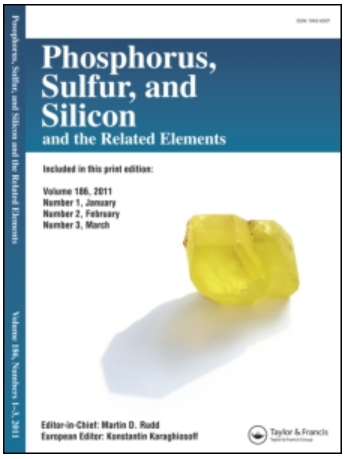

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The Formation of Thiocarbonyl Compounds by The Thermal Decomposition of Heteroaryl Substituted Sulfoxides

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The thermal reaction of phenacyl sulfoxide bearing some heterocycles in the presence of butadiene afforded the thiapyarn derivatives, which is considered to be formed by the Diels Alder reaction of diene with thiocalbonyl compound.

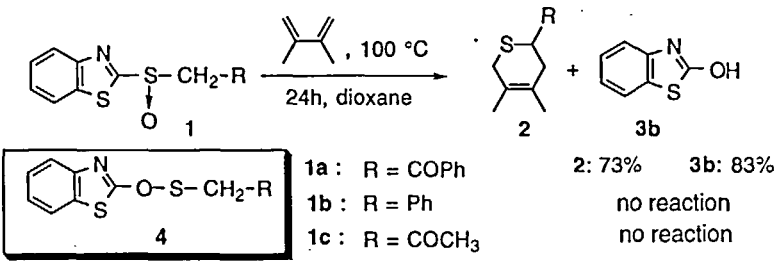
INTRODUCTION

It is well kown that, in usual alkyl system, Ei elimination fo sulfoxides having β-hydrogen affords sulfenic acid and olefin, and in particuler system, such as allylic and acetylenic sulfoxide, some time the rearrangement reaction takes place.

In this paper, we report that the thermal reaction of phenacyl sulfoxide bearing heterocycles, such as benzothiazolyl and 1,2,3,4-tetrazolyl groups in the presence of 2,3-dimethyl-1,3-butadiene afford dihydro thiapyran derivatives.

RESULTS AND DISCUSSIONS

Recenty, we found that the thermal reaction of 2-benzothiazolyl phenacyl sulfoxide (**1a**) in dioxane at 100°C for 24h in the presence of 10 eq. of 2,3-dimethyl-1,3-butadiene affrded 6-benzoyl-5,6-dihydro-3,4-dimethyl-2*H*-thiapyran and hydroxy substituted hereroaromatics in good yield. (Scheme 1)



Scheme 1

The dihydro-thiapyran derivatives is considered to be formed by the reaction of diene with thioaldehyde formed by the decomposition of phenacyl sulfoxide derivatives.

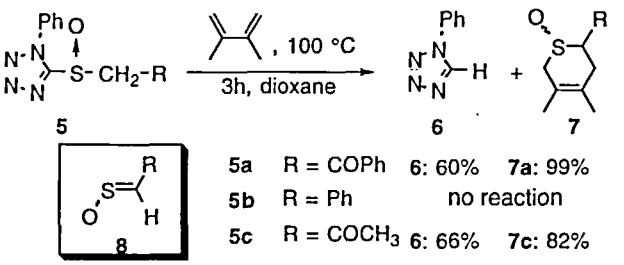
As synthetic procedures for thioaldehyde, the dehydrochlorination from sulfenyl

halide[1] and the photolytic reaction of phenacyl sulfide[2] are well known.

In order to study the scope and the limitations of these reaction, the sulfoxide derivatives were prepare and the thermal reaction were carried out. However, the thermal reaction of benzyl (**1b**) and even ethoxycarbonylmethyl sulfoxide (**1c**) bearing benzothiazoly group did not proceed at all.

The only plausible mechanism for this reaction seems to proceed through sulfenic ester intermediate **4** in view of the product formation, though the direct detection of the intermediate by NMR spectrometry was not successful, probably suggesting the rapid decomposition of sulfenic ester intermediate **4** to products. In this reaction mechanism nitrogen containing heteroaryl group would provide the sufficient driving force for the rearrangement to the corresponding sulfenic ester **4** and then also for the elimination reaction forming the stable hydroxy heteroaromatics.

In order to get further examples of this reaction, the thermal reaction of the sulfoxide bearing other heterocycles were carried out under simillar condition. Unexpectedly, the reaction of phenacyl sulfoxide **5a** and acetyl methyl sulfoxide **5c** afford **6** and dihydro thyapyran S-oxide derivatives **7a** and **7c**, respectively, which is considered to be formed by the Diels-Alder reaction of diene with sulfine formed initially by the thermal decomposition of the sulfoxide, while the reaction of 5-(1-phenyl)-1,2,3,4-tetrazolyl benzyl sulfoxide did not proceed at all. (Scheme 2)



Scheme 2

From these preliminaly results the plausible mechanism of this reaction is considered as following: first the nitrogen of heteroaryl group of the sulfoxide abstracts a α-hydrogen atom to give the intermediate and succeedingly this intermediate affords the sulfine **8** by elimination of a heterocycle. Finally the unstable sulfine **8** formed initially is soon trapped by the hetero-Diels-Alder reaction with 2,3-dimethyl-1,3-butadiene.

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