J.Serb.Chem.Soc. 68(4–5)313–320(2003) UDC 547.592+546.26.027:66.095.11.095.252+66.092.21
JSCS – 3047 *Original scientific paper*

Synthesis of tetrahydrokhusitone. Annulation of the cyclohexane ring by free radical and carbanionic sequence of reactions*

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(Received 16 December 2002)

Abstract: The synthesis of norcadinane sesquiterpene tetrahydrokhusitone **1** has been achieved by a new method for annulation of cyclohexane ring involving a sequence of free radical δ-alkylation of the non-activated carbon atom and intramolecular carbanionic alkylation. (–)-Menthol was used as the starting compound.

Keywords: khusitone, norcadinanes, annulation of the cyclohexane ring, 1,5-hydrogen transfer, cycloalkylation, isomerization, tetrahydrokhusitone.

The Robinson annulation and 4+2 cycloaddition reactions are the most important synthetic methods for the construction of the cyclohexane ring. In addition to these classical reactions, we recently discovered a new sequence of free radical and carbanionic reactions for the annulation of the cyclohexane ring involving carbon-carbon bond formation on the non-activated carbon atom (Scheme 1).[1]

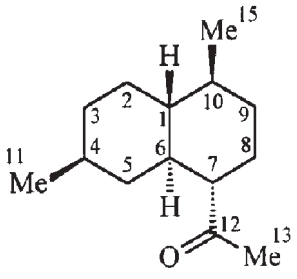
Scheme 1.

This new methodology for cyclohexane ring formation was applied in the synthesis of norcadinane (C_{14}) sesquiterpene tetrahydrokhusitone **1**.

Khusitone **2** is a bicyclic 14-norsesquiterpene isolated from the north Indian vertiver oil (*Vetiveria zizanioides*, L.) which belongs to the large group of cadinene sesquiterpenes.[2] Cadinenes are widely distributed in nature, while khusitone is a rare C_{14} terpenoid possessing the same stereochemistry at the C_1, C_6 and C_7 atoms as the ε-cadinenes subgroup of terpenes.[3] The synthesis of khusitone **2** starting from 4-acetyldecaline-1,6-dione has been described, however synthesis of its tetrahydroderivative was not realized.[4]

* Dedicated to Professor Miroslav Gašić on the occasion of his 70th birthday.

\# Serbian Chemical Society active member.



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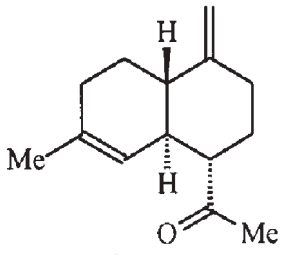
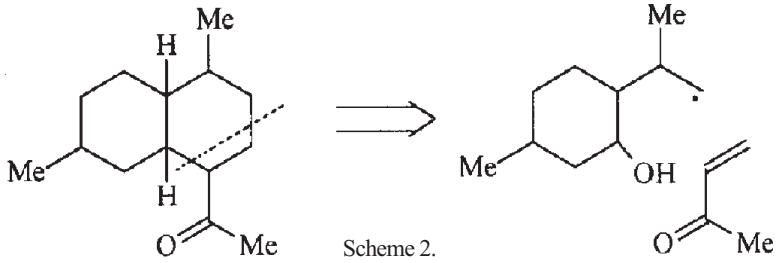


2

Herein a new synthetic method for the construction of the cyclohexane ring by tandem of free radical alkylation of the non-activated δ-carbon atom[5] and a subsequent intramolecular carbanion cycloalkylation[6] was applied for the construction of the bicyclic skeleton of 14-norcadinane derivatives.

