a well-defined configuration. Results are reported in Table 3.

With secondary alcohols (Tables 1 and 3), the chlorination reaction seemed to be superseded by the formation of alkenes. As seen with other secondary alcohols, the temperature has no influence on the nature and the proportion of the products.

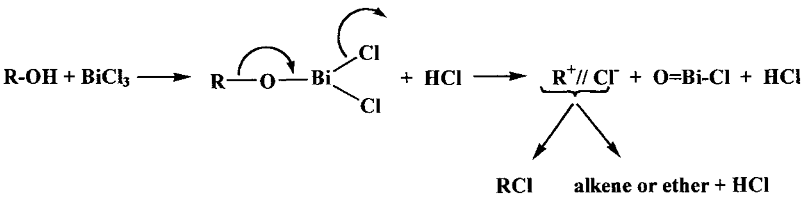
To evaluate the influence of the $BiCl_3$ concentration, some

Table 3. Chlorination of cyclic secondary alcohols by $BiCl_3$ (1 equiv.) in CCl_4 at reflux

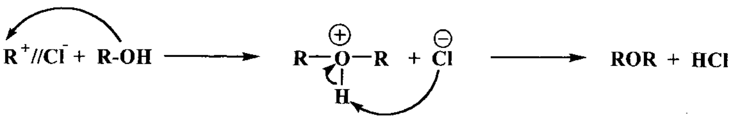
Alcohols (1 equiv.)	Reaction times	Conversion (%)	Products
cis-2-methylcyclohexanol	15 min	100	32% 1-Chloro-1-methylcyclohexane+68% 1-methylcyclohex-1-ene
trans-2-methylcyclohexanol	1 h	100	30.3% *Trans*-1-chloro-2-methylcyclohexane+6% *cis*-1-chloro-2-methylcyclohexane+8.9% 1-chloro-1-methylcyclohexane+42.4% 1-methylcyclohex-1-ene+6.3% 1-methylcyclohex-2-ene+6.2% cyclohexylidene
Menthol	4 h	100	35% Menthyl chloride+65% menthenes

Table 4. Chlorination of alcohols by $BiCl_3$ (1/3 equiv.) in CCl_4.

Alcohols (1 equiv.)	*T* (°C)	Reaction times	Conversion (%)	Products
Octan-2-ol	Reflux	45 h	100	40% 2-Chlorooctane+19% 3-chlorooctane+6% 4-chlorooctane+13% oct-2-ene+12.5% oct-3-ene+6% oct-4-ene+3.5% oct-1-ene
cis-2-Methylcyclohexanol	Reflux	1 h	100	33% 1-Chloro-1-methylcyclohexane+67% 1-methylcyclohexene
2-Methylpropan-2-ol	25°C	2 h 30	100	100% 2-Chloro-2-methylpropane
1-Phenylethanol	25°C	1 h	100	30% 1-Chloro-1-phenylethane+70% bis (1-diphenylethyl)ether



Scheme 1.



Scheme 2.

alcohols were treated with a third of one equivalent of $BiCl_3$ to give the results reported in Table 4.

The use of smaller quantities of $BiCl_3$ did affect neither the nature nor the ratio of the products but increases the reaction times. However, 2-methylpropan-2-ol was completely converted into 2-chloro-2-methylpropane showing that the three chlorine atoms of $BiCl_3$ are usable in the chlorination reaction.

From all these results, we have considered two possible mechanisms.

The first mechanism involves the formation of alkoxybismuthane intermediates and proceeds via a carbocation derived from the alcohol.

The second mechanism assumes the alcohol activation by means of complexes between the oxygen of the alcohol and the bismuth atom.

2.1.1. Mechanism A. The mechanism (Scheme 1) was inspired from that proposed in the alcohols chlorination by boron trichloride.[8]

The action of $BiCl_3$ on the alcohol would lead to formation of the dichloroalkoxybismuthane with liberation of HCl. This intermediate would then give bismuth oxychloride and an ion pair. The isomeric chlorides obtained in the reactions would arise from a carbocation rearrangement. Ether formation would result from the reaction between the carbocation and unreacted alcohol molecules (Scheme 2).

Finally, the deprotonation of the carbocation would produce alkenes and hydrogen chloride (Scheme 3).

If such a mechanism occurs, it would imply: (a) the formation of a carbocation, (b) the liberation of HCl, (c) the formation of oxychloride.

