μ-Oxo-bis(chlorotriphenylbismuth): a Mild Reagent for the Oxidation of the Hydroxy Group, Especially in Allylic Alcohols

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Summary μ-Oxo-bis(chlorotriphenylbismuth) is an effective reagent for the oxidation of the hydroxy group under exceptionally mild conditions; it is especially applicable to allylic alcohols.

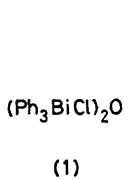
THE oxidizing capability inherent in the bismuth(V)—bismuth(III) change has been exploited only to a very limited extent in organic synthesis.[1,2] We conceived that triarylbismuth derivatives, such as μ-oxo-bis(chlorotriphenylbismuth) (**1**), would be expected to have the correct combination of solubility in organic solvents and oxidizing power. The reagent (**1**) is crystalline, easily prepared by the action of alkali on dichlorotriphenylbismuth,[3] and readily soluble in dichloromethane, chloroform, and benzene.

In a typical oxidation procedure, the alcohol (0·25 mmol) and the reagent (**1**) (0·20 mmol) in dichloromethane (2 ml) are stirred with an excess of K_2CO_3 or $NaHCO_3$ (200 mg) until reaction is complete. The product is readily separated from triphenylbismuth by chromatography on silica gel. Alternatively, all bismuth containing products may be solubilised by heating with acetic acid. Rigorously anhydrous conditions are unnecessary for the oxidation. Unlike manganese dioxide,[4] and silver carbonate–celite,[5] an excess of reagent is not required.

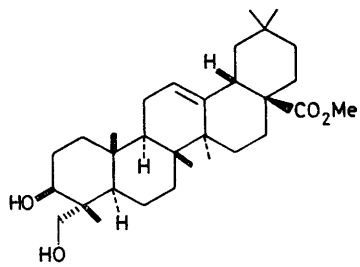
TABLE

Alcohol	Time/h	Temp./°C	Base	Product	Yield/%
Allylic					
Cinnamyl alcohol	15	21	K_2CO_3	Cinnamaldehyde	83[a]
Geraniol	15	21	K_2CO_3	Geranial	95[a]
Vitamin A alcohol	15	21	$NaHCO_3$	Vitamin A aldehyde	68[a]
Crotyl alcohol	5	60	$NaHCO_3$	Crotonaldehyde	76[a]
Cholest-1-en-3β-ol	6	21	K_2CO_3	Cholest-1-en-3-one	85
Cholest-4-en-3β-ol	6	21	K_2CO_3	Cholest-4-en-3-one	89
(−)-Carveol	6	21	K_2CO_3	Carvone	84[a]
3-Methyl-but-2-en-1-ol	2	60	$NaHCO_3$	3-Methylbut-2-enal	90[a]
Benzyl					
Benzyl alcohol	15	21	K_2CO_3	Benzaldehyde	82[a]
p-Nitrobenzyl alcohol	1	60	$NaHCO_3$	*p*-Nitrobenzaldehyde	87[a]
Anisyl alcohol	1	60	$NaHCO_3$	Anisaldehyde	75[a]
Primary					
1-Pentanol	6	60	$NaHCO_3$	Pentanal	79[a]
Secondary					
Cholestanol	30	21	K_2CO_3	Cholestanone	75
Tigogenin	4	60	$NaHCO_3$	Tigogenone	80
Testosterone	4	60	$NaHCO_3$	Androst-4-ene-3,17-dione	88
α-Amyrin	15	21	K_2CO_3	α-Amyrone	86
21-Acetoxy-9α-fluoro-11β,17α-dihydroxy-16β-methylpregna-1,4-diene-3,20-dione	15	60	$NaHCO_3$	21-Acetoxy-9α-fluoro-17α-hydroxy-16β-methylpregna-1,4-diene-3,11,20-trione	80
Cholestane-3β,6β-diol	15	21	K_2CO_3	Cholestan-3β-ol-6-one,	50
				Cholestan-3,6-dione	25
Methylhederagenin (**2**)	24	21	K_2CO_3	Methylhederagonate (**3**)	36
α-Glycol cleavage					
meso-Hydrobenzoin	3	21	K_2CO_3	Benzaldehyde	80[a]
Diacetone mannitol	0·25	60	$NaHCO_3$	Prop-2-ylideneglyceraldehyde	76

[a] Isolated as the 2,4-dinitrophenylhydrazone.



(1)



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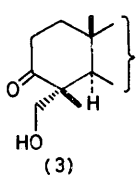

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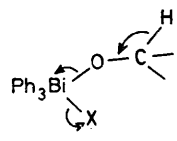

(4)

Examination of the data in the Table reveals that good yields of aldehydes and ketones can be obtained under very mild conditions of pH and temperature from a variety of hydroxy containing compounds. In particular, the reagent is especially effective for the oxidation of allylic alcohols. The oxidation of methyl hederagenin (**2**) to the ketone (**3**) represents a significant improvement over the published literature yield.[6] We have also observed that cleavage of 1,2-glycols is an easy process. From the mechanistic standpoint, the preferential oxidation of the more hindered 6β-hydroxy group in cholestane-3β,6β-diol would suggest that the normal rate determining step for the reaction is the breakdown of an intermediate of type (**4**).

We are currently examining the scope of the reagent (**1**) and of its congeners.[7]

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