# Radical low-temperature oxidation of dibenzyl sulfide with the triphenylbismuth—*tert*-butyl hydroperoxide system

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The reaction of  $Ph_3Bi$  with Bu<sup>4</sup>OOH in a mole ratio of 1 : 3 in hydrocarbon solvents affords the  $\eta^2$ -peroxo complex of triphenylbismuth  $Ph_3Bi(\eta^2O_2)$  which oxidizes the C—H bonds of the methylene group of dibenzyl sulfide. The reaction proceeds *via* the radical mechanism with the formation of intermediate unstable sulfur-containing hydroperoxide. Its decomposition is accompanied by the C—S bond cleavage, resulting in benzaldehyde.

**Key words:** dibenzyl sulfide,  $\eta^2$ -peroxo complexes, triphenylbismuth, *tert*-butyl hydroperoxide, oxidation, radical mechanism, benzaldehyde, organobismuth compounds.

Oxygen activation on metallic centers of transition and nontransition metals in low-temperature (20 °C) oxidation is one of the most important problems of organic catalysts. Metal-containing compounds of the ozonide type  $(Bu^{t}O)_{n-1}MOOOBu^{t}$  (n = 3,  $M = Al;^{1,2}$ n = 4,  $M = Ti^{2,3}$ ) and the bismuth  $\eta^{2}$ -peroxo complex Ph<sub>3</sub>Bi( $\eta^{2}$ -O<sub>2</sub>) (1)<sup>4,5</sup> serve as the sources of electron-excited dioxygen. Ozonides are formed upon the reaction of the corresponding metal *tert*-butoxides with *tert*-butyl hydroperoxide 2 in a mole ratio of 1 : 2, whereas  $\eta^{2}$ -peroxo complex 1 is formed due to the thermal decomposition of di(*tert*-butylperoxy)triphenylbismuth 3 at room temperature. Compound 3 is a product of the reaction of triphenylbismuth (4) with hydroperoxide 2 in a mole ratio of 1 :  $3^{4,5}$  (Scheme 1).

Scheme 1

3 Bu<sup>t</sup>OOH + Ph<sub>3</sub>Bi 
$$\longrightarrow$$
  
2 4  
 $\longrightarrow$  Ph<sub>3</sub>Bi(OOBu<sup>t</sup>)<sub>2</sub> + Bu<sup>t</sup>OH + H<sub>2</sub>O  
3  
3  $\xrightarrow{\Delta, 20 \circ C}$  Ph<sub>3</sub>Bi $\subset_{O}^{O}$  + 2 Bu<sup>t</sup>O<sup>\*</sup>  
1

 $\eta^2$ -Peroxo complex 1 selectively oxidizes the methylene groups of alkanes to form carbonyl groups *via* the radical mechanism<sup>4,5</sup> (Scheme 2).

#### Scheme 2

$$>C \stackrel{H}{\xrightarrow{}} \frac{1}{-Ph_{3}Bi} \left[ \stackrel{\cdot}{>} C - H + OH \right] \xrightarrow{} C = O$$

Peroxo complex 1 and the ozonides mentioned above are efficient low-temperature oxidants of C-H bonds<sup>4</sup> featuring by the reaction conditions and, especially, by the final products. Dioxygen coordinated on the metal atom acts as a direct oxidant.

The purpose of the present work is to obtain comparative data on the reactivity of the peroxide derivatives of bismuth and aluminum in the low-temperature (20 °C) oxidation of the C—H bonds in the benzyl group using dibenzyl sulfide and ethylbenzene as examples. The choice of Bn<sub>2</sub>S is due to the fact that, on the one hand, no oxidation products of the benzylic C—H bonds were observed upon its interaction with ozonides  $(Bu^{t}O)_{n-1}MOOOBu^{t}$  (n = 3, M = Al; n = 4, M = Ti).<sup>6</sup> On the other hand, it is known<sup>7</sup> that the oxidation of this sulfide with oxygen, under the conditions of radio frequency discharge or irradiation with a Xe—Hg lamp sensibilized by zinc tetraphenylporphine, results in its destruction at the C—S bond to benzaldehyde.

## Experimental

Solvents (analytical and reagent grade) were purified as follows: benzene and ethylbenzene were distilled over  $P_2O_5$  (stored above metallic sodium) and chlorobenzene was distilled and stored over  $Na_2SO_4$ . Dibenzyl sulfide (pure grade) was recrystallized from

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ethanol. Triphenylbismuth (4) was synthesized according to a known procedure.<sup>8</sup> The synthesis and properties of aluminum tri*tert*-butoxide were described previously.<sup>2</sup> *tert*-Butyl hydroperoxide (2) was synthesized by a known procedure,<sup>9</sup> providing Bu<sup>t</sup>OOH with an active oxygen content of 99.5–99.8%.