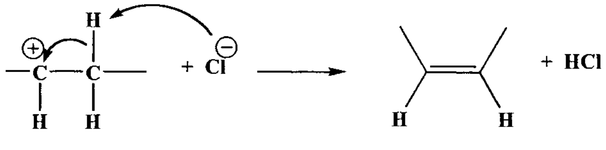
Also the formation of ethers or alkenes would result from a reaction involving $BiCl_3$.

We have successively examined each of these points.

(i) To verify the existence of a carbocation intermediate, we have compared reaction times of the benzyl alcohol and the 4-methylbenzyl alcohol. If a carbocation was formed, the presence of the methyl group in *para* position should enhance the reaction rate. In fact, when the reaction was performed in the standard conditions (1 equiv. of $BiCl_3$ in CCl_4 at 25°C), the benzyl alcohol disappeared faster than the 4-methyl derivative, reaction times being 30 and 55 min, respectively. Those results are inconsistent with the formation of a carbocation.

Moreover, if there was a carbocation, *cis*- and *trans*-2-methylcyclohexanol (Table 3) would lead to the same carbocation and, consequently should then give the same product mixtures which is not the case.

Additionally, Table 2 showed a rearrangement of allylic alcohols. Thus at reflux, both but-2-en-1-ol and but-3-en-2-ol led roughly to the same chlorobutene mixture (70/30



Scheme 3.

and 75/25, respectively). This result could suggest the passage through two carbocations in a fast equilibrium. However, if this was the case, the secondary chloride corresponding to the more stable carbocation should be expected. The experiment showed the opposite: 1-chlorobut-2-ene was roughly three times more abundant than 2-chlorobut-3-ene. On the contrary, a slow equilibrium between both carbocations should not give the same mixture of chlorides.

All those experimental observations should preclude the formation of a carbocation as reaction intermediate.

(ii) This mechanism involves the formation of HCl. We were never able to detect HCl. Thus, 2-methylpropan-2-ol (*t*BuOH), was reacted at 25°C in CCl_4 with 1 equiv. of $BiCl_3$ and 1 equiv. of 2,3-dimethylbut-2-ene to trap HCl. The reaction rate was strongly reduced (30 min instead of 5 min) but no 2-chloro-2, 3-dimethylbutane traces could be detected. At this stage, we have found no evidence for the production of HCl.

(iii) According to this mechanism, bismuth oxychloride (O=Bi–Cl) should be formed at the end of the reaction.

When reactions were performed in the presence of 1 equiv. of BiOCl in CCl_4 at reflux, the alcohols were recovered unchanged. Thus BiOCl is totally inactive towards alcohols. To verify the formation of BiOCl, the chlorination of *t*BuOH by $BiCl_3$ (1 mol equiv.) was performed in CCl_4 at room temperature. Upon completion of the reaction, a solid was recovered, washed with CCl_4 and reacted with another equivalent of *t*BuOH. This gave the corresponding chloride proving thus that the recovered solid was not BiOCl.

Also we have observed (Table 4) that *t*BuOH (1 equiv.) was totally converted into *t*BuCl by 1/3 equiv. of $BiCl_3$. Thus the stoichiometry $3ROH/1BiCl_3$ was observed which is inconsistent with mechanism A.

(iv) Thus, in this mechanism the first steps are common for the formation of chlorides, ethers or alkenes. Whatever the product, $BiCl_3$ would be consumed. The reaction of 3 equiv. of 1-phenylethanol with 1 equiv. of $BiCl_3$ gave chloride (30%), ether (70%) and a solid. According to mechanism A, this solid should not be able to chlorinate an alcohol. This solid was recovered, washed with CCl_4 and reacted with another equivalent of 1-phenylethanol. This reaction led to the corresponding chloride and ether in the same proportion as shown previously. This was not compatible with mechanism A.

In conclusion, mechanism A had to be discarded.

2.1.2. Mechanism B.

This mechanism suggests the formation of a complex between the alcohol and $BiCl_3$ followed by different routes leading either to the chloride, the ether or the alkene.

2.1.2.1. Etherification.

Proposals described above (see iv) indicate that this reaction does not consume chlorine of $BiCl_3$. Then, this last would play only a catalytic role.

