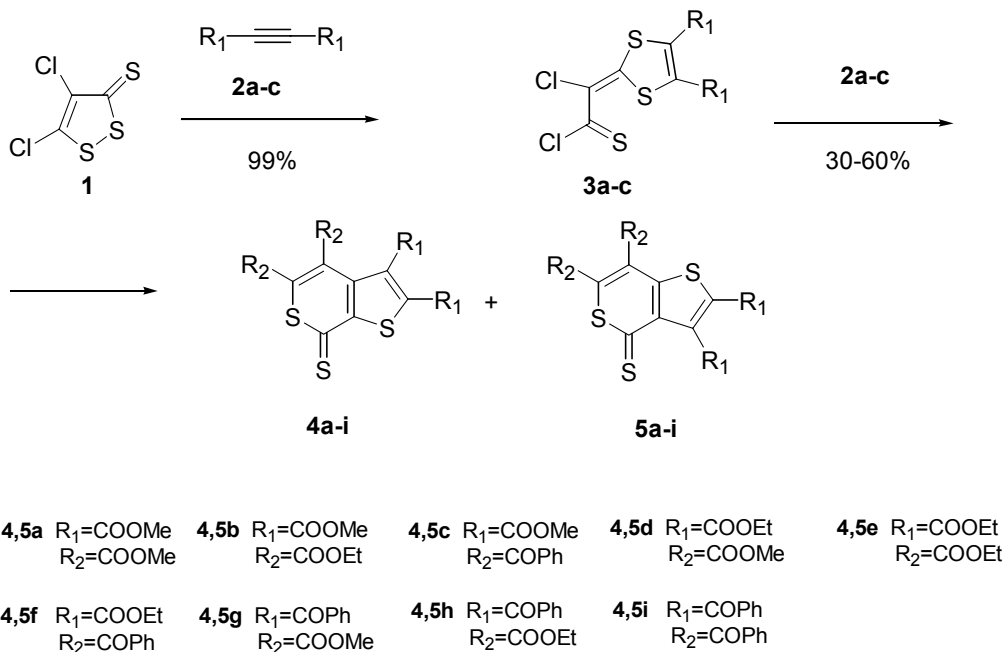


First Synthesis of Thieno[2,3-*c*]thiopyranethiones

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One of the most interesting properties of 1,2-dithiole-3-thiones is their ability to react with alkynes as 1,3-dipoles [1]. The first cycloaddition reaction was accomplished by heterocyclic ring opening to give 1,3-dithioles, which sometimes add a second alkyne in Diels-Alder reaction to give spiro 1,4-dihydrothiopyran. We found that 4,5-dichloro-1,2-dithiol-3-thione **1** reacts with acetylene derivatives **2a-c** at room temperature to give surprisingly stable, rare thioacyl chlorides **3a-c**. However, heating **3a-c** with an excess of alkyne in xylene leads not to expected spiro 1,4-dihydrothiopyrane, but to a new heterocyclic systems – thieno[2,3-*c*]-thiopyranthiones (**4a-i** and **5a-i**) in ratio ~1:1.



We have isolated both types of isomers **4** and **5** by flash chromatography on silica gel and by fractional crystallization. The structure of **4a** and **5e,f,h** was strictly confirmed by X-ray analysis. ¹³C NMR shifts are in good agreement with calculated data.

Thienothiopyrans **4a,c,i** and **5a,c,i** can be prepared in one-pot by refluxing of **1** with an excess of corresponding acetylene **2a-c** in xylene. The mechanism of these unusual transformations is proposed.

[1] C. Th. Pedersen, *Ad. Heterocycl. Chem.*, 1982, **31**, 63.