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## Synthesis of Ketene Butyltelluro(phenylseleno)acetals by the Al/Te exchange reaction.

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Abstract: Hydroalumination of acetylenic selenides occurs regiospecifically and the vinyl alanes obtained as intermediates were transformed into ketene butyltelluro (phenylseleno) acetals by the Al/Te exchange reaction using  $C_4H_9$ TeBr as electrophile. The stereoselectivity of the hydroalumination of chalcogeno acetylenes was confirmed by performing the hydrolysis of the vinyl alane intermediates that results in formation of the correponding Z phenylseleno alkenes with good yields.

Vinylic tellurides are of great interest for chemists since they are precursors of vinyl lithium<sup>1-8</sup> and vinyl copper<sup>8-11</sup> reagents utilized for chain elongation. We have recently developed in our laboratory several methodologies to obtain vinylic tellurides with total control of the regio and stereo chemistry of the products obtained. (*E*)-Vinylic tellurides were formed by the Al/Te<sup>12</sup> or Zr/Te<sup>7,13</sup> exchange reactions, while the isomers of *Z* configuration were obtained by the hydroalumination<sup>12</sup> or by the hydrozirconation<sup>14</sup> of acetylenic tellurides. A new approach to the isomeric 1-(butyltelluro)-1-(organyl) ethenes was also developed by the aluminotelluration of terminal acetylenes.<sup>12</sup> These methodologies permit the preparation of several disubstituted vinylic tellurides that are difficult to prepare by others methods.<sup>2-6,14-16</sup>

We have special interest in the study of the reactivity of an organyltellurium moiety in the presence of another organochalcogene group (Te, Se or S) attached at one double bond since it is expected that tellurium removal using several types of reagents must be an extremely selective reaction. However, few compounds containing these difunctionalizations are known.<sup>8,17-19</sup> Previous attempts to prepare the 1-butyltelluro-2-phenylselenoethenes by the telluroalumination/selenenylation of acetylenes were unsuccessful.<sup>12</sup> On the other hand, Braga et al<sup>18</sup> described the reaction of a selenoacetylene with butylcyano cuprate followed by capture of the intermediate with C<sub>6</sub>H<sub>5</sub>TeBr to give the unique known compound containing the telluro and seleno groups attached to the same sp<sup>2</sup>

carbon atom. The stereochemistry observed by these authors show the tellurium moiety and the alkyl group bonded in adjacent carbons on the same side of the double bond formed. The importance of both vinylic tellurides<sup>20</sup> and vinylic selenides<sup>21,22</sup> as useful synthetic intermediates provided an additional incentive for preparation of the practically unknown ketene butyltelluro (phenylseleno) acetals.<sup>18</sup>

We wish to report here on the synthesis of ketenes butyltelluro(phenylseleno)acetals by the hydroalumination of phenylseleno acetylenes. Treatment of the vinyl alane intermediate 1 with  $C_4H_9TeBr.LiCl^{12}$  results in the formation of a mixture of 2 and 3 in yields indicated in table 1. The Al/Te exchange reaction was performed at room temperature and this transformation was never total, so that the remaining vinyl alane 1 was transformed into the (Z)-vinyl selenide 2 at the aqueous work-up (Table 1; column 4).



Phenylseleno acetylenes (1.0 mmol) were reduced with DIBAL-H in dry hexane (2.0 ml) under reflux for two hours, furnishing the corresponding vinyl alanes 1. After this time, the vinyl alane was treated with a solution of  $C_4H_9TeBr.LiCl^{12}$  (1.0 mmol). When the reaction was stirred for two hours at room temperature after the addition of  $C_4H_9TeBr$  and followed by the addition of water, the yields were poor (never more than 15 %) furnishing as major product the Z-vinylic selenides. When the reaction time was increased to 24 hours, the yields observed were improved substantially (22-50 %), but the Z-vinyl selenides were still isolated (see Table 1; columns 2 and 4). Compounds 2 and 3 were separated by flash chromatography. In other experiments, treatment of vinyl alanes 1 directly with water results as expected, exclusively into the vinylic selenides of Z configuration in good yields (Table 1; column 5). In all cases studied (Table 1), only one regio or stereo isomer was detected by the analytical methods employed (<sup>1</sup>H NMR, <sup>13</sup>C NMR and CG/MS).

