THE REACTION OF ALLYLTRIMETHYLSILANE WITH SELENIUM-STABILIZED CARBON ELECTROPHILES.

Bernard HERMANS and Laszlo HEVESI*

Department of Chemistry, Facultés Universitaires N-D de la Paix 61, Rue de Bruxelles, 5000 NAMUR

Abstract: Lewis acid activation of bis(methylseleno)alcanes makes them react with allylsilane to produce the corresponding homoallyl selenides in moderate to good yields, depending on the structure of the starting selenoacetals.

It has been demonstrated in recent years that carbenium-like intermediates bearing stabilizing selenium moieties at the α position are able to react with a variety of nucleophiles in order to bring about C-C bond formation ¹. In a number of cases, the isolated methylseleno- or phenylselenoalkylated products proved to be interesting synthetic intermediates ^{1a,d,e,g}. Exploring further the usefulness of these selenium-stabilized carbon electrophiles in organic synthesis, we report here our preliminary results on their reaction with allyltrimethylsilane.

In a typical experiment, a dichloromethane (1,5 ml) solution of 300 mg (1 mmol) of 2,2bis(methylseleno)octane **1f** is added slowly to a solution of 520 mg (2 mmol) of tin tetrachloride in the same solvent (3 ml), maintained under argon at -40 °C. The yellow solution is stirred for 5 min., then 228 mg (2 mmol) of allyltrimethylsilane dissolved in 2 ml of dry dichloromethane are added. The reaction medium bleaches and a white precipitate appears. After 1.5 h of reaction at -40 °C, 10 ml of ether and 10 ml of 1 N sodium hydroxide are added and stirred vigorously, the organic layer is separated, washed twice with saturated brine, dried over MgSO₄, filtered and concentrated. The crude product (272 mg) is purified by PLC (SiO₂, eluent ether / pentane 5 / 95) to give 171 mg (69 % yield) of 4-methyl-4-methylseleno-1-decene **2f** as a pale yellow liquid, in all respect identical to an authentic sample ². The other results, obtained in a similar manner are gathered in Scheme 1.



Analogous allylation reactions have been performed using oxo-carbenium type electrophiles 5, and more recently thionium ions 6. It follows therefore that homoallylic ethers (alcohols), sulfides and selenides can now be preparated in a connective fashion trough the same methodology.

Although it is well documented that fluoride ions promote this type of reaction in numerous occasions ⁷, this was not observed in our case. None of the homoallyl selenide <u>2a</u> could be isolated when the reaction of the acetal <u>1a</u> was conducted under the same conditions as in Scheme 1a but in the presence of TBAF (tetrabutylammonium fluoride). On the other hand, 2,2-bis(methylseleno)octane <u>1f</u> did react in the presence of 1 equ. of TBAF, but the yield in homoallyl selenide <u>2f</u> dropped to 31 % only. Transmetallation reactions occurring between allylstannanes and Lewis acids have been reported recently ⁸. Such a reaction may also take place between allyltrimethylsilane and tin tetrachloride ^{8b, 9}, and is likely to be accelerated by fluoride ions. This would explain the yield depressing effect of TBAF in our reactions, in agreement with the observation that no trace of selenide <u>2f</u> was produced when 2 equ. of SnCl4 and 1 equ. of allyltrimethylsilane were reacted (-40 °C/1 h) prior to the addition of the selenoacetal <u>1f</u>. Indeed, admitting that the metathesis reaction proceeds with an appreciable rate under these conditions ⁹, the selenoacetal (eventually complexed with SnCl4) finds itself in the presence of allyltrichlorostannane which does not react. To some respect, similar behaviour has

been reported recently in the case of addition of allylstannane to aldehydes in the presence of tin tetrachloride 10

Scheme 1 shows that selenoacetals derived from ketones (especially methyl ketones or cyclohexanone) react easier and give better yields in homoallylic selenides than do selenoacetals derived from aldehydes (Scheme 1, compare entries f, h, j to entries a-c), or from internal ketones (Scheme 1, entries f, h vs. g, i).

These findings parallel the observations made for the Lewis acid mediated reactions of selenoacetals with silyl enol ethers 1a, i.e. electronic effects (stabilization of the incipient carbenium ion) and steric crowding around the electrophilic center influence considerably these reactions. It is also interesting to note the somewhat contradictory reports about the allylation of thioacetals : using allylsilane and AlCl₃ as Lewis acid, higher yields in homoallylic sulfides were obtained with thioacetals derived from aldehydes than with thioacetals derived from ketones 6g, whereas the reverse was observed using allylstannanes and DMTSF [dimethyl(methylthio)sulfonium fluoroborate] as Lewis acid 11.

Besides the formation of the main products 2, a few side-reactions could be identified in some instances : i) bis-allylation has been observed in the sole case of selenoacetal <u>1k</u>, and gave 4-methyl-4-phenyl-1, 6-heptatriene in ± 10 % yield; ii) homoallylic silylselenides have been detected in low (2-3 %) yield in several instances presumably arising from β -silyl cation type intermediates (Scheme 2).



Further work is being done in order to extend the reaction to substituted allylsilanes, and to establish the scope and limitations of this new homoallyl selenide synthesis.

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- Spectral (IR, ¹H NMR, MS) data of all the compounds 2 are in agreement with the proposed structures. Elemental analyses are as follows: <u>2c</u> : calcd. C : 58.67; H : 6.27, found C : 58.14; H : 6.30; <u>2d</u> : calcd. C : 60.25; H : 6.74, found C : 60.44; H : 6.87; <u>2j</u> : calcd. C : 55.29; H : 8.35, found C : 55.80; H : 8.50; <u>2k</u> : calcd. C : 60.25; H : 6.74, found C : 60.43; H : 6.89; <u>2a</u> and <u>2f</u> : see ref 2
- These are crude yields estimated by ¹H NMR, compounds <u>2e</u> and <u>2k</u> undergo extensive decomposition during chromatographic (SiO₂) purification.
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- 9) We have indeed observed the reaction of allyltrimethylsilane with SnCl4 to be solvent dependent : 4 h at 25 °C in CCl4, very rapid at 25 °C in CDCl3 and very rapid at -40 °C in CH2Cl2, but we have not yet investigated the effect of fluoride ions on these reaction rates.
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