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A short review on the synthesis of selena and tellurasteroids

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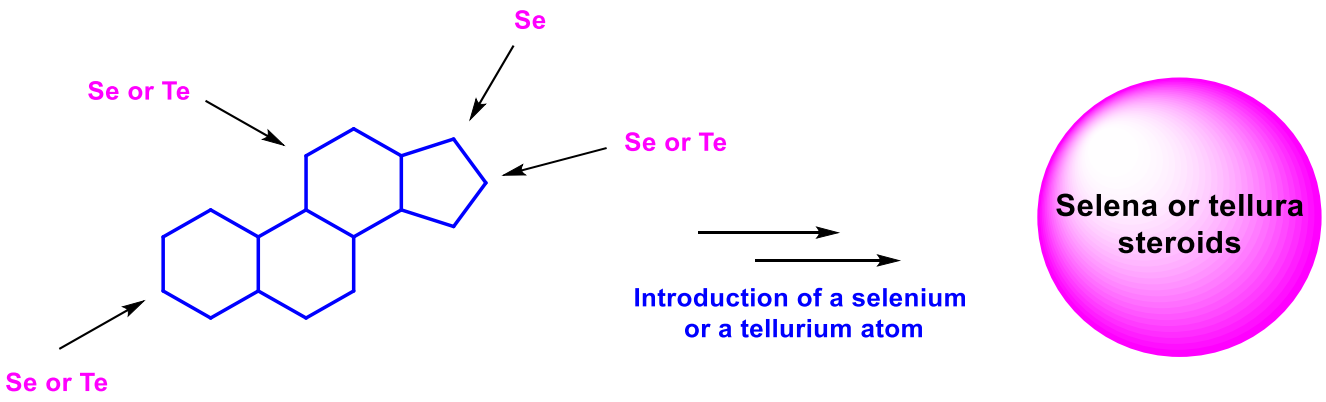
Abstract

Recently hetero steroids have received much attention for pharmacological interest. Indeed, the replacement of one or more carbon atoms of a steroid molecule by a heteroatom often results in useful alterations to its biological activity because this modification affects the chemical properties of this steroid. Compounds containing a selenium, or a tellurium atom can possess biological properties and so have a great potential for the creation of a new library of molecules important for biological applications. Some of them have been used as antibacterial, antiviral, antihypertensive, or chemopreventive anticancer agents. Recent developments in the syntheses of selena and tellurasteroids are described herein.



Keywords: steroid; heteroatom; intramolecular Diels-Alder, Bistro, orthoquinodimethane.

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1. Introduction

Steroids constitute an extensive and important class of biologically active polycyclic compounds that are widely used for therapeutic purposes.[1-20] Even after decades of research, the total synthesis of steroid nuclei by improved strategies continues to receive considerable attention. Numerous methods[21-27] have been exploited for the total synthesis of steroids which are widely distributed in nature, and which possess practical medical importance. Research into steroid total synthesis continues to this day.[28-31]

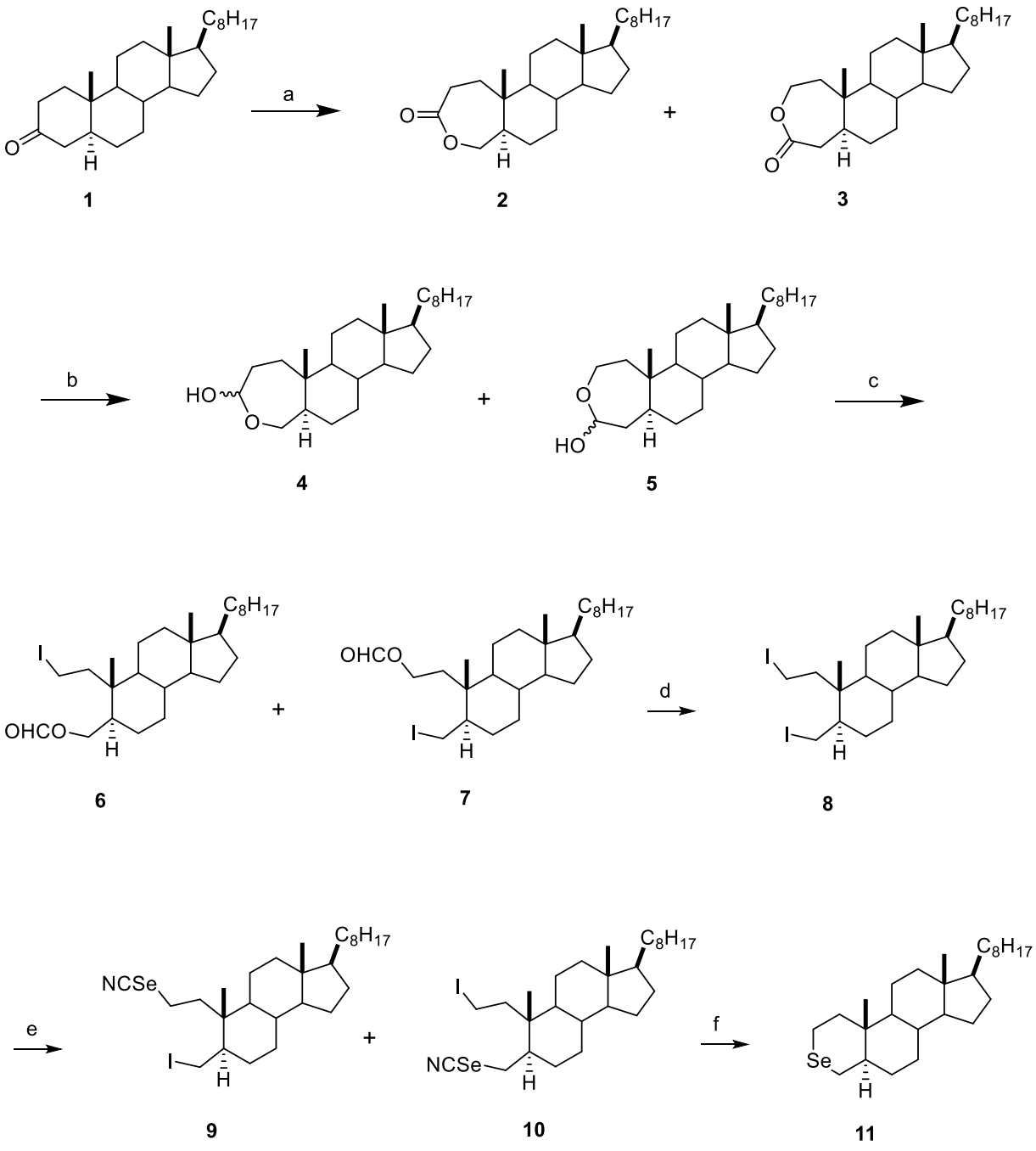
The fact that the introduction of a heteroatom in steroid structures can cause extensive changes in biological activity has long intrigued medicinal chemists. Naturally occurring steroid nuclei have been modified in several ways to recognize the structural and stereochemical features required for the display of specific, selective physiological activity and for finding more active compounds, free from undesirable or harmful side effects. Among the many known analogs of steroids, compounds containing either heteroatoms within the steroid nucleus itself or heterocyclic rings condensed with the cyclopentanoperhydrophenanthrene nucleus, have received much attention because of their different and interesting biological activities. The introduction of heteroatom or replacement of one or more carbon atoms in a steroidal molecule by a heteroatom often results in alterations of its biological activities, which sometimes may be useful. Indeed, this modification affects the chemical properties of that particular steroid.

