THE REACTIONS OF (+)-2- AND (+)-3-CARENES WITH THE RETENTION OF THE BICYCLIC FRAMEWORK

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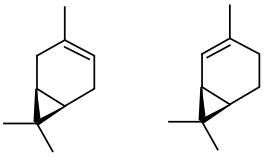
Abstract: Carane-type compounds have attracted attention in recent years due to their practical importance. This review is focused on describing the developments in the synthesis of trimethylbicyclo[4.1.0]heptanes and their unsaturated analogues from monoterpenes (+)-2- and (+)-3-carenes published mostly during the last decade.

Keywords: (+)-2- carene, (+)-3-carene, trimethylbicyclo[4.1.0]heptanes, trimethylbicyclo[4.1.0]hept-3-enes, organic synthesis.

1. Introduction

Progress of modern synthetic organic chemistry is determined by two general tendencies – profound study of biological processes and natural products as the ground for the creation of new effective bioregulators (drugs, pharmaceuticals, diagnostic materials, pesticides et al.) and the use of natural substances as the starting materials (raw materials) for the synthesis of new optically active compounds including bioregulators. The development of new enantiopure compounds, in particular new medicals having chiral centers in a molecule (such substances are found in about, the third part of all drugs and in more than 75% of new pharmaceuticals) is connected with the requirements of obtaining high molecular purity. It is well known that one of the tasks of the synthesis of a bioactive compound is the preparation of the required enantiomer in an optically pure form. Bicyclic monoterpenes (+)-3-carene **1a** and (+)-2-carene **1b** are widely used for resolving this type of problems [1-7]. A structural feature of both compounds is the presence of the reactive C=C double bond and bicyclic bridging system. This fact opens perspectives for a new synthesis with the retention of the bicyclic framework of monoterpenes **1a,b**. The main attention in this review is focused on the articles published during the last decade, and on those not mentioned in the above references. Data on skeleton transformation as well as a gradual fragmentation of the terpenes framework are published in works [8-13] and will be not considered hereafter.

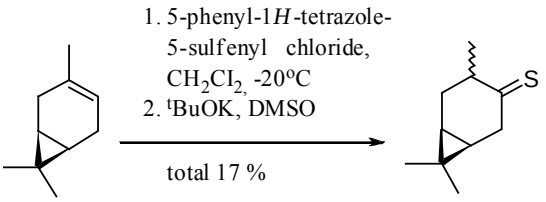


1a **1b**

2. Synthesis on the basis of (+)-3-carene with the retention of the carane framework

Sulfur containing terpenoids derivatives, which have a number of important properties, are not found in nature. The regioselective method for obtaining epimeric sulfides **2** is described in [14] and it is based on the hydrolysis of the product of sulfenyl chloride addition to (+)-3-carene **1a** (scheme 1).

***Scheme* 1**

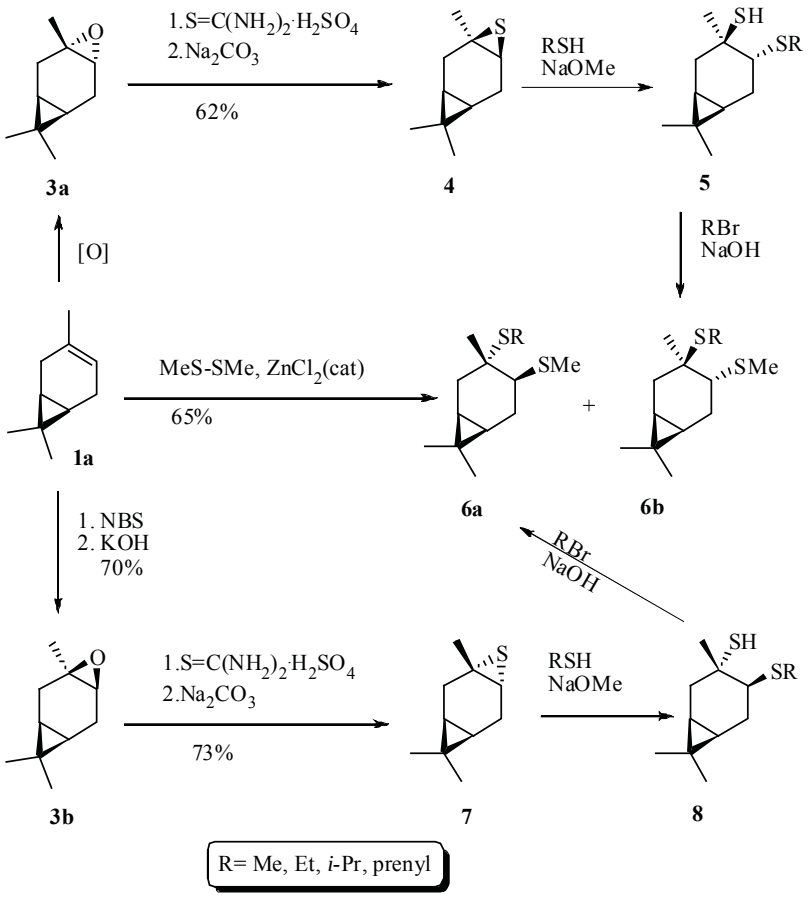


1a **2**

In order to perform the introduction of the thio-group into position 3 of the carane framework it is suggested to use the addition of $(MeS)_2$ to carene **1a** or thio-caranes **4**,**7** (scheme 2).

The $ZnCl_2$ catalyzed addition of $(MeS)_2$ yields a mixture of isomeric products **6a,b** (R=H) [15,16]. For the synthesis of similarly built substances, the α- and β-thio-oxides of 3-carene epoxides **3a** and **3b** have been prepared. The latter gave the carane derivatives **5** and **8** upon the interaction with mercaptans. The respective homologues **6a,b** (R=Me, Et, i-Pr or prenyl) are formed at alkylation of mercaptans in alkaline conditions with alkyl halides.

***Scheme* 2**



Initial epoxides **3a** can be obtained using peroxy acids, dimethyloxirane, by the oxidization with H_2O_2 or O_2 catalyzed by transition metals [22-50]. One of the most used epoxidation methods is the stoichiometric peracid route using such acids as peracetic acid and *m*-chloroperbenzoic acid. The employment of peroxy acids is not a clean method as equivalent amounts of acid waste are produced. The safety issues associated with handling peracids are also a matter of concern. The use of hydrogen peroxide as a cheap, environmentally clean and easily handled oxidant in conjugation with robust and easily obtainable synthetic metalloporphirins, transition metal Schiff base complexes of various metals, heteropoly acids, transition metal substituted heteropoly acids as catalysts led to procedures, which help to perform epoxidation reaction. However, the chemo- and stereoselectivity of the oxidation reactions were not high. Moreover, the separation of the catalysts is usually troublesome and not economical for application. Dimethyldioxirane epoxidation of (+)-3-carene **1a** gave the corresponding epoxide **3a** (yield 100%). In pilot conditions, carene **1a** is oxidized into epoxide **3a** (yield 93%) by pinane hydroperoxide in the presence of molybdenum catalysts [51]. Epoxide **3b** is synthesized in two steps with a 70% yield [52].

Synthesized tiocaranes as well as (+)-3-carene **1a** itself show an antifungal activity [53].

Hydroxymercaptans and sulfides **9-12,** that are of interest as physiologically active compounds and reagents, have been synthesized from epoxides **3a**,**b** [54,55] (scheme 3).

It has been established that the interaction of oxides **3a**,**b** with thioglycolic acid proceeds along with the formation of isomeric diols **10a,b** in mixture with acids **9a,b**. The given reactions allow the synthesis of disulfide **11** and enantiomers **12a**,**b**. However, the yield of these products is low.

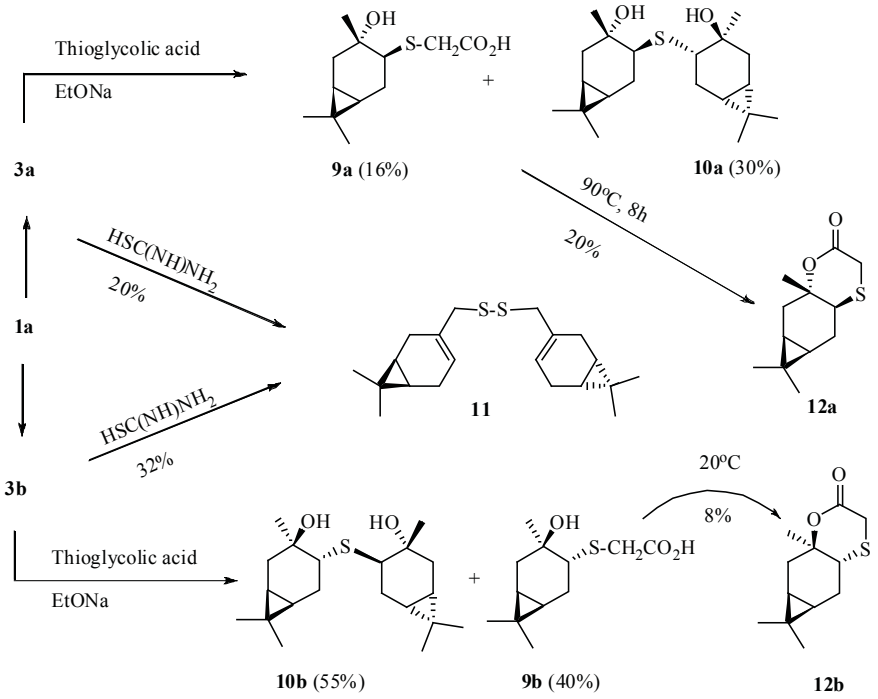
cis-Diol **13** can be synthesized by direct hydroxylation of 3-carene **1** with $KMnO_4$ or OsO_4 [56, 57].

