A Catalytic Method for α-Glycol Cleavage

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Summary α-Glycols are smoothly cleaved by a catalytic amount of triphenylbismuth in the presence of potassium carbonate and a little water, using *N*-bromosuccinimide (or another N-bromo-reagent) for the oxidation of Bi^{III} to Bi^{V}.

THE efficient cleavage of α-glycols by a stoicheiometric amount of triphenylbismuth carbonate also gives a virtually quantitative recovery of triphenylbismuth. A catalytic cycle based on trivalent bismuth[1,2] should be possible. We now report the realisation of this concept by use of *N*-bromosuccinimide[3] (or *N*-bromoacetamide) as oxidant for triphenylbismuth. The presence of potassium carbonate and a small amount of water is essential.

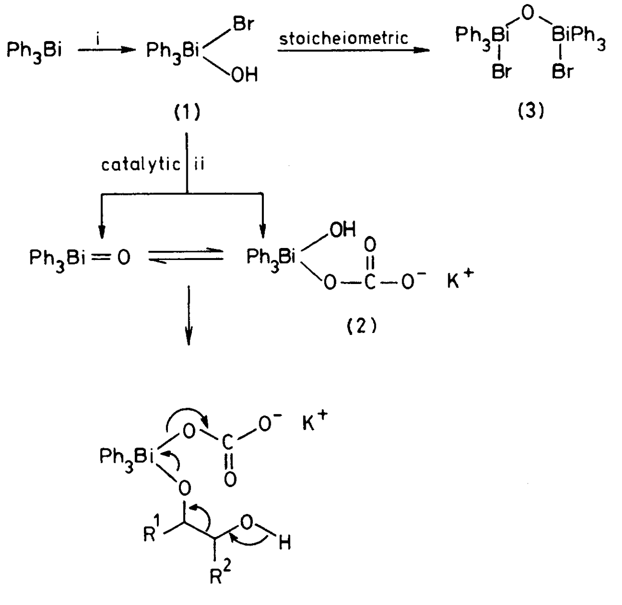
The results for a variety of vicinal diols (Table) indicate that preparatively useful yields of aldehydes and ketones can be obtained using only 1% of triphenylbismuth. Under our normal reaction conditions, no cleavage is observed in the absence of this catalyst. The reaction is rapid and yields are generally comparable with, or superior to, those obtained by use of lead tetra-acetate or sodium periodate. *N*-Bromoacetamide or bromine can also be used as oxidant, although the latter reagent proved to be less successful. Sodium bismuthate[4] is also known to cleave glycols under acidic conditions. It does not, however, function as an organobismuth catalyst in our system. In contrast with the use of lead tetra-acetate,[5] the addition of an organic base does not lead to a faster reaction rate. We have in fact observed that addition of diethylamine (1 mmol/mol of substrate) and, to an even greater extent, dimethylaniline (0·1 mmol) and triethylamine (0·01 mmol) prevent complete reaction. This may well be owing to competitive but

TABLE. α-Glycol cleavage catalysed by triphenylbismuth.

Diol	Triphenylbismuth (equiv.)	Time[a] (min)	Product	% Yield
$Me_2C(OH)C(OH)Me_2$	0·01	90	Me_2CO[b]	100
$Ph_2C(OH)C(OH)Ph_2$	0·01	190	Ph_2CO	84
meso-PhCH(OH)CH(OH)Ph	0·10	5	PhCHO	89
,,	0·05	10	,,	91
,,	0·01	20	,,	85
cis-Cyclopentane-1,2-diol	0·01	90	Pentane-1,5-dial	63
cis-Cyclohexane-1,2-diol	0·01	99	Hexane-1,6-dial	71
cis-Decalin-9,10-diol	0·10	120	Cyclodecane-1,6-dione	72
,,	0·01	360	,,	68
trans-Decalin-9,10-diol	0·10	165	Cyclodecane-1,6-dione	77
,,	0·01	360	,,	54
1,2:5,6-Di-*O*-isopropylidene-D-mannitol	0·1	30	$(\mathrm{D})\text{-OHC-}\overline{\mathrm{C(H)OC(Me_2)\ OCH_2}}$	72
,,	0·05	45	,,	70
,,	0·01	90	,,	65
,,	0·01	90	$(+)\text{-HOCH}_2\text{-}\overline{\mathrm{C(H)OC(Me)_2OCH_2}}$[c]	70
Dibenzyl L-tartrate	0·01	90	Benzyl glyoxylate	83

[a] The specified time denotes the time of addition of *N*-bromosuccinimide. Reactions were generally stirred for an additional period equal to one quarter of the addition time. [b] Isolated as the 2,4-dinitrophenylhydrazone derivative. [c] Isolated after reduction with sodium borohydride.

