

## Studies on Peroxy Compounds

V. The Introduction of the *t*-Butoxy Group into TetrahydrofuranSVEN-OLOV LAWESSON, CURT BERGLUND  
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The benzoyloxy group may be introduced into olefins by the copper salt catalyzed decomposition of *t*-butyl perbenzoate, according to the Kharasch-Sosnovsky<sup>1,2</sup> method whereby the benzoyloxy group enters exclusively the allylic position without the occurrence of isomerisation. Denney *et al.* have proposed a mechanism based on studies with *t*-butyl perbenzoate (carbonyl <sup>18</sup>O) and Lawesson and Berglund have found that the benzoyloxy group is introduced into benzyl ethers<sup>3,4</sup> and benzyl sulphides<sup>5</sup> without fragmentation or dimerisation of the respective substrates. In our further studies of the Kharasch-Sosnovsky reaction with various types of ethers we have found that under suitable conditions tetrahydrofuran gives 2-*t*-butoxy tetrahydrofuran. (Found: C 66.57; H 10.93. Calc. C 66.63; H 11.18), b. p. 127°C,  $n_D^{20} = 1.4194$ . That the *t*-butoxy group enters mainly (possibly exclusively) the 2-position is inferred by the chemical and physical evidence, details of which will be given in a subsequent publication. Contrary to tetrahydrofuran, 1,4-dioxane gives 2-benzoyloxy-1,4-dioxane. (Found: C 63.57; H 5.84. Calc. C 63.45; H 5.81), m. p. 51–52°C and di-*n*-butyl ether gives 2-benzoyloxy-di-*n*-butyl ether. (Found: C 72.25; H 8.91. Calc. C 71.97; H 8.86), b. p. 97–98°C/0.3 mm Hg,  $n_D^{20} = 1.4837$ . Although there are indications that the benzoyloxy group is first introduced also into tetrahydrofuran, the main product isolated is the *t*-butoxy compound.

At this juncture, we do not want to discuss any theoretical or other aspects of this reaction; however, by extending this work, we are exploring the Kharasch-Sosnovsky reaction more fully and any detailed discussion will be postponed until further experimental work has been completed.

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1. Kharasch, M. S. and Sosnovsky, G. *J. Am. Chem. Soc.* **80** (1958) 756.
2. Kharasch, M. S., Sosnovsky, G. and Yang, N. C. *J. Am. Chem. Soc.* **81** (1959) 5819.
3. Denney, D. B., Denney, D. Z. and Feig, G. *Tetrahedron Letters* **15** (1959) 19.
4. Lawesson, S.-O. and Berglund, C. *Tetrahedron Letters* **2** (1960) 4.
5. Lawesson, S.-O. and Berglund, C. *Arkiv Kemi* **15** (1960). *In press.*
6. Lawesson, S.-O. and Berglund, C. *To be published.*

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On the Crystal Structures of  
(BiO)<sub>2</sub>SeO<sub>4</sub>·H<sub>2</sub>O, (BiO)<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O,  
BiOHCrO<sub>4</sub> and BiOHSeO<sub>4</sub>·½H<sub>2</sub>OBENGT AURIVILLIUS, OLOV von HEIDENSTAM  
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In the bismuth oxide salts whose structures have hitherto been reported, a characteristic structural element is frequently present, *viz.* infinite two-dimensional layers of the composition Bi<sub>2</sub>O<sub>3</sub>. The layers consist of sheets of oxygen atoms which are arranged to form squares. The bismuth atoms are situated alternately above and below the centres of the latter as illustrated in Fig. 1. Each oxygen atom of the sheets is thus tetrahedrally surrounded by four bismuth atoms. The arrangement can also be described geometrically as built up of OBi<sub>4</sub> tetrahedra linked together to form the Bi<sub>2</sub>O<sub>3</sub> layers by sharing four edges.

The bismuth oxide compounds reported to contain Bi<sub>2</sub>O<sub>3</sub> layers include several bismuth oxide halides<sup>1</sup>, some bismuth oxide salts of fatty acids<sup>2</sup>, several mixed oxides of bismuth and titanium, niobium or tantalum<sup>3</sup> and one oxide carbonate of bismuth<sup>4</sup>.