Compounds containing selenium have great potential, insofar as they can possess biological properties. They have been used as antihypertensive, antiviral, antibacterial, or chemopreventive anticancer agents.[32-36] There are several reports in the literature describing the antitumoral activity of selenium derivatives via apoptosis in cancer cells induced by the generation of ROS in a pro-oxidant fashion.[37-40] In the same way, compounds containing tellurium are interesting for the creation of a new library of molecules important for biological applications. Organotellurium compounds have attracted a great deal of attention because of their potential synthetic.[41-43]

This review is an update on the partial and total synthesis of selena and tellurasteroids. Recently, Jastrzebska and coworkers[44] reported a review on the synthesis of selenosteroids, hybrid molecules for which the selenium atom is outside the steroidal skeleton. Also, to the best of our knowledge and much to our surprise, there are no reports on this subject. Otherwise, selena and tellurasteroids constitute an important class of steroids. The main emphasis of this review is on the synthetic studies leading to selena or tellurasteroids and therefore, many publications that describe only biological activities are not included.

2. Synthesis of Selenasteroids

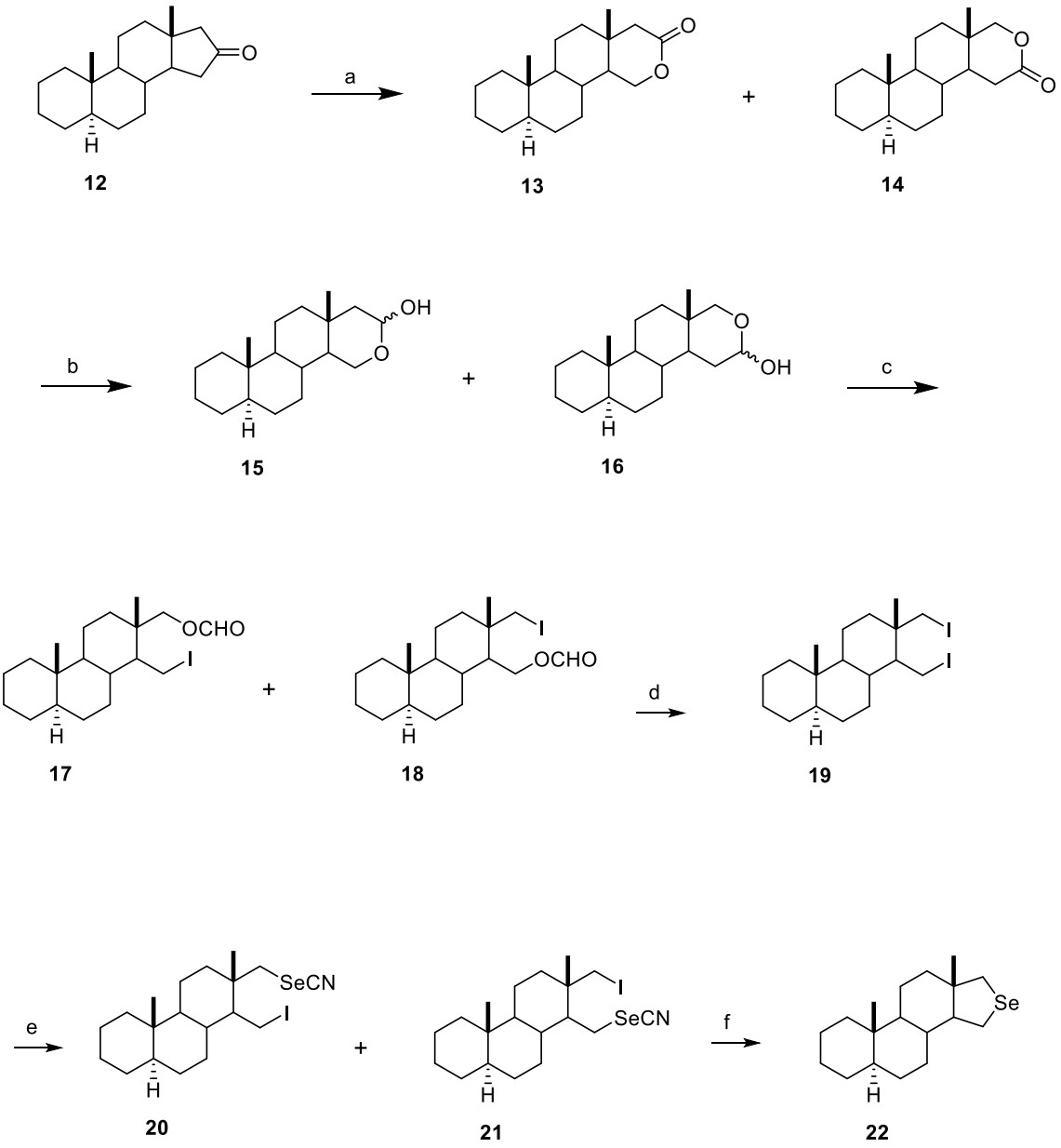
In 1990, Suginome and coworkers[45] reported the synthesis of 3-selena and 16-selenasteroids from respectively, 5α-cholestan-3-one and 5α-androstan-16-one.