Salakhutdinov *et al* published the synthesis of compound **13** using *cis*-opening of epoxide **3a** [58]. This approach gave *cis*-diol avoiding skeleton rearrangements, which were noticed with β-epoxide **3b**.

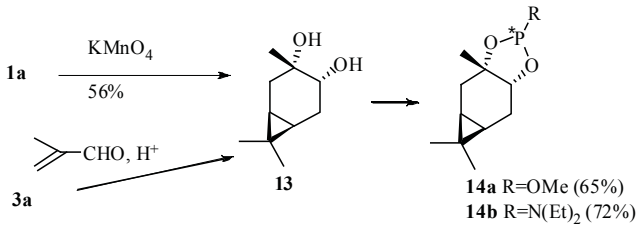
We designed and synthesized novel *P**-chiral monodentate phosphite ligands, having five-membered phosphacycles and OMe (or NEt_2) exocyclic substituents (scheme 4) [59, 60].

These can be easily prepared by direct phosphorylation of the appropriate **13** and purified by vacuum distillation. Carene-based compounds **14a,b** are characterized by rather small contents of the minor epimer. The major stereoisomer has the *R* - configuration at the *P** - stereocenter.

***Scheme* 3**

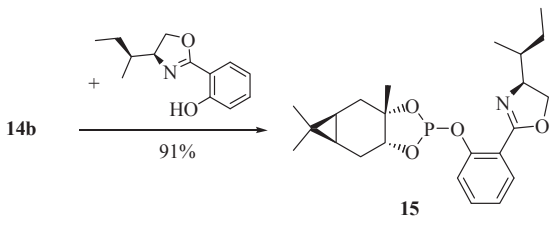


***Scheme* 4**



One of the approaches to enhance asymmetrising activity of chiral phosphite-type compounds is the synthesis of the respective *P,N*-bidentate ligands with additional *C** - stereocenters in the side chain *N*-containing group. In particular, oxazolinophosphite **15** has been prepared using phosphoramidite **14b** as a phosphorylating reagent (scheme 5).

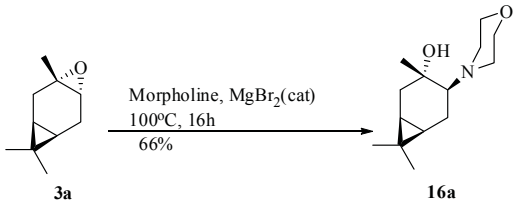
***Scheme* 5**



Using these novel ligands, up to 91% *ee* was achieved in the Pd-catalysed asymmetric allylic amination [59, 60].

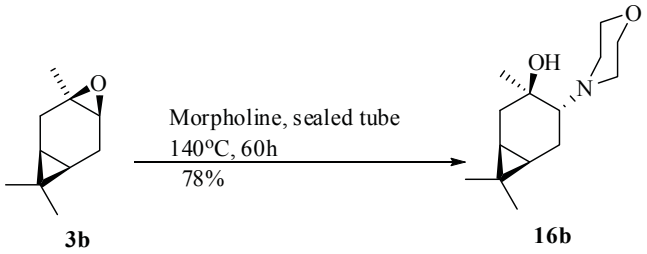
β-Hydroxyamine **16**, obtained by the interaction of epoxide **3a** with morpholine [61-63], was an effective catalyst in addition of diethylzinc to aromatic aldehydes in the synthesis of optically active alcohols (up to 98% ee) (scheme 6).

***Scheme* 6**



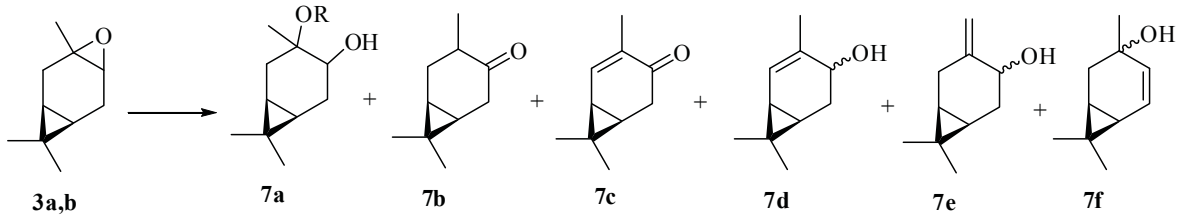
Diastereomeric compound 1**6b** has been synthesized from epoxide **3b** and morpholine [64] (scheme 7).

***Scheme* 7**



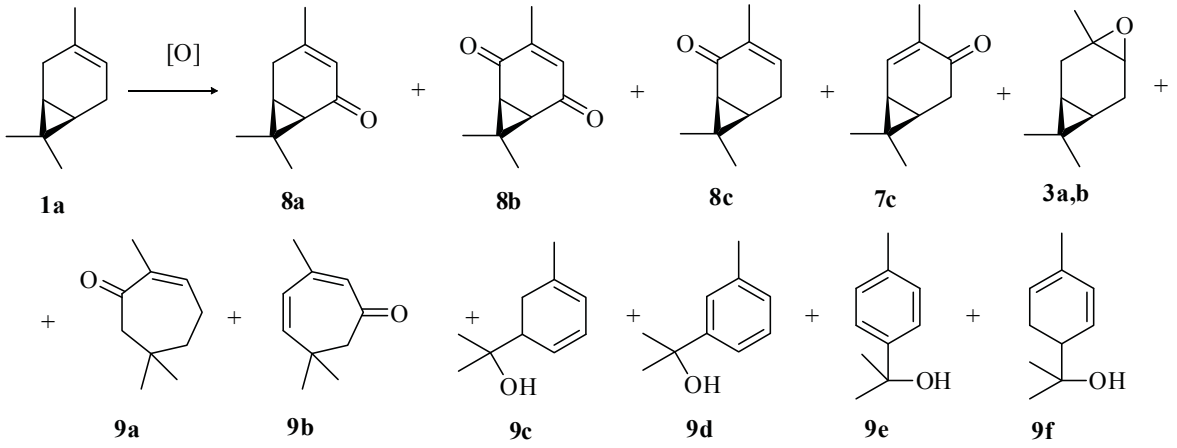
Another, no less interesting group of carane derivatives **7a-d**, has been synthesized from oxide **3a,b** (scheme 8). It should be noted that in most cases the syntheses are not selective, though they have been carried out in various proton solvents during catalysis with inorganic or organic acids, oxides of heavy metals, or under photolysis [57, 43, 65-77].

***Scheme* 8**



Acid-catalysed opening of the epoxide **3a** involves the cleavage of a more highly substituted C-O bond and affords as a rule compound **7a** accompanied by trace amounts of the opposite 4-alkoxy-3-caranols. The treatment of oxide **3a** with both mineral acids and acetic acid provides 4-caranone **7b**. The rearrangement of epoxide **3a** has been made using boron trifluoride etherate, which resulted in the mixture of the 4-caranone (43%) with menth-3-en-2-one (28%).

***Scheme* 9**



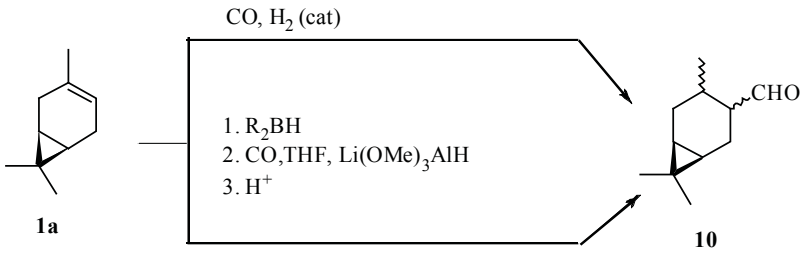
The treatment of the isomeric epoxide **3b** under identical conditions provides product **7b** with 66% yield. In contrast with the epoxide **3a**, which gives major trans-diols **7a** (R=H) on the acid-catalyzed hydrolysis – epoxide **3b** was noted to give both the expected cis- and trans-diols **7a** (R=H) in 26% and 53%, respectively. The repetition of the experiment in acidic MeOH provides both regio-isomeric hydroxy ethers in total yield 80%. The treatment of the isomeric epoxides **7a,b** with oxides of heavy metals or under photosensitized conditions provides the mixture of isomeric carenes **7c-f** .

