Di(*tert*-butylperoxy)triphenylbismuth and the triphenylbismuth—*tert*-butyl hydroperoxide system as efficient oxidants of alcohols

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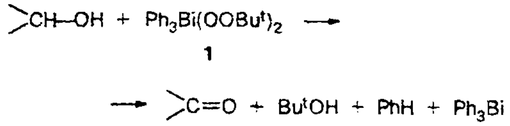
Di(*tert*-butylperoxy)triphenylbismuth and the triphenylbismuth—*tert*-butyl hydroperoxide system react with aliphatic alcohols and cyclohexanol to give carbonyl compounds in high yields. The oxidation occurs as the radical dehydrogenation of alcohols; Bi derivatives serve as the sources of free radicals.

Key words: alcohols, aldehydes, ketones, di(*tert*-butylperoxy)triphenylbismuth, *tert*-butyl hydroperoxide, triphenylbismuth, oxidation, radical dehydrogenation.

The oxidative ability of organic derivatives of bismuth(v) is well known. Thus Bi^V acyl derivatives efficiently oxidize alcohols to carbonyl compounds, and Bi^V is simultaneously reduced to Bi^{III}.[1,2] In this work, we study the oxidative properties of di(*tert*-butylperoxy)triphenylbismuth (**1**) and a system consisting of triphenylbismuth (**2**) and *tert*-butyl hydroperoxide (**3**) in a molar ratio of 1 : 3 with respect to alcohols. In a previous study, it was found[3] that the interaction of compounds **2** and **3** taken in this molar ratio yields diperoxide **1**.

As has been shown previously,[4,5] peroxide **1** and the **2**—**3** system efficiently oxidize aliphatic and aromatic hydrocarbons at 10—15 °C. Under these mild conditions, hydrocarbons are oxidized to carbonyl compounds by the oxygen generated upon homolytic cleavage of peroxide **1**, which is coordinated to the bismuth atom. Primary and secondary aliphatic and alicyclic alcohols were the objects of the present study.

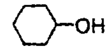
These alcohols were subjected to oxidation by $Ph_3Bi(OOBu^t)_2$ at 10—15 °C (Table 1). It was found that only in some cases did the reaction products contain small amounts of hydroperoxide **3**; this indicates that the probability of the alcoholysis of the initial peroxide is low. Aldehydes were obtained as volatile reaction products in the reactions with primary alcohols, while ketones, together with *tert*-butyl alcohol and benzene, were formed in the case of secondary alcohols. The isolated yields of these products were about 2 moles per 1 mole of peroxide **1**.



$$\rangle CH{-}OH + \underset{\mathbf{1}}{Ph_3Bi(OOBu^t)_2} \longrightarrow \rangle C{=}O + Bu^tOH + PhH + Ph_3Bi$$

It is noteworthy that the reactions of primary alcohols gave no carboxylic acids or their derivatives resulting from more extensive oxidation of the aldehydes formed, although acids are formed in the reactions with other heteroorganic peroxides.[6,7] The solid residue obtained in the reactions consisted of compound **2** and another compound with a high content of bismuth (up to 60%), which

Table 1. Products of the reactions of $Ph_3Bi(OOBu^t)_2$ (**1**) with alcohols (10—15 °C, 30 h)

Alcohol	Products (moles per mole of **1**)					Bi-containing residue	
	Bu^tOH	PhH	>C=O	Bu^tOOH	Ph_3Bi	g per g of **1**	Bi (%)
Pr^iOH	1.83	1.83	1.78	0.07	0.05	0.50	59.09
Bu^nOH	1.94	1.90	2.08	0.07	0.15	0.44	62.67
Bu^iOH	1.61	1.58	1.72	0.11	0.14	0.50	57.90
Bu^sOH	1.88	1.93	1.88	—	0.05	0.46	62.94
	1.57	1.72	1.59	0.04	0.13	0.34	74.22
$PhCH_2OH$	2.00	2.32	1.84	—	0.07	0.36	77.10

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was insoluble in ordinary organic solvents (diethyl ether, benzene, hexane, acetone, chloroform, *etc.*) and did not melt on heating to 250 °C. Among the products of thermolysis of this compound (175—200 °C, 8—10 h), benzene, acetone, *tert*-butyl alcohol, and isobutylene were detected.

