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# Phosphorus, Sulfur, and Silicon and the Related Elements

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## Electrophilic Cyclization of Alkenyl B-Dicarbonyl Compounds: a Comparative Study

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This work describes a comparative study between PhSeBr, ArTeCl<sub>3</sub>and I<sub>2</sub> toward the electrophilic cyclization of some unsaturated  $\beta$ -keto esters and  $\beta$ -diketones. The oxidation/elimination reaction of the obtained selenides was also studied.

Keywords: Cyclofunctionalization; Selenium; Iodine; Cyclic ethers;  $\beta$ -Dicarbonyl compounds

### INTRODUCTION

In recent works we reported the results of the telluro- and iodocyclization of a series of alkenyl substituted  $\beta$ -keto esters<sup>[1]</sup>, as well as the iodocyclization of their analogous  $\beta$ -enamino esters<sup>[2]</sup>. Among the substrates investigated by us are the  $\beta$ -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)<sup>(1)</sup>. The reaction of the  $\beta$ -diketone **8** with p-methoxyphenyltellurium trichloride was also performed by us<sup>[3]</sup> (Scheme 2, Eq. 2).

Although the selenocyclization of several alcohols and carboxylic acids is a well-known reaction<sup>[4]</sup>, there are not many examples dealing with the reaction of  $\beta$ -dicarbonyl compounds with selenium electrophiles<sup>[5]</sup>. 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  $\beta$ -keto esters 1-2 and of the  $\beta$ -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<sub>3</sub> and I<sub>2</sub>) 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).





The starting alkenyl-substituted  $\beta$ -dicarbonyl compounds 1, 2, 8 and 9 were obtained by known procedures<sup>[6]</sup>. All the cyclization products were identified by <sup>1</sup>H and <sup>13</sup>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 <sup>1</sup>H and <sup>13</sup>C-NMR analysis<sup>[7,8]</sup>. The bicyclic products obtained from 1 and 2 exhibit *cis*-fused rings, as a consequence of the mecanism of the electrophilic

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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 sclenides 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<sup>[9]</sup>.



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





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

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