Liquid-phase oxidative conversions of carene **1a** are technologically perspective but it is difficult to make them, just like the previous ones, due to the low selectivity of the process, which results in a low yield and a difficult identification of the enones **8a-d, 9a,b,** epoxides **3a,b**, diene **9c** and aromatic hydrocarbons **9d-f** [78-80].

The introduction of functional groups in the C4 position of caranes is required for the elaboration of approaches to obtain practically important *gem*-dimethylcyclopropanes, e.g to fragrant substances [81-84].

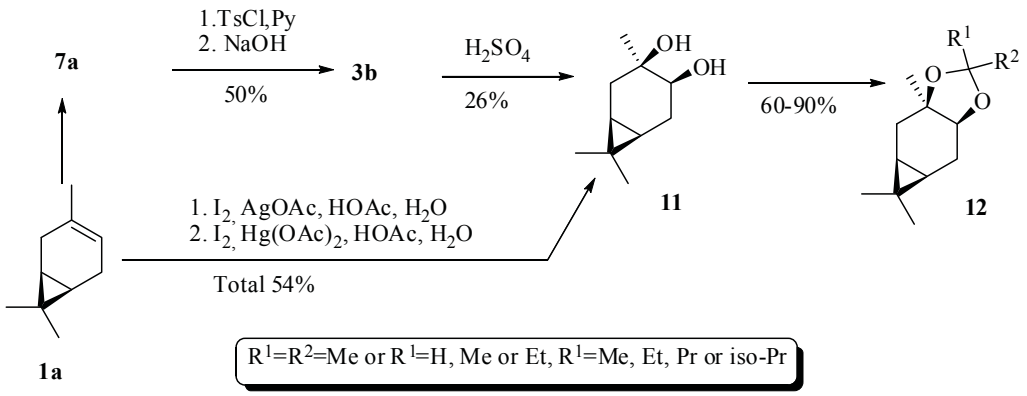
Overall yield of 4-formylcarane **10** at hydroformylation or carbonylation has not exceeded 40% (scheme 10) [85, 86].

***Scheme* 10**



The approach to acetals and ketals **12** [87] has been performed on the basis of the well-known 3β,4β-carandiol **11** [76, 88, 89].

***Scheme* 11**



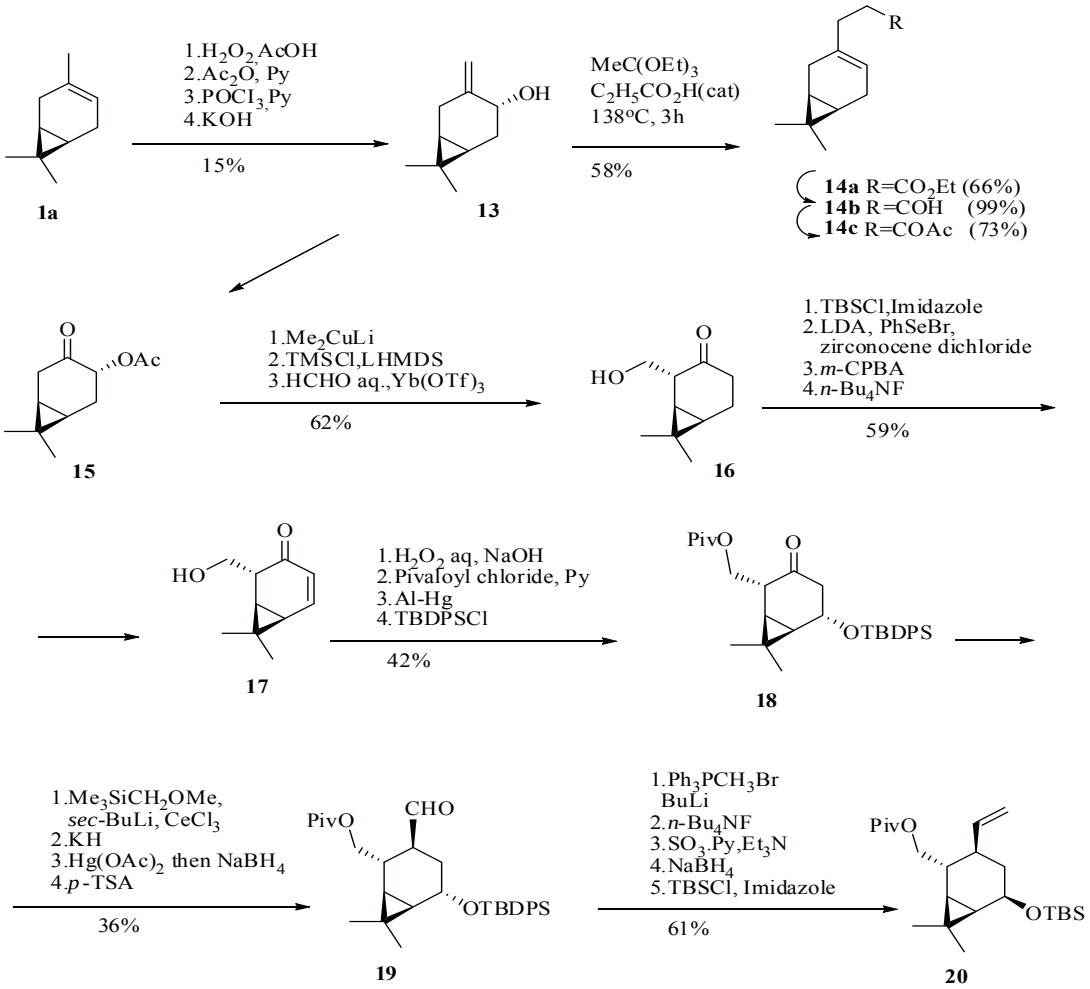
Target products have been obtained by the treatment of diol **11** and the corresponding aldehyde or ketone with catalytic amounts of sulfuric or *p*-toluenesulfonic acids. These acetals and ketals had odour characteristics and in these conditions the *gem*-dialkyl group created pleasant, floral-balsamic or floral-wood odours. Acetals had markedly less odour.

Odorants **14a-c** have been synthesized from 4-hydroxy-3(10)-carene **13** (scheme 12) [90, 91].

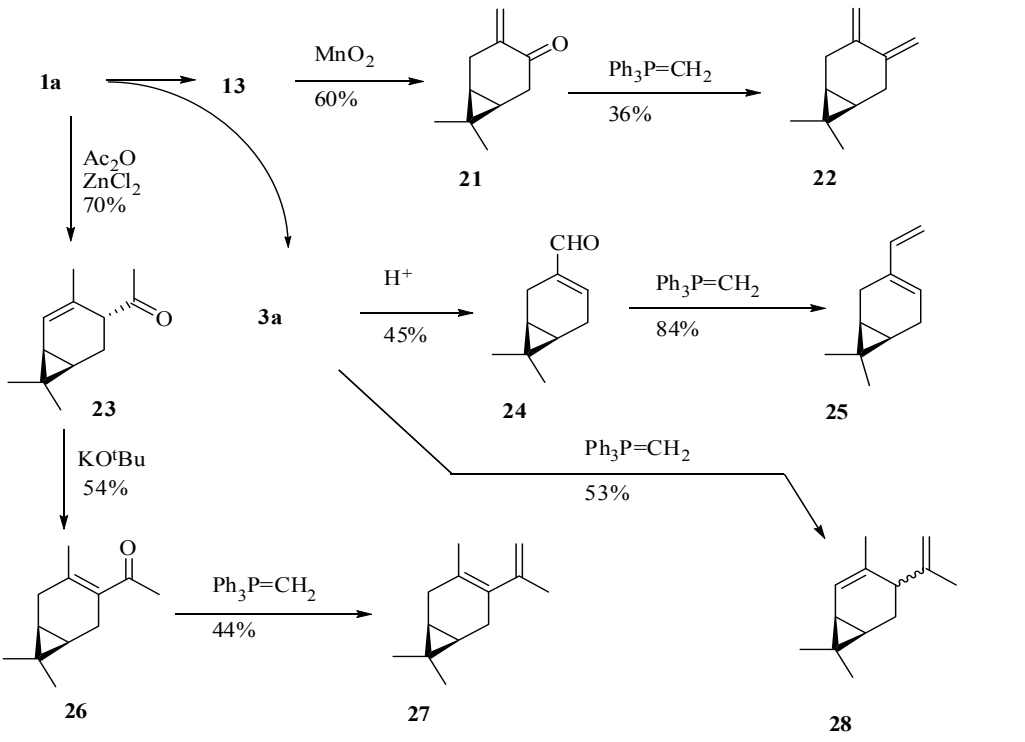
Another group [92] has described the stereoselective route from an alcohol **13** to functionalized ketone **15,** olefines **17, 20,** and aldehyde **19**.