Reaction conditions : (a) MCPBA, APTS, CH_2Cl_2; (b) DIBAL, CH_2Cl_2; (c) HgO-I_2, pyridine, C_6H_6, hν; (d) Me_3SiCl, CCl_4; (e) KSeCN, acetone; (f) $NaBH_4$, THF, EtOH.

Scheme 1. Synthesis of selenasteroid **11** from 5α-cholestan-3-one **11**.

The synthesis of 3-selenasteroid is depicted in Scheme 1. The starting compound **1** was transformed into the corresponding lactones **2** and **3** by a Baeyer-Villiger oxidation using MCPBA in dichloromethane. A reduction of steroidal lactones **2** and **3** using DIBAL led to the corresponding lactols **4** and **5**, which irradiation in benzene in the presence of HgO-I_2 gave iodo formates **6** and **7** in good yield. Treatment of these latter with trimethylsilyl iodide[46] in carbon tetrachloride, afforded 2,3-diiodo-2,3-seco-A-nor-5α-cholestane **8** in 93% yield. The reaction of the diiodide **8** with 1 equiv of potassium selenocyanate[47-48] in acetone gave a mixture of the monoselenocyanates **9** and **10**. Upon treatment of these selenocyanates with sodium borohydride in ethanol-tetrahydrofuran, the crystalline 3-selena-5α-cholestane **11** was obtained in a 78% yield.



Reaction conditions : (a) MCPBA, APTS, CH_2Cl_2; (b) DIBAL, CH_2Cl_2; (c) HgO-I_2, pyridine, C_6H_6, hν; (d) Me_3Si, CCl_4; (e) KSeCN, acetone; (f) $NaBH_4$, THF, EtOH.

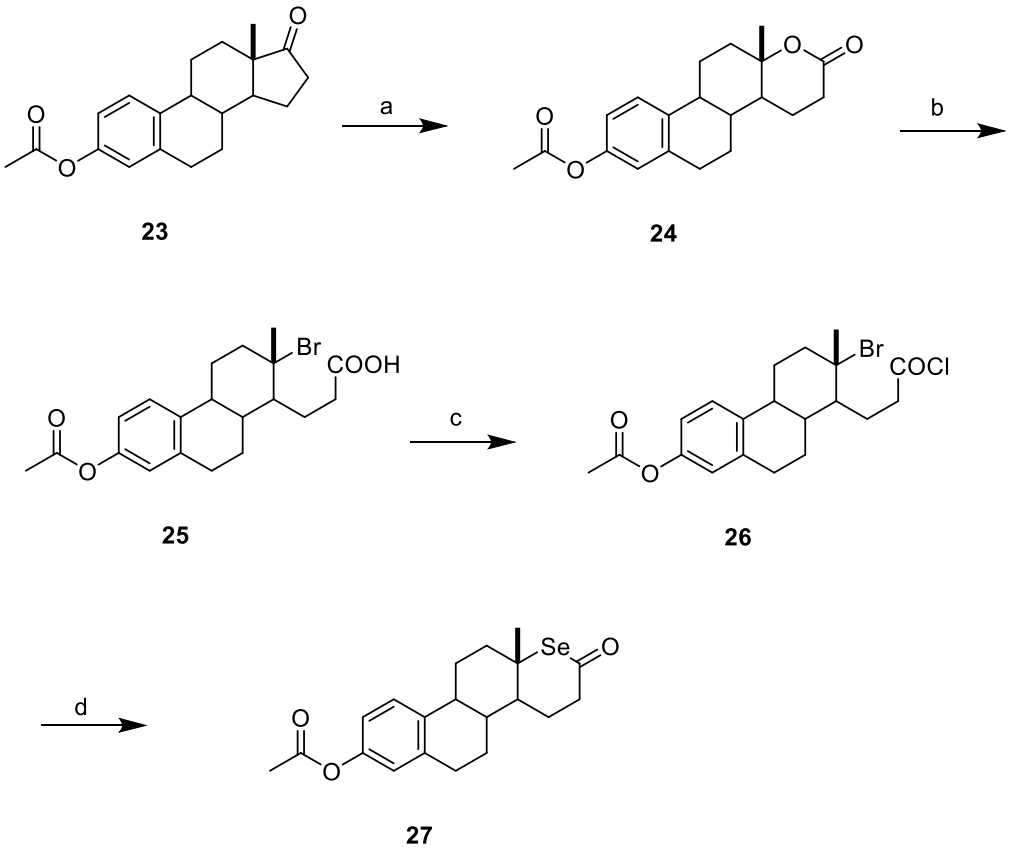
Scheme 2. Synthesis of selenasteroid **22** from 5α-androstan-16-one **12**.

This synthesis constitutes the first synthesis of 3-selenasteroid having a natural steroid skeleton.

The transformation of steroidal 16-one derivative **12** into 16-selenasteroid can be achieved similarly as depicted previously in Scheme 2. Thus, a mixture of iodo formates **17** and **18**[49] was obtained from 5α-androstan-16-one **12** in three steps and good overall yield. Treatment of these latter with trimethylsilyl iodide in carbon tetrachloride at 60 °C for 48 h led to 15,16-diiodo-15,16-seco-D-nor-5α-androstane **19** in 96% yield. An oily mixture of the isomeric monoselenocyanates **20** and **21** was obtained in 79% yield, upon dissolution of the diiodide **19** in acetone containing potassium selenocyanate and heated under reflux for 3 h. Treatment of this mixture, dissolved in tetrahydrofuran-ethanol, with $NaBH_4$ at 40 °C for 70 h, provided the crystalline 16-selena-5α-androstane **22** in good yield.