*tert*-Butyl alcohol was identified on an LKhM-80 chromatograph at 80 °C on a 3000 mm column packed with dinonyl phthalate (30%) on Chromaton N-AW-DMCS. Benzaldehyde and acetophenone were analyzed at 110–120 °C on a 2400 mm column with 10% Reoplex-400 on Inerton AW-DMCS. Biphenyl and benzyl benzoate were identified at 240 °C on a 2000 mm column packed with 5% SE-30 on Inerton AW. Helium served as the carrier gas.

The determination of  $Bn_2S$  and  $Ph_3Bi$  (4) was carried out on a Knower liquid chromatograph equipped with a UV spectrophotometer using a 150 mm column packed with Serapon SGX C18. The calculation was performed by the internal normalization method.

Carbonyl compounds were transformed into their 2,4-dinitrophenylhydrazones, which were identified by TLC using Silpearl on the aluminum foil (Silufol UV-254) as the sorbent and benzene as the eluent.

The ESR spectrum was recorded on a Bruker ER200D-SRC spectrometer equipped with an ER 4105 DR double resonator and an ER 4111 VT thermocontrolling unit. Diphenylpicrylhydrazyl was used as the standard in the determination of the g factor.

The mass spectrum was obtained on a Hewlett—Packard mass spectrometer combined with an HP-5890 gas chromatograph, an HP-5972 mass-selective detector, and a working station equipped with a software and the NIST98.L and WILEY 138.L mass-spectral databases Ultra-2 (25 000 mm column of the HP-5MS type, injector temperature 280 °C).

Reaction of  $Bn_2S$  with the  $Ph_3Bi$  (4)— $Bu^4OOH$  (2) system. Hydroperoxide 2 (6.4 mmol) and  $Bn_2S$  (2.1 mmol) were added to a solution of compound 4 (2.1 mmol) in benzene (14 mL). The reaction mixture was kept for 1 day at ~20 °C, after which the solvent and volatile reaction products were condensed into a trap cooled with liquid nitrogen. The volatile fraction contained  $Bu^4OH$ (5.2 mmol) and PhCHO (0.5 mmol). The solid residue in the flask was washed with THF, and the solution was decanted. The GLC method showed PhCHO (0.5 mmol),  $Ph_2$  (0.1 mmol), and benzyl benzoate (0.1 mmol). Unreacted  $Bn_2S$  (0.8 mmol) and compound 4 (0.6 mmol) were identified by liquid chromatography.

## **Results and Discussion**

The oxidation of  $Bn_2S$  was carried out by the systems **4**–2 and aluminum tri-*tert*-butoxide (5)–2 in ethylbenzene and "unoxidizable" solvents (benzene and chlorobenzene) at room temperature and the ratio of components chosen earlier by the study of the oxidation of the C–H bonds of hydrocarbons:  $1: 3^{4,5}$  and  $1: 2, ^{1,2,4}$ respectively.

The reaction of  $Bn_2S$  with the **4**-2 system in benzene affords benzaldehyde and benzyl benzoate in 51 and 5% yields, respectively. A similar reaction in ethylbenzene afforded benzaldehyde (31%) and acetophenone (oxidation product of the solvent, 14%). The reaction of  $Bn_2S$ with the **5**-2 system in benzene and ethylbenzene gave sulfone  $Bn_2SO_2$  in 99% yield, and the reaction was accompanied by self-heating of the reaction mixture and completed within 1 h.

Taking into account the earlier data<sup>1,4</sup> on the oxidation of the C—H bonds of hydrocarbons by the **4**—2 and **5**—2 systems *via* the radical mechanism, we assume that the primary act of Bn<sub>2</sub>S oxidation is the abstraction of the hydrogen atom from the methylene group of the substrate (Scheme 3).

## Scheme 3

$$PhCH_{2}SCH_{2}Ph \xrightarrow{1}_{-Ph_{3}Bi} \left[Ph\dot{C}HSCH_{2}Ph + \dot{OOH}\right] \longrightarrow 6$$

$$\longrightarrow \left[PhCHSCH_{2}Ph \\ OOH \right]$$
7

The ESR method using 2-methyl-2-nitrosopropane (MNP) as a spin trap was used to identify assumed radical **6**. The analysis was carried out in chlorobenzene in the temperature interval from +25 to  $-60 \,^{\circ}$ C. The signals (Fig. 1) of the spin-adduct of MNP with the phenyl radical  $\stackrel{\text{PhNBut}}{\overset{}{}_{\text{O}}}$  ( $a_{\text{N}} = 1.23 \,\text{mT}$ ,  $a_{2\text{H}}^{\text{M}} = 0.09 \,\text{mT}$ ,  $a_{3\text{H}}^{\text{O},\text{P}} = 0.21 \,\text{mT}$ , g = 2.0060, <sup>10</sup> ( $a_{\text{N}} = 1.54 \,\text{mT}$ )<sup>2</sup>) formed by the reaction of compound **3** and di(*tert*-butyl)nitroxyl radical  $\stackrel{\overset{}{\overset{}{}_{\text{O}}}{\overset{}{}_{\text{O}}}$ , which is the product of MNP self-reduction under irradiation ( $a_{\text{N}} = 1.54 \,\text{mT}$ ),<sup>2</sup> were identified at  $-13 \,^{\circ}$ C. The intermediate formation of the phenyl radical is also indicated by the presence of biphenyl (5–11%; reaction in benzene) or chlorobiphenyl (qualitatively identified by GLC, reaction in chlorobenzene) in