The present study was undertaken in order to find out whether the Bi<sub>2</sub>O<sub>3</sub> layers are also present in compounds containing tetrahedral anions.

Since only preliminary determinations have been made of the positions of the

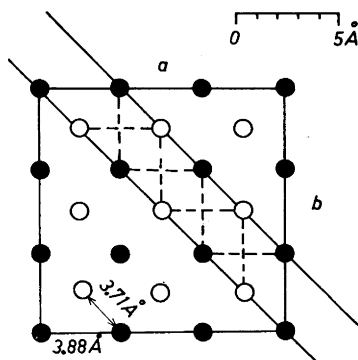


Fig. 1. Projection of the bismuth atom positions in a  $\text{Bi}_2\text{O}_3$  layer on the  $ab$  plane. Circles and filled circles mark Bi atoms at the heights zero and 2.50 Å respectively. The Bi-Bi distances are given for  $\text{BiOCl}$ .

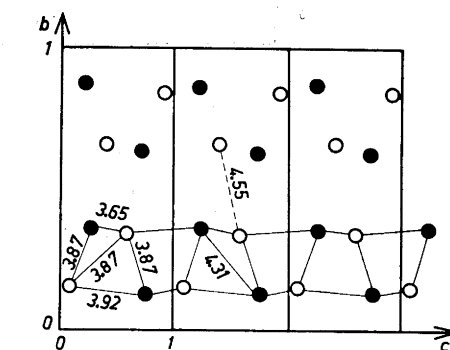


Fig. 2. Projections of the bismuth atom positions in  $(\text{BiO})_2\text{SeO}_4 \cdot \text{H}_2\text{O}$  on the  $bc$  plane. Circles and filled circles denote the positions of the atoms  $\text{Bi}_1$  and  $\text{Bi}_2$ .

oxygen atoms, the formulae given in the title must as yet be regarded as empirical. However, from the positions found for the Bi atoms, the following conclusions can be drawn:

1. The arrangement of the bismuth atoms in  $(\text{BiO})_2\text{SO}_4 \cdot \text{H}_2\text{O}$  and  $(\text{BiO})_2\text{SeO}_4 \cdot \text{H}_2\text{O}$  have features in common with their arrangement in  $\text{Bi}_2\text{O}_3$  layers. In fact, in these compounds, idealized bismuth atom positions can be deduced from their arrangement in these layers.

2. The arrangements of the bismuth atoms in  $\text{BiOHCrO}_4$  and  $\text{BiOHSeO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  are not compatible with that in  $\text{Bi}_2\text{O}_3$  layers.

$(\text{BiO})_2\text{SeO}_4 \cdot \text{H}_2\text{O}$  and  $(\text{BiO})_2\text{SO}_4 \cdot \text{H}_2\text{O}$

The compounds  $(\text{BiO})_2\text{SeO}_4 \cdot \text{H}_2\text{O}$  and  $(\text{BiO})_2\text{SO}_4 \cdot \text{H}_2\text{O}$  are isostructural. Space group:  $P2_1/c$  (No. 14). The unit cells contain four formula units. The following point positions and parameters were derived:

$(\text{BiO})_2\text{SeO}_4 \cdot \text{H}_2\text{O}$ ;

$$\begin{aligned}
 &4 \text{ Bi}_1 \text{ in } 4(e): \\
 &\quad \pm(x, y, z); \quad \pm(x, \frac{1}{2} - y, \frac{1}{2} + z); \\
 &\quad x = 0.034, y = 0.156, z = 0.087 \\
 &4 \text{ Bi}_2 \text{ in } 4(e): \\
 &\quad x = 0.299, y = 0.134, z = 0.235 \\
 &4 \text{ Se in } 4(e): \\
 &\quad x = 0.366, y = 0.634, z = 0.087
 \end{aligned}$$

$(\text{BiO})_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ;

$$\begin{aligned}
 &4 \text{ Bi}_1 \text{ in } 4(e): \\
 &\quad x = 0.037, y = 0.155, z = 0.088 \\
 &4 \text{ Bi}_2 \text{ in } 4(e): \\
 &\quad x = 0.310, y = 0.135, z = 0.218
 \end{aligned}$$

