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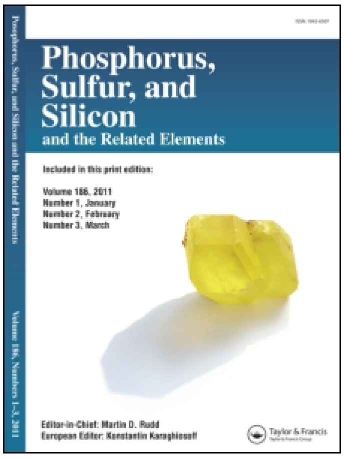

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The Role of Thietane-2-Ones in the Synthesis of the New Types of Sulfur Heterocycles

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THE ROLE OF THIETANE-2-ONES IN THE SYNTHESIS OF THE NEW TYPES OF SULFUR HETEROCYCLES

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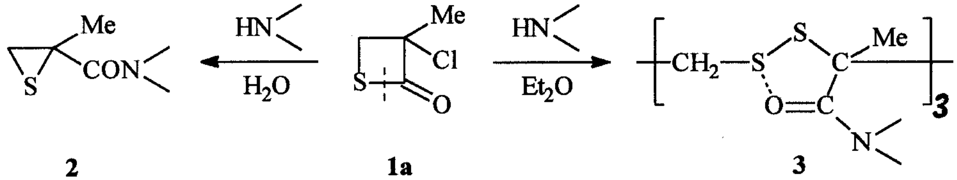
Abstract Thiiranecarboxylic acids, 1,2-dithiolane-3-ones, 1,2-dithiol-3-ones, 1,2-oxathiolane-5-one-2-oxides and the other hardly available S-heterocycles were obtained from thietane-2-ones.

INTRODUCTION

It is well known that thietane-2-ones (**1**) have been firstly synthesized by M.G.Lin'kova via intramolecular cyclization of β-mercaptocarboxylic acids or β-halocarbonyl chlorides. We offered a novel synthesis of (**1**) by the reaction between 1,2-dithiolane-3-ones and phosphines. The reactivity of (**1**) has received little attention.

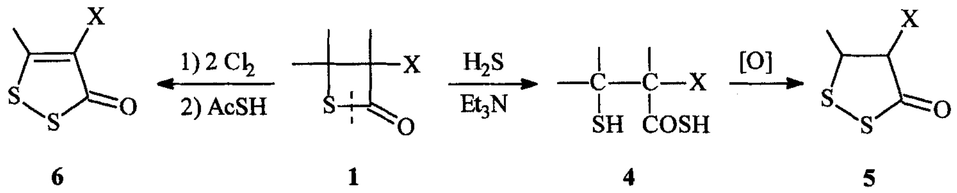
RESULTS AND DISCUSSION

We have found that a way of the reaction of 3-chloro-3-methylthietanone (**1a**) with secondary amines depends on solvent. A number of new α-methylthioglycidic acid amides (**2**) were obtained in high yields in water. A cyclic trimer (**3**) with >C=O···S coordination was obtained as a product of the disproportionation of (**2**) in organic solvent.[1]



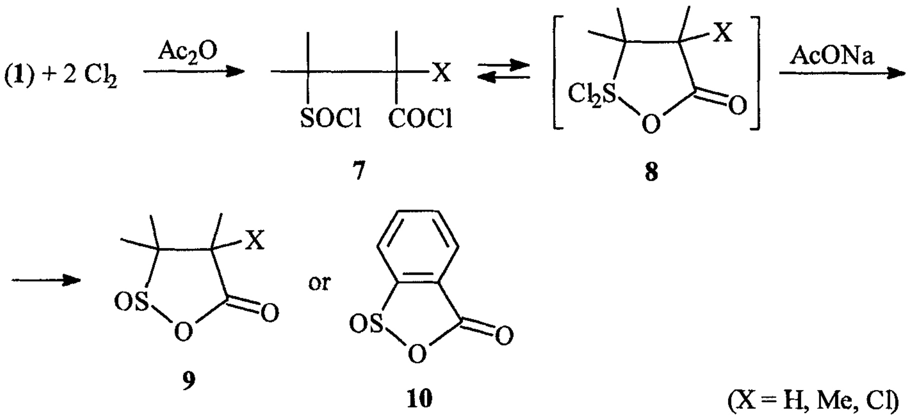
2 **1a** **3**

Interaction of **1** with hydrogen sulfide in the presence of triethylamine is a novel reaction of thietane-2-ones resulting to β-mercaptothiolalkanoic acids (**4**). Oxidation of **4** gives 1,2-dithiolane-3-ones (**5**).[2] Desired 1,2-dithiol-3-ones (**6**) were synthesized in two stage by chlorination of **1** and following heterocyclization with thioacetic acid in the presence of catalyst ($ZnCl_2$).



(X = H, Me, Cl, NHAc)

Recently we have found[3] the other novel reaction of **1** - oxidative chlorination affording β-(chlorosulfinyl)alkanoyl chlorides (**7**). Due to mutual coordination of >S=O···>C=O, it is possible a tautomeric conversion of the stable **7** to the labile dichlorosulfuran **8**. The saponification of **7** by action of $NaHCO_3$ and subsequent cyclization of the formed bis-Na salt with oxalylchloride leads to previously unknown 1,2-oxathiolane-5-one-2-oxides (**9**) and also new 2,1-benzoxathiol-3-one-1-oxide (**10**).[4] It has been found a novel general synthesis **9** (including X=Cl) and **10** by interaction **7** with sodium acetate.[5]



(X = H, Me, Cl)

The reaction of **9** and **10** with nucleophiles are similar by aminolysis or different by alcoholysis. The compounds with intramolecular H-bonds >S=O···HN< have been revealed among some products of aminolysis.[4]

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