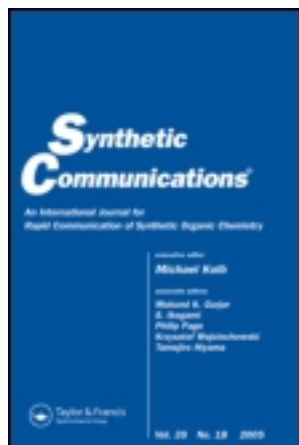


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BiCl₃: An Efficient Agent for Selective Chlorination of Alcohols or for Halogen Exchange Reaction

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BiCl₃ : AN EFFICIENT AGENT FOR SELECTIVE CHLORINATION OF ALCOHOLS OR FOR HALOGEN EXCHANGE REACTION

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Abstract: BiCl₃ was found to be an effective reagent for an improved chlorination of alcohols and for a convenient halogen exchange reaction.

The usefulness of bismuth in organic synthesis has been little recognized until the last decade, when intensive works revealed the uniqueness and promising potential of bismuth derivatives as reagents for organic transformations¹. Bismuth(V) derivatives constitute interesting reagents developed in organic synthesis¹. On the other hand, the use of Bi(III) complexes as catalysts in organic reactions has rarely been reported and poorly documented. Some recent examples concern oxidation², condensation reactions³ hydrolysis of esters⁴ and regeneration of carbonyl compounds⁵. In our ongoing research on glycosyl halide preparation for the formation of the glycosidic bond, we recently reported a new procedure for a mild halogenation of glycosyl peracetates⁶. This new approach, previously described by Dubac⁷ for the halogenation of alcohols, involves a catalytic amount of bismuth (III) halides in the presence of halogenosilanes.

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Those preliminary results prompted us to explore new possibilities in the use of Bi(III) halides, not only as a catalyst but also as halogenating reagents in order to understand the role played by those Bi(III) halides. We particularly focused on BiCl₃ and tested its activity as chlorinating reagent for alcohols. We herein present our preliminary results. No example of the use of BiCl₃ as reagent for alcohol chlorination has, to our knowledge, been previously reported.

A series of alcohols (primary, secondary, tertiary) were reacted in CCl₄ under an inert atmosphere (N₂) at room temperature (unless stated) with an equimolar amount of BiCl₃. The reaction is heterogeneous since BiCl₃ is not soluble in CCl₄. The results concerning chloride formation are presented in the Table.

Table.- Chlorination of alcohols^a : $\text{R-OH} \xrightarrow[\text{CCl}_4]{\text{BiCl}_3} \text{R-Cl}$

Entry	ROH	T°C	Reaction Time	Yield (%)
1	2-methylpropanol	Reflux	48 h	no reaction
2	hexanol	Reflux	48 h	no reaction
3	2-ethylhexanol	Reflux	48 h	no reaction
4	octan-2-ol	Reflux	3 h	65 ^b
5	cyclohexanol	Reflux	5 mn	> 99
6	2-methyl-2-propanol	25	5 mn	100
7	2-methyl-2-butanol	25	5 mn	100
8	benzyl alcohol	25	20 mn	25 ^c
9	1-phenylethanol	25	30 mn	30 ^c

^a General reaction conditions : anhydrous CCl₄^d (5 ml) was stirred in the presence of BiCl₃ (1.25 mmole) and the alcohol (1.25 mmole) at 25°C (or reflux) under nitrogen atmosphere. The reaction was followed by GC until complete alcohol consumption. The mixture was filtered and solvent evaporation led to chlorides in the yields shown. The products were analyzed by GC, ¹HNMR, and their spectral data compared with those of authentic samples. ^b The by-product in that reaction was solely the E-oct-2-ene. ^c The main-products in those reactions were corresponding ethers. ^d The same reaction can be realized with other solvents (CH₂Cl₂ or cyclohexane). CCl₄ was used for the convenience to analyse directly by ¹HNMR an aliquot of the reaction media.

Cyclic secondary and tertiary alcohols (entries 5, 6 and 7) afforded the corresponding chlorides in good yield. However 2-octanol (entry 4) was entirely converted after a 3 h reaction at reflux and the 2-chlorooctane was formed in 65% yield : the by-product being the corresponding 2-octene. The new BiCl_3 chlorinating agent shows an interesting selectivity. Thus, primary alcohols (entries 1, 2 and 3), did not react in the presence of BiCl_3 and were recovered unchanged after 48 h at reflux. This result agrees with that previously reported⁷ in the chlorination of alcohols by chloromethylsilanes in the presence of catalytic amounts of BiCl_3 : no chlorination reaction was observed with primary alcohols.

It is noteworthy that with benzylic alcohols (entries 8 and 9), the corresponding halides were formed only in 25% and 30% yield respectively; the main products being the dibenzyl ether (75%) and the di-(1-phenylethyl) ether (70%)⁸. Due to the high reactivity of benzyl halides, we thought that the chloride formed during the reaction reacted with the remaining alcohol to afford the corresponding ether. To check this point, a reaction was carried out in the presence of the 1-phenylethanol and the commercially available 1-bromoethylbenzene but without BiCl_3 . After 72 h, only 20% of the corresponding ethers were obtained. In spite of the higher reactivity of the bromide compared to the chloride, the etherification reaction is a very slow reaction without BiCl_3 . The fast ether formation observed (entries 8 and 9) should result from a catalysis of that reaction by BiCl_3 . To verify, we repeated the same reaction (1-bromoethylbenzene and 1-phenylethanol) in adding a catalytic amount of BiCl_3 (0.05 eq). The reaction led after 6 h to a mixture of the ether (0.5 eq) and 1-phenylethyl halides (1 eq.) constituted by the bromide (85%) and the chloride (15%). Since halides were totally recovered, that means that the etherification reaction takes place solely from the alcohol by an unclear mechanism.

Furthermore, right at the start of this reaction we observed a change in the colour of the catalyst in suspension in the medium ; this catalyst, BiCl_3 , which is a white powder, became yellow (the typical colour of BiBr_3). It appeared that an halogen exchange took place between the 1-bromoethylbenzene and BiCl_3 . Then, we carried out a reaction in the presence of BiCl_3 (0,4 mmole) and the 1-bromophenylethane (1.2 mmole) at 25°C in CCl_4 . After a few seconds, there was a colour change (white to yellow). After 4 h , $^1\text{HNMR}$ analysis of the medium revealed the presence of the 1-chloroethylbenzene (80%) and the bromide (20%). Clearly there was a fast halogen exchange between the bromide and chlorine atoms. The composition of the organic halides resulting from that exchange did not reflect a statistical distribution since 50% of each halogen derivatives could be expected by this reaction. Clearly, we reached a value beyond that distribution ; these results are most likely related to the higher affinity of bromine for bismuth than for carbon, compared to that of chlorine.

To the best of our knowledge, no example in the literature reports the halogen exchange from BiCl_3 . Further investigations are at present underway to elucidate the particular behaviour of bismuth.

In conclusion, the new reaction described here offers a simple, one-pot, quick, convenient, highly efficient and straightforward procedure which affords chlorides from secondary cyclic and tertiary alcohols. It represents the first examples where a Bi(III) halide is used as a reagent in an halogenation reaction. Furthermore, those preliminary results indicate that Bi(III) derivatives could constitute a good agent for the specific halogen exchange. Further investigations in these areas are now underway.

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