In 1996, Siddiqui and coworkers[50] reported the synthesis of 3β-acetoxy-17α-selena-D-homo-1,3,5(10)-estratrien-17-one **27** from 3β-acetoxy-1,3,5(10)-estratrien-17-one **23**.

The synthesis is depicted in Scheme 3. The Baeyer-Villiger oxidation of 3β-acetoxy-1,3,5(10)-estratrien-17-one **23** with perbenzoic acid in the presence of *p*-toluenesulfonic acid led to 3β-acetoxy-17α-oxa-D-homo-1,3,5(10)-estratrien-17-one **24**, which was treated with hydrobromic acid in acetic acid to provide 3β-acetoxy-seco-13-bromo-1,3,5(10)-estratrien-16-oic acid **25**. This latter was treated with thionyl chloride to give 3β-acetoxy-seco-13-bromo-1,3,5(10)-estratrien-17 acid chloride **26** in a quantitative yield. Treatment of the acid chloride **26** with selenium and sodium borohydride in a 1:2 ratio in ethanol afforded 3β-acetoxy-17α-selena-D-homo-1,3,5(10)-estratrien- 17-one **27** in a good yield.



23 **24** **25** **26** **27**

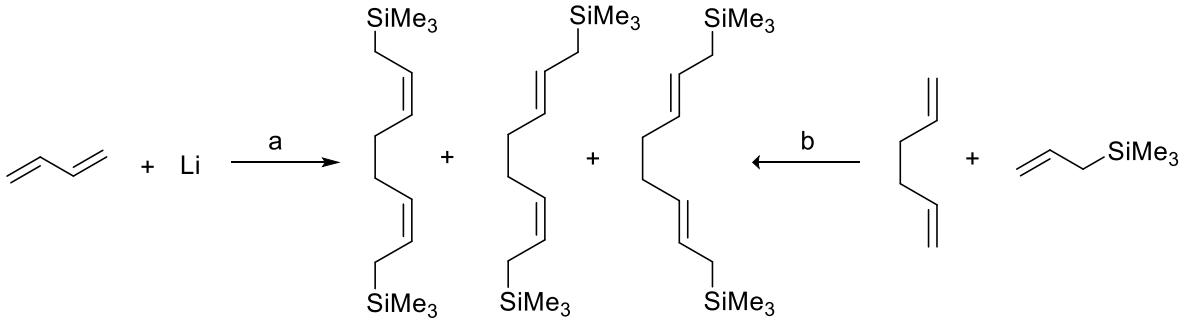
Reaction conditions : (a) MCPBA, PTSA, $CHCl_3$; (b) HBr, AcOH, r.t., 4 h;
(c) $SOCl_2$, dioxane, r.t., 1 h; (d) Se powder, $NaBH_4$, EtOH, reflux, 6 h.

Scheme 3. Synthesis of 3β-acetoxy-17α-selena-D-homo-1,3,5(10)-estratrien-17-one **27**.

In 2009, Ibrahim-Ouali[51] reported the first total synthesis of 11-selena steroids via an intramolecular Diels–Alder cycloaddition of *o*-quinodimethanes as the key step and using 1,8-bis(trimethylsilyl)-2,6-octadiene (BISTRO) **28** as starting material (Scheme 5).

1,8-Bis(trimethylsilyl)-2,6-octadiene (BISTRO) **28** was obtained by reduction with lithium from 1,3-butadiene in the presence of chlorotrimethylsilane.[52] A mixture of the (*Z,Z*) isomer (ca. 50%), the (*Z,E*) isomer (ca. 40%) and the (*E,E*) isomer (4%), contaminated with about 6% of 1,6-bis(trimethylsilyl)-2,7-octadiene was obtained.[53]

More recently, the author showed that BISTRO **28** can be obtained by simple acyclic cross-metathesis CM from allytrimethysilane and 1,5-hexadiene using Grubbs's ruthenium catalyst. The CM reaction of 1,5-hexadiene and allyltrimethysilane was done by treatment with a catalytic amount of Grubbs's catalyst [$(Cy_3P)_2Cl_2Ru$=CHPh] (10 mol %) in dichloromethane at room temperature under argon atmosphere. BISTRO **28** was isolated as the sole product, after stirring for 12 h, in a fair yield of 45%. Moreover, it was found that 5 mol % of catalyst was sufficient to complete this reaction at the same time. Otherwise, this key compound was here isolated as a mixture of (*Z,Z*) and (*E,E*) isomers in a 60:40 ratio (Scheme 4).