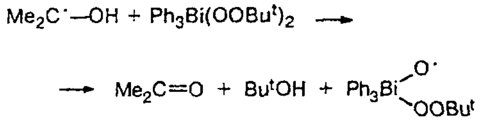
In our opinion, the reaction products are produced in the following way. The Ph—Bi and O—O bonds in peroxide **1** are known to readily undergo homolytic cleavage yielding phenyl and *tert*-butoxyl radicals,[8] for example

$$\underset{\mathbf{1}}{Ph_3Bi(OOBu^t)_2} \longrightarrow Ph^{\cdot} + Bu^tO^{\cdot} + [Ph_2Bi(O)OOBu^t].$$

The resulting radicals abstract a hydrogen atom from a molecule of an alcohol, for example, isopropyl alcohol, to give benzene or *tert*-butyl alcohol and an α-hydroxyalkyl radical.

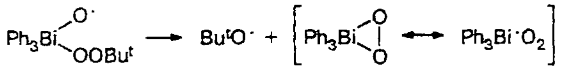
$$Me_2CH{-}OH + Ph^{\cdot}\ (Bu^tO^{\cdot}) \longrightarrow$$
$$\longrightarrow PhH\ (Bu^tOH) + Me_2C^{\cdot}{-}OH \qquad (1)$$

The latter attacks a molecule of the starting peroxide and thus induces its decomposition; this affords a carbonyl compound and a new bismuth-containing peroxide radical.



$$Me_2C^{\cdot}{-}OH + Ph_3Bi(OOBu^t)_2 \longrightarrow Me_2C{=}O + Bu^tOH + Ph_3Bi(O^{\cdot})(OOBu^t)$$

The latter can directly participate in the oxidation of the alcohol serving as the source of both free radicals and oxygen, coordinated at the bismuth atom.



These oxygen atoms easily oxidize a methylene group in hydrocarbons;[4,5] in our experiments with alcohols, they attack the same C—H bond in an alcohol molecule as do free radicals (see Eq. (1)).

The oxidative ability of the system consisting of compounds **2** and **3** was studied in the reactions with isobutyl alcohol (**4**), isopropyl alcohol (**5**), cyclohexanol, and 1,2-diphenylethanol (**6**) at 10—15 °C (Table 2).

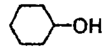
Since compound **2** is poorly soluble in alcohols, these reactions were carried out in toluene or CCl_4; the reactants **2**, **3**, and ROH were taken in a molar ratio of 1 : 3 : 1. The products of the oxidation of alcohols **4**—**6**, namely, isobutyraldehyde, acetone, and benzyl phenyl ketone, respectively, were isolated in yields of 0.30—0.35 moles per mole of compound **2**. The yields of other products were similar to those obtained in the reactions of these alcohols with peroxide **1**. An exception is benzene, whose yield was much lower (0.50—0.70 moles per mole of compound **2**). The reaction in a CCl_4 solution was accompanied by the formation of chlorobenzene (0.25 mol), which confirms a radical mechanism of the process.

It is noteworthy that in the case of 1,2-diphenylethanol, whose methylene group is converted relatively easily into an oxo group on treatment with the **2**—**3** system,[5] oxidation afforded only benzyl phenyl ketone. However, more extensive oxidation is also possible. Indeed, benzil (0.04 mole per mole of compound **2**) was detected among the reaction products by TLC and GLC.

When the reaction of the **2**—**3** system was carried out in a mixture of toluene and an alcohol (**4**, **5**, or cyclohexanol) taken in a ratio of 1 : 1 (v/v), an increase in the concentration of the alcohol in the reaction mixture resulted, as should be expected, in a substantial increase in the yield of the oxidation products (see Table 2).