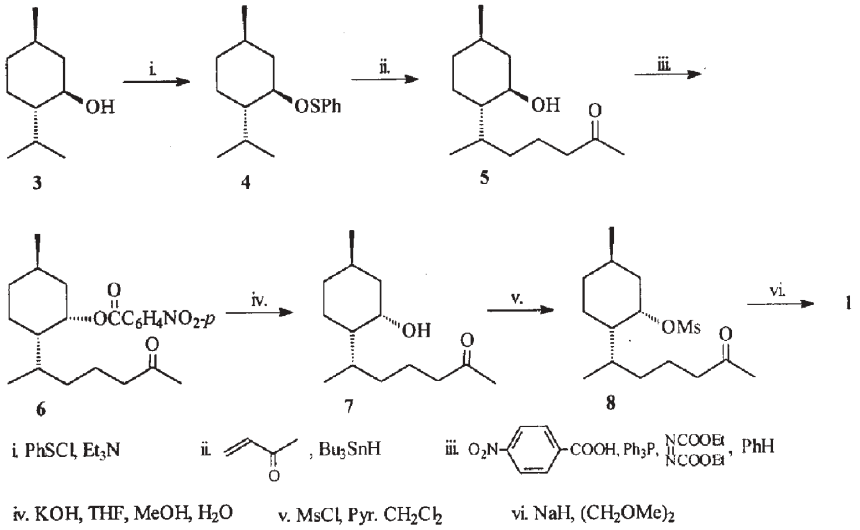
The synthetic approach to the khusitone skeleton, by application of our annulation method was conveniently realized using (–)menthol **3** as starting compound (Scheme 2).



Scheme 2.

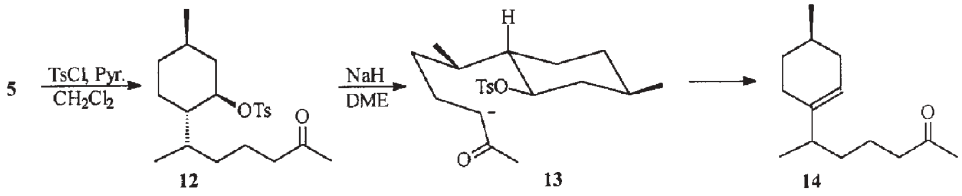
(–)-Menthol was converted to the (–)-menthyl benzenesulfenate ester **4** by reaction with phenylsulfenyl chloride (Scheme 3).[7] (–)-Menthyl benzenesulfenate **4** is a good precursor of the menthyloxy radical intermediate, necessary for the free radical alkylation of the non-activated methyl group of the side isopropyl group. Introduction of the functonalized alkyl chain onto the non-activated methyl group was achieved in the reaction of (–)-menthyl benzenesulfenate **4** with tributyltin hydride in the presence of 10 molar equivalents of methyl vinyl ketone, under irradiation conditions.[5] Thus, in the key step of this synthesis of tetrahydrokhusitone, the hydroxy ketone **5**, as a synthetic intermediate, was isolated in 32 % yield.

In the hydroxy ketone **5** procarbanionic (electron donor) and procarbocationic (electron acceptor) carbon atoms are suitably disposed for intramolecular alkylation and cyclohexane ring closure. Thus, the hydroxy group in the alkylated poroduct **5** was transformed to the corresponding *p*-toluenesulfonate ester **12** (Scheme 4). In the subsequent reaction of the tosylate **12** with sodium hydride in dimethoxy ethane, under equilibrium reaction conditions, the corresponding enolate anion **13** was formed. It was expected that the intramolecular alkylation may occur with closure of a new cyclohexane ring, possessing an exocyclic acetyl group. However, an elimination reaction rather than a cycloalkylation reaction occurs and the unsaturated ketone **14** was obtained as the only reaction product. The



Scheme 3.

intramolecular alkylation of the keto tosylate **12** is a S_N2 type of reaction, however the stereochemistry of the keto tosylate, possessing a bulky toluenesulfonyl group in the equatorial position, does not allow the side chain to adopt the conformation necessary for substitution of the tosyl group by a nucleophilic carbon atom and elimination of the proton from the adjacent tertiary carbon atom occurs instead.

