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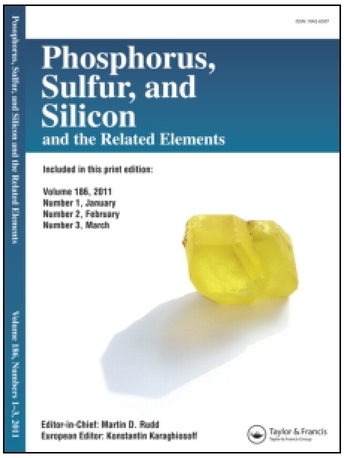

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Access to New Reactive Unsaturated Cycloalkenethiones by Flash Vacuum Thermolysis

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Access to New Reactive Unsaturated Cycloalkenethiones by Flash Vacuum Thermolysis

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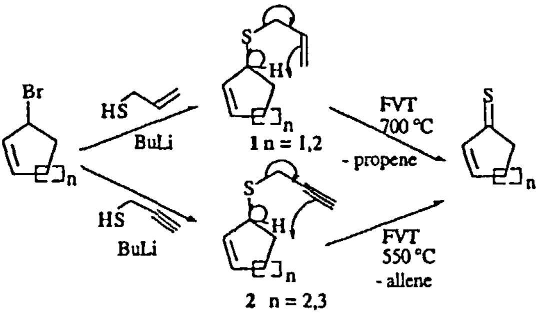
The reactive conjugated cycloalkenethiones (3, 4, 5) have been synthesized from the corresponding cycloalkenylsulfanyl compounds under flash vacuum thermolysis (FVT) conditions. The nonconjugated cycloalkenethiones (8, 9) were prepared in the same way, the tautomerisation into cycloalkadienethiols (10, 11) occurred at 77 K. As for the cyclobutenethione 13, only the ring opening products were observed at 77 K.

Keywords: flash vacuum thermolysis; retro-ene; cycloalkenethione; vinylthioketene

Conjugated cycloalkenethiones have been prepared when stabilized by the presence of a methyl group in the β-position [1]. The generation by flash vacuum thermolysis (FVT) of the most reactive thioketones has been also reviewed [2]. Among these compounds, the simplest unsaturated cycloalkenethiones have been little investigated [3].

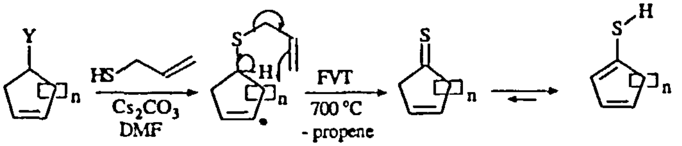
Starting from the sulfanyl precursors **1**, **2**, prepared as in the scheme below, we initiated the generation of conjugated cycloalkenethiones **3**, **4**, **5**, by retro-ene reaction under FVT conditions [4]. The structure of these products was assigned on the basis of the infra-red, ultra-violet spectra at 77 K, NMR ^1H spectrum at -100 °C, and mass spectra.



n	cpd
1	3
2	4
3	5

To facilitate the retro-ene reaction, and reduce the thermolysis temperature, the allyl group is replaced by a propargyl one [5]. In that case, the β-elimination reaction, forming cycloalkadiene and propargyl mercaptan, is quite non-existent.

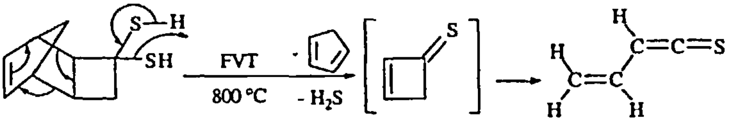
The preparation of non-conjugated cycloalkenethiones (**8**, **9**), was undertaken.



n	Y	n	Cpd	n	Cpd	n	Cpd
1	OMs	1	**6**	1	**8**	1	**10**
2	Br	2	**7**	2	**9**	2	**11**

The sulfanyl precursors **6** and **7** were thermolysed at 700 °C. Infra-red study at 77 K, shows a broad band at 2460 or 2500 cm^{-1} corresponding to the thiol **10** and **11**, respectively. Tautomerisation of the thioketones **8** and **9** occurred rapidly, the presence of which is confirmed by UV/visible spectroscopy at 77 K. The presence of conjugated cyclopentenethione **3** is detected in the NMR spectra of the FVT products of **6**.

With regard to the preparation of cyclobutenethione **13**, due to the instability of cyclobutenic cycles, we performed simultaneously β-elimination and retro Diels- Alder processes to generate the C=S and C=C bonds. The gem-dithiol **12** was prepared according to a general procedure [7].



12 **13** **14**

The products of thermolysis at 800 °C, were trapped at 77 K. Cyclobutenethione **12** itself wasn't detected. In fact, vinylthioketene **13** (given by ring opening) acts in accordance with typical absorption bands in infra-red at 1740 and 1600 cm^{-1} [6].

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