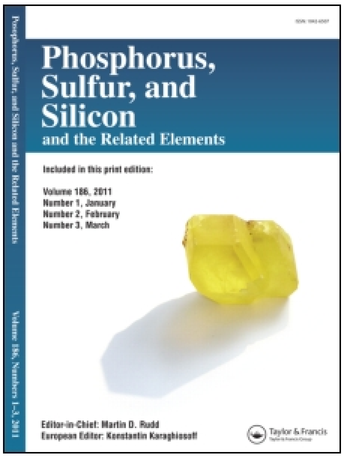

Phosphorus, Sulfur, and Silicon and the Related Elements

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Electrophilic Cyclization of Alkenyl β-Dicarbonyl Compounds: A Comparative Study

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Electrophilic Cyclization of Alkenyl ß-Dicarbonyl Compounds: a Comparative Study

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This work describes a comparative study between PhSeBr, $ArTeCl_3$and I_2 toward the electrophilic cyclization of some unsaturated β-keto esters and β-diketones. The oxidation/elimination reaction of the obtained selenides was also studied.

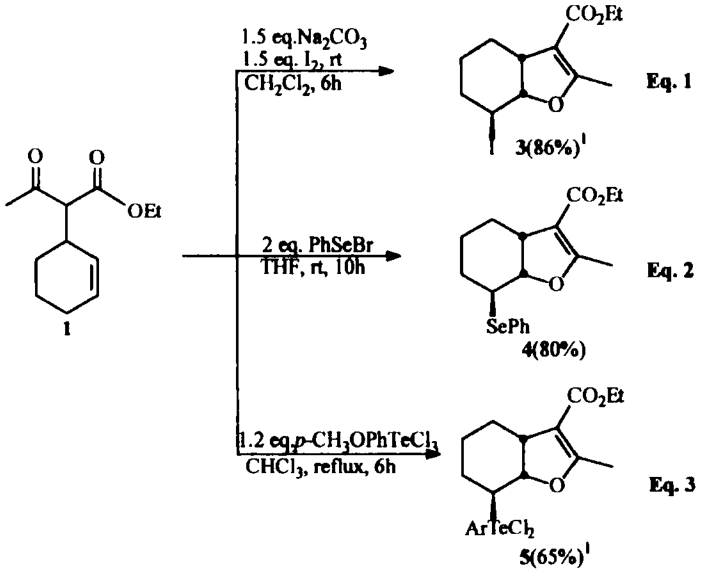
Keywords: Cyclofunctionalization; Selenium; Iodine; Cyclic ethers; β-Dicarbonyl compounds

INTRODUCTION

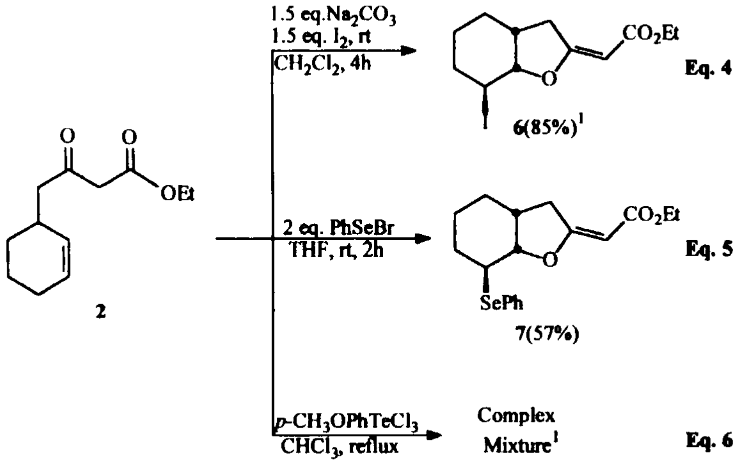
In recent works we reported the results of the telluro- and iodocyclization of a series of alkenyl substituted β-keto esters[1], as well as the iodocyclization of their analogous β-enamino esters[2]. Among the substrates investigated by us are the β-keto esters **1** and **2**, which gave the cyclic products **3** and **6**, respectively, in good yields, when treated with iodine (Scheme 1, Eq.1 and 4). However, only the substrate **1** was able to undergo tellurocyclization, while **2** gave decomposition products under the same reactional conditions (Scheme 1, Eq. 3 and 6)[1]. The reaction of the β-diketone **8** with p-methoxyphenyltellurium trichloride was also performed by us[3] (Scheme 2, Eq. 2).

Although the selenocyclization of several alcohols and carboxylic acids is a well-known reaction[4], there are not many examples dealing with the reaction of β-dicarbonyl compounds with selenium electrophiles[5]. These substrates can react through the enolic form, to give the product of an O-cyclization (kinetic control), or through the keto form, giving the thermodynamically controled product of a C-cyclization, depending upon the reaction conditions. The reaction of the β-keto esters **1-2** and of the β-diketones **8-9** with electrophilic selenium reagents has not been reported yet.

