Organometallic Chemistry

Cleavage of the carbon—carbon bond in α-glycols under the action of bismuth(v) derivatives

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Di(*tert*-butylperoxy)triphenylbismuth and the triphenylbismuth—*tert*-butyl hydroperoxide system react with 2,3-dimethylbutane-2,3-diol, benzopinacol, butane-2,3-diol, and ethane-1,2-diol with the cleavage of the C—C bond of α-glycol to form carbonyl compounds. Both heterolytic (through formation of cyclic triphenylbismuth glycolate) and homolytic cleavage occur.

Key words: α-glycol, triphenylbismuth, *tert*-butyl hydroperoxide, oxidation, carbonyl compounds.

It is well known that bismuth(v) derivatives are efficient oxidants of organic compounds, in particular, of hydroxyl-containing derivatives. Thus, monohydric alcohols are readily oxidized by triphenylbismuth diacylates to give the corresponding carbonyl compounds in high yields.[1] Unlike monohydric alcohols, glycols undergo phenylation at one hydroxyl group under the action of triphenylbismuth diacetate.[2] It has been established that under more severe conditions, tertiary glycols are oxidized by triphenylbismuth diacetate with the cleavage of the C—C bond. Thus, a solution of pinacol in toluene or acetonitrile[3] at 80—100 °C gave acetone in a yield of up to 83%. Previously,[4,5] triphenylbismuth carbonate, triphenylbismuth dichloride, and the triphenylbismuth—bromosuccinimide system have been used as oxidants of α-glycols. In all cases, oxidation was carried out in the presence of potassium carbonate. According to one of the schemes suggested previously,[5] oxidation proceeds through formation of an intermediate cyclic derivative, namely, triphenylbismuth glycolate, whose decomposition is accompanied by reduction of triphenylbismuth and cleavage of the C—C bond of α-glycol to yield carbonyl compounds.

The aim of this work is to search for readily available and efficient oxidizing systems based on bismuth(v). We studied oxidation of α-glycols (2,3-dimethylbutane-2,3-diol (**1**), benzopinacol (**2**), butane-2,3-diol (**3**), and ethane-1,2-diol (**4**)) by the triphenylbismuth (**5**)—*tert*-butyl hydroperoxide (**6**) system. Oxidation of compound **1** by system **5**—**6** at molar ratios of the components in the range from 1 : 1 to 1 : 12 was studied in most detail (Table 1).

Among the reaction products, acetone is the only carbonyl compound. At all the ratios of the components of the oxidizing system used, the yield of acetone was high and amounted to 6.86 mole per mole of Ph_3Bi at the ratio of 1 : 8. The high concentration of compound **5** in the reaction mixture and the large amount of hydroperoxide **6** consumed in the reaction are indicative that the process is a cyclic one in the course of which com-

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Table 1. Products of the reaction of pinacol with the Ph_3Bi—Bu^tOOH system (moles per mole of Ph_3Bi)

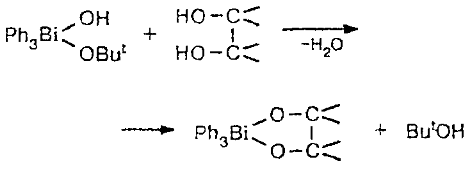
Product	Concentration of the products							
	1 : 1	1 : 2	1 : 3	1 : 4	1 : 5	1 : 6	1 : 8	1 : 12
Me_2CO	1.17	2.84	3.68	4.28	4.90	5.28	6.86	5.82
Bu^tOH	0.90	1.54	2.20	2.48	3.17	2.63	4.13	3.20
PhH	0.23	0.04	0.06	0.13	0.17	0.23	0.32	0.18
Ph_3Bi	0.67	0.85	0.80	0.78	0.67	0.59	0.44	0.38
Bu^tOOH	0.10	0.27	0.27	0.36	0.72	1.30	2.78	4.44
Bi-containing residue*	$\frac{0.12}{54.71}$	$\frac{0.23}{53.70}$	$\frac{0.33}{51.72}$	$\frac{0.38}{50.10}$	$\frac{0.40}{53.97}$	$\frac{0.11}{52.86}$	$\frac{0.18}{65.95}$	$\frac{0.07}{73.15}$

*B (g/g_{Ph_3Bi})/(% Bi).

pound **5** is continuously regenerated. Based on the results obtained, we suggested the following scheme of oxidation of α-glycols **1**—**4** by system **5**—**6**. As was demonstrated previously,[6] at the first stage compound **5** is oxidized by hydroperoxide **6** to a bismuth(V) derivative:

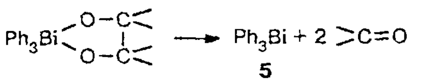
$$\underset{\mathbf{5}}{Ph_3Bi} + \underset{\mathbf{6}}{Bu^tOOH} \longrightarrow Ph_3Bi(OH)(OBu^t) \qquad (1)$$

The adduct obtained reacts with α-glycols to form unstable triphenylbismuth glycolate:



(2)

Triphenylbismuth glycolate decomposes to the carbonyl derivative (2 mol), accompanied by regeneration of **5**:



(3)

Based on the scheme suggested, the low yield (1.24 mol) of benzophenone compared to other α-glycols (Table 2) obtained in reaction (2) with the use of system **5**—**6** is attributable to steric hindrances, which prevent the formation of cyclic glycolate. This scheme also agrees well with the published data.[5]

In addition to the reaction with α-glycols, the hydroxy-*tert*-butoxy derivative obtained (Eq. (1)) can react with hydroperoxide **6** to form di(*tert*-butylperoxy)triphenylbismuth **7**:[6]

$$Ph_3Bi(OH)(OBu^t) + 2\ Bu^tOOH \longrightarrow$$

$$\longrightarrow \underset{\mathbf{7}}{Ph_3Bi(OOBu^t)_2} + Bu^tOH + H_2O \qquad (4)$$

It is known that product **7** is an efficient oxidant of various organic compounds, including hydrocarbons.[7,8]

Table 2. Products of the reactions of α-glycols with $Ph_3Bi(OOBu^t)_2$ and with the Ph_3Bi—Bu^tOOH systems (moles per mole of the organobismuth derivative)

Product	Concentration of the products						
	$Ph_3Bi(OOBu^t)_2$			Ph_3Bi—Bu^tOOH (1 : 3)			
	1	**2**	**3**	**1**	**2**	**3**	**4**
>C=O	3.51	1.87	2.67	3.68	1.24	2.14	3.28
PhH	0.23	0.51	0.13	0.94	0.06	0.37	0.13
Bu^tOH	1.71	1.51	0.98	2.75	2.20	1.80	2.64
Ph_3Bi	0.67	0.31	0.63	0.80	0.50	0.69	0.62
Bu^tOOH	0.01	0.09	0.86	0.27	0.04	0.82	0.11
Bi-containing residue*	$\frac{0.12}{54.71}$	$\frac{0.41}{54.70}$	$\frac{0.15}{70.36}$	$\frac{0.31}{57.44}$	$\frac{0.33}{61.72}$	$\frac{0.34}{60.77}$	$\frac{0.16}{64.65}$

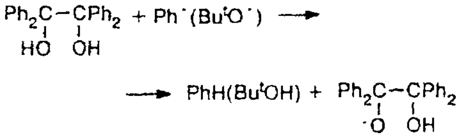
Note: **1** is 2,3-dimethylbutane-2,3-diol; **2** is benzopinacol; **3** is butane-2,3-diol; and **4** is ethane-1,2-diol.

* B (g/g_{Ph_3Bi})/(% Bi).

Therefore, it can be assumed that in addition to conversion of α-glycols according to reactions (2) and (3), their oxidation by peroxide **7** can also occur.

We studied oxidation of glycols **1**—**3** by diperoxide **7** (see Table 2). As can be seen from Table 2, in this case α-glycols were also oxidized with cleavage of the C—C bond to form carbonyl compounds in rather high yields. A comparison of the compositions of the mixtures obtained by oxidation of α-glycols **1** and **2** by system **5**—**6** and by diperoxide **7** demonstrated that in the case of the reactions with diperoxide, the yield of benzene was higher for compound **2** and the concentration of Ph_3Bi was lower for the both compounds. These reactions also produced *tert*-butyl alcohol in high yields. These results suggest that oxidation of glycols by diperoxide **7** is a radical reaction.

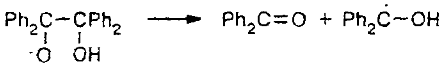
It is known that $Ph_3Bi(OOBu^t)_2$ undergoes homolysis at the Ph—Bi and O—O bonds even at room temperature.[9] The phenyl and *tert*-butoxyl radicals thus generated react with α-glycols, for example, with tertiary glycol:



$$\underset{HO\ \ \ OH}{Ph_2C{-}CPh_2} + Ph^{\cdot}(Bu^tO^{\cdot}) \longrightarrow$$

$$\longrightarrow PhH(Bu^tOH) + \underset{{}^{\cdot}O\ \ \ OH}{Ph_2C{-}CPh_2} \qquad (5)$$

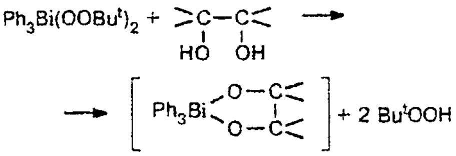
The oxygen-centered radical formed decomposes into benzophenone and a new carbon-centered radical:



$$\underset{{}^{\cdot}O\ \ \ OH}{Ph_2C{-}CPh_2} \longrightarrow Ph_2C{=}O + Ph_2\dot{C}{-}OH \qquad (6)$$

The reaction of the carbon-centered radical with initial peroxide **7** results in induced decomposition of **7** and conversion of the radical to the carbonyl derivative.

