

[D0002]

COMPARISON OF THE REACTIVITY BETWEEN NITROTHIOPHENES AND NITROSELENOPHENES IN POLAR CYCLOADDITION REACTIONS.

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Abstract. Dienophilic behaviour of nitrothiophenes and nitroselenophenes towards Diels-Alder reactions with dienes of medium nucleophilicity is studied under thermal conditions. While nitrated thiophenes reacted via Hetero Diels-Alder, nitrated selenophenes followed the normal process.

Keywords: nitrothiophenes, nitroselenophenes, Diels-Alder

Introduction

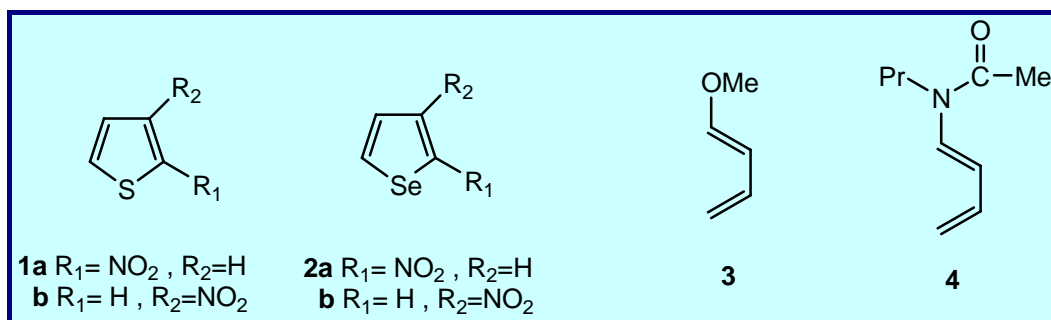
The nitrocompounds are versatile reagents whereby they are object of extensive applications in organic synthesis due to this substituent can be transformed in one great variety of functional groups.

We have recently reported that aromatic nitroheterocyclic act as dienophiles in Diels-Alder reactions.^{1,2,3} A very strong electron-acceptor group, such as nitro group, push the dienophilic character of these heterocyclics and owing to this substituent is easily extruded under thermal conditions makes this reaction sequence a simple method of organic compound's families with heteroatom rings preparation.

In this manuscript, we would like to compare the different behaviour of nitrothiophenes and nitroselenophenes in thermal reaction with 1-methoxy-1,3-butadiene and 1-*N*-acetyl-*N*-propylamino-1,3-butadiene as dienes.

Results and discussion

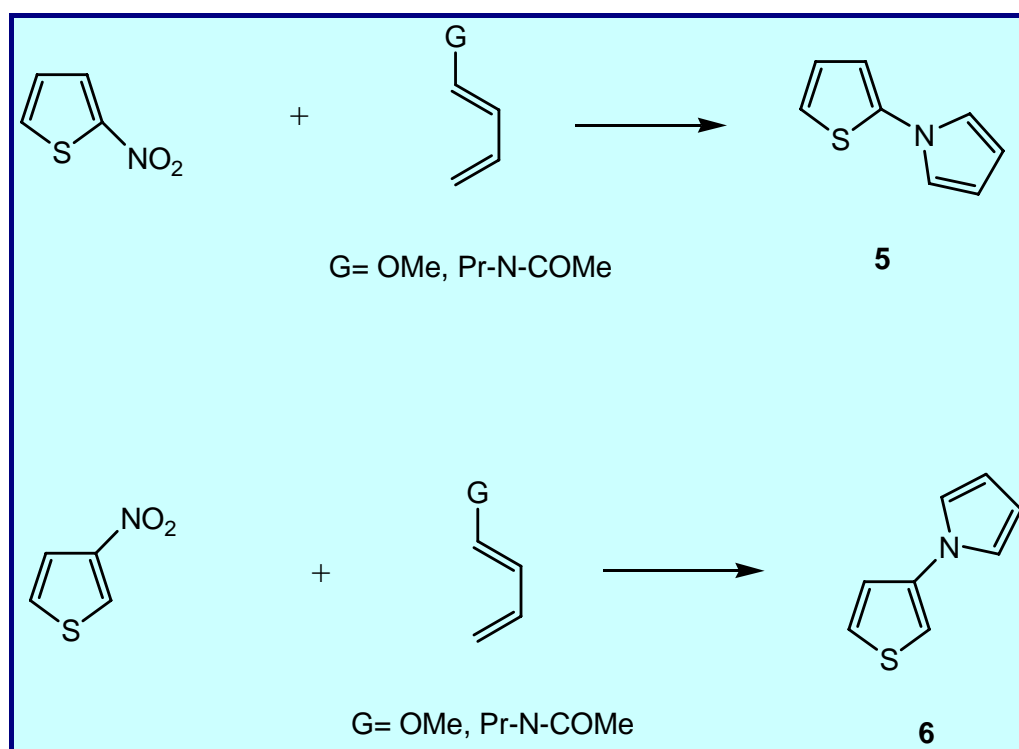
The dienophiles used were 2-nitrothiophene (**1a**), 3-nitrothiophene (**1b**), 2-nitroselenophene (**2a**) and 3-nitroselenophene (**2b**). 1-Methoxy-1,3-butadiene (**3**) and 1-*N*-acetyl-*N*-propylamino-1,3-butadiene (**4**) were chosen as diene partners (Scheme 1).