Bistro 28

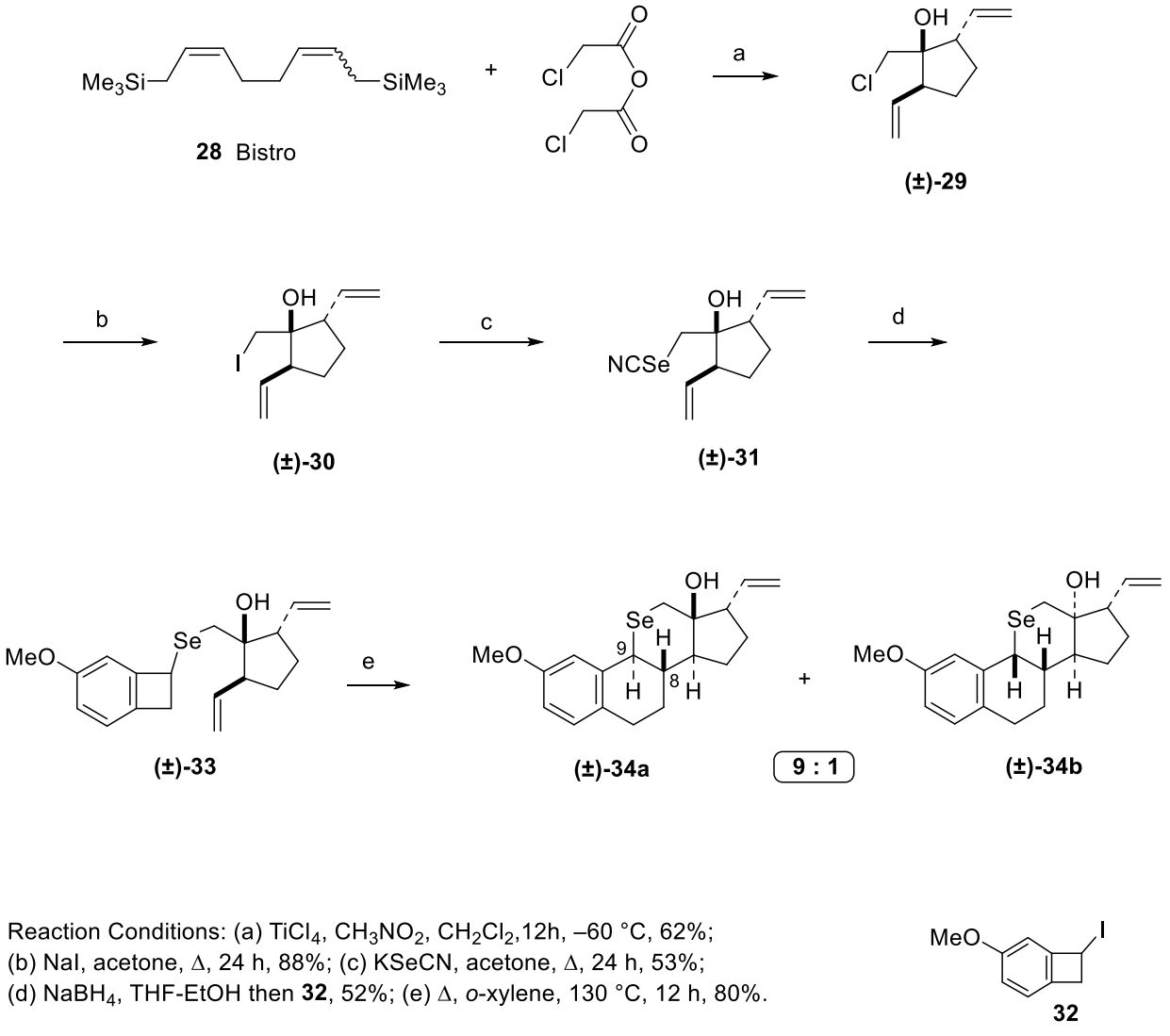
Reaction Conditions: (a) $ClSiMe_3$, THF,10 h at 0 °C then 18 h at r.t., 60%;
(b) 5 mol% [$(Cy_3P)_2Cl)_2Ru$=CHPh], CH_2Cl_2, r.t., 12 h, 45%.

Scheme 4. Synthesis of Bistro **28**.

The key reactions leading to these new hetero steroids are depicted in Scheme 5. A convergent steroid synthesis, based on the approach A + D -> AD -> ABCD was adopted by the author.

This strategy is based on an intramolecular cycloaddition of *o*-xylylenes to generate the BC ring system, which was developed by Oppolzer[54-56] and Kametani et al.[57-59] The condensation of BISTRO **28** with chloroacetic anhydride provided the (*d,l*)-2,5-divinylcyclopentan-1-ol **29**. This latter was then heated with NaI in acetone to give **30** in good yield. The resulting iodohydrine **30** was dissolved in acetone which contained potassium selenocyanate and was heated under reflux for 48 h. Thus, the selenocyanate **31** was isolated in a 53% yield. In the next step, the seleno derivative **31** was dissolved in tetrahydrofuran-ethanol, and treated with $NaBH_4$ at rt for 24 h. The resulting reduced product generated in this manner has been alkylated *in situ* with 1-iodo-5-methoxybenzocyclobutene **32**. This step constitutes a convenient way to produce (*d,l*)-cyclobutene **33**, which thermolysis afforded a mixture of two selena steroids **34a** and **34b** in 80% yield and a 9:1 ratio. The latter were easily separable by flash chromatography on silica gel.

The steroids **34a** and **34b** have, respectively, a *trans–anti–trans* and a *cis–anti–cis* ring fusion. Interesting is to note that the main product **34a** matches the *trans–anti–trans* ring fusion configuration of natural products.



Reaction Conditions: (a) $TiCl_4$, CH_3NO_2, CH_2Cl_2,12h, –60 °C, 62%;
(b) NaI, acetone, Δ, 24 h, 88%; (c) KSeCN, acetone, Δ, 24 h, 53%;
(d) $NaBH_4$, THF-EtOH then **32**, 52%; (e) Δ, *o*-xylene, 130 °C, 12 h, 80%.

