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VINYL SELENIDE ANIONS. NEW SYNTHESIS OF VINYL ALKYL SELENIDES

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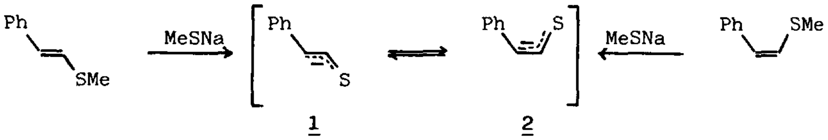
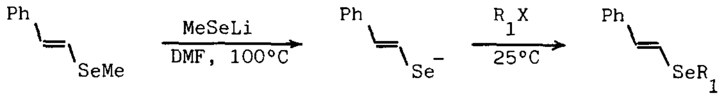
Abstract. Vinyl selenide anions, generated in DMF at 100°C, maintain the configuration of the vinyl methyl selenides from which they are produced by demethylation. This property has been used to effect an efficient three steps one pot stereospecific synthesis of vinyl alkyl selenides from unactivated vinyl halides.

Alkenyl selenides have a considerable synthetic importance since they are valuable precursors for the preparation of several organic compounds.[1] The synthesis of vinyl selenides has therefore attracted the attention of several workers[1] and new methods have been proposed in the last few years.[2,3] Very recently we have described a very simple procedure consisting in a nucleophilic vinylic substitution effected by methyl and aryl selenide anions in unactivated vinyl halides.[4,5] We now report a very versatile synthesis of vinyl alkyl selenides based on the observation that vinyl selenide anions, produced by demethylation of the vinyl methyl selenides, retain the configuration of the starting products.

In a previous work[6] we reported that vinyl methyl sulphides react with excess MeSNa to give a solution of the enethiolate anion as a result of a nucleophilic aliphatic substitution. When the demethylation reaction was applied to the pure (E)- or (Z)-ß-(methylthio)styrenes, the same equilibrium mixture of the (E)- and (Z)- anions, 1 and 2, was obtained:



We now report that when the ß-(methylselenyl)styrenes[4] are treated with lithium methyl selenide, in DMF at 100°C, they are very easily demethylated to the corresponding selenide anions which, on treatment with an alkyl halide, give a new vinyl alkyl selenide with complete retention of configuration.[7]



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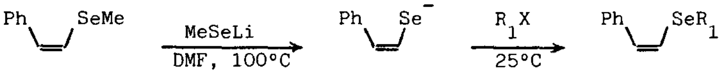

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This indicates that, under the experimental conditions employed, the vinyl selenide anions 3 and 4 are configurationally stable and do not interconvert; in this respect the behaviour of 3 and 4 is quite different from that observed in the case of the corresponding sulphur anions 1 and 2.

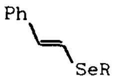
This peculiar property of these vinyl selenide anions is not only conceptually interesting, but it can also be fruitfully employed to develop a very simple and efficient stereospecific synthesis of vinyl alkyl selenides starting from unactivated vinyl halides. This procedure is a three steps one pot synthesis since the three reactions which occur, and which are indicated below, take place in the same flask:

$$\text{R-CH=CH-X} + \text{MeSeLi} \longrightarrow \text{LiX} + \text{R-CH=CH-SeMe}$$

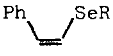
$$\text{R-CH=CH-SeMe} + \text{MeSeLi} \longrightarrow \text{Me}_2\text{Se} + \text{R-CH=CH-SeLi}$$

$$\text{R-CH=CH-SeLi} + \text{R}_1\text{X} \longrightarrow \text{LiX} + \text{R-CH=CH-SeR}_1$$

Thus, the reactions of the ß-bromostyrenes with an excess of MeSeLi and the appropriate alkyl iodide or bromide gave the products 5 - 10 with the yields indicated in parentheses.[8]



5: R = CH_2CH_3 (93%)
6: R = $CH(CH_3)_2$ (81%)
7: R = $CH_2CH=CH_2$ (74%)

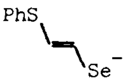


8: R = CH_2CH_3 (88%)
9: R = $CH(CH_3)_2$ (78%)
10: R = $CH_2CH=CH_2$ (83%)

A typical experimental procedure was as follows. To a solution of MeSeLi[5] (0.04 mol), in DMF (20 ml), the vinyl halide (0.01 mol) was added and the mixture was stirred under nitrogen at 100°C for 1 hr. The progress of the reaction was monitored by glc and tlc. The reaction mixture was cooled to 25°C and the alkyl halide (0.04 mol) was added. After half an hour the reaction mixture was worked up in the usual way and the products were separated and purified by column chromatography on silica gel.[9]

The procedure described above to synthetize compounds 5 - 10 is extremely convenient since the direct preparation of these compounds from the ß-bromostyrenes would require the ethyl, isopropyl and allyl selenide anions which cannot be easily obtained.

Moreover, other vinyl halides react similarily with lithium methyl selenide. Thus the intermediate anions 11 - 14 were produced from the (E)- and (Z)-1-phenylthio-2-chloroethylene, PhSCH==CHCl, and from the (E)- and (Z)-1-phenylselenyl-2-chloroethylene, PhSeCH==CHCl, respectively. The addition of ethyl iodide to the reaction mixtures afforded the corresponding ethyl vinyl selenides 15 - 18 in good yields.[8]



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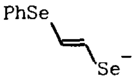

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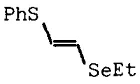

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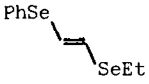

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In conclusion, the interesting experimental finding that the vinyl selenide anions do not interconvert, under the conditions employed in the present work, has open the way to a very simple and extremely convenient general method for a new stereospecific synthesis of vinyl alkyl selenides.[10]

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References and Notes

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7) The anions **3** and **4** can be produced from the ß-(methylselenyl)styrenes (or from other ß-(alkylselenyl)styrenes) also by treatment with sodium in HMPA or DMA; in this case the anions are very likely formed through the fragmentation of the radical anions[5] of the starting products. The reactions of the ß-(methylselenyl)styrenes with MeSNa did not produce the anions **3** and **4**, but afforded the ß-(methylthio)styrenes as a result of a stereospecific nucleophilic vinylic substitution in which the MeSe acts as the leaving group. This interesting different behaviour between sulphur and selenium nucleophiles will be discussed in a separate paper.

8) Yields are based on isolated products after column chromatography and are calculated from the amount of the vinyl halide employed.

9) In every case the reaction mixtures and the isolated products were analyzed by glc and nmr and the reactions were found to be completely stereospecific (less than 2% of the undesired stereoisomer was present). The (E)- or (Z)- configurations could be easily assigned on the basis of the value of the coupling constant between the two ethylenic protons.

10) The interest of these reactions is further increased by the fact that the vinyl selenide anions also react with unactivated vinyl halides. This represents a new and peculiar example of stereospecific nucleophilic vinylic substitutions which also have considerable synthetic importance. In this way, in fact, symmetrical and unsymmetrical divinyl selenides can be easily obtained (Unpublished observation from this laboratory).

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