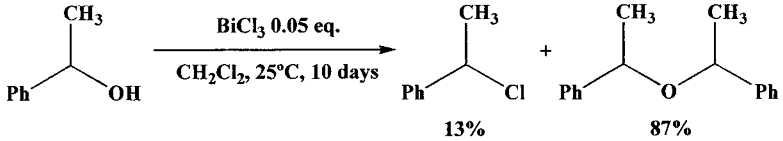
To confirm this catalytic role played by $BiCl_3$ in the benzylic alcohols etherification, 1-phenylethanol was reacted with a catalytic amount of $BiCl_3$ (5% mol equiv.). The reaction proceeds to completion in 10 days leading to 1,1-diphenylethylether (87%) and 1-chloro-1-phenylethane (13%) (Scheme 4).

The alcohol was completely consumed showing that $BiCl_3$ acts as catalyst in the ether formation. Its reaction mechanism is shown in Scheme 5.

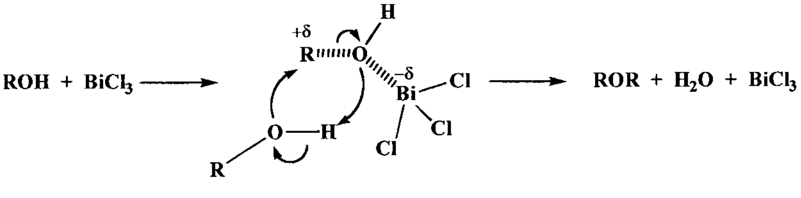
The studies of Lewis acidity of Bi(III) compounds, especially if the bismuth bears electronegative atoms, has led to the identification of numerous complexes[9] formed with amines, alcohols, amides, esters, carbonyl group,...

Such structures reported in those complexes lend additional support to our mechanistic proposal.

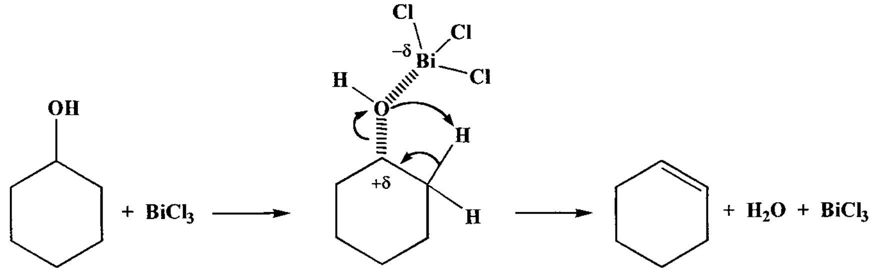
The interaction between the lone electron pair of the alcohol oxygen and the electronic deficiency of bismuth involve the elongation and the weakening of the C–O bond turning the hydroxy-bearing carbon into an electrophilic centre. The oxygen atom of a second alcohol molecule acting as nucleophile attacks this positively carbon atom affording thus to the ether formation with loss of water and that, without direct $BiCl_3$ consumption.



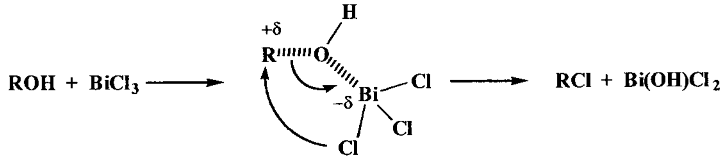
Scheme 4.



Scheme 5.



Scheme 6.



Scheme 7.

2.1.2.2. Elimination. When the elimination occurs, for example with the cyclohexanol, it would proceed through a similar catalytic process to that postulated for the etherification reaction according to Scheme 6.

2.1.2.3. Chlorination. The alcohol/$BiCl_3$ complex may evolve according to a third way. The carbon atom bearing the hydroxyl group can be attacked by one of chlorine atom of $BiCl_3$. In the bismuth atom an exchange between chlorine atom and the hydroxyl group occurs involving a four-centre transition state already previously mentioned in the halogen exchange reactions.[5] The expected chloride was formed with a new species of bismuth, '$BiCl_2OH$'. This reaction would occur according to an S_{Ni} mechanism (Scheme 7).

Since one mole of $BiCl_3$ can convert 3 mol of *t*BuOH into the corresponding chloride, we should therefore admit that the bismuth could exchange successively its chlorine atoms according to an analog process.

In summary, $BiCl_3$ plays a catalytic role in etherification and elimination reactions and acts as a reagent in the chlorination reaction.