Table 1 - Ketenes butyltelluro(phenylseleno)acetals obtained by the Al/Te exchange reaction.					
]	Product <sup>*</sup>	Yield(%) <sup>b</sup>	Vinylic selenide <sup>a,b</sup>	Yield(%) <sup>a,b,c</sup>	Yield(%) <sup>a,b,d</sup>
C <sub>3</sub> H <sub>7</sub>	$= \begin{pmatrix} SeC_6H_5 \\ \\ \\ TeC_4H_9 \end{pmatrix}$	35	C <sub>3</sub> H <sub>7</sub> SeC <sub>6</sub> H <sub>5</sub>	40	60
C₄H <sub>9</sub>	ScC <sub>6</sub> H <sub>5</sub>	31	C <sub>4</sub> H <sub>9</sub> SeC <sub>6</sub> H <sub>5</sub>	43	65
C <sub>6</sub> H <sub>13</sub>	SeC <sub>6</sub> H <sub>5</sub>	50	C <sub>6</sub> H <sub>13</sub> SeC <sub>6</sub> H <sub>5</sub>	24	60
C <sub>7</sub> H <sub>15</sub>	SeC <sub>6</sub> H <sub>5</sub> TeC₄H <sub>9</sub>	22	C <sub>7</sub> H <sub>15</sub> SeC <sub>6</sub> H <sub>5</sub>	35	78
C <sub>10</sub> H <sub>21</sub>	SeC <sub>6</sub> H <sub>5</sub>	32	C <sub>10</sub> H <sub>21</sub> SeC <sub>6</sub> H <sub>5</sub>	23	60
	TeC <sub>4</sub> H9	45	CeHeSe	15	68
C <sub>6</sub> H <sub>5</sub>	SeC <sub>6</sub> H <sub>5</sub>	30	C <sub>6</sub> H <sub>5</sub>	32	64

<sup>a</sup>-Purified by flash chromatography. <sup>b</sup>-Isolated products. <sup>c</sup>-Separated from 3.<sup>d</sup> Vinylic selenides obtained by direct treatment of 1 with water.

Formation of the ketene butyltelluro (phenylseleno) acetals was confirmed by analysis of the <sup>1</sup>H NMR spectrum, where compounds with the obtained double bond bearing an alkyl group (entries 1-5; Table 1) presented only one triplet at 6,6-6,9 ppm and J=7 Hz corresponding to the coupling constant of the vinylic proton with the methylenic hydrogens of the allylic carbon. Since the stereochemistry of the obtained products showed the tellurium moiety and the organyl group bonded in trans at the new double bond, our method permits to obtain the opposite stereoisomer described by Braga et al.<sup>18</sup> Addition of DIBAL-H to the carbon-carbon triple bond is syn and the Al is added to the carbon bearing the selenium moiety and the hydride is transferred to the adjacent carbon. This fact is in accordance with the stabilization of  $\alpha$ -negatives charges by the selenium atom.<sup>22</sup> In this way, vinyl alane 1 intermediates are easily formed as demonstrated by the production of vinylic selenides of Z configuration in good yields after hydrolysis.

In conclusion, we described here a novel approach to difunctionalized, trisubstituted olefins containing selenium and tellurium with 100% of regio and stereoselectivity. We are currently exploring the selective removal of the tellurium moiety in the presence of the selenium group in compounds 3 and other experimental conditions, as well as new methodologies (for example: by the Zr/Te exchange reaction<sup>14</sup>) to obtain compounds of type 3 with improved yields.

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