When peroxide **7** reacts with α-glycols that possess a more reactive H atom than monohydric alcohols, peroxide 7 can enter into the replacement of the *tert*-butylperoxy group to form cyclic glycolate (A):


A

(7)

Triphenylbismuth glycolate decomposes to form Ph_3Bi and a carbonyl compound (see Eq. (3)).

This conversion was observed in the reaction with 2,3-butanediol, which contains the most reactive H atom as evidenced by the high concentration of Bu^tOOH (up to 0.86 mol) in the reaction products (see Table 2).

Therefore, it was established that α-glycols are oxidized by the $Ph_3Bi—Bu^tOOH$ system as well as by peroxide $Ph_3Bi(OOBu^t)_2$ with cleavage of the C—C bond to form carbonyl compounds. When the $Ph_3Bi—Bu^tOOH$ system is used as the oxidizing agent, the reaction proceeds predominantly through formation of cyclic triphenylbismuth glycolate. Subsequent decomposition of the latter affords carbonyl derivatives, and Ph_3Bi is regenerated. The side reaction involves formation of unstable peroxide $Ph_3Bi(OOBu^t)_2$ as the intermediate. Oxidation of α-glycols by the above-mentioned peroxide can occur both through homolytic and heterolytic pathways.

Experimental

All reactions were carried out in solutions of toluene at 10—15 °C over a period of 30—40 h. Chromatographic analysis was carried out on a Tsvet-205 instrument with a flame ionization detector. A 3×1200-mm column was used. 15% Reoplex-400 on Chromaton N-AW-DMCS was used as the stationary phase. The temperature was 80—170 °C; helium was used as the carrier gas.

Reactions of 2,3-dimethylbutane-2,3-diol, butane-2,3-diol, and ethane-1,2-diol with the $Ph_3Bi—Bu^tOOH$ system. A mixture of Ph_3Bi (2.5 mmol) and Bu^tOOH (7.5 mmol) was added to a solution of one of the above-mention α-glycols (10 mmol) with cooling with ice water. After completion of the reaction, the solvent was recondensed in a receiver cooled with liquid nitrogen. The condensate was analyzed iodometrically (Bu^tOOH) and by GLC (benzene, Bu^tOH, and carbonyl compounds). In addition, carbonyl compounds were identified as 2,4-dinitrophenylhydrazones. In all cases, the derivatives obtained had melting points close to the published data. Samples mixed with certain hydrazones obtained gave no depression.

After the removal of the solvent and volatile products, the nonvolatile residue was carefully washed with ether. Ph_3Bi was quantitatively determined in the filtrate. A product (m.p. 77 °C) was obtained. A sample mixed with pure Ph_3Bi melted without depression of the melting point. The ether-insoluble solid residue was an amorphous brown powder that did not melt when heated to 250 °C and was insoluble in commonly used organic solvents (benzene, ether, acetone, carbon tetrachloride, *etc.*). The bismuth content of the product was no more than 50%.

Products of the reaction of 2,3-dimethylbutane-2,3-diol with the $Ph_3Bi—Bu^tOOH$ system (the ratio of the components was varied from 1 : 1 to 1 : 12) were analyzed analogously.

Reactions of 2,3-dimethylbutane-2,3-diol and butane-2,3-diol with $Ph_3Bi(OOBu^t)_2$. A solution of α-glycol (8 mmol) was added with cooling to a solution of diperoxide[9] (5 mmol) in toluene. The reaction mixture was kept for 30 h. Products were isolated and identified analogously to the procedure described above.

Reaction of benzopinacol with the $Ph_3Bi—Bu^tOOH$ system. Ph_3Bi (2.5 mmol), Bu^tOOH (7.5 mmol), and benzopinacol (3.0 mmol) were mixed. After completion of the reaction, the liquid products were recondensed under reduced pressure. The condensate was analyzed for Bu^tOOH, Bu^tOH, and C_6H_6. The nonvolatile residue was distilled with water vapor. The condensate was extracted with CCl_4, and benzophenone was found in the solution. The solid residue was washed with ether. Ph_3Bi was found in the ethereal solution. The ether-insoluble infusible amorphous brown powder contained up to 55% bismuth.

Analysis of the product of the reaction of benzopinacol with $Ph_3Bi(OOBu^t)_2$ was carried out analogously.

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