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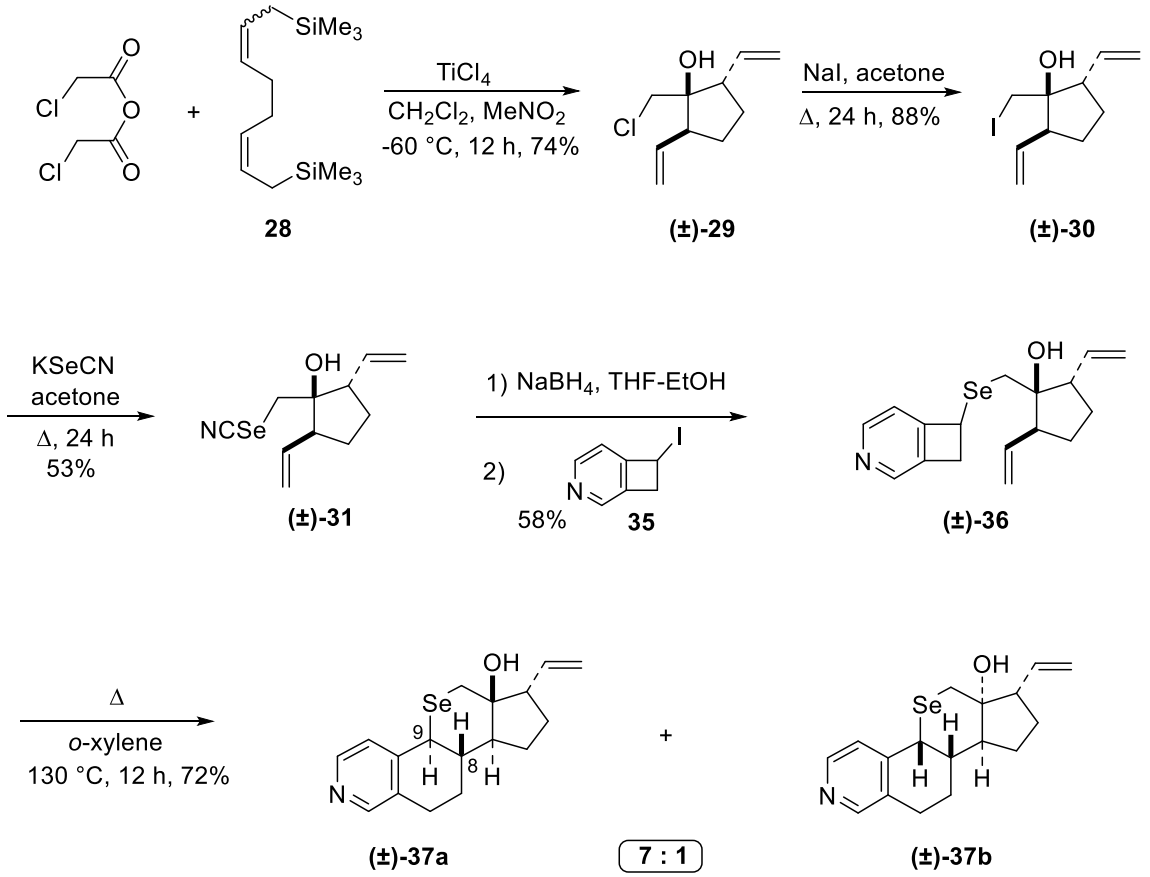
Scheme 5. Synthesis of selenasteroids **34**.

The same strategy was used efficiently to obtain 3-aza-11-selena-1,3,5(10)-trieno steroids[60] as depicted in Scheme 6. Thus, the starting selenocyanate **31** was easily accessible by the procedure reported above in 53% yield. This latter was then reduced with $NaBH_4$ at rt and the resulting product has been alkylated *in situ* with 3-aza-7-iodo-bicyclo[4.2.0]octa-1,3,5-triene[38,61] leading to (*d,l*)-cyclobutene **36**. Thermolysis of derivative **36** provided a mixture of two selena steroids **37a** and **37b** in a 7:1 ratio and 72% yield, which were easily separable by flash chromatography on silica gel.

These steroids **37a** and **37b** have, respectively, a "*trans-anti-trans*" and a "*cis-anti-cis*" ring fusion. It's worth to note that here too the main product **37a** matches the "*trans-anti-trans*" ring fusion configuration of natural products.



Scheme 6. Synthesis of 3-aza-11-selenasteroids **37**.

3. Synthesis of Tellurasteroids

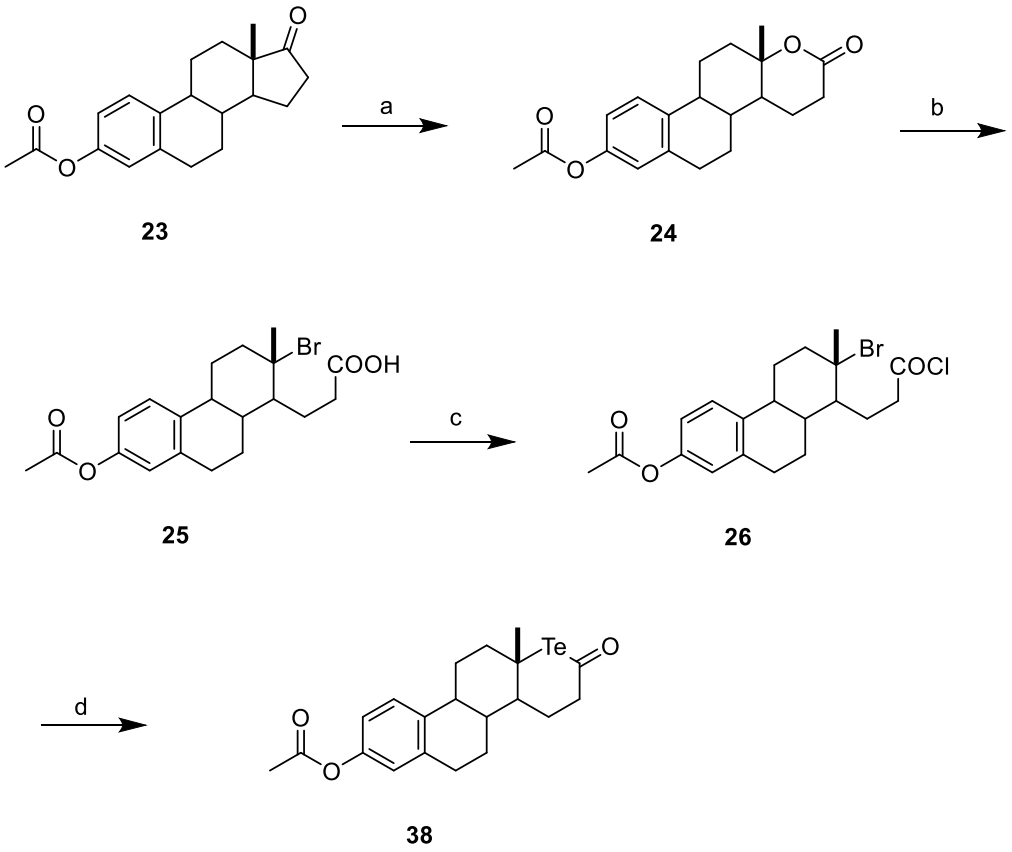
In 1996, Siddiqui and coworkers[50] also reported the synthesis of 3β-acetoxy-17α-tellura-D-homo-1,3,5(10)-estratrien-17-one **38** from 3β-acetoxy-1,3,5(10)-estratrien-17-one **23** using the same strategy described above for selenasteroid **27**.

The reaction of 3β-acetoxy-*seco*-13-bromo-1,3,5(10)-estratrien-17 acid chloride **26** with tellurium in the presence of sodium borohydride led to 3β-acetoxy-17α-tellura-D-homo-1,3,5(10)-estratrien-17-one **43** in a good yield (60%), as depicted in Scheme 7.