**Fig. 1.** ESR spectrum recorded in the  $Bn_2S$ — $Ph_3Bi$ — $Bu^tOOH$  (1:1:3) system in the presence of 2-methyl-2-nitrosopropane in chlorobenzene at -13 °C (the sample was degassed).

the reaction mixture. No radical **6** was found. Perhaps, the radical pair that formed interacts in the solvent cage with a higher rate than radical **6** interacts with the spin trap.

Sulfur-containing hydroperoxide 7 was not isolated in the individual state. It is most likely that it readily decomposes with the C—S bond cleavage to benzaldehyde and benzylmercaptane. The latter, as well known,<sup>11</sup> is easily oxidized, under mild conditions, at the sulfur atom by hydrogen peroxide or a CuCl<sub>2</sub>—air system to unstable sulfenic acid and dibenzyl disulfide, which was qualitatively found by mass spectrometry combined with chromatography. We also identified benzyl thiolbenzoate PhC(O)SCH<sub>2</sub>Ph, which is the product of radical ketonization of the methylene group of the benzyl fragment of the starting sulfide (*cf.* Scheme 2).

In addition, the reaction products always contain high-boiling compounds, presumably the corresponding benzyl thiosulfinate and benzyl thiosulfonate, which are formed<sup>7</sup> due to the transformations of sulfenic acid.

Differences in chemiselectivity that appear in the oxidation of dibenzyl disulfide by the **4**–**2** and **5**–**2** systems are caused by the method of generation of electron-excited dioxygen on the metal atom. Dioxygen coordinated on the aluminum atom oxidizes the sulfur atom of the sulfide with the intermediate formation of thiadioxirane,<sup>6</sup> which is further transformed into sulfone. We assume that dioxygen of  $\eta^2$ -peroxo complex **1** is more strongly retained in the coordination sphere of bismuth in the form of the ligand.<sup>12</sup>

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## References

- V. A. Dodonov, L. P. Stepovik, *Zh. Obshch. Khim.*, 1992, **62**, 2630 [*J. Gen. Chem. USSR*, 1992, **62** (Engl. Transl.)].
- L. P. Stepovik, I. M. Martynova, V. A. Dodonov, V. K. Cherkasov, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 590 [*Russ. Chem. Bull., Int. Ed.*, 2002, 51, 638].
- L. P. Stepovik, M. V. Gulenova, I. M. Martynova, *Zh. Obshch. Khim.*, 2005, **75**, 545 [*Russ. J. Gen. Chem.*, 2005, **75** (Engl. Transl.)].
- V. A. Dodonov, E. A. Zaburdaeva, N. V. Dolganova, L. P. Stepovik, T. I. Zinov´eva, *Zh. Obshch. Khim.*, 1997, **67**, 988 [*Russ. J. Gen. Chem.*, 1997, **67** (Engl. Transl.)].
- T. I. Zinov´eva, N. V. Dolganova, V. A. Dodonov, I. G. Prezhbog, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 681 [*Russ. Chem. Bull.*, 1998, 47, 659 (Engl. Transl.)].
- V. A. Dodonov, E. A. Zaburdaeva, L. P. Stepovik, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 1663 [*Russ. Chem. Bull., Int. Ed.*, 2004, 53, 1729].
- 7. E. J. Corey, C. Ouannes, Tetrahedron Lett., 1976, 4263.
- K. A. Kocheshkov, A. P. Skoldinov, N. N. Zemlyanskii, *Metody* elementoorganicheskoi khimii. Sur´ma, vismut [Methods of Organoelement Chemistry. Stibium, Bismuth], Nauka, Moscow, 1976, p. 402 (in Russian).
- 9. V. Karnozhitskii, Organicheskie perekisi [Organic Peroxides], Izd. Inostr. Lit., Moscow, 1961, 156 (in Russian).
- 10. V. E. Zubarev, *Metod spinovykh lovushek* [*Method of Spin Traps*], Izd. Mosk. Gos. Univ., Moscow, 1984, 188 (in Russian).
- S. Hauptmann, I. Eraefe, H. Remane, Organische Chemie, VEB Deutscher Verlag f
  ür Grundstoffindustrie, Leipzig, 1976.
- S. Wallenhauer, D. Leopold, K. Seppelt, *Inorg. Chem.*, 1993, 32, 3948.

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