Cell dimensions:

$$\begin{aligned}
 &(\text{BiO})_2\text{SeO}_4 \cdot \text{H}_2\text{O}; \\
 &a = 7.92 \text{ \AA}, b = 14.04 \text{ \AA}, c = 5.64 \text{ \AA}, \beta = 108.8^\circ \\
 &(\text{BiO})_2\text{SO}_4 \cdot \text{H}_2\text{O}; \\
 &a = 7.67 \text{ \AA}, b = 14.00 \text{ \AA}, c = 5.70 \text{ \AA}, \beta = 109.2^\circ
 \end{aligned}$$

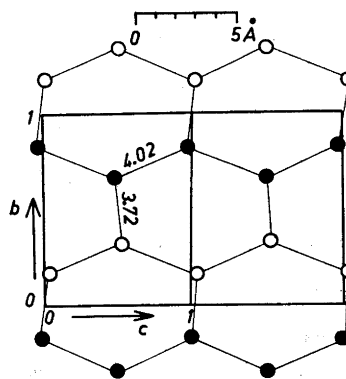


Fig. 3. Projection of the bismuth atom positions in  $\text{BiOHCrO}_4$  on the  $bc$  plane. Circles and filled circles mark Bi atoms at  $x = 0.16$  and  $x = 0.16$ , respectively.

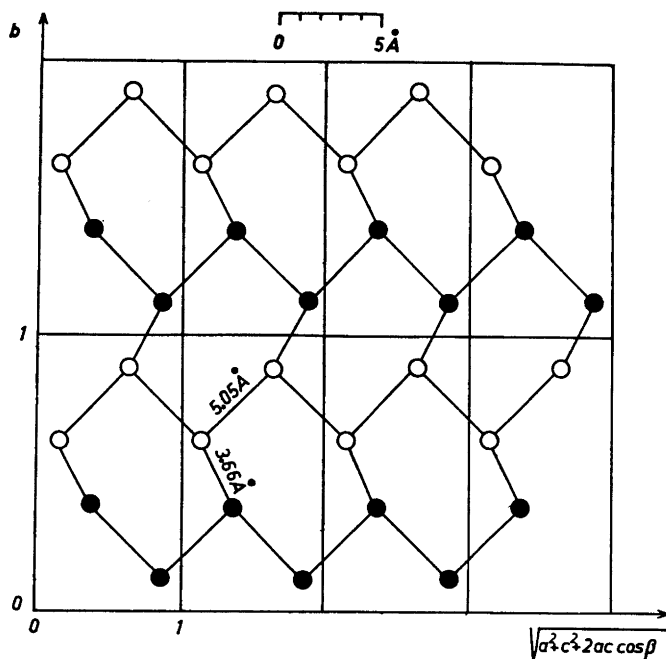


Fig. 4. Projection of the bismuth atom positions of one layer in  $\text{BiOHSeO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  on the plane (101) along the line  $[10\bar{1}]$ . The bismuth atoms occur at two heights along  $[10\bar{1}]$ , the difference in the heights being 0.68 Å. Circles and filled circles represent bismuth atoms at different levels.

The bismuth atom positions projected on the  $bc$  plane are shown in Fig. 2. As seen, the bismuth atoms form double chains along the  $c$  axis of the unit cell. These chains can be described as being formed by linked tetrahedra, each sharing two opposite edges. A corresponding chain of Bi atoms occurs in the  $\text{Bi}_2\text{O}_3$  layers and is marked in Fig. 1. Thus the arrangements of the bismuth atoms in  $(\text{BiO})_2\text{SeO}_4 \cdot \text{H}_2\text{O}$ ,  $(\text{BiO})_2\text{SO}_4 \cdot \text{H}_2\text{O}$  and in  $\text{Bi}_2\text{O}_3$  layers are quite similar. In the structures of this selenate and sulphate,  $\text{OBi}_4$  tetrahedra with reasonable distances O—Bi are geometrically possible.