The first total synthesis of 11-tellurateroids was reported in 2010 (Scheme 8). The author Ibrahim-Ouali[62] has succeeded in introducing for the first time a tellurium atom onto the steroid skeleton by using of a simple synthetic sequence based on an intramolecular cycloaddition of *o*-xylylene. Moreover, the tellurium atom occupies a position of established biological importance.[63-64]

The methodology based on an intramolecular cycloaddition of o-xylylenes has a remarkable advantage for the formation of the B/C cycle. The starting compound **30** was the same as described above (see Scheme 5). Thus, iodohydrine **30** was dissolved in a solution of dry ethanol containing sodium telluride[65] and heated under reflux for 48 h, to lead to an intermediate which was alkylated *in situ* with 1-iodo-5-methoxybenzocyclobutene **32**, providing a convenient way to produce the (*d,l*)-cyclobutene **39**. This constitutes a very interesting result, despite the fair yield to obtain compound **38**. Indeed, an 8/2 mixture of two diastereoisomers **40a** and **40b** in a

58% overall yield was isolated by thermolysis of (*d,l*)-cyclobutene **39**. These tellurasteroids were easily separated by flash chromatography on silica gel (Scheme 7).

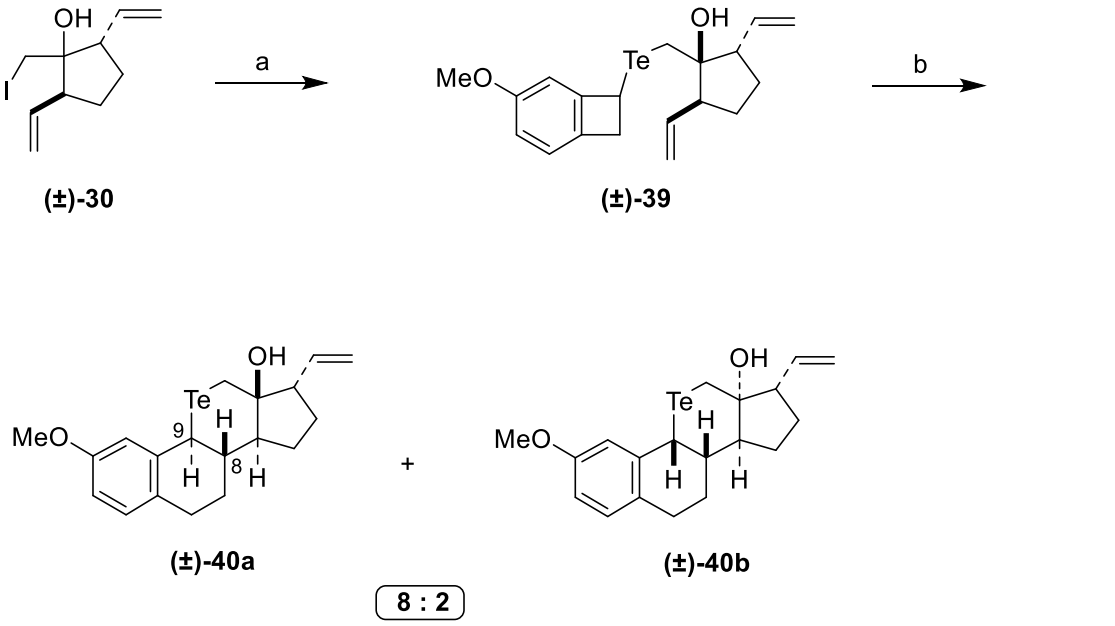


Scheme 7. Synthesis of 3β-acetoxy-17α-tellura-D-homo-1,3,5(10)-estratrien-17-one **38**.

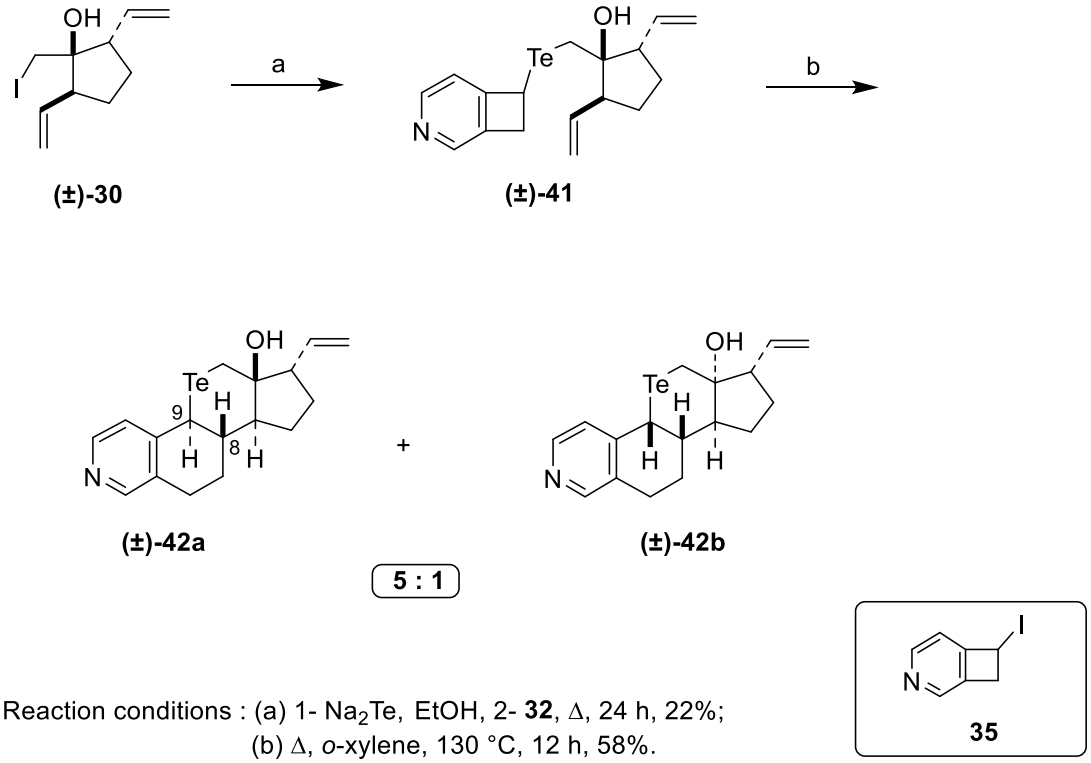
The steroids **40a** and **40b** have, respectively, a "*trans-anti-trans*" and a "*cis-anti-cis*" ring fusion. Interestingly, the main product **40a** matches the "*trans-anti-trans*" ring fusion configuration of natural products. The torquoselectivity in the electrocyclic conversion of benzocyclobutenes into *o*-xylylenes has been previously discussed.[66] A pronounced preference for outward rotation is generally observed in the case of electron–donating substituents borne by the benzocyclobutene.