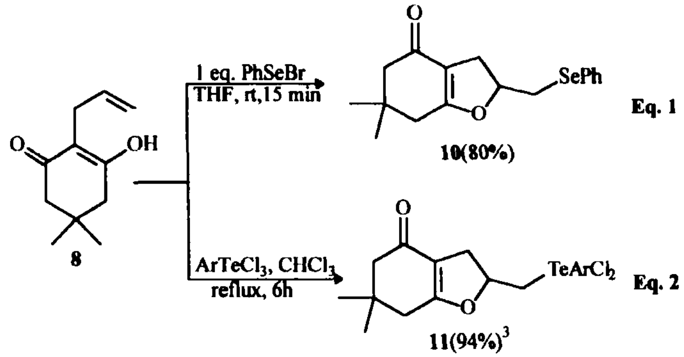
We then decided to study the behavior of these substrates toward phenyl selenenyl bromide, as a matter of comparison between this reagent and the others ($ArTeCl_3$ and I_2) previously studied. The results are shown in Schemes 1(Eq. 2 and 5) and 2(Eq. 1 and 3). The diketone **9** was also submitted to treatment with iodine, giving the cyclic product **13** (Scheme 2, Eq.4).

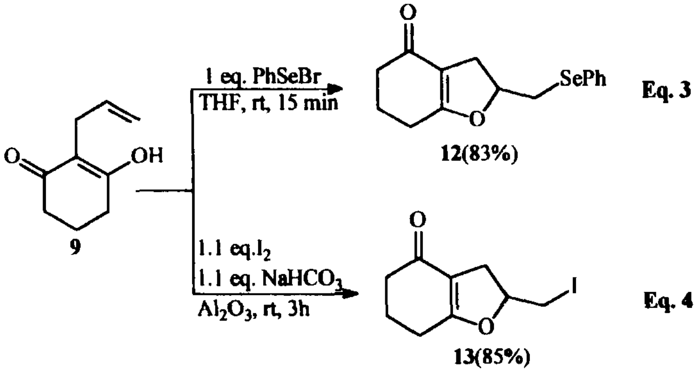


SCHEME 1



SCHEME 2



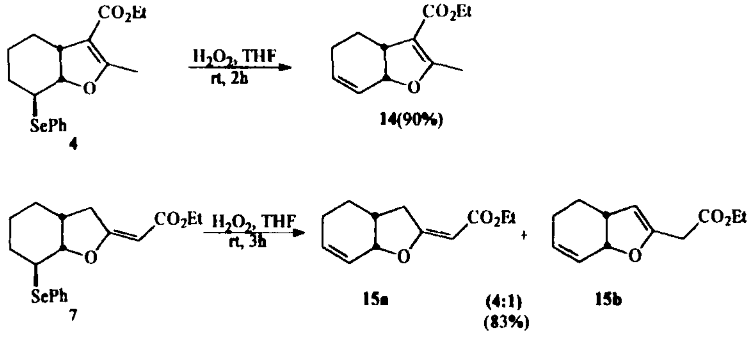


The starting alkenyl-substituted β-dicarbonyl compounds **1**, **2**, **8** and **9** were obtained by known procedures[6]. All the cyclization products were identified by ^{1}H and ^{13}C-NMR spectroscopy and by mass spectrometry.

It is noteworthy that the cyclization of the substrate **2** led exclusively to the E-exocyclic double bond, as deduced by ^{1}H and ^{13}C-NMR analysis[7,8]. The bicyclic products obtained from **1** and **2** exhibit *cis*-fused rings, as a consequence of the mecanism of the electrophilic cyclization, which proceeds *via* a *trans*-diaxial addition to the double bond.

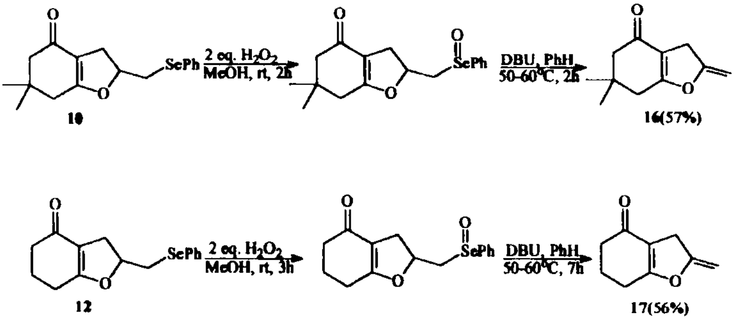
One of the most useful applications of the selenium chemistry is the oxidation-elimination reaction of organic selenides, which smoothly furnishes olefins, usually in very good yields.

Thus, the selenides **4** and **7**, when treated with H_2O_2 in THF promptly gave the corresponding olefins, in good yields, as shown in Scheme 3. The products **14** and **15a** thus obtained are identical to those previously prepared by dehydroiodination of **3** and **6** [9].



SCHEME 3

Since the selenides **10** and **12** are primary, they do not undergo elimination under the usual conditions[10]. Thus, the intermediate selenoxides were just isolated and then treated with DBU in benzene[11], to furnish the elimination products **16** and **17**, in moderate yields, as shown in Scheme 4.



SCHEME 4

In conclusion, the cyclization reactions here described seem to be of general validity, the yields ranging from moderate to very good.

ACKNOWLEDGEMENTS

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