Finally, another proof of the validity of mechanism B has been given by the stereochemical study of the chlorinating reaction of optically alcohols [(*S*)-(−)-1-phenylethanol and (+)-butan-2-ol] in the presence of $BiCl_3$ in CCl_4 at reflux; chlorides were isolated and their optical rotations measured (Table 5).

These findings will suggest that in the chlorination reactions, $BiCl_3$ attacked the 1-phenylethanol and the butan-2-ol mainly in a S_{Ni} mechanism (retention of configuration), which agrees with the four-centre reaction mechanism proposed above and, therefore, with the mechanism B.

We have now to explain the formation of different isomer chlorides during the chlorination reactions which results were already reported in preceding tables.

The formation of these different chlorides could be explained in considering the geometry of the $BiCl_3$–ROH complex in which several parameters should be taken in consideration, namely:

the location of positively charges-bearing carbons;
the position of chlorine atoms of $BiCl_3$ compared to these electrophilic centres;
steric hindrance susceptible to interfere with the chlorine approach;
the size of bismuth atom.

In considering these different parameters, we can partly explain the regioselectivity of the chlorination and thus the formation of several positional isomers. For example, the hexan-2-ol leads to the 2- and 3-chlorohexane in the ratio 2:1 roughly (see Table 1). Let us consider the hexan-2-ol/$BiCl_3$ complex (Scheme 8).

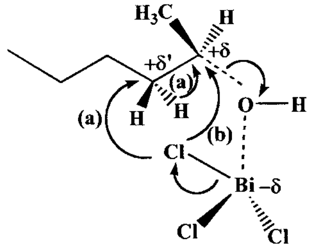
We have attempted to explain our experimental results from those criteria.

The Bi–O interaction creates a positive charge on the C2. This charge can be spread partially toward the C3. Since the

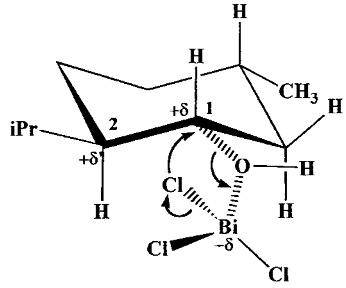
Table 5. Chloriantion of optically alcohols by $BiCl_3$ (1 equiv.) in CCl_4 at reflux

ROH	$[\alpha]_D$	RCl[a]	$[\alpha]_D$[b]	$[\alpha]_D$[10,11]
(*S*)-(+)-butan-2-ol	+12° *c*=5; MeOH	(*S*)-(+)-2-chlorobutane	+24.9° *c*=15.6; MeCN	+24.7° *c*=15.6; MeCN
(*S*)-(−)-1-phenylethanol	−45° *c*=10; MeOH	(*S*)-(−)-1-chloro-1-phenylethane	−45° *c*=5.4; EtOH	−45° *c*=5.4; EtOH

[a] Chlorides isolated from the reaction mixture.
[b] Optical rotations were measured at 20°C.



Scheme 8.



Scheme 9.

$BiCl_3$ size and its position with respect to the alcohol, chlorine atoms of $BiCl_3$ are close to these two attack centres (C2 and C3) and chloride mixture was ensued via a four- or a five-centre transition state, respectively. The attack on the C2, more positively polarized, is predominant. On the other hand, menthol afforded only one chloride which could be explained with the help of the menthol/$BiCl_3$ complex (Scheme 9) involving a four-centre intermediate.

From the menthol structure, $BiCl_3$ is relatively bulky and there is a strong steric hindrance with the isopropyl group. Thus $BiCl_3$ can only adopt only one well-precise position with respect to the ring. So, $BiCl_3$ is located under the ring and far from it. Thus, the chlorine approach could happen only on the C1, which should be the less-hindered side. Since $BiCl_3$ is situated far from the ring, the chlorination reaction was disfavoured leading thus to a higher alkene formation.

Also the observed transposition with allylic alcohols (Table 2) can result from the chlorine atom transfer involving a six-centre (Scheme 10) transition state. Thus, it appears that the size of the bismuth atom can permit the passage through a four-, five- or six-centre transition state.

It is worthwhile to mention that in the case of aliphatic secondary alcohols, the chlorination never concerns the primary carbon atom (see Table 1) whatever the position of the hydroxyl group.

Finally, the mechanism B would explain part of experimental results namely:

the 3 chlorine atoms of $BiCl_3$ are available and exchangeable to achieve the chlorination reaction.

This reaction occurs according to a S_{Ni} mechanism and depends of the steric hindrance of the bismuth–alcohol complex.