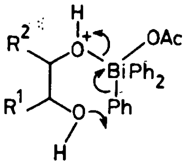
non-productive complexation of the organobismuth reagent and the amine, without oxidation.[2] 2,3-*O*-Isopropylidene-D-glyceraldehyde, a useful chiral synthon,[6] was obtained without racemisation $\{[\alpha]_D + 64{\cdot}8^\circ$ (c 1·28, C_6H_6), lit.[7] $[\alpha]_D + 68{\cdot}1^\circ$ (c 0·4, C_6H_6)$\}$. Glyoxylates, easily prepared from the corresponding tartrates, are important reagents for bicyclic β-lactam synthesis.[8]



SCHEME. *Reagents*, i, *N*-bromosuccinimide–H_2O, ii, K_2CO_3.

In a typical procedure, *N*-bromosuccinimide (4·4 mmol) in acetonitrile (40 ml) containing 1% of water was added dropwise over a period of 1·5 h to a well stirred mixture of 1,2:5,6-di-*O*-isopropylidenemannitol (4 mmol), triphenylbismuth (0·04 mmol), and potassium carbonate (6 g) in moist acetonitrile (40 ml) in the dark; stirring was continued for a further 0·5 h. The reaction mixture was filtered and the solvent removed *in vacuo* at room temperature. Distillation of the residue (oil bath temperature, 100 °C, 4 mmHg) into a trap cooled in an ice–salt bath gave 2,3-(isopropylidenedioxy)propanal. Alternatively, the crude reaction product may be purified either by addition of diethyl ether to precipitate succinimide or by column chromatography.

As recently described,[9] *N*-iodosuccinimide cleaves simple α-glycols in a light-catalysed reaction. We find however that this reagent gives a complex mixture on attempted cleavage of 1,2:5,6-di-*O*-isopropylidenemannitol. Moreover, reaction of PhCH(OH)CH(OH)Ph with *N*-bromosuccinimide (2 equiv.) in tetrahydrofuran or acetonitrile gives benzil (98%). This reaction is also catalysed by the light from a tungsten lamp.



(5)

A plausible mechanism (Scheme) involves initial formation of the bromohydrin (**1**) and subsequent attack of carbonate anion to give triphenylbismuth oxide or its carbonate equivalent (**2**) as the active organobismuth oxidant. Support for this proposal comes from the observation that treatment of triphenylbismuth with *N*-bromosuccinimide in acetonitrile containing water gives μ-oxobis(bromotriphenyl-bismuth) (**3**) in high yield (83%). We also find that *cis*-decalin-9,10-diol is cleaved at the same rate as the rigid *trans*-decalin-9,10-diol as compared with the selective rate of 100:1 which is found for lead tetra-acetate.[10] This would suggest that very efficient cleavage can occur without the necessity of formation of a cyclic intermediate.

David and Thiéffry[11] have recently made the interesting observation that α-glycols react with triphenylbismuth diacetate to give monoaryl ethers in good yield. Presumably, the initial intermediate (**5**) in this reaction can undergo either direct reductive elimination or, more likely, participation by the neighbouring hydroxy-group in the sense indicated. The difference between (**4**) and (**5**) lies either in the basicity of the medium or, more probably, in the effect of the fifth ligand (carbonate or hydroxy-group *vs.* acetate) on the breakdown of the bismuth(v) intermediate.[12] We have previously commented on the importance of the carbonate ligand in bismuth(v) chemistry.[2]

In view of the compatability of organobismuth oxidants with many other functional groups, and the practical simplicity of this inexpensive procedure, we feel that this method of α-glycol cleavage should find use in organic synthesis.

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