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Selenophene derivatives as dienophiles in diels-alder reactions

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Introduction

It has been demonstrated that aromatic heterocycle compounds, for example, furan, pyrrol and thiophene, despite its aromaticity and relative chemical inertia can act as dienophiles in cycloaddition reactions (Wenkert and Piettre, 1988; Wenkert *et al.*, 1988; Della Rosa *et al.*, 2004, 2005). Such behaviour is verified when the mentioned substrates are substituted by electron-withdrawing groups, which induce their dienophilic behaviour in Diels-Alder reactions with normal electron requirement.

In this investigation we have extended the study of these atypical dienophiles using selenophene derivatives (2-nitroselenophene and 2-acetyl-4-nitroselenophene) in Diels-Alder reactions, compared to dienes of different nucleophilicity [isoprene, 1-methoxy-3-(trimethylsilyloxy)-1,3-butadiene and 1-(diethylamino)-3-(*tert*-butyldimethylsilyloxy)-1,3-butadiene] (Fig. 1). This allows us to draw conclusions regarding the participation of this new dienophile in Diels-Alder reactions, and likewise, to perform a comparative study with the rest of the heterocycles used.

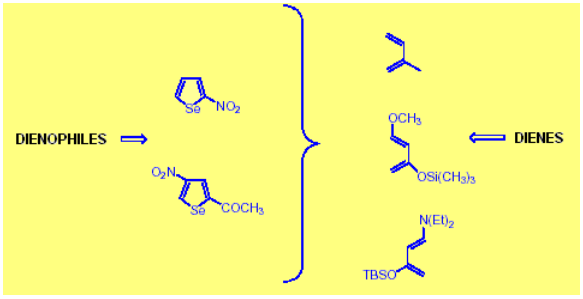

Figure 1

Experimental

Experiences were carried out in closed ampules, using benzene as solvent. Reaction time (72 h) and work temperatures (in the range of 120ºC-200ºC) were fixed taking into account the stability of the different dienes used. The work-up of the reaction was carried out by separation in a silicagel column chromatography, using *n*-hexane-ethyl acetate as eluent.

Products were identified by spectroscopic techniques (NMR, IR and MS).

Results y Discussion

The reactions of 2-nitroselenophene are shown in Fig. 2.

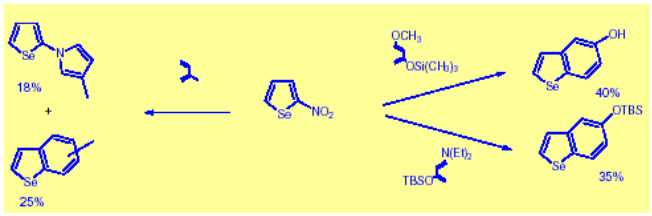

Figure 2

The product of the hetero Diels-Alder reaction (*N*-selenoarylpyrrol) was in a low yield, when using isoprene as diene, *vs* the adduct of the normal Diels-Alder reaction, unlike the behaviour shown by 2-nitrothiophene. In the case of more reactive dienes the result is in agreement with that expected, obtaining bicycles derived from the Diels-Alder reaction, followed by nitrous acid extrusion and aromatization.

When the acetylated selenophene derivative at position 2 with nitrogen at position 4 was used, normal addition's products were observed without taking into account the type of diene used (Fig. 3).

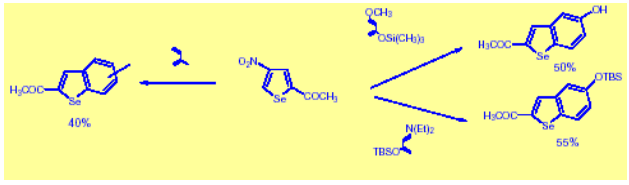

Figure 3

It should be noted the regioselectivity observed in the adducts obtained with Danishefsky's diene and that of Rawal.

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Conclusions

►It has been shown the dienophilic nature of nitro derivatives of selenophene when involved in cycloaddition reactions with dienes of different reactivity.

►*A priori*, and unlike expected, these dienophiles show a reactive behaviour, which is in agreement with that of nitrofurans than nitrothiophenes.

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