Following these results, we supplemented our investigations in studying the reactivity of two other bismuth(III) halides ($BiBr_3$ and BiI_3) towards alcohols.

2.2. Reactivity of $BiBr_3$ and BiI_3

1-phenylethanol was reacted with 1 equiv. of $BiBr_3$ in CCl_4 at 25°C. Within 15 min the alcohol was totally consumed, giving bis-(1-phenylethyl)ether in 100% yield. $BiBr_3$ does not seem to be a brominating reagent. To verify this point, this work has been extended to a series of alcohols (primary, secondary, tertiary, benzylic and allylic). Results are reported in Table 6.

From these results, we can make the following remarks:

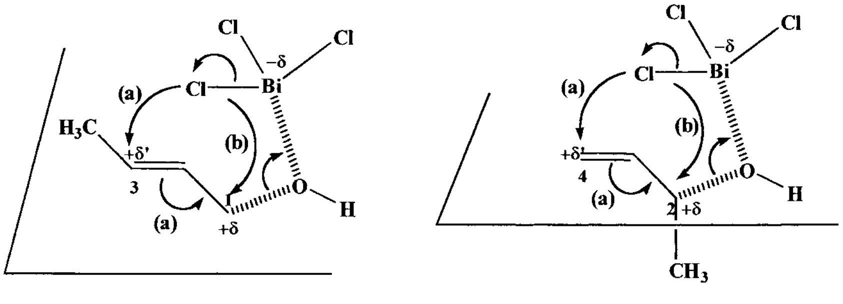
Like with $BiCl_3$, primary alcohols did not react in the presence of $BiBr_3$.

Secondary and tertiary alcohols afforded exclusively the corresponding alkenes. Even tertiary alcohols which are converted into chlorides in 100% yield by $BiCl_3$, react with $BiBr_3$ to lead quantitatively the corresponding alkenes.

Benzylic and allylic alcohols led to the corresponding ethers without bromide formation, with reaction times shorter than those obtained with $BiCl_3$. As previously noted, but-2-en-1-ol and but-3-en-2-ol gave mixture of symmetrical and unsymmetrical ethers.

$BiBr_3$ is not a reagent for the bromination of alcohols and it does not give its bromine atoms.

Those results can be explained on the base of the Hard and Soft Acids and Bases concept[12] (HSAB principle): soft acids prefer to bond to soft bases. The Bi^{3+} ion is considered as a


But-2-enol **But-3-en-2-ol**

Scheme 10.

Table 6. Reactivity of $BiBr_3$ (1 equiv.) towards alcohols in CCl_4

Alcohols (1 equiv.)	Reaction times	Conversion (%)	Products
Hexan-1-ol[a]	7 days	0	
Octan-1-ol[a]	7 days	0	
Cyclohexanol[a]	1 h	100	100% Cyclohexene
cis-2-Methylcyclohexan-1-ol[a]	1 h 30	100	100% 1-Methylcyclohex-1-ene
Pentan-3-ol[a]	2 h	100	100% Pent-2-ene
2-Methylpropan-2-ol[b]	5 min	100	100% 2-Methylprop-1-ene
2-Methylbutan-2-ol[b]	5 min	100	100% 2-Methylbut-2-ene
1-Methylcyclohexan-1-ol[b]	5 min	100	100% 1-Methylcyclohex-1-ene
Benzyl alcohol[b]	30 min	100	100% Dibenzylether
1-Phenylethanol[b]	20 min	100	100% Bis-(1-phenylethyl)ether
2-Phenylpropan-2-ol[a]	15 min	100	100% Bis-(2-phenylprop-2-yl)ether
Prop-2-en-1-ol[a]	4 h	100	100% Bis-(prop-2-enyl)ether
But-2-en-1-ol[a]	30 min	100	58.4% (But-2-enyl)(1-methylprop-2-enyl)ether +11.6% bis-(1-methylprop-2-enyl)ether +30% bis-(but-2-enyl)ether
But-3-en-2-ol[b]	30 min	100	63.4% (But-2-enyl)(1-methylprop-2-enyl)ether +18.3% bis-(1-methylprop-2-enyl)ether +18.3% bis-(but-2-enyl)ether

[a] Reaction performed at 60°C.
[b] Reaction achieved at 25°C.

soft (or eventually borderline) acid and should prefer to bond to soft bases like I^- or Br^- rather than with a hard base. It is worthwhile pointing out that Cl^- and OH^- are two hard bases approximatively equivalent, which would explain why $BiCl_3$ can behave as chlorinating agent. In other words, $BiCl_3$ is able to exchange chlorine atom against hydroxyl group, while $BiBr_3$ does not exchange bromine with hydroxyl group.

