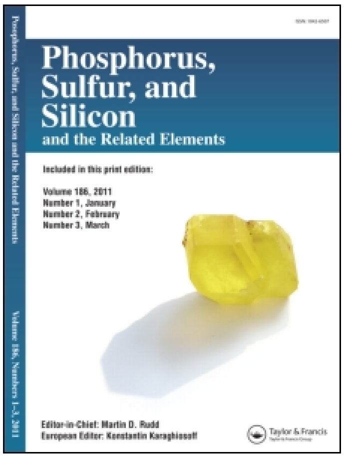

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SYNTHESIS OF THIOALDEHYDES, THIOKETONES AND THIOKETENES BY FLASH VACUUM THERMOLYSIS

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SYNTHESIS OF THIOALDEHYDES, THIOKETONES AND THIOKETENES BY FLASH VACUUM THERMOLYSIS

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Abstract Our last results concerning the synthesis of reactive thiocarbonyl componds using the retro-Diels-Alder reaction under flash vacuum thermolysis conditions are presented.

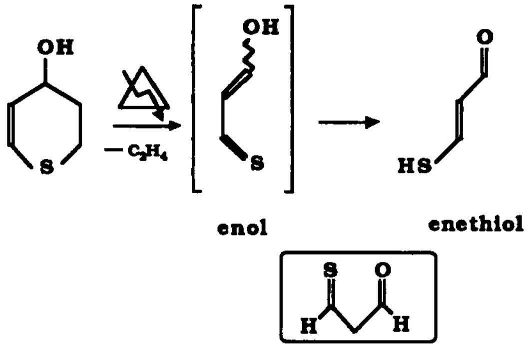
INTRODUCTION

Flash vacuum thermolysis is an efficient gas phase method for the synthesis of reactive species[1], allowing spectroscopical and chemical investigations, either in the gas phase or after trapping at low temperature. We report herein some applications of this technique to the synthesis of thioaldehydes, thioketones and thioketenes.

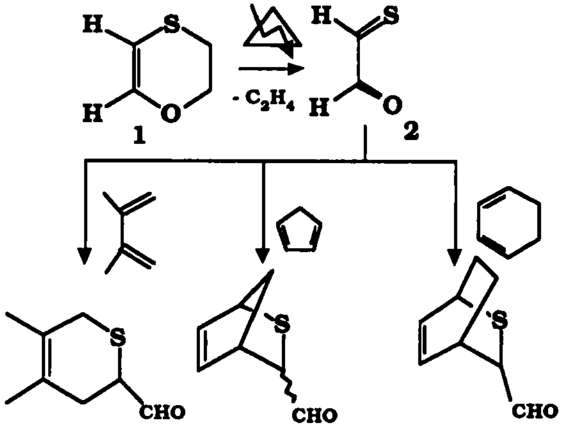
OXOTHIOALDEHYDES AND THIOKETONES

The retro-Diels-Alder reaction of simple cyclohexenes and heterocyclohexenes can, in principle, be used to synthesize conjugated dienes and heterodienes. However, due to the high temperatures required for such cycloreversions, this remained scarcely used until now.

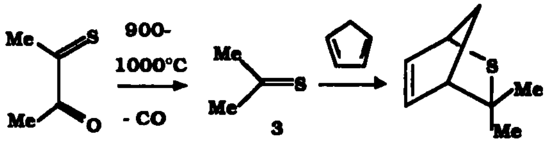
It has been shown in our laboratory[2] that the FVT of 2,3-dihydro-4-hydroxythiin gives transient 3-hydroxypropenethial, the enol form of the simplest β-oxothiocarbonyl compound, 3-thioxopropanal. However the isolated product was 3-mercaptopropenal, the enethiol form of 3-thioxopropanal.



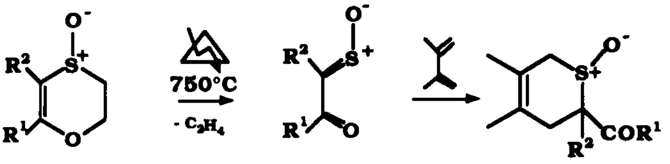
In the case of α-oxothiocarbonyl compounds, the needed precursors were the easily available 2,3-dihydro-1,4-oxathiins. For instance, we have thermolysed the unsubstituted heterocycle **1** at 850°C. Transient thioxoethanal **2** was formed and trapped with various dienes in the gas phase^3.