The first total synthesis of 3-aza-11-tellura-1,3,5(10)-trieno steroids was described by the same author.[60] The key reactions leading to these compounds are schematically depicted in Scheme 9.

Also here, iodohydrine **30** was treated with sodium telluride[65] in dry ethanol and heated under reflux for 48 h, to provide an intermediate which was alkylated *in situ* with 3-aza-7-iodo-bicyclo[4.2.0]octa-1,3,5-triene **35**. The key intermediate **41**, sensitive to oxygen, was then isolated and used without further purification in the following step. Thermolysis of this latter led to a 5/1 mixture of two diastereoisomers **42a** and **42b** in a 55% overall yield. These tellura steroids were easily separated by flash chromatography on silica gel and can be stored under an argon atmosphere (Scheme 8).



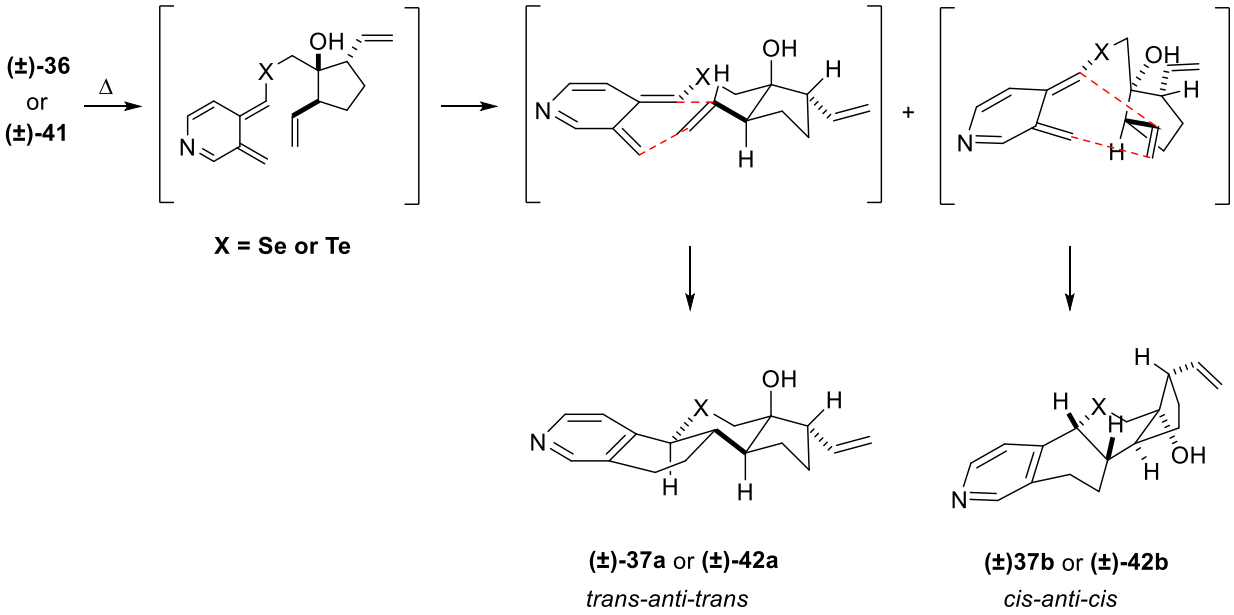
Scheme 8. Synthesis of tellurasteroids **40**.



Scheme 9. Synthesis of 3-aza-11-tellurasteroids **42**.

The steroids **42a** and **42b** have, respectively, a "*trans-anti-trans*" and a "*cis-anti-cis*" ring fusion. As indicated above, in the two cases the main product **37a**/**42a** matches the "*trans-anti-trans*" ring fusion configuration of natural products. The steroid **37a**/**42a**, which exhibits "*cis-anti-cis*" ring fusion stereochemistry, comes from a cycloaddition process involving the vinyl group *syn* to the benzocyclobutene moiety. This steroid could result from an *endo* approach of the (*E*)-*o*-xylylene intermediate. The cycloadducts **37a** and **42b** result from an *exo* approach of the (*E*)-*o*-xylylene intermediate during the cyclization (Scheme 10).

It is worth pointing out the similarity of the results between 3,11-dihetero steroids and 11-hetero steroids. By introducing a new heteroatom, the authors observed that the isomer's ratio obtained is quite the same and on top of that in favor of the isomer matching the ''*trans-anti-trans*'' ring fusion of natural product. Interesting is also to note the good stereoselectivity of the thermolysis step. Indeed, the relative configurations of five stereogenic centers were controlled during the cycloaddition process.



Scheme 10. Stereochemistry of major and minor isomers **37** and **42**.

4. Conclusions

Since it has been proven that the introduction of a heteroatom in the steroidal moiety could have a biological impact, heterosteroids have been known to have a revival of interest. Presented here is up-to-date literature on the syntheses of selena and tellurasteroids reported during the last years. Several of these syntheses may be useful, and the strategy involving the intramolecular cycloaddition of *o*-xylylenes to generate the BC ring of the steroidal system, developed by Oppolzer and Kametani, seems to be very efficient to synthesize selena and tellurasteroids. Currently, interest in steroids and related molecules continues because of the emerging bioactivity and structural diversity inherent in this class of compounds.

5. Acknowledgements

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