Scheme 1

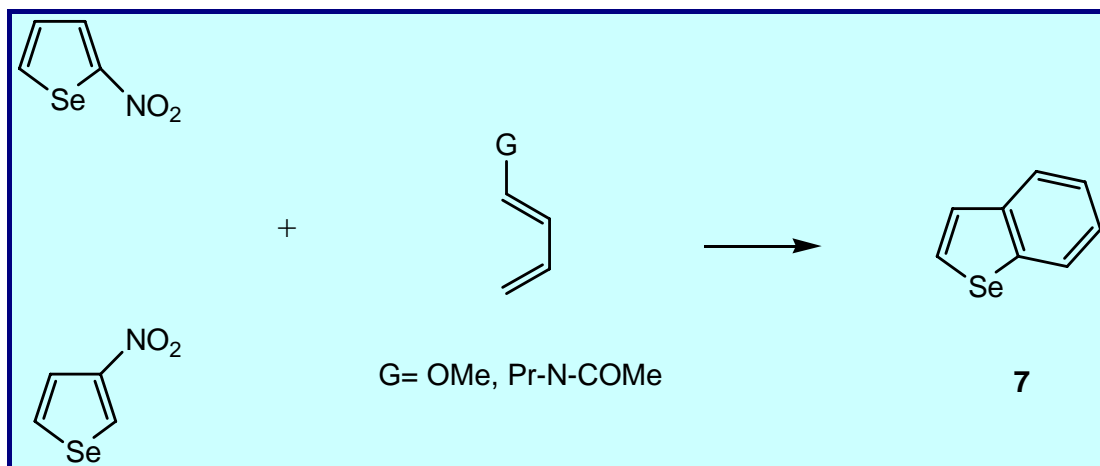
The thermal reactions of 2-nitrothiophene **1a** with **3** in a sealed ampoule at 150 °C or 200 °C for 72 h using benzene as solvent afforded the pyrrolyl derivative **5** as unique product. It is assumed that these nitroaromatic compound can react through the heterodienophilic fragment NO by a hetero Diels-Alder reaction (HAD). This unexpected behaviour was also found with nitronaphthalenes as dienophiles.⁴ Likewise, exposure of **1a** to dienamide **4** produced the same compound **5** with very good yield. It is necessary to take in account that in these processes the group G is losted in the aromatization.

Similarly, in the reactions under thermal conditions of 3-nitrothiophene **2b** with **3** and **4** the corresponding pyrrolyl-thiophene **6** are obtained (Scheme 2).



Scheme 2

On the other hand, exposure under thermal conditions of 2-nitroselenophene **2a** with **3** afforded the benzoselenophene **7** with moderate yield (Scheme 3).



Scheme 3

This fact shows the nitroselenophene behaviour as normal dienophile.² The ease of thermal extrusion of nitrous acid accompanying the DA process. Moreover, the DA reactivity of nitroselenophene appears as opposed to that reported for nitrothiophene when isoprene was used as diene.⁵ No pyrrolyl-derivatives from hetero DA were detected.

Again, the same conduct is observed when **2a** reacted with dienamide **4**. The results of this type of DA reactions indicate a possible sequential pathway where the ease of thermal extrusion of nitrous acid accompanying the DA reaction would lead to the 4-substituted-dihydro adduct, which would undergo thermal aromatization by losing the *N*-acetyl-*N*-alkylamino substituent.⁶ Identical results are observed when dienophile **2b** reacted with dienes **3** and **4**.

Conclusions

The above results demonstrate that the presence of nitro group in these dienophilic structures induce two possible reaction paths: normal Diels-Alder reaction or hetero Diels-Alder reaction. A combination of structural factors, the aromaticity is one of them, are responsible of these behaviours.^{7,8}

Acknowledgement

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