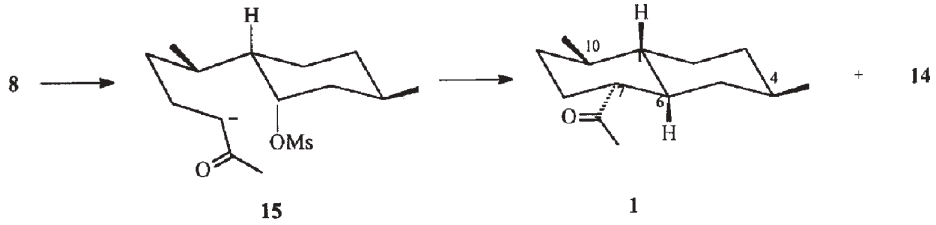


Scheme 4.

In order to achieve the cycloalkylation reaction leading to the tetrahydrokhusitone skeleton it was necessary to adjust the stereochemistry of the hydroxy group for realization of the intramolecular substitution reaction (S_N2 type). In hydroxy ketone **5** it was necessary to epimerize the equatorial hydroxy group into an axial hydroxy group and thus set up the leaving group in the axial position.

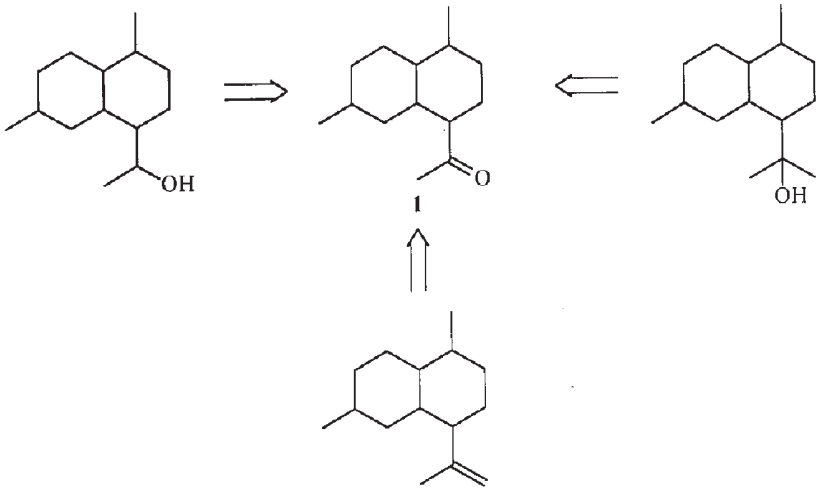
Inversion of the stereochemistry was achieved by a modified Mitsunobu reaction *via* the *p*-nitrobenzoate ester.[8] The δ-alkylated product **5** was treated with *p*-nitrobenzoic acid in the presence of triphenyl phosphine and diethyl azodicarboxylate. Under these conditions, esterification with isomerization takes place, and 6-[(1*S*, 2*S*, 4*R*)-2-(*p*-nitrobenzoyloxy)-4-methylcyclohexyl]-heptan-2-one (**6**) is obtained in 82 % yield. Hydrolysis of the *p*-nitrobenzoate ester **6** under basic conditions gives the epimerized hydroxy ketone **7** (97 %) with an axial hydroxy group. In the reaction of **7** with methanesulfonyl chloride in the

presence of pyridine, the corresponding mesylate ester **8** was obtained (Scheme 3). The enolate anion **15**, derived from the epimerized oxygen function of the keto mesylate ester with the appropriate stereochemistry and an axial leaving group, undergoes intramolecular substitution to give the tetrahydrokhusitone **1** in 53 % yield (Scheme 5). In addition to the bicyclic product, the unsaturated ketone **14** was also formed in 34 % yield as a product of elimination.



Scheme 5.

It is well known that the intramolecular cycloalkylation reaction is less favourable when the leaving group (*i.e.*, the sulfonate ester group) is attached to a secondary carbon atom and in such cases the elimination reaction becomes a serious side reaction.



Scheme 6.

The stereochemical course of the cycloalkylation reaction involves the inversion of the configuration of the procarbocationic carbon atom and the two cyclohexane rings, in the bicyclic system **1** are *trans*-jointed. The side acetyl group is at the more stable equatorial position. The 11-methyl group retains the equatorial position as in the starting (–)-menthol. A new chiral center at the C10 carbon atom is formed in the free radical alkylation of the (–)-menthyl benzenesulfenate and the ratio of the isomers with equatorial 15-methyl group (10*R*) and axial 15-methyl group (10*S*) is 5 : 1.