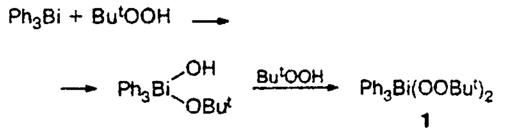
The oxidation of alcohols by the **2**—**3** system, like the oxidation by peroxide **1**, occurs apparently *via* their radical dehydrogenation. Bismuth diperoxy derivative **1**

Table 2. Products of the reactions of alcohols with the Ph_3Bi (**2**)—Bu^tOOH (**3**) system (1 : 3) in various solvents (10—15 °C, 40 h)

Alcohol	Products (moles per mole of 2)					Bi-containing residue	
	Bu^tOH	PhH	>C=O	Bu^tOOH	Ph_3Bi	g per g of 2	Bi (%)
				Toluene			
Pr^iOH	2.18	0.52	0.30	0.06	0.21	0.65	52.04
Bu^iOH	1.50	0.70	0.34	0.60	0.40	0.37	69.99
				CCl_4*			
$PhCH(OH)CH_2Ph$	2.81	0.75	0.31	0.13	0.11	0.65	67.13
			A mixture of equal volumes of toluene and alcohol				
Pr^iOH	2.21	0.75	1.00	0.13	0.08	0.60	56.73
Bu^iOH	2.32	0.64	1.23	0.60	0.33	0.54	63.49
	2.27	1.37	1.35	0.60	0.18	0.52	73.44

* Chlorobenzene (0.25 moles per mole of **2**) is also formed.

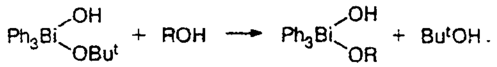
arising at the first stage of the reaction serves as the source of free radicals[3].



$$Ph_3Bi + Bu^tOOH \longrightarrow Ph_3Bi\begin{smallmatrix}OH\\ OBu^t\end{smallmatrix} \xrightarrow{Bu^tOOH} Ph_3Bi(OOBu^t)_2$$

1

However, in a solution containing an excess of an alcohol, the hydroxy(*tert*-butoxy)phenylbismuth formed initially can react not only with hydroperoxide **3**, but also with the alcohol, and thus gives a new alkoxy derivative.



$$Ph_3Bi\begin{smallmatrix}OH\\ OBu^t\end{smallmatrix} + ROH \longrightarrow Ph_3Bi\begin{smallmatrix}OH\\ OR\end{smallmatrix} + Bu^tOH. \qquad (2)$$

It cannot be ruled out that the alkoxide participates in the formation of the carbonyl compound, as has been found previously.[2] The presence of hydroperoxide **3** in the reaction mixture (up to 35% of its initial amount in the case of alcohol **4**) indicates that it is not completely converted due to the competing reaction of $Ph_3Bi(OH)OBu^t$ with ROH (Eq. (2)).

These results provided grounds for believing that an increase in the reaction time would increase the yield of peroxide **1** and, hence, the yield of the carbonyl compound. In fact, the series of reactions carried out for the **2**—**3** system dissolved in isobutyl alcohol showed that the content of **2** in the reaction mixture considerably decreases as the reaction time increases, whereas the yields of aldehyde, benzene, and *tert*-butyl alcohol increase (Table 3); in this case, the yields of the two former compounds approach those attained in the reaction with peroxide **1**.

Thus, it was found that primary and secondary alcohols are oxidized by peroxide **1** or the **2**—**3** system to carbonyl compounds. This transformation of alcohols occurs most likely by their radical dehydrogenation. Aldehydes and ketones are formed in high yields and, what appears fairly important, these oxidants do not cause any further transformations of the resulting aldehydes.

Experimental

Triphenylbismuth (m.p. 77—78 °C) was prepared by the reaction of phenylmagnesium bromide with bismuth trichloride,[9] di(*tert*-butylperoxy)triphenylbismuth (**1**) was synthesized by a procedure described previously,[10] and 1,2-diphenylethanol (m.p. 66 °C) was obtained by the reaction of benzylmagnesium chloride with benzaldehyde.[11] The *tert*-butyl hydroperoxide (**3**) used in the experiments was 98.00—98.50% pure. Chromatographic analysis was performed on a Tsvet-205 instrument with a flame ionization detector, a 3 m×3 mm column, and 15% Reoplex-400 on Chromaton-N-AW-DMCS as the stationary phase; the temperature varied from 70 to 180 °C; helium was used as the carrier gas.

