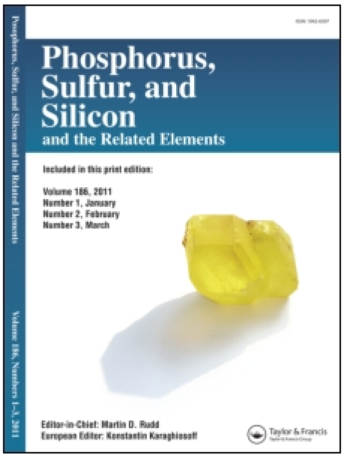

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Synthesis, Crystal and Molecular Structures of the Novel Compounds 4,7-Dithio-5,6-Diselenocino- [1,2b:3,4b']-Diimidazolyl-1,3,8,10-Tetrabutyl 2,9-Dithione and -2,9-Diselone

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SYNTHESIS, CRYSTAL AND MOLECULAR STRUCTURES OF THE NOVEL COMPOUNDS 4,7-DITHIO-5,6-DISELENOCINO-[1,2b:3,4b']-DIIMIDAZOLYL-1,3,8,10-TETRABUTYL 2,9-DITHIONE AND -2,9-DISELONE

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The sulfurization reaction with Lawesson's reagent on a series of 1,3-dialkyl imidazolidine-2-selone-4,5-diones in toluene gave depending on the reaction conditions, the compounds 4,7-dithio, 5,6-diselenocino[1,2b:3,4b']di-imidazolyl-1,3,8,10-tetraalkane-2,9-dithione and -2,9-diselone. The structural characterization of the tetrabutyl derivatives are reported.

Keywords: thiones, selones, thiocino-selenocino, X-ray.

INTRODUCTION

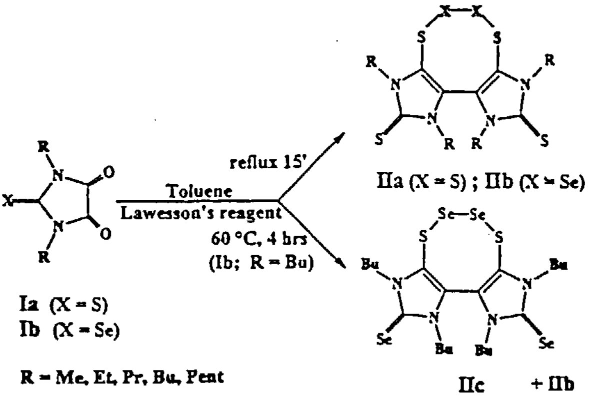
The sulfurization with Lawesson's reagent or P_4S_{10} of several 1,3 dialkyl imidazolidine 2-thione -4,5 diones (Ia) does not produce the expected trithiones but the class of compounds 4,5,6,7 tetrathiocino [1,2b; 3,4b'] diimidazolyl-1,3,8,10-tetraalkane-2,9-dithiones (IIa)[1], which show interesting donor properties towards dihalogens[2] and transition metals[3].

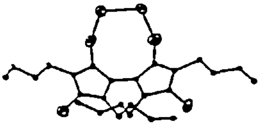
These molecules have been tested as anticancer agents; preliminary results are very promising[4] and further experiments are in progress. In order to obtain similar tetrathiocino derivates, containing Se atoms in 2,9 position, in view of checking their ability as ligands and achieving better biological activity, we have reacted in the same conditions 1,3-dialkylimidazolidine-2-selone-4,5-dione (Ib) with Lawesson's reagent.

Results and discussion

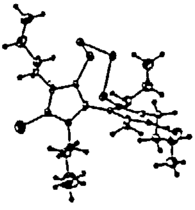
The reaction of Ib with Lawesson's reagent in toluene gave surprisingly a compound in which two selenium atoms were not located in the expected 2,9 positions, but inserted in the 5,6 positions of the octaatomic ring (IIb). Working in milder conditions and in the tetrabutyl case, a compound containing four Se atoms in 2,9 and 5,6 positions was also isolated (IIc). The reason why this happens is difficult to explain. We can only tentatively suggest that the Lawesson's reagent could in part exchange sulfur atoms with the selenium atoms of Ib and then it could act as sulfurating and seleniating agent at the same time. The I.R. spectra of IIb and IIc in the tetrabutyl derivative are nearly superimposable in the medium I.R. region. The FT-Raman spectra instead are diagnostic to distinguish the different compounds in the region characteristic of the interchalcogen vibrations. In fact IIa shows a strong peak at 425 cm^{-1} attributable to the S-S vibration, IIb shows a peak at 316 cm^{-1} due to the S-Se vibration and IIc two peaks at 306 cm^{-1} and at 258 cm^{-1} attributable to C-Se and Se-Se vibrations. The molecular structures of IIb and IIc are similar. Both the thio and selenocino octaatomic rings adopt a chair configuration. The imidazolidinic rings are planar due to a π-electronic delocalization, but they lie on different planes. The intramolecular Se-Se interactions are observed.

This class of compounds behaves as donors towards dihalogens and transition metals and the adducts with diiodine (in which the thio- or selenochetonic groups are involved in the coordination) have been isolated. Moreover they are able to coordinate transition metal atoms. The complexes of Cu(II) are in course of characterization.





Molecular structure of IIb



Molecular structure of IIc

Experimental

The 1,3 dialkylimidazolidine-2-selone-4,5-dione derivatives (Ib; R=Me-Et-Pr-Bu-Pent) were prepared from CH_2Cl_2 solutions of the correspondent N,N'dialkylselenoureas (obtained through a new method [5]) on dropping the equivalent amounts of oxalyl chloride at 0°C in presence of two equivalents of triethylamine. The red-purple solutions were extracted three times with water, dried with Na_2SO_4 and evaporated to dryness. The red residues were eluted in a wet silica gel column using petroleum ether/ethyl ether 3:2 as eluent to give red crystals of Ib. They were refluxed 15' in dry toluene under nitrogen with a 1:1.2 molar ratio of Lawesson's reagent. The dark-brown resulting solutions were rotary evaporated to dryness and the oily residues extracted with methanol. The undissolved solids were recrystallized from CH_2Cl_2/MeOH to give orange crystal of IIb (approx. yield 40%)

When the reaction with Lawesson's reagent was performed at 60° for 4 hours, the same treatment gave (R=Bu) a mixture of orange and red-orange crystals of IIb and IIc. They were separated by fractionated crystallization from CH_2Cl_2/MeOH. The compound IIc precipitated first (approx. yield 10%). All the compounds gave CHNS analytical results satisfactory

Crystal of IIb and IIc (R=Bu) suitable for X-ray structure determination were obtained by slow evaporation of CH_2Cl_2/MeOH solutions.

FT-IR spectra were recorded as KBr pellets on a Bruker IFS55 spectrometer working at room pressure and using a flow of dried air.

FT-Raman spectra have been recorded on a Bruker RFS100 spectrometer (excitation line: 1064 nm).

CHNS analyses were performed on a Fisons instrument mod. EA1108.

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