HYDROLYSIS OF CARBAMATES AND CARBONATES OF 3-HYDROXYTHIOLANE 1,1-DIOXIDE

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Alkylcarbamates of 3-hydroxy-thiolane 1,1-dioxide are hydrolyzed in the presence of bases to give alkyl(1,1-dioxo-3-thiolanyl)amines and 2-thiolene 1,1-dioxide (I). Aryl esters undergo hydrolysis to give sulfone I and 3-hydroxythiolane 1,1-dioxide (II). The corresponding alkyl- and arylcarbonates also form sulfone I and a very small amount of hydroxy derivative II under these conditions.

It is known that amines and alcohols (or phenols) are formed in the hydrolysis of N-alkyl- and N-phenylcarbamates in neutral and alkaline media. The reaction proceeds through the intermediate formation of an oxy anion via nucleophilic attack on the carbonyl group by hydroxide ion [1, 2].

We have established that 3-(N-alkylcarbamoyl)thiolane 1,1-dioxides (I) are hydrolyzed when they are refluxed in water to give 3-alkylamino-thiolane 1,1-dioxides (II), 2-thiolene 1,1-dioxide (III), and a small amount of 3-hydroxythiolane 1,1-dioxide (IV). Hydrolysis of 3-(N-phenyl-carbamoyl)thiolane 1,1-dioxide in the presence of alkali metal hydroxides or tertiary amines leads to the formation of a mixture of III, IV, and aniline. The difference in the behavior of carbamates I can be explained if one assumes that they react with water via general scheme (a) and anomalously via scheme (b) with splitting out of a carbamic acid and the formation of III, which then adds the alkylamines that are formed during the reaction:

\[
\begin{align*}
\text{O} & \text{C} - \text{NHR} \quad \text{H}_2\text{O} \quad \[
\begin{align*}
\text{O} & \text{C} - \text{NHR} \quad \text{OH} \quad \rightarrow \quad \text{OH} \quad \text{CO}_2 \quad \text{RNH}_2 \quad (a) \\
\text{O} & \text{NHRCO}_2\text{H} \\
\text{O} & \text{NHR} \\
\end{align*}
\end{align*}
\]

Aniline does not add to III under the hydrolysis conditions; this is in agreement with the data in [3].

The elimination of a carbamic acid is due to the increased C–H acidity of the methylene group of the 1,1-dioxothiolane ring in the 2 position and probably takes place in the same way as the splitting out of carboxylic acids from 3-acetoxythiolane 1,1-dioxides via a carbamion mechanism [4]. The addition of catalytic amounts of alkali accelerates the elimination reaction. Hydration of sulfone III takes place very slowly in dilute solutions of alkali and amines [5], and it may therefore be assumed that IV, which is detected in the products of hydrolysis of carbamates, is produced primarily via scheme (a).

In contrast to carbamates I, carbamates V are hydrolyzed in aqueous solutions of sodium carbonate, alkali, and amines via the general scheme of the cleavage of carbamates with the formation of 3-aminothiolane 1,1-dioxide (VI):


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TABLE 1. Products of Hydrolysis of N-Phenylcarbamates I and Carbonates VII

<table>
<thead>
<tr>
<th>Type of compound</th>
<th>Starting compound R</th>
<th>Base</th>
<th>Solvent</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>III</td>
</tr>
<tr>
<td>VII</td>
<td>CH₂</td>
<td>KOH</td>
<td>H₂O</td>
<td>84.1</td>
</tr>
<tr>
<td>VIII</td>
<td>CH₃</td>
<td>Na₂CO₃</td>
<td>H₂O</td>
<td>86.4</td>
</tr>
<tr>
<td>VII</td>
<td>CH₃</td>
<td>(C₂H₅)₂N</td>
<td>H₂O</td>
<td>76.1</td>
</tr>
<tr>
<td>VII</td>
<td>C₆H₅</td>
<td>KOH</td>
<td>Dioxane–water, 1:1</td>
<td>85.0</td>
</tr>
<tr>
<td>I</td>
<td>C₂H₅</td>
<td>KOH</td>
<td>Dioxane–water, 1:1</td>
<td>84.3</td>
</tr>
<tr>
<td>I</td>
<td>C₂H₅</td>
<td>(C₂H₅)₃N</td>
<td>Dioxane–water, 1:1</td>
<td>86.0</td>
</tr>
</tbody>
</table>

We also observed dual reactivity in the case of 1,1-dioxo-3-thiolanyl carbonates (VII) during their hydrolysis in the presence of sodium carbonate, alkalis, and tertiary amines.

Carbonates VII (R = C₆H₅) form IV via a common (with respect to alkylcarbonates) scheme (a) [6], as well as III as a consequence of 2,3 elimination of the substituent. Sulfones III and IV and the corresponding alkoxy derivatives VIII are formed with alkylcarbonates VII (R = CH₃).

The results in conjunction with data on the chemistry of ethers [7] and esters IV [4], make it possible to conclude that the increased C–H acidity of the adjacent methylene group in the 2 position has a decisive effect on the course of the hydrolysis of 3-substituted derivatives of thiolane 1,1-dioxides with an oxygen atom attached to the ring.

EXPERIMENTAL

Gas-chromatographic analysis (GLC) was performed with a Tsvert-1 chromatograph with a thermal-conductivity detector on SE-30 siloxane polymer applied to Chezasorb AWNMBDS; the column temperature was 196°C, the vaporizer temperature was 250°C, and the carrier gas (helium) flow rate was 73 ml/min. Thin-layer chromatography (TLC) was carried out on activity II A1203 in a loose layer on 20 by 10 cm glass plates with elution with ether and development with iodine vapors.

Hydrolysis of 1,1-Dioxo-3-thiolanyl Butylcarbamate (I). A solution of 7.05 g (0.03 mole) of carbamate I in 50 ml of water was refluxed for 10 h, after which it was evaporated to half its original volume. It was established that the distillate contained 1.09 g (0.015 mole) of butylamine (titration with 0.1 N HCl). The residue was neutralized with 3% hydrochloric acid, and the mixture was evaporated at no higher than 40°C. The residue was treated with 50 ml of acetone, and the precipitated butyl(1,1-dioxo-3-thiolanyl)amine hydrochloride was separated to give 3.23 g (48%) of a product with mp 149-150°C. Vacuum distillation of the residue gave 1.5 g (52%) of sulfone III with bp 95-100°C (1 mm) and mp 49-50°C. According to the TLC data, IV was present in the residue.