Thus, from this HSAB principle, $BiBr_3$ would be unchanged at the end of the reaction with alcohols and would act only as an efficient catalyst for the elimination and etherification reactions.

To verify that, 1-phenylethanol was reacted with 0.05 equiv. of $BiBr_3$ in CCl_4 at 25°C. The alcohol was totally converted to ether after 8 h. At the end of this reaction, the solid was recovered, washed with CCl_4 and reacted with one another equivalent of 1-phenylethanol. The corresponding ether was again obtained after 8 h. Therefore $BiBr_3$ is really a catalyst for the etherification reaction of allylic and benzylic alcohols.

The catalytic role played by $BiBr_3$ in the elimination reaction was also confirmed by examining the reaction of cyclohexanol with 0.05 equiv. of $BiBr_3$ in CCl_4 at reflux. The alcohol was completely converted to cyclohexene within 24 h. Therefore $BiBr_3$ is also a catalyst for the elimination reaction.

Otherwise we have observed that under indentical experimental conditions in the presence of $BiBr_3$, benzyl alcohol give the corresponding ether faster than the 4-methylbenzyl alcohol (40 and 65 min, respectively). Such a behaviour is not consistent with mechanism involving a carbocation as intermediate.

From these results it appears that $BiBr_3$ proceeds through similar catalytic processes to that postulated for the same reactions described above for the etherification and elimination reactions catalysed by $BiCl_3$.

We tried to extend to BiI_3 experiments achieved with $BiBr_3$. However whatever the considered alcohol, BiI_3 was not able to convert any of them. Alcohols were recovered unchanged after reaction in the presence of BiI_3. Two factors can explain this result:

> According to the HSAB principle. I^- being a soft base and OH^- a hard base, BiI_3 is not able to play the role of reagent (iodination reaction), which is in agreement with $BiBr_3$ behaviour.
> Furthermore, the bulky iodine atoms around the bismuth metal lead to a compact structure,[13] which prevent any alcohol molecule approach and the Bi–OH interaction creation. Thus, BiI_3 can act neither as reactant nor as catalyst.

3. Conclusions

In conclusion, this study concerning the bismuth(III) halides reactivity towards alcohols has shown the following points:

> Experimental results are better explained by the postulated mechanism B which implies the preliminary formation of a complex between the alcohol and BiX_3.
> $BiCl_3$ has two behaviour patterns. It plays the role of reagent for the chlorination of alcohols and intervenes as catalyst for both the etherification and the elimination reactions.

The chlorination by $BiCl_3$ would involve a S_{Ni} process, which agrees with the already proposed[5] four-centre reaction mechanism. Due to the bismuth atom large size and the steric hindrance of the $BiCl_3$–alcohol complex, chlorination can also involve a five- or six-centre transition state.

The steric hindrance affects strongly the reaction: a large steric interference leads to a low chloride formation and consequently to a large alkene or ether amount.

$BiBr_3$ behaves only as an efficient catalyst for both the etherification and the elimination reactions.

BiI_3 is totally inactive towards alcohols.

Furthermore the difference in the halogenation ability between $BiCl_3$ and $BiBr_3$ or BiI_3 is in agreement with HSAB principle.

Further studies on the application of Bi(III) derivatives to others reactions are in progress.

4. Experimental

^{1}H NMR was recorded in a BRUCKER ACE-250 instrument at 250 MHz in $CDCL_3$ solutions. GC analysis was performed with a DELSI 330 apparatus. Optical rotations were measured using a PERKIN ELMER 241 polarimeter with specific rotations determined at 20°C. All starting materials, alcohols, optically active alcohols, $BiCl_3$, $BiBr_3$, BiI_3, BiOCl, were commercially available (Aldrich).

Whatever the bismuth derivative ($BiCl_3$, $BiBr_3$, BiI_3, BiOCl), halogenation reactions were performed following the general procedure previously described.[4] The same method was used for the reaction achieved in the presence of the 2,3-dimethylbut-2-ene.