#### $\text{BiOHCrO}_4$

Space group:  $P2_1/c$  (No. 14). The unit cell contains four formula units. The following point positions and parameters were arrived at for the bismuth and chromium atoms:

$$\begin{aligned} 4 \text{ Bi in } 4(e): \\ \pm(x, y, z); \quad \pm(x, \frac{1}{2}-y, \frac{1}{2}+z); \\ x = 0.162, y = 0.170, z = 0.014 \end{aligned}$$

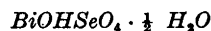
$$\begin{aligned} 4 \text{ Cr in } 4(e): \\ x = 0.270, y = 0.580, z = 0.177 \end{aligned}$$

Cell dimensions:

$$a = 5.61 \text{ \AA}, b = 9.54 \text{ \AA}, c = 7.44 \text{ \AA}, \beta = 93.15^\circ$$

The projection of the bismuth atom positions on the  $bc$  plane is given in Fig. 3. As seen, the bismuth atoms form puckered sheets made up of hexagons along the  $bc$  planes. The shortest distance between bismuth atoms belonging to different sheets is 5.61 Å. A tetrahedral arrangement  $\text{OBi}_4$  with reasonable distances O—Bi is not possible in this structure and the arrangement of the bismuth atoms does not seem to have any relation to the bismuth arrangement occurring in  $\text{Bi}_2\text{O}_3$  layers.

Judging from the Bi—Bi distances, there seems to exist a weak tendency for the bismuth atoms to form pairs in this structure.



Space group:  $P2_1/n$  (No. 14). The unit cell contains four formula units. The following point positions and parameters were derived for the bismuth and selenium atoms:

4 Bi in 4(e):

$$\pm(x, y, z); \pm(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z);$$

$$x = 0.586, y = 0.118, z = 0.151$$

4 Se in 4(e):

$$x = 0.094, y = 0.165, z = 0.165$$

Cell dimensions:

$$a = 6.64 \text{ \AA}, b = 13.60 \text{ \AA}, c = 6.08 \text{ \AA}, \beta = 112.2^\circ$$

The bismuth atoms form nearly planar sheets parallel to the plane (101). The sheets are made up of hexagons with the edges 3.66 Å and 5.05 Å (Fig. 4). The shortest distances between bismuth atoms in adjacent layers is 5.77 Å. The arrangement of the bismuth atoms in  $\text{BiOHSeO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  does not bear any resemblance to the quadratic layers of bismuth atoms in the  $\text{Bi}_2\text{O}_3$  sheets. The tendency of pair formation for the bismuth atoms is more pronounced in this structure than in  $\text{BiOHCrO}_4$ .

These investigations will be continued in order to refine the parameters and to determine the positions of the oxygen atoms. A full account will be published later.

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1. Sillén, L. G. *Diss.*, Stockholm 1940.
2. Aurivillius, B. *Acta Chem. Scand.* **9** (1955) 1213.
3. Aurivillius, B. *Diss.*, Stockholm 1951.
4. Lagercrantz, Å. and Sillén, L. G. *Arkiv Kemi, Mineral. Geol.* **25A** (1948) No. 20.

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## Electrophilic Replacement of Bromine by Hydrogen

### Debromination of 2,4,6-Tri-*t*-butylbromobenzene

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When 2,4,6-tri-*t*-butylbromobenzene (*I*) is heated in the presence of a strong acid a mixture of products including 1,3,5-tri-*t*-butylbenzene (*II*) and 3,5-di-*t*-butylbromobenzene is formed. If an acceptor for  $\text{Br}^+$  such as bromide ion is present in the acid and the resulting bromine is entrained from the solution, *II* is the chief product. In principle, any compound which formally serves as a reducing agent for  $\text{Br}^+$  and is otherwise inert is suitable for use as an acceptor. Reactive aromatic hydrocarbons prove to be very efficient for this purpose. Trifluoroacetic acid has been used in most experiments because of its high acidity and relatively good solvent properties; however, the reaction occurs with a variety of acids.

The debromination of *I* is viewed as an electrophilic replacement of bromine by hydrogen or the reverse of aromatic bromination. That *I* should undergo electrophilic debromination was by no means unexpected. The observed strong isotope effect in the "positive" bromination<sup>1</sup> of *II* coupled with the known facts about other electrophilic substitutions by hydrogen<sup>2</sup> led us to investigate this reaction possibility. The isotope effect in the bromination of *II* has been explained in terms of steric effects which cause the velocity of step 2 to become less than that of step -1. It is apparent that steric repulsion energy increases as this reaction proceeds towards products. As a result, the energy differ-

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