

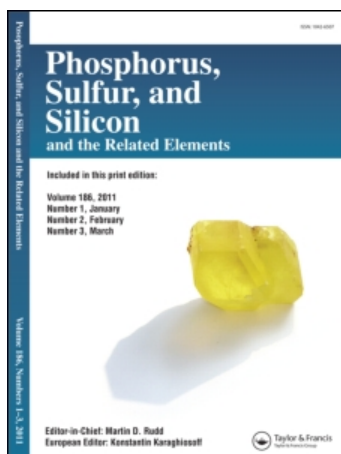
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New Reactions of Sulfur-Centered 1,3-Dipoles Generated from Thioketones in Three-Component Reactions with Phenyl Azide and an Electron-Deficient Dipolarophile

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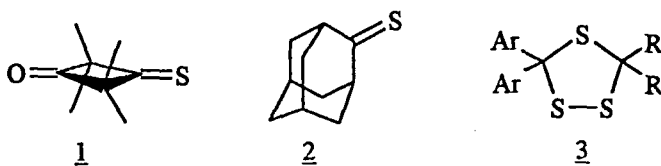
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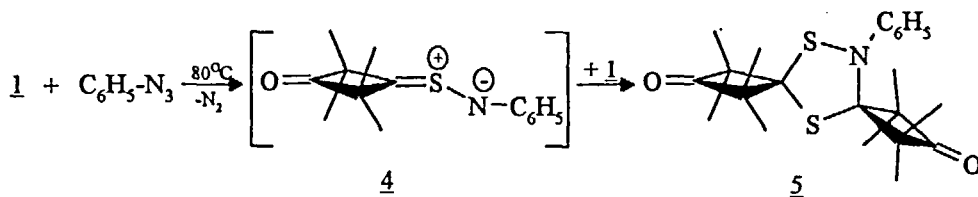
ABSTRACT: Reactions of cycloaliphatic thioketones with phenyl azide in the presence of an electron-deficient C-C-dipolarophile have been studied. It was shown that the course of the reactions and the structures of the products depend strongly on the type of the dipolarophile used. Only in the case of fumaronitrile the interception product of the intermediate thiocarbonyl-S-imide was obtained.

KEY WORDS: thioketones, thiocarbonyl-S-imides, thiocarbonyl-S-ylides, 1,3-dipolar cycloaddition, 1,5-electrocyclization.

Previously we described the behaviour of cycloaliphatic thiones **1** and **2** in three-component systems with phenyl azide and an aromatic thioketone; thiofluorenone and thiobenzophenone were involved in these studies. At 80°C, evolution of nitrogen was observed and mixed trithiolanes **3** were isolated as the major products [1].



The two-component reaction of sterically crowded **1** with phenyl azide afforded 1,4,2-dithiazolidine **5** as the product of interception of the intermediate thiocarbonyl-S-imide **4** by the unconsumed starting material **1** [2].



The goal of the present study was to determine if the intermediate **4** can also be

The ν_{CO} region in the I.R. spectra of the title compounds shows the existence of a doublet whose relative intensities are practically constant in solvents of low dielectric constant such as $n\text{-C}_6\text{H}_{14}$, CCl_4 and CHCl_3 , being the higher frequency component the most intense. A reversal of the relative intensities of the doublet is observed in more polar solvents CH_3CN and DMSO . This unusual effect is not an evidence of the rotational isomerism. However, the comparison between the fundamental and the 1st overtone ν_{CO} regions in CCl_4 indicates the existence of the cis-gauche isomerism. The agreement between the *ab-initio* relative rotamer populations and the I.R. data for compound (1) indicates that the higher frequency component of the doublet for the title compounds corresponds to the more abundant polar cis rotamer and the lower one is the less polar gauche rotamer.

The decrease of the cis rotamer population in solvents of high polarity along with the unusual negative carbonyl cis shifts ($\Delta\nu_{\text{C}}$) of the title compounds suggest the existence of an intramolecular complex between the $\text{C}=\text{O}$ and $\text{S}=\text{O}$ dipoles for (1) and (2). This complex should dissociate in more polar solvents favoring the gauche rotamer.

The I.R. data of (1) and (2) are in good agreement with both the *ab-initio* calculations which indicate a predominance of the cis conformer over the gauche one and the X-ray diffractogram of (1) which shows that the cis rotamer is the only one present in the solid state. The reversal of the $n_{\text{O}(\text{CO})}/\pi_{\text{SO}}$ energy levels ordering in the P.E. spectrum of (1) along with the increase of the $n_{\text{O}(\text{CO})}$ and the decrease of the π_{SO} ionization energy values in relation to the reference compounds are in line with the ground state $\text{SO} \leftarrow \text{O}/\text{CO}$ charge transfer which stabilizes the cis conformation. This interaction is supported by shorter intramolecular contact between the oxygen and the sulfur atom in relation to the sum of their van der Waals radii.

It seems reasonable to admit that the cis rotamers of the α -sulfinylacetophenones are more stable than the same rotamers in the α -sulfinylacetones due to an increasing carbonyl oxygen electron density in the acetophenone derivatives as a consequence of the π_{ϕ} and π_{CO} conjugation which leads to a stronger $n_{\text{O}(\text{CO})} \rightarrow \text{SO}$ charge transfer complex.

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- 3) P.R.Olivato, S.A.Guerrero and E.Bueno (to be published).