3(10)-Caren-4-on **21** [67], 4α-acetyl-2-carene **23** [93], 3-caran-10-al **24** [94-96] and 4-acetyl-3-carene **26** [93] have been selected [97-99] for the construction of intermediates **22, 25, 27, 28** of the optically active tri- and tetracyclic analogues of sesquiterpenes from *Nardostachys jatamansi* and *Aristolochia debilis* [100], and the homologues of some crop protection agents (scheme 13) [5, 101- 103].

***Scheme* 12**



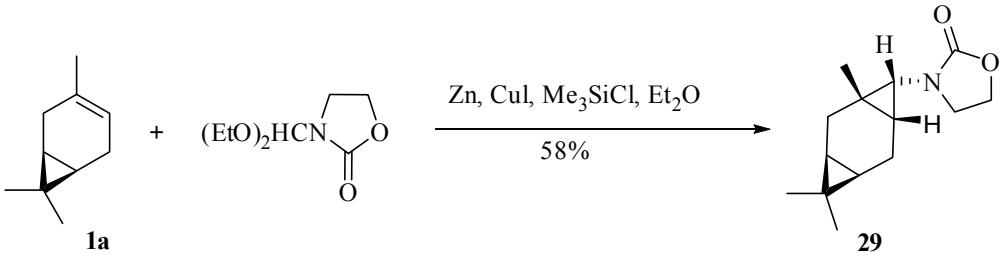
***Scheme* 13**



The synthesis of cyclic products on the basis of compounds **22, 25-28** has been discussed in the review [6], so it will not be considered hereafter.

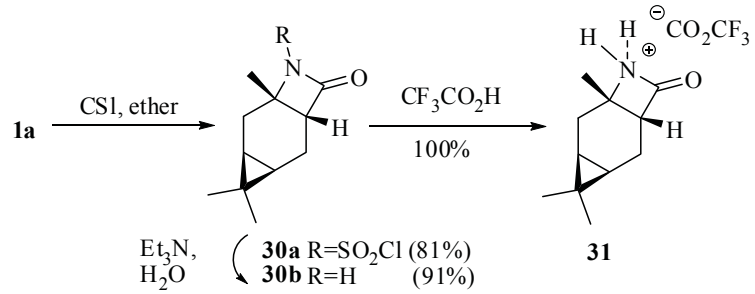
The direct amidocyclopropanation of (+)-3-carene **1a** using organozinc carbenoids gives a single isomer **29** [104-106]

***Scheme* 14**



A pathway for preparing optically active lactam functionalized ionic liquid **31** was demonstrated by scheme 15 [107].

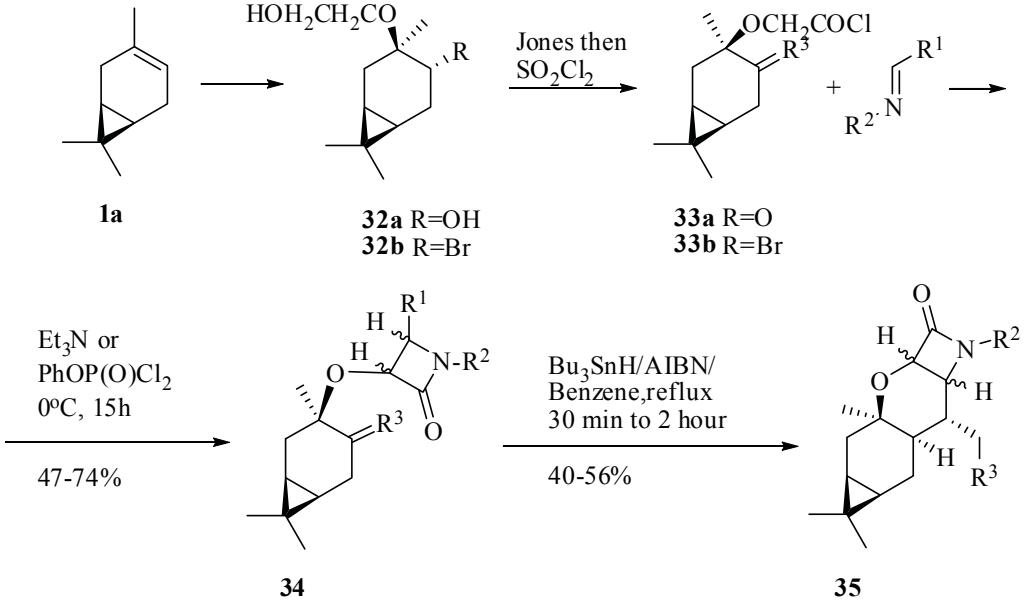
***Scheme* 15**



The reaction of chlorosulfonyl isocyanate addition to compound **1a** proceeds regio- and stereoselectively with the formation of β-lactam **30a.** The hydrolysis of compound **30a** has yielded the product **30b** [108].

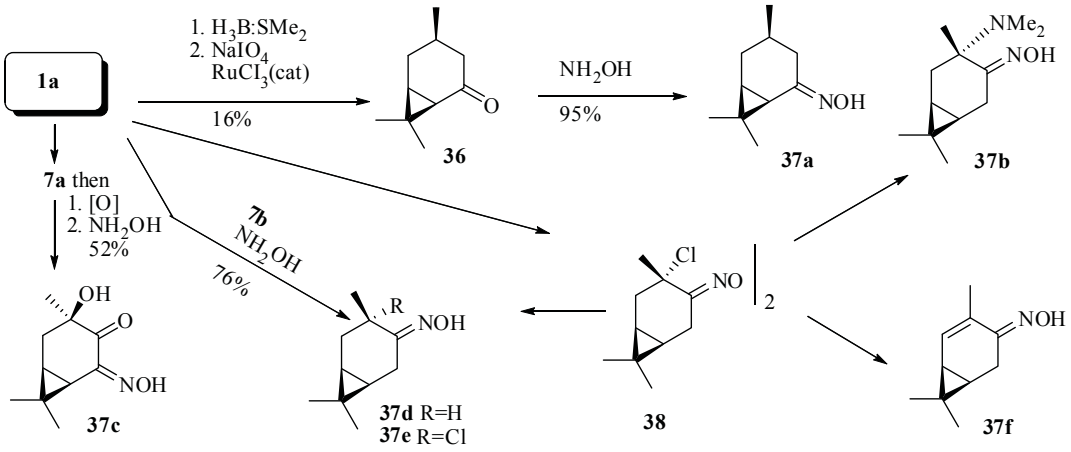
The synthesis of lactams **34**, **35** included the preliminary constructing of the diol **32a** or the bromohydrine **32b** with following cycloaddition of anhydrides **33a,b** to imines (scheme 16) [109-111].

***Scheme* 16**



The ketoximes of the carane series should also be mentioned (scheme 17) [112, 115-120].

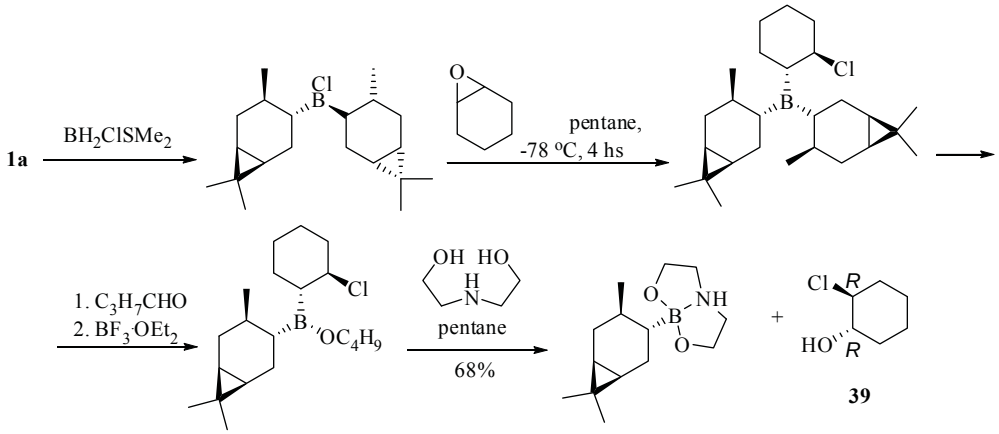
***Scheme* 17**



Substances **37a,c,d** have been classically synthesized from ketones **7b** and **36**, while the homologues **37b**,**f** have been obtained on the basis of the adduct **38**.

