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

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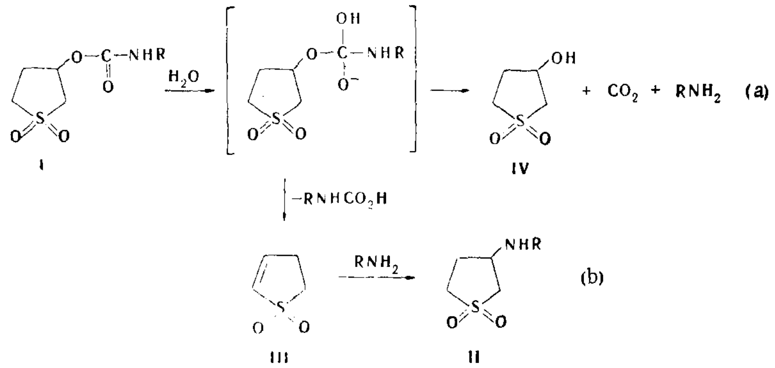
Alkylcarbamates of 3-hydroxy-thiolane 1,1-dioxide are hydrolyzed in the presence of bases to give alkyl(1,1-dioxo-3-thiolanyl)amines and 2-thiolene 1,1-dioxide (I). Aryl esters undergo hydrolysis to give sulfone I and 3-hydroxythiolane 1,1-dioxide (II). The corresponding alkyl- and arylcarbonates also 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:



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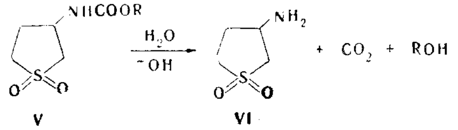
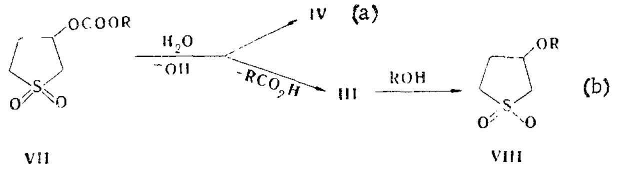
TABLE 1. Products of Hydrolysis of N-Phenylcarbamates I and Carbonates VII

Type of compound	Starting compound R	Base	Solvent	Yield, %		
				III	IV	VIII ($R=CH_3$)
VII	CH_3	KOH	H_2O	84,1	6,5	2,6
VII	CH_3	Na_2CO_3	H_2O	86,4	1,5	1,7
VII	CH_3	$(C_2H_5)_3N$	H_2O	76,1	2,2	1,8
VII	C_6H_5	KOH	Dioxane—water, 1 : 1	85,0	1,4	
I	C_6H_5	KOH	Dioxane— water, 1 : 1	84,3	8,8	
I	C_6H_5	$(C_2H_5)_3N$	Dioxane— water, 1 : 1	86,0	2,4	



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.



$R = CH_3, C_6H_5$

Carbonates VII ($R = C_6H_5$) 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 ($R = CH_3$).

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 Tsvet-1 chromatograph with a thermal-conductivity detector on SE-30 siloxane polymer applied to Chezasorb AWhMDS; 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 Al203 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.

Hydrolysis of Methyl 1,1-Dioxo-3-thiolanylcarbamate (V). A solution of 19.3 g (0.1 mole) of carbamate V and 6 g (0.11 mole) of KOH in 100 ml of water was refluxed for 20 h, after which it was cooled and filtered. The filtrate was evaporated, and the residue was dissolved in chloroform. Dry HCl was passed into the solution at no higher than 10-15°C until it became acidic. The precipitated hydrochloride of VI was separated to give 14.2 g (83%) of a product with mp 218-219°C.

Hydrolysis of Phenylcarbamates I and Carbonates VII. This reaction was carried out by refluxing 0.02-0.2 M solutions of the compounds in water or a mixture of solvents in the presence of equimolar amounts of bases for 5 h. The solutions were evaporated, and the residues were dissolved in acetone and analyzed by GLC. The results of hydrolysis are presented in Table 1.

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DIHYDRO-1,2,3-TRIALKOXYCARBONYLCYCLOPENTA[b]-1,4-BENZOTHIAZINES

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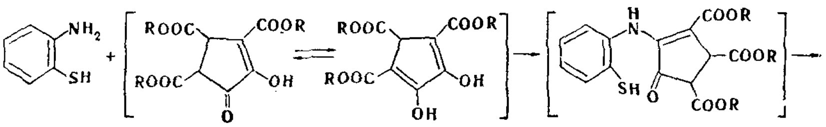
3a,9-Dihydro-1,2,3-trialkoxycarbonylcyclopenta[b]-1,4-benzothiazines, the structures of which were established on the basis of the absorption, fluorescence, PMR, and IR spectra and quantum-chemical calculations, were synthesized by condensation of o-aminothiophenol with 1,2-dihydroxy-3,4,5-trialkoxycarbonyl-2,5-cyclopentadienes.

Little study has been devoted to 1,4-benzothiazines, and they have not yet found any practical application [1]. Several cyclopenta-1,4-benzothiazines, which were obtained by condensation of o-aminothiophenol with 2-chlorocyclopentanone [2], 3-chlorocyclopentane-1,2-dione [3], indanedione [4], and 2-hydroxytrialkoxycarbonylcyclopentadienone [5], are described in the literature. We have found that the condensation of o-aminothiophenol with 1,2-dihydroxy-3,4,5-trialkoxycarbonyl-2,5-cyclopentadienes* leads to 3a,9-dihydro-1,2,3-trialkoxycarbonylcyclopenta[b]-1,4-benzothiazines (V) [7]:



I II III

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*The compounds exist in solution in the form of a tautomeric mixture of the keto enol and the dienediol [6].

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