References

1. (a) Suzuki, H.; Igekami, T.; Matano, Y. *Synthesis* **1997**, 249. (b) Desmurs, J. R.; Labrouillère, M.; Le Roux, C.; Gaspard, H.; Laporterie, A.; Dubac, J. *Tetrahedron Lett.* **1997**, *38*, 8871. (c) Repichet, S.; Le Roux, C.; Dubac, J.; Desmurs, J. R. *Eur. J. Org. Chem.* **1998**, 2743. (d) Repichet, S.; Roux, C.; Hernandez, P.; Dubac, J. *J. Org. Chem.* **1999**, *64*, 6479.
2. Irwing-Sax, N.; Bewis, R. J. In *Dangerous Properties of Industrial Materials*; Van Nostrand Reinhold: New York, 1989; pp 283 (also pages 284, 522 and 523).
3. (a) Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; *Comprehensive Coordination Chemistry*, Pergamon Press: London, 1987; Vol. 3, pp. 292. (b) Manhart, M. D. *Rev. Infect. Dis.* **1990**, *12*, 311. (c) Kozak, R. W.; Waldmann, T. A.; Atcher, R. W.; Gansow, O. A. *Trends Biotechnol.* **1985**, *4*, 259. (d) Baxter, G. F. *Chem. Ber.* **1992**, *28*, 445.
4. Boyer, B.; Keramane, E. M.; Montéro, J. L.; Roque, J. P. *Synth. Commun.* **1998**, *28*, 1737.
5. Boyer, B.; Keramane, E. M.; Arpin, S.; Montéro, J. L.; Roque, J. P. *Tetrahedron* **1999**, *55*, 1971.
6. Boyer, B.; Keramane, E. M.; Roque, J. P.; Pavia, A. A. *Tetrahedron Lett.* **2000**, *41*, 2891.
7. Labrouillère, M.; Le Roux, C.; Oussard, A.; Gaspard-Iloughmane, H.; Dubac, J. *Bull. Soc. Chim. Fr.* **1995**, *132*, 522.
8. (a) Hudson, H. R.; Kinghorn, R. R. F.; Murphy, W. S. *J. Chem. Soc.* **1971**, 3593. (b) Gerrard, W.; Hudson, H. R.; Murphy, W. S. *J. Chem. Soc.* **1964**, 2314. (c) Gerrard, W.; Lappert, M. F. *J. Chem. Soc.* **1951**, 1020. (d) Gerrard, W.; Lappert, M. F. *J. Chem. Soc.* **1955**, 3084.
9. (a) Lange, K. C. H; Klapotke, T. M. In *The Chemistry of Arsenic, Antimony and Bismuth Compounds*; Pataï, S., Ed.; Wiley: New York, 1994; pp 315. (b) Majafuji, T.; Mutoh, T.; Satoh, K.; Tsunenari, K. *Organometallics* **1995**, *14*, 3848. (c) Carmalt, C. J.; Clegg, W.; Elsegood, M. R. J.; Errington, R. J.; Havelock, J.; Lightfoot, P.; Norman, N. C.; Scott, A. J. *Inorg. Chem.* **1996**, *35*, 3709. (d) Di Vaira, M.; Mani, F.; Stoppioni, P. *Eur. J. Inorg. Chem.* **1999**, 833. (e) Kallal, K.; Coin, C.; Dunach, E.; Postel, M. *New J. Chem.* **1997**, *21*, 495 (and references cited therein). (f) Genge, A. R. J.; Levason, W.; Reid, G. *Chem. Commun.* **1998**, 2159. (g) Murray, B.; Hvoslef, J.; Hope, H.; Power, P. P. *Inorg. Chem.* **1983**, *22*, 3421. (h) Althaus, H.; Breunig, H. J.; Rosler, R.; Lork, E. *Organometallics* **1999**, *18*, 328.
10. Holcomb, H. L.; Nakanishi, S.; Flood, T. C. *Organometallics* **1996**, *15*, 4228.
11. Moss, R. A.; Baicerzak, P. *J. Am. Chem. Soc.* **1992**, *114*, 9386.
12. (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. (b) Pearson, R. G. *Science* **1966**, *151*, 172. (c) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512. (d) Pearson, R. G. *J. Chem. Educ.* **1987**, *64*, 561.
13. Fisher, G. A.; Norman, N. C. The Structures of the Group 15 Element (III) Halides and Halogeanions. In *Advances in inorganic chemistry*; Academic Press: San Francisco, 1994; Vol. 14, pp 336 (and references cited therein).