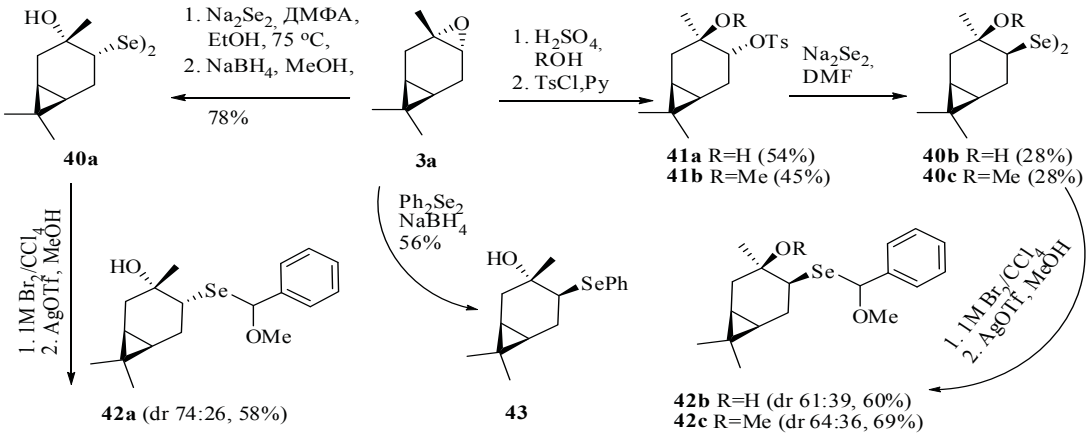
Asymmetric ring opening of *meso*-epoxide with *B*-halobis(2-isocaranyl)boranes affords chlorohydrine **39** with 19% ee enantioselectivity (scheme 18) [121].

***Scheme* 18**



A convenient method for the syntesis of optically active trans-hydroxyselenodes **40a-c, 43** from oxide **3a** on the reactions of sodium selenide or sodium diselenide was described (scheme 19) [122].

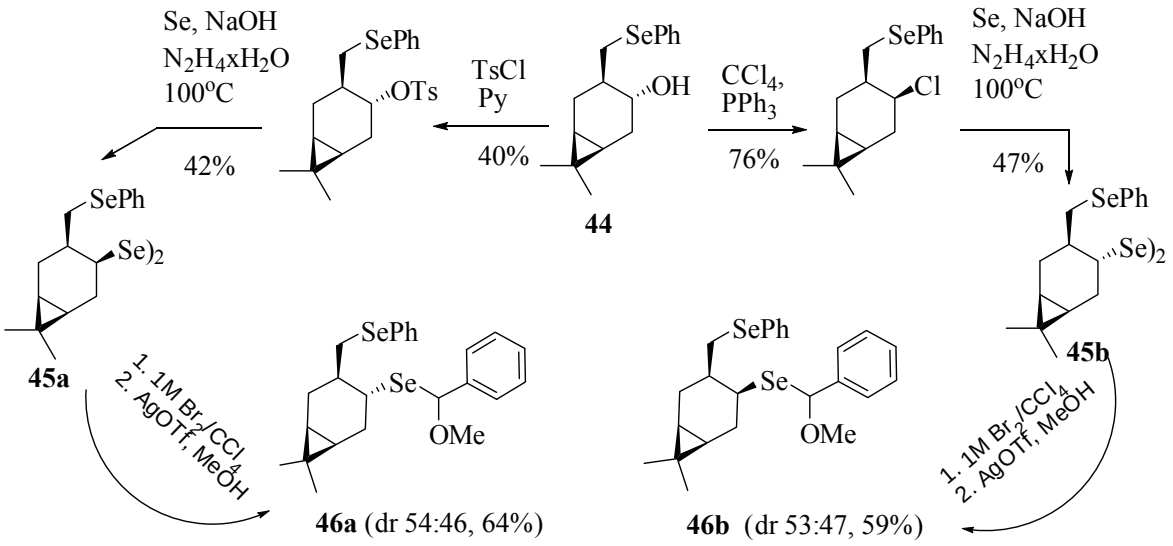
***Scheme* 19**



The cis-hydroxy and cis-methoxydiselenides **40b,c** were obtained in the reaction of sodium diselenide with the corresponding hydroxy- and methoxytosylates **41a,b**.

New chiral selenium-caranes **45a,b** as well as **46a,b** can be synthesized from hydroxyselenide **44** [123].

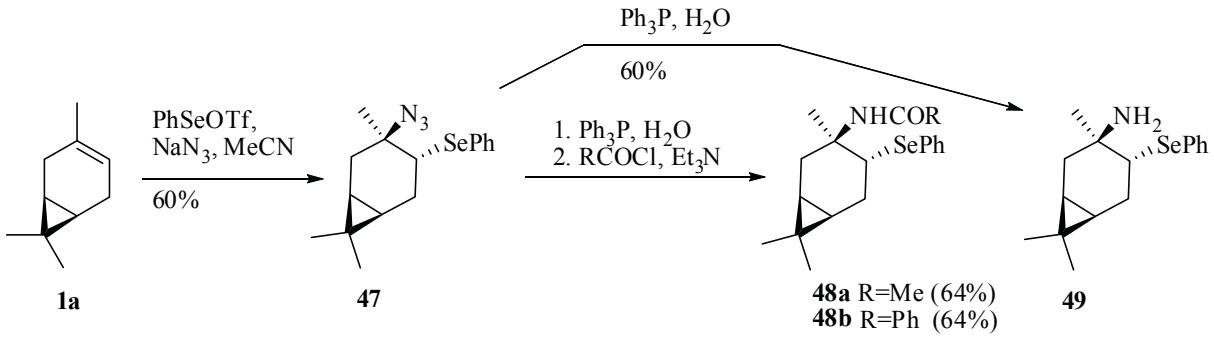
***Scheme* 20**



The diselenides were used for asymmetric selenenylation of sterene and selenocyclization with o-allylphenol with moderate yield but low diastereoselectivety.

(+)-3-Carene **1a** has been easily converted into β-azidoselenide **47** by addition of PhSeOTf in the presence of NaN_3 [123].

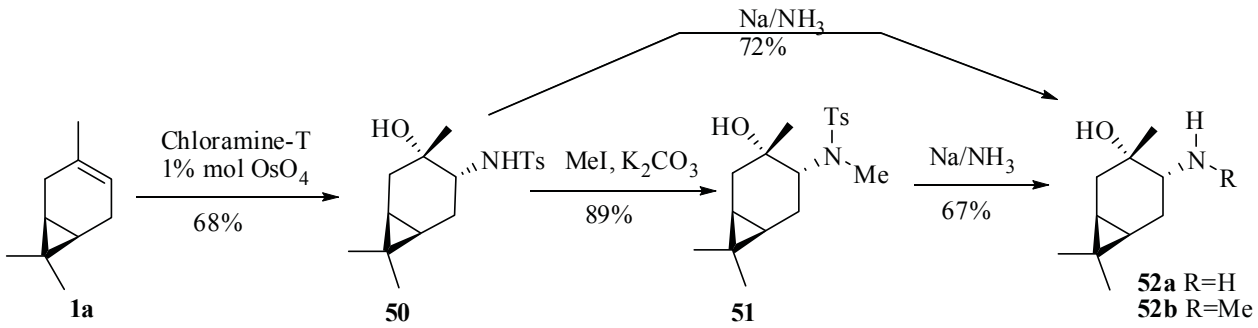
***Scheme* 21**



Using classical procedures, compound **47** was converted into amidoselenides **48a,b** and aminoselenide **49**.

The regio- and stereoselective aminohydroxylation of monoterpene **1a** into hydroxytoluenesulfonamide **47** was reported [124].

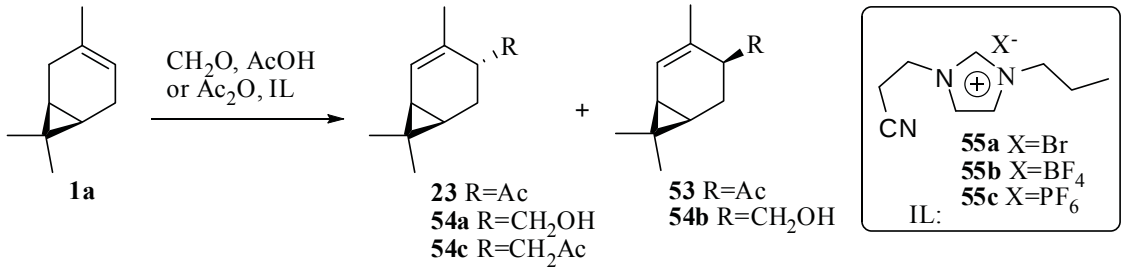
***Scheme* 22**



The methylation of compound **50** gives the corresponding product **51.** The sulfonamides **50, 51** were reduced with sodium in liquid ammonia to give the corresponding cis-amino alcohols **52a,b**.