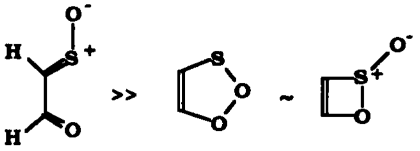


When submitted to FVT experiments at higher temperature (900-1000°C), α-oxothiocarbonyl compounds are cleaved to carbon monoxide and simple thials or thiones. For example, we have been able to trap propanethione **3** by cyclopentadiene :



We have also studied the FVT of dihydrooxathiin S-oxides. In this case α-oxosulfines were obtained and characterised by low temperature IR spectroscopy, ^{1}H NMR and/or trapping with 2,3-dimethylbuta-1,3-diene.



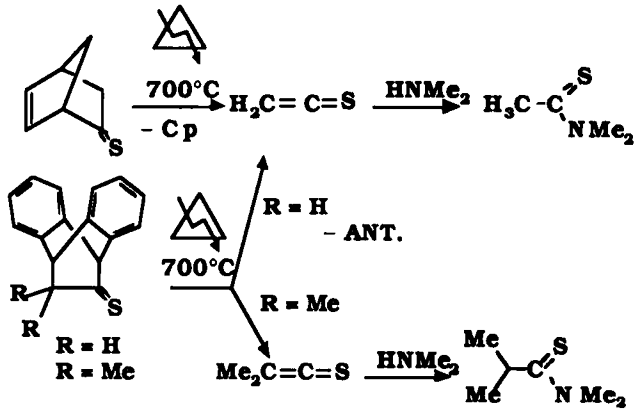


Furthermore, the relative stability of the parent compound (thioxoethanal S-oxide) and of its cyclic isomers was evaluated using MNDO calculations (in collaboration with G. Pfister-Guillouzo, Pau). It was found that the open stucture is more stable than the cyclic ones by 42 kcal mol^{-1}. The β-sultine and 3-thia-1,2-dioxole were found at nearly the same energetic level.

THIOKETENES

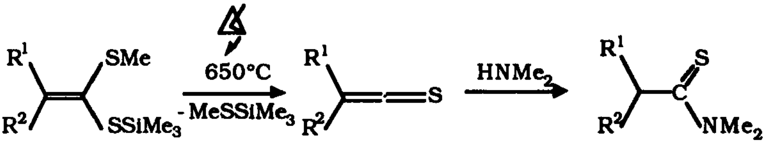
We have applied the retro-Diels-Alder reaction under FVT conditions to the synthesis of reactive thioketenes[4].

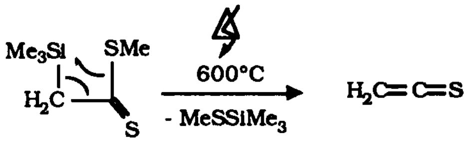
The precursors were obtained by thionation of the corresponding ketones, and submitted to FVT at 700°C.



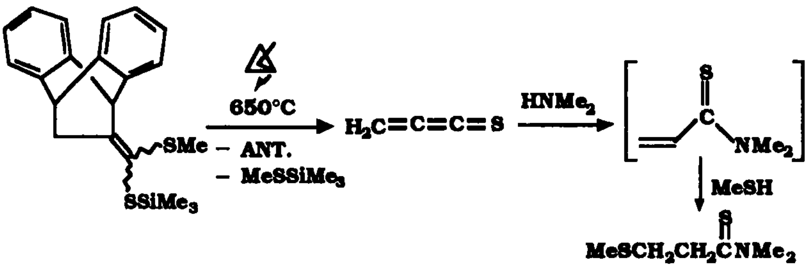
The obtained thioketenes were characterized by low temperature IR spectroscopy ($\nu_{CCS} \approx 1750\ cm^{-1}$), and trapped in the gas phase by dimethylamine.

Alternatively, these heterocumulenes can be obtained by elimination of methylthiotrimethylsilane from silylated ketenedithioacetals, and in the case of thioketene itself, from methyl trimethylsilyldithioacetate.





Association of a retro Diels-Alder reaction with an elimination of $MeSSiMe_3$ gave propadienethione. Upon trapping with $HNMe_2$, this cumulene gave a thioacrylamide which reacted with the methanethiol formed in situ : the isolated product was a β-methylthio-thioamide.



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