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Bismuth (III) Chloride¹; an Efficient and Selective Catalyst for Deprotection of 1,1-Diacetates

I. Mohammadpoor-baltork ^a & H. Aliyan ^a

^a Department of Chemistry, Esfahan University, Esfahan, 81744, Iran Published online: 25 Sep 2007.

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BISMUTH (III) CHLORIDE¹; AN EFFICIENT AND SELECTIVE CATALYST FOR DEPROTECTION OF 1,1-DIACETATES

I. Mohammadpoor-Baltork^{*} and H. Aliyan

Department of Chemistry, Esfahan University, Esfahan 81744, Iran

ABSTRACT: A variety of 1,1-diacetates are easily and efficiently deprotected in the presence of catalytic amounts of bismuth(III) chloride affording the corresponding aldehydes in high yields.

Selective introduction and removal of protecting groups is of vital importance in synthetic organic chemistry. 1,1-Diacetates have attracted considerable attention during recent years since these compounds are moderately stable², easily prepared²⁻¹¹ and can act as protecting groups for the selective protection of aldehydes. They are also important starting materials for the synthesis of dienes for Diels-Alder cycloaddition reactions¹².

Various methods such as alcoholic sulfuric¹³ or hydrochloric¹⁴ acid, sodium hydroxide or potassium carbonate², boron triiodide-N, N-diethylaniline

^{*} To whom correspondence should be addressed.

complex¹⁵, ceric ammonium nitrate coated on silica-gel¹⁶, neutral alumina under microwave irradiation¹⁷, potassium phenoxides¹⁸, montmorillonite K 10^{19} , expansive graphite²⁰, montmorillonite K 10^{21} or KSF²² under microwave irradiation and scandium triflate²³ have been reported for the conversion of 1,1diacetates to the corresponding aldehydes. However, some of these methods suffer from disadvantages such as high acidity, long reaction time, low yield of the product and requirement for an additional microwave oven.

The applications of bismuth compounds to organic transformations have been extensively investigated²⁴. Recently we have introduced an efficient and convenient method for the conversion of oxiranes to thiiranes in the presence of bismuth(III) chloride¹. In connection with our work on bismuth(III) chloride catalysis we now report an efficient deprotection of 1,1-diacetates under catalysis of bismuth(III) chloride in refluxing chloroform.

As shown in the Table different 1,1-diacetates including those with electronwithdrawing substituents are converted to the corresponding aldehydes in the presence of 0.1-0.2 molar ratio of bismuth(III) chloride in high yields. It is important to note that aryl aldehyde diacetates are selectively deprotected in the presence of phenolic acetate function (Entries 14, 15). We have also tried the reaction of 1,1-diacetoxyheptane as an example of aliphatic aldehyde diacetate in refluxing chloroform for 1 h in the presence of the catalyst. Only 8% of conversion to heptanal was observed under this condition. Therefore, the present procedure is a selective deprotection of aryl aldehyde diacetates to aryl aldehydes in the presence of aliphatic aldehyde diacetate and phenolic acetate.

Table. Deprotection of 1,1-Diacetates in the Presence of BiCl₃ in Refluxing CHCl₃

Entry	R	Time(min.)	BiCl ₃ /Diacetate	Yield(%) ^{a,b}
1	C.H.		0.1	90
2	2-MeOC.H.	10	0.1	90
2	2-McOC ₆ 11 ₄	10	0.1	97 08
3	4-IMEOC ₆ 11 ₄	10	0.1	90
4	$4-CIC_6H_4$	25	0.1	99
5	$4-BrC_6H_4$	15	0.1	97
6	4-MeC ₆ H ₄	10	0.1	99
7	2,5-(MeO) ₂ C ₆ H ₃	10	0.1	99
8	$2-O_2NC_6H_4$	30	0.15	98
9	$3-O_2NC_6H_4$	40	0.15	95
10	4-O ₂ N C ₆ H ₄	40	0.15	99
11	C ₆ H ₅ CH=CH	15	0.1	97
12	5-Me-2-Furyl	15	0.1	96
13	l-Naphthyl	20	0.1	99
14		15	0.15	8 0 (15°)
15		30	0.2	80 (5°)

^aAll products were identified by comparison of their physical and spectral data with those of authentic samples . ^bIsolated yield. ^cYield for deprotection of both acetoxyl and diacetate groups.

In conclusion, we have developed a simple and efficient method for the selective deprotection of aryl aldehyde diacetates. In addition, high yields of the products, short reaction times, ease of work-up and non-toxicity of the catalyst make this method a useful addition to the present methodologies.

EXPERIMENTAL

Deprotection of 1,1-Diacetates; General Procedure

To a solution of 1,1-diacetates (1 mmol) in chloroform (5 mL) was added bismuth(III) chloride (0.1-0.2 mmol) and the mixture was stirred under reflux condition for the time indicated in the Table. The reaction was followed by GLC. Water (10 mL) was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with chloroform (2x10 mL). The combined extracts were dried on MgSO₄ and evaporated. Purification of the crude material on a silica-gel plate (eluent: CCl_4/Et_2O : 4/1) afforded the pure product; yield 80-99% (Table).

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