The ionic-liquids **55a-c** [125-128] catalyzed Kondakov and Prince reactions of monoterpene **1a** were described [129].

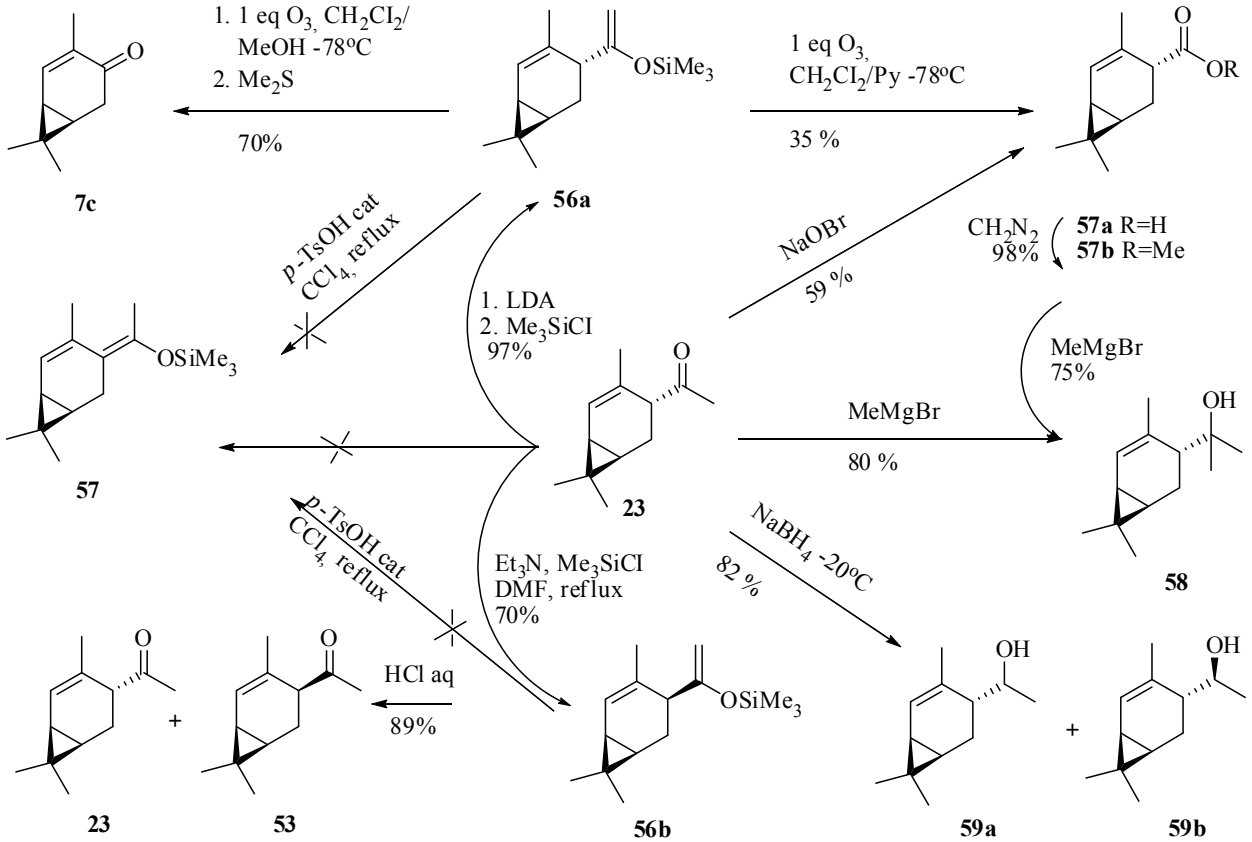
***Scheme* 23**



The reaction of carene **1a**, with Ac_2O in the presence of ionic liquid **55a** at 50°C gave the mixture of 4α- and 4β-acetyl-2-carenes **23,54** (ratio 95:5). All the attempts of hydroxymethylation of **1a** using paraformaldehyde in the presence or in the solution of ionic-liquids **55a-c** have failed. Only the addition of the AcOH to the indicated mixture has contributed to the proceeding of Prins's reaction with the formation of 4α-hydroxymethyl-2-carenes **53a,c** and 4α-acetoxymethyl-2-carenes **53b** as well.

The silylation of compound **23** was carried out in both conditions of kinetic and thermodynamic control of the reaction [130-132]. The reaction of compound **23** with chlorotrimethylsilane afforded silyl enol ether **56a** [133,134].

***Scheme* 24**

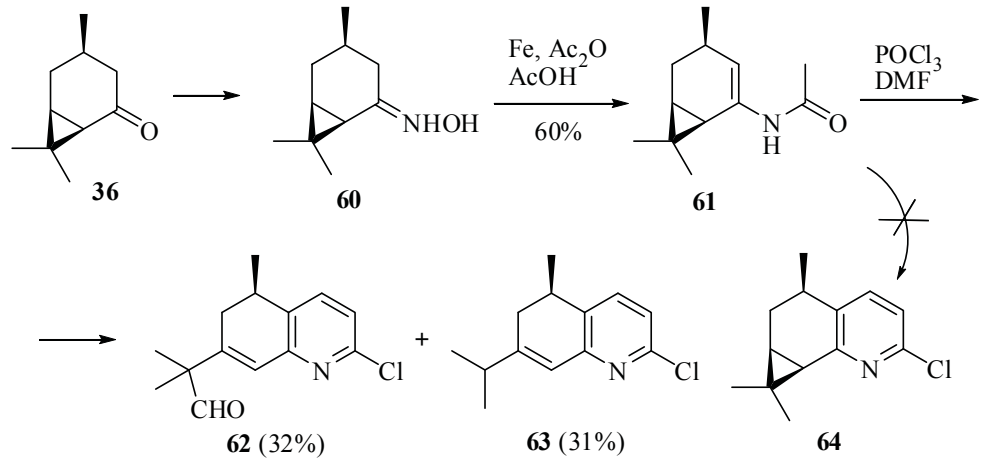


An interaction of ketone **23** with the mixture of Et_3N-chlorotrimethylsilane in DMF gave an epimer **56b**. The attempts to isomerize ethers **56a,b** into isomer **57** have failed. The product of hydrolysis has represented a

mixture of 4α- and 4β-acetyl-2-carenes **23, 53** (ratio 5:95). Ozonolysis of the ether **56a** in the mixture of CH_2Cl_2/MeOH followed by the decomposition of peroxides with Me_2S proceeds with the formation of well-known [135-138] car-2-en-4-one **7c**. As far as the stability of ethers **56a,b** towards isomerization is concerned, it is most probable that the rearrangement of intermediary products occurs during ozonization. The acid **57a** has been synthesized from the ketone **23** in the condition of hypobromide oxidation as well as by ozonolysis of the ether **56a** [139,140]. The ester **57b** or the ketone **23** could react with MeMgBr to give the alcohol **58**. Crystalline epimer **59a** is easily separated from the oil-like alcohol **59b** by the crystallization from hexane [141-143].

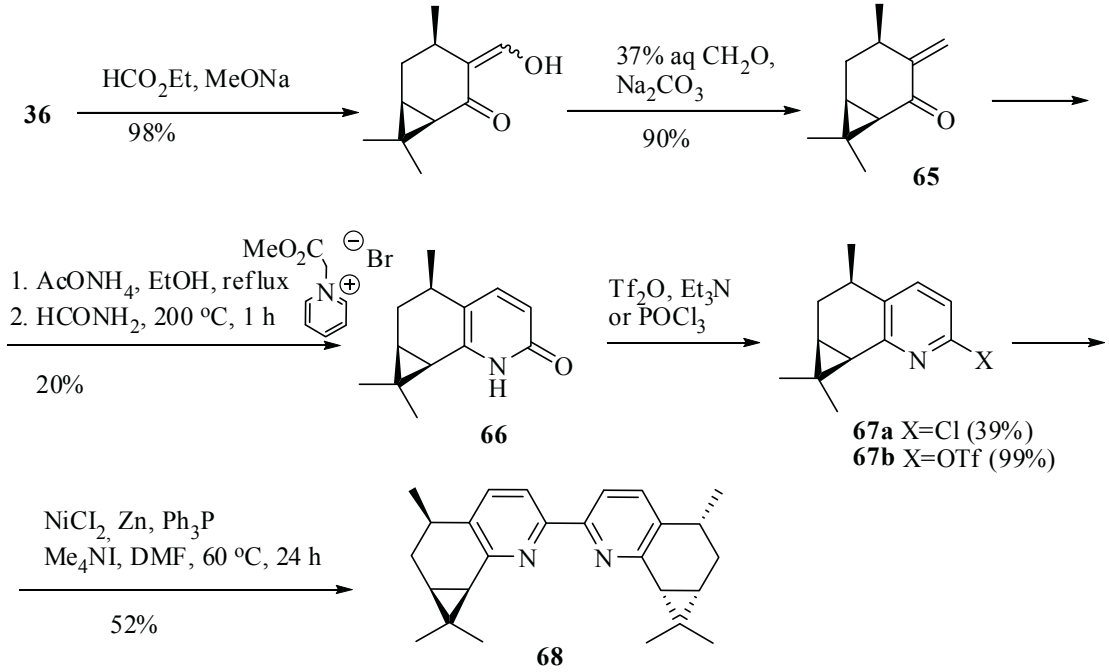
To develop new efficient routes to functionalized pyridines, amide **61** was tested as starting chirone [144].

