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

$BiOHSeO_4 \cdot \frac{1}{2}\ H_2O$

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:
$a = 6.64$ Å, $b = 13.60$ Å, $c = 6.08$ Å, $\beta = 112.2°$

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 $BiOHSeO_4 \cdot \frac{1}{2}H_2O$ does not bear any resemblance to the quadratic layers of bismuth atoms in the Bi_2O_2 sheets. The tendency of pair formation for the bismuth atoms is more pronounced in this structure than in $BiOHCrO_4$.

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.

These studies form part of a research program on bismuth oxide salts financially supported by the *Swedish Natural Science Research Council.*

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.

Received May 16, 1960.

Electrophilic Replacement of Bromine by Hydrogen

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

PHILIP C. MYHRE*

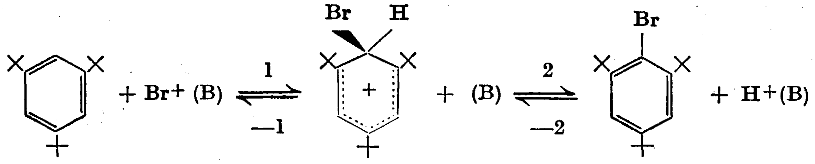
Nobel Institute of Chemistry, Stockholm 50, Sweden

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 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 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 [1] of *II* coupled with the known facts about other electrophilic substitutions by hydrogen [2] 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-

---

* U.S. National Science Foundation Postdoctoral Fellow, 1958—1960.



ence between the products and the transition state would be expected to be less for a highly hindered compound such as *I* than for a less hindered alkylbromobenzene. Consequently, one would predict that the reverse reaction, debromination, would become energetically more favorable in highly hindered systems. It should be stressed that the existence of an isotope effect in the bromination of *II* does not imply that the reaction is reversible. However, steric effects serve to explain both the isotope effect and the facile debromination.

Since there are numerous examples in the literature of acid-induced dehalogenations of highly reactive unhindered aromatic compounds such as amines and phenols[3,4], it is important to establish that the lowering of the free energy of activation for the debromination of *I* is in a large measure due to the above mentioned steric effects and not simply to a general activation of the aromatic ring by the alkyl group substituents. Consequently, the possible debromination of 2-bromomesitylene (*III*), a compound whose substituents have as a first approximation similar electron releasing properties but greatly reduced steric hindrance, was investigated. No debromination could be detected when *III* was subjected to conditions which caused extensive debromination of *I* (refluxing trifluoroacetic acid and excess bromide ion). In the course of this work it has been shown that mesitylene is a far better acceptor of Br+ than bromide ion. Therefore, it could be argued that debromination of mesitylene would be difficult to detect because of the rapid back reaction (bromination). A more conclusive test was devised. An equimolar mixture of mesitylene-α-H^3_1, specific activity 228, and inactive 2-bromomesitylene was heated at reflux in trifluoroacetic acid for one hour; this is approximately one half-life for the debromination of *I*. The specific activities of the isolated mesitylene and bromomesitylene were 226 and 3, respectively. From these results it is concluded that *III* does not appreciably debrominate under conditions which lead to extensive debromination of *I*. The results also preclude the exchange of hydrogen in the methyl groups of mesitylene under the reaction conditions.

The facile debromination of *I* led us to investigate the possibility that the reported[5] failure of the iron catalyzed bromination of *II* to yield *I* (only 3,5-di-*t*-butylbromobenzene has been isolated) was due to two competing reactions: the first, a readily reversible bromination at an aromatic carbon bearing a hydrogen; the second, an irreversible bromination at an aromatic carbon bearing a *t*-butyl group. A necessary condition of this proposed scheme is that *I* be converted to 3,5-di-*t*-butylbromobenzene under iron catalyzed bromination conditions. This conversion has been shown to take place. It remains to be shown that *I* is transiently formed in this bromination reaction.

1. Myhre, P. C. *Acta Chem. Scand.* **14** (1960) 219.
2. Schubert, W. M. and Myhre, P. C. *J. Am. Chem. Soc.* **80** (1958) 1755.
3. Nicolet, B. H. *et al. J. Am. Chem. Soc.* **43** (1921) 1796; **49** (1927) 1796, 1801, 1806.
4. Meerwein, H. J., Hofmann, P. and Schill, F. *J. prakt. Chem.* **154** (1940) 266.
5. Bartlett, P. D., Roha, M. and Stiles, R. M. *J. Am. Chem. Soc.* **76** (1954) 2349.

Received May 19, 1960.