

Studies on Peroxy Compounds

V. The Introduction of the *t*-Butoxy Group into Tetrahydrofuran

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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^{1,2} 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 ¹⁸O) and Lawesson and Berglund have found that the benzoyloxy group is introduced into benzyl ethers^{3,4} and benzyl sulphides⁵ 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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On the Crystal Structures of (BiO)₂SeO₄·H₂O, (BiO)₂SO₄·H₂O, BiOHCrO₄ and BiOHSeO₄·½H₂O

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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 Bi₂O₂. 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 OBi₄ tetrahedra linked together to form the Bi₂O₂ layers by sharing four edges.

The bismuth oxide compounds reported to contain Bi₂O₂ layers include several bismuth oxide halides¹, some bismuth oxide salts of fatty acids², several mixed oxides of bismuth and titanium, niobium or tantalum³ and one oxide carbonate of bismuth⁴.

The present study was undertaken in order to find out whether the Bi₂O₂ layers are also present in compounds containing tetrahedral anions.

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