***Scheme* 25**



However, the heterocyclisation step leads to the cyclopropane ring opening reaction with the formation of two types of pyridines **62, 63** without target **64**. This problem was solved by replacing direct heterocyclisation step with a Krohnke annulation. The *exo*-methylene functionality was prepared via Claisen condensation followed by transaldolization. The reaction of enone **65** with Krohnke salt afforded pyridone **66**. The treatment of the latter derivative with $POCl_3$ produced the target chloride **67a** in a modest yield. By contrast, the conversion into the triflate **67b** occurred almost quantitatively. The triflate **67b** was then coupled using the Ni/Zn to afford the required bis-pyridine **68**.

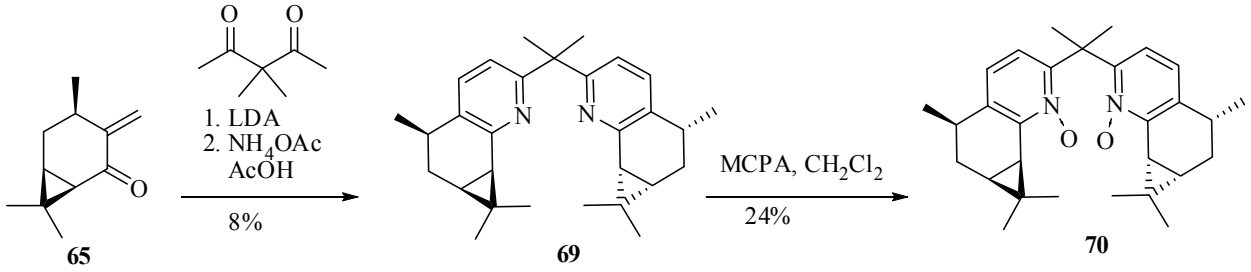
***Scheme* 26**



A moderate yield of asymmetric allylic oxidation of cycloalkenes catalyzed by Cu-complexes of chiral ligand **57** was observed.

The synthesis of more functionalized bis-pyridine **69, 70** was realized from the enone **65** [145,146]. The reactions carried out successfully are detailed in scheme 27.

***Scheme* 27**



The allylation of aldehydes with allyltrichlorosilane promoted by new chiral dipyridylmethane N-oxides **70** was realized with moderate yield (58%) and good (83%) enantioselectivity.

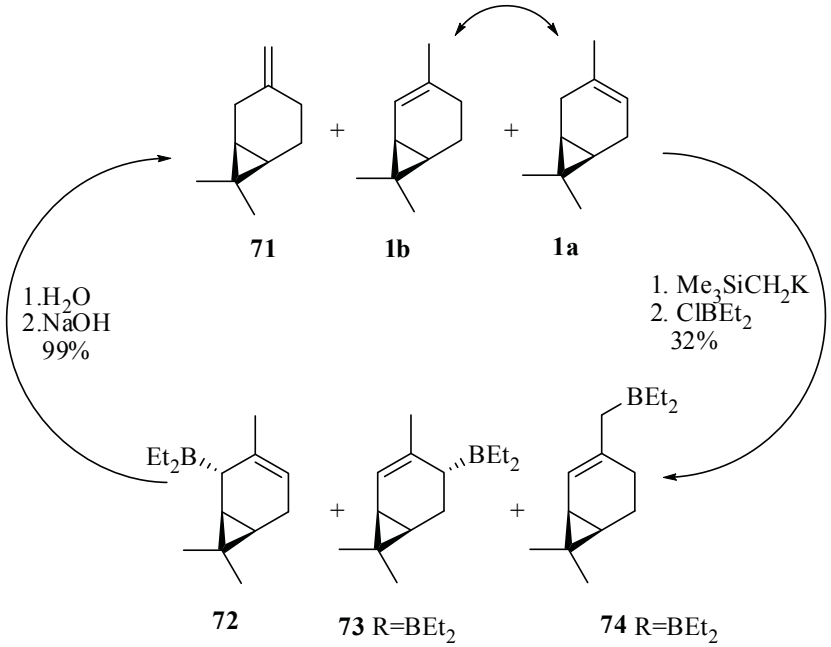
Thus, it has been shown that the functionalization of carene's π-bond with subsequent conversions gives compounds with carane skeleton in the molecule.

3. Synthesis on the basis of 2-carenes with carane skeleton retention

As has been mentioned above, the 2-carene **1b** is a convenient initial compound for a purposeful synthesis. A heterogeneous catalyzed isomerization on inorganic materials (zeolites in the basic form, nickel catalysts on SiO_2) or via hydrogenation of (+)-3-carene **1a** was described [147-150]. In all cases the mixture of **1a,b** separated with a great difficulty was obtained.

The transformation of (+)-3-carene **1a** into mixture diethylboranes **72-74** and hydrolysis resulted in the mixture of carenes **1a** (yield 9%), **1b** (yield 9%) and **71** (yield 82%) (scheme 28) [151].

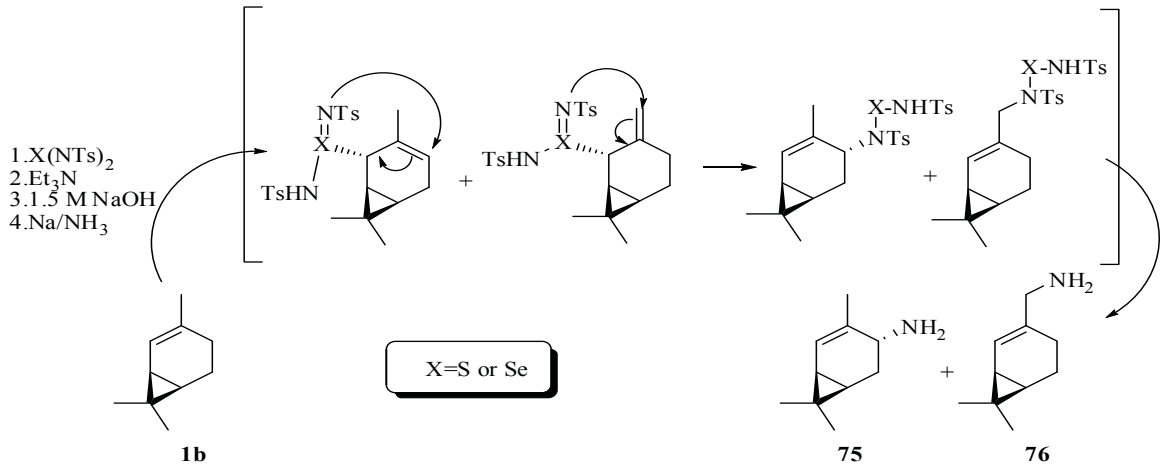
***Scheme* 28**



Amino homologues **75, 76** have been synthesized from 2-carene **1b** [152, 153].

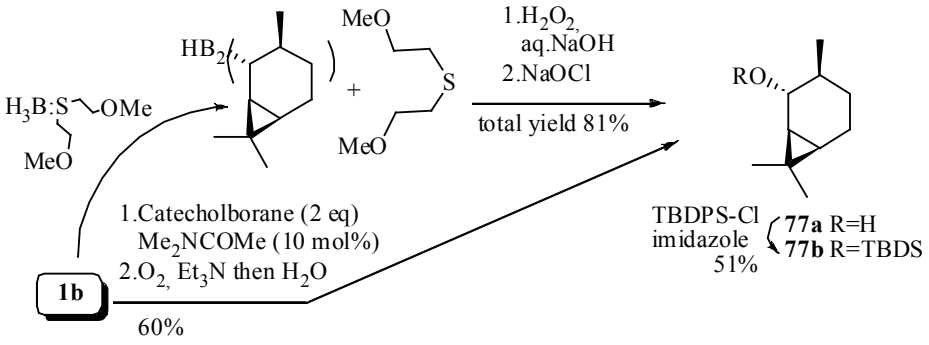
The initially formed mixture of regioisomeric imides is subjected to [2,3]-sigmatropic rearrangement, and its subsequent hydrolysis leads to a pair of amines **75** (yield 11%), **76** (yield 5%).