The reaction of alcohols with $Ph_3Bi(OOBu^t)_2$ (1) (see Table 1). Compound **1** (2.50 mmol) was dissolved in 10—15 mL of an alcohol cooled by ice water. The mixture was kept at 10—15 °C for 30 h. Then the volatile products and the solvent were recondensed under reduced pressure into a trap cooled with liquid nitrogen. The condensate was analyzed for *tert*-butyl hydroperoxide by iodometry. The quantities of *tert*-butyl alcohol, benzene, and the corresponding carbonyl compounds in the condensate were found by GLC. The carbonyl compounds were also converted into the corresponding 2,4-dinitrophenylhydrazones; their melting points were close to the published values, and the melting points of their mixtures with authentic samples were undepressed.

The nonvolatile residue obtained after removal of the solvent and the volatile products was washed with diethyl ether. The ethereal extract was analyzed for the content of triphenylbismuth. The solid residue insoluble in ether was a light-brown amorphous powder. It did not melt on heating to 250 °C, and was insoluble in benzene, chloroform, acetone, tertrahydrofuran, or *n*-hexane; the contents of bismuth in the residues obtained in reactions with different alcohols varied from 57 to 77%.

The reaction of isopropyl (5) and isobutyl (4) alcohols with the Ph_3Bi (2)—Bu^tOOH (3) system (see Table 2). A mixture of compounds **2** (2.50 mmol), **3** (7.50 mmol), and an alcohol (2.50 mmol) was dissolved in 15 mL of toluene, and the mixture was kept for 40 h at 10—15 °C. When the reaction was completed, the volatile products and the solvent were removed under reduced pressure. The subsequent analyses of the liquid fraction and the nonvolatile residue were carried out as described for the reactions of alcohols with peroxide **1**.

The products that formed in the reactions of the **2**—**3** system with alcohols **4** and **5** taken in excess amounts (10 mL) at an ROH : toluene ratio equal to 1 : 1 were analyzed in a similar way.

Table 3. Products of the transformation of the Ph_3Bi (**2**)—Bu^tOOH (**3**) system in isobutyl alcohol (10—15 °C)

Time	Products (moles per mole of **2**)					Bi-containing residue	
/h	Bu^tOH	PhH	>C=O	Bu^tOOH	Ph_3Bi	g per g of **2**	Bi (%)
				2 : **3** = 1 : 2			
60	1.89	1.15	1.00	0.22	0.45	0.37	65.74
				2 : **3** = 1 : 3			
20	1.51	0.21	0.44	1.00	0.40	0.35	67.87
40	1.80	0.89	0.94	0.83	0.43	0.42	65.93
60	1.94	1.80	1.52	0.96	0.32	0.45	64.62
160	2.43	1.73	1.61	0.48	0.25	0.45	71.48

The reactions of cyclohexanol and 1,2-diphenylethanol with the Ph_3Bi (2)—Bu^tOOH (3) system (see Table 2). The reactions of compounds 2 (2.50 mmol) and 3 (7.50 mmol) with alcohols (2.50 mmol) were carried out in toluene or in tetrachloromethane at 10—15 °C. After 40 h, the solvent and the volatile products were recondensed into a trap cooled with liquid nitrogen. The content of Bu^tOOH in the condensate was determined by iodometry, and those of *tert*-butyl alcohol, benzene, and chlorobenzene (for reactions in CCl_4), by GLC. The nonvolatile residue was washed with CCl_4, and the extract was analyzed by chromatography for the content of cyclohexanone or benzyl phenyl ketone for reactions with cyclohexanol or 1,2-diphenylethanol, respectively. In the same extract, the content of Ph_3Bi was determined. The residue insoluble in CCl_4 was a sand-colored amorphous powder, which did not melt upon heating to 250—260 °C, was insoluble in ordinary organic solvents, and contained up to 70% bismuth.

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