The Stability of 1,1-Dibromoacetone

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1,1-Dibromoacetone can be prepared according to Hughes, Watson and Yates in about 30% yield by bromination of bromoacetone. It is found that a sample of this compound kept at room temperature undergoes rearrangement, while a sample kept in the dark in a refrigerator for 2 months is only little affected.

Rearranged samples were analyzed by NMR-techniques and the following compounds identified: monobromoacetone, 1,1-dibromoacetone, 1,3-dibromoacetone and 1,1,3-tribromoacetone. The relative amounts of the different products were determined.

Two samples were studied. One sample (A) was kept in a light place for 50 days and the percentages of the different products found are given in Table 1.

In order to ascertain if the rearrangement was catalyzed by light, a sample of 1,1-dibromoacetone (B) was kept in the dark at room temperature for 13 and for 20 days. The compositions after these times were determined and are given in Table 1.

The occurrence of monobromoacetone and 1,1,3-tribromoacetone indicates that the rearrangement is intermolecular, but no details of the mechanism are known. Bromoketones are known to undergo a halogen rearrangement, and in these examples the rearrangements were found to be catalyzed by free hydrogen bromide; see Ref. 2 where references are collected.

It is interesting to note that the rearrangement of 1,1-dibromoacetone gives products with one more and one less bromine atom, as in the rearrangement of 3-bromo- to 5-bromolavulic acid.

Although no equilibrium is reached and the results are preliminary, one can notice that the main product of the rearrangement is the symmetrical dibromoketone. The amount of monobromoacetone appears to be constant during the procedure.

The author has started to study this rearrangement in more detail, particularly with regard to its mechanism and kinetics, and the results will be published elsewhere.

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Table 1.

<table>
<thead>
<tr>
<th></th>
<th>CH₃COCBr₂</th>
<th>CH₂COC₃Br</th>
<th>CH₂BrCOC₃Br</th>
<th>CH₂BrCOCBr₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A (50 days)</td>
<td>6</td>
<td>21</td>
<td>68</td>
<td>6</td>
</tr>
<tr>
<td>Sample B (13 days)</td>
<td>42</td>
<td>18</td>
<td>26</td>
<td>14</td>
</tr>
<tr>
<td>Sample B (20 days)</td>
<td>33</td>
<td>21</td>
<td>33</td>
<td>14</td>
</tr>
</tbody>
</table>

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