***Scheme* 29**



Brown and co-workers have proposed a stereocontrolled synthesis of caranol **77a** *via* hydroboration of (+)-2-carene **1b** [154].

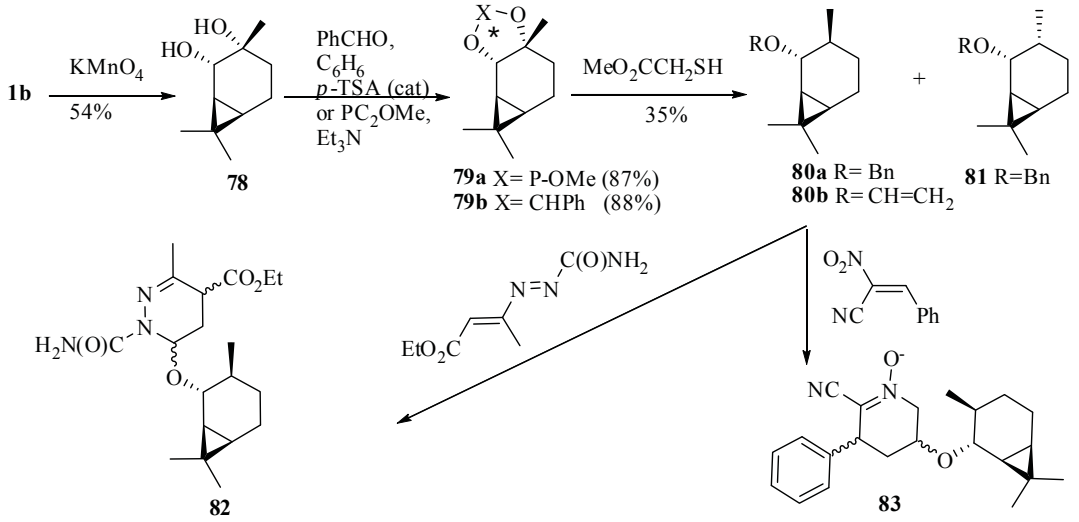
***Scheme* 30**



Another group has established that oxygen oxidizes the aryl(alkyl)boronates up to hydroxylated product **77a**, however this method is less selective [155]. The alcohol is characterized as ether **77b**.

A new and readily available modular phosphate ligand **79a** with P*-stereocentre has been prepared from caran-2,3-diols **78** [60]. The acetals **79b** were transformed into chiral intermediates **80a,b** and **81** (scheme 31) [156].

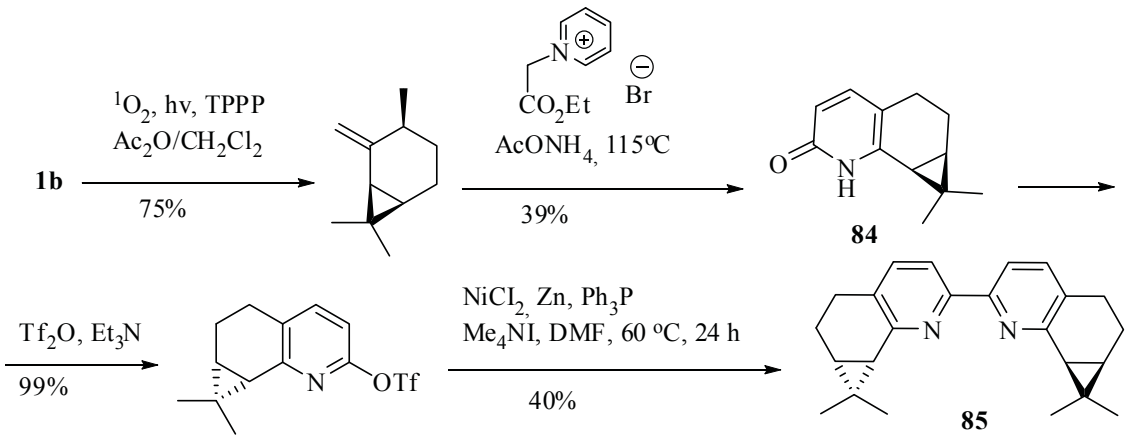
***Scheme* 31**



The synthesis of more functionalized ether **82, 83** via two different [4+2] cycloaddition reactions in aqueous medium is presented [157,158].

Bis-pyridine **85** was obtained *via* an initial transformation of (+)-2-carene **1b** into pyridone **84** [144]. The treatment of the latter compound with Tf_2O following the coupling affords the compound **85**. Asymmetric allylic oxidation of cyclic olefins with good conversion rates and acceptable enantioselectivity (67% ee) was registered by Cu-complexes of ligand **85.**

***Scheme* 32**

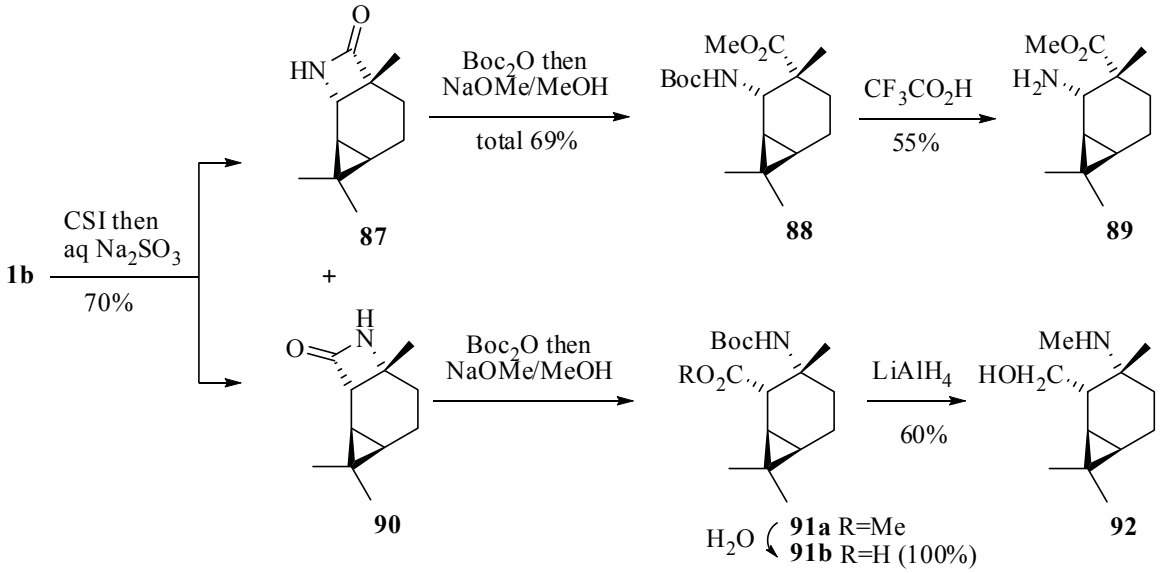


Mixtures of lactams **87**, **90** have been obtained by addition to monoterpene **1b** chlorosulfonyl isocyanate [159].

It was reported that isomers **87**, **90** could not be separated in a pure form and significant amounts. Analytically pure samples were isolated after fractional recrystallization from hexane.

In general, tricyclic compounds **87**, **90** gave a number of derivatives of β-amino acids **88**, **89**, **91a,b** and **92**. It is to be noted that, in contrast to amino ester **88** its region-isomer **91a** was readily hydrolyzed to the acid **91b** under the NaOMe catalyzed methanolysis as well as in the presence of even small amounts of water. The mixture of compounds **91a,b** can be reduced with a reasonable yield to amino alcohol **92** with $LiAlH_4$.

***Scheme* 33**



4. Conclusion

It is clear from the above relative reactivity data of monoterpenes (+)-2- and (+)-3-carenes that there are good posibilities of establishing objective or sets criteria which help decide whether electrophilic addition or dipolar cycloadditions to carbon-carbon double bonds involve the synthesis with the retention of the bicyclic framework. Although the coupling reactions should be optimised and the cyclisation of such compounds has not been attempted, one can rely on the results obtained with the polycyclic compounds. The synthesized compounds can be further converted

into the substances of known pharmaceutical interest and the obtained molecules can also display interesting biological properties.

In conclusion, it might be stated that the actual details of the transformation of bicyclic monoterpenes employing a stereoselective functionalized of the cyclohexene rings are yet to be clarified on the basis of more definitive studies.

5. Acknowledgements

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