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INTRAMOLECULAR DIELS-ALDER REACTION OF FURANS WITH ALLENYL ETHERS FOLLOWED BY METHYLTHIO GROUP 1,4-REARRANGEMENT

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Key Words: Intramolecular Diels-Alder Reaction; Furans; Allenyl Ether; Methylthio Group 1,4-Rearrangement.

Abstract: The base-catalyzed intramolecular Diels-Alder reactions of the furfuryl propargyl ethers **1a-1e** gave compounds **6a-6e** as the major product respectively, a novel reaction involving an intramolecular Diels-Alder reaction followed by a methylthio group 1,4-rearrangement.

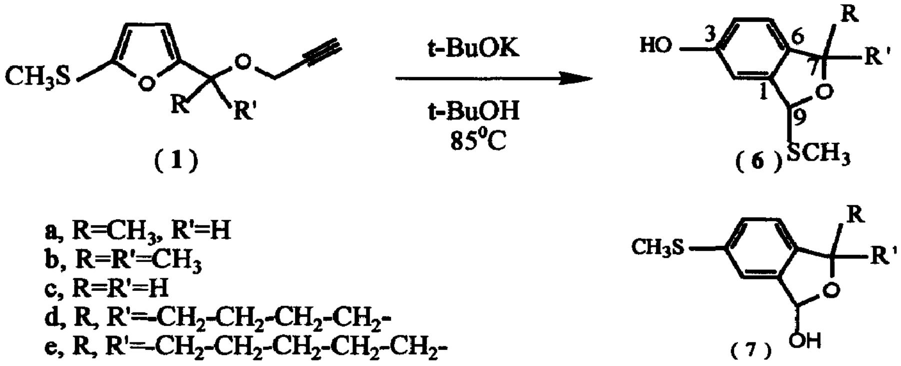
The intramolecular Diels-Alder reaction has been a central topic in modern organic synthesis.[1] The vast majority of the work reported in this area has dealt with reactions utilizing ethylenic and acetylenic dienophiles. However, the intramolecular Diels-Alder reaction of allene has received less attention.[2] Several years ago, Kanematsu et al demonstrated that the allene unit is a versatile synthon as a dienophile in the intramolecular cycloaddition due to the absence of unfavorable nonbonded interactions in the transition state.[3] Afterward, they developed a furan ring transfer reaction via the intramolecular Diels-Alder reaction of furan diene and allenyl ether dienophile.[4] For the purpose of furan ring transfer reaction, in all of their cases there were only one carbon atom and one oxygen atom connection between the furan diene and the allene dienophile for the cycloaddition.

In order to understand the effect of the chain length between the furan diene and the allenyl ether dienophile on the structure and reactivity of the cycloadducts, we accomplished the intramolecular Diels-Alder reactions by varying the chain length.[5] In this letter we report here a novel reaction involving an intramolecular Diels-Alder reaction followed by a methylthio group 1,4-rearrangement.

Treatment of the propargyl ether **1a** with potassium *t*-butoxide in refluxing *t*-butyl alcohol (85 °C) for five hours gave **6a** in 90% yield. The ^{1}H and ^{13}C nmr spectra of **6a** revealed that **6a** was a mixture of two diastereomers in a ratio of 1:1. The ^{1}H nmr spectrum of **6a** showed two singlets at δ 1.98 and 1.87 for the methylthio protons, two doublets at δ 1.49 and 1.41 for the methyl protons, two singlets at δ 6.38 and 6.29 for the methine proton at C_9 and two quartets at δ 5.39 and 5.27 for the methine proton at C_7. The large chemical shift difference (0.11 ppm) for the methylthio protons indicates that the methylthio group locates on C_9 rather than on C_3 of the aromatic ring.

Reaction of the propargyl ethers **1b**,**1c**, **1d** and **1e** under the same reaction conditions gave compounds **6b**, **6c**, **6d** and **6e** as the major product respectively, Scheme I.

Scheme I

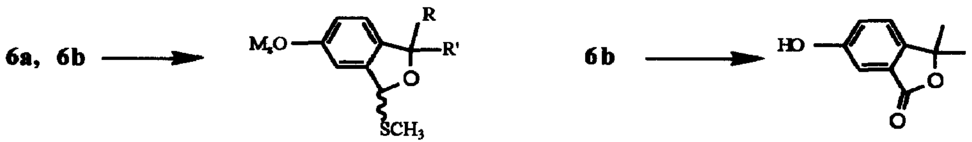


(1) (6) (7)

a, $R=CH_3$, $R'=H$
b, $R=R'=CH_3$
c, $R=R'=H$
d, R, $R'=-CH_2-CH_2-CH_2-CH_2-$
e, R, $R'=-CH_2-CH_2-CH_2-CH_2-CH_2-$

To prove the structure of the product of this reaction to be **6** instead of **7**, some chemical transformations of the reaction products were performed. Mesylation of **6a** and **6b** with methanesulfonyl chloride in pyridine at room temperature for 3 hours gave compounds **8a** and **8b** respectively. The ^1H nmr spectra of **8a** and **8b** revealed that the aromatic protons shifted down field from δ 6.96-6.71 to 7.22-7.10. Oxidation of **6b** with *m*-chloroperbenzoic acid in dichloromethane at room temperature gave the lactone **9**, Scheme II. Finally, the structure was proved by X-ray analysis[6] of the crystalline compound **6b** (Figure 1).

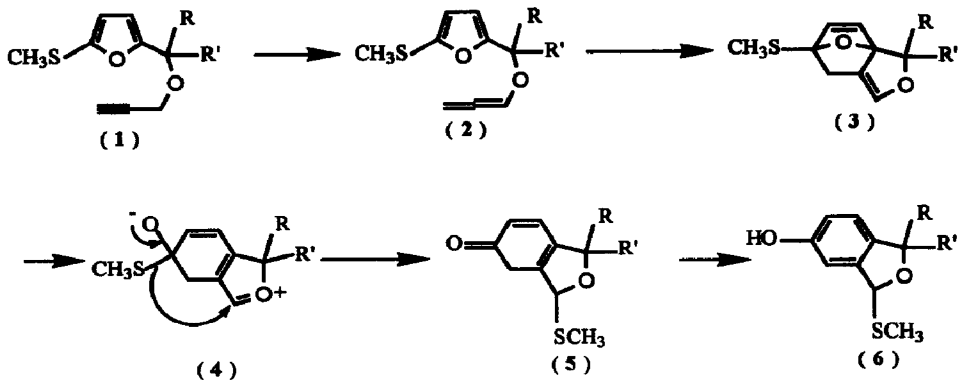
Scheme II



8a, 8b **9**

A mechanism was proposed for this reaction. The intramolecular Diels-Alder reactions of **1a**-**1e** gave **6a**-**6e** as the major product respectively, presumably via the corresponding allenyl ethers **2a**-**2e** and the cycloadducts **3a**-**3e**. We proposed that the cycloadducts are highly strained and they easily undergo ring opening of the bridged oxygen atom to form the zwitter ions **4a**-**4e** as the reaction intermediates. Repelling the methylthio group by the alkoxide ion followed by nucleophilic attack of the methylthio group on the oxonium ion gave the rearranged intermediates **5a**-**5e**, which underwent aromatization to give **6a**-**6e** as the major product respectivity, Scheme III.

Scheme III



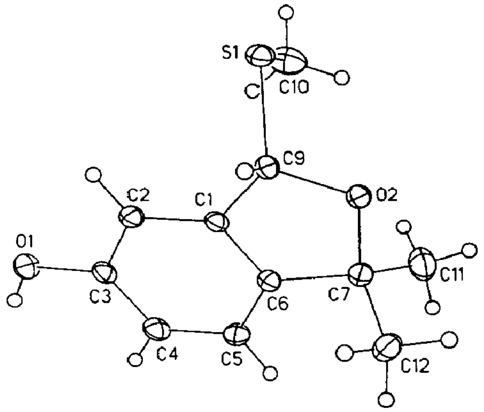


Fig.1. X-ray structure of **6b**

Thus we found a novel reaction involving an intramolecular Diels-Alder reaction followed by a methylthio group 1,4-rearrangement.

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6. The final coordinates for the X-ray analysis of **6b** have been deposited at Cambridge.

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