The prepared tetrahydrokhusitone **1** may be considered as a synthetic intermediate in the synthesis of 14-norcadinane derivatives. This synthetic methodology for construction

of the 14-norcadinane skeleton, involving a free radical and ionic squence of reactions, offers a new approach for the synthesis of a number of norcadinane and cadinane derivatives possessing a variety of functional groups. In Scheme 6 the synthetic routes of some terpenes possessing a norcadinane or cadinane structure are illustrated.

EXPERIMENTAL

The solvents used in all of the experiments were purified by distillation before use (benzene distilled over calcium hydride and dichloromethane over phosphorus pentoxide). Purifications and separations of the reaction products were carried out by distillation and column chromatography using silica gel 100–200 mesh (60 Å) and by dry flash chromatography using silica gel (60 Å). The reactions were monitored by TLC using silica gel (TLC 60 Å) or by GC (Varian 3400, column OV-101 1 % on Chromosorb W–AW). IR spectra (ν_{max} in cm^{-1}) were recorded on a Perkin-Elmer 457 grating instrument. ^{1}H-NMR spectra (ppm in δ-values) were recorded (in $CDCl_3$) at 200 MHz, using a Varian Gemini 200. ^{13}C-NMR spectra were recorded on the same instrument at 50 MHz. Mass spectra were recorded on a Finnigan ITDS 700 instrument.

*(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl benzenesulfenate [(–)-menthyl benzenesulfenate] (***4***)*

A mixture of (–)-menthol (3.0 g, 19.2 mmol) and triethylamine (4.8 g, 48.0 mmol) in dichloromethane (140 ml) was cooled to –78 ºC, in an argon atmosphere and benzenesulfenyl chloride (3.3 g, 23.0 mmol) was added with stirring during 10 min. The reacting mixture was then stirred at the same temperature for an additional 40 min. The mixture was left to attain room temperature and then dichloromethane (400 ml) was added. The resulting solution was washed successively with 2 M hydrochloric acid (50 ml), saturated aqueous sodium bicarbonate (50 ml) and water. The solution was dried over anhydrous Na_2SO_4 and solvent was evaporated under reduced pressure. The residual yellow-green oil was distilled under reduced pressure and 4.4 g (87 % yield) of (–)-menthyl benzenesulfenate was obtained, b.p. 108–110 ºC / 0.07 mm Hg, $[\alpha]_D^{22} = -256.7$ (*c* = 1, $CHCl_3$). The purity of the compound was 92 % (determined by ^{1}H-NMR spectrum). Micro analysis was not performed because the compound decomposes with explosion in the Pregl apparatus. IR (neat, cm^{-1}): 3062, 2000–1600, 1583, 1477, 1455, 1440, 1387, 1370, 1345, 1097, 1024, 1004, 981, 959, 914, 851, 778, 738, 690. ^{1}H-NMR (200 MHz) δ: 0.62 (*d*, *J* = 7.0 Hz, 3H), 0.87 (*d*, *J* = 7.2 Hz, 3H), 0.88 (*d*, *J* = 7.2 Hz, 3H), 0.72–1.00 (*m*, 3H), 1.20–1.38 (*m*, 2H), 1.54–1.66 (*m*, 2H), 2.18–2.38 (*m*, 2H), 3.37 (*td*, J_1 = 10.7 Hz, J_2 = 4.4 Hz, 1H), 7.10–7.40 (*m*, 5H). ^{13}C-NMR (50 MHz) δ: 141.29, 128.52, 126.65, 125.37, 87.01, 48.62, 40.88, 34.10, 31.50, 25.06, 22.93, 22.03, 20.87, 15.59.

*6-[(1*S*,2*R*,4*R*)-2-Hydroxy-4-methylcyclohexyl]-heptan-2-one (***5***)*

A solution of (1*R*,2*S*,5*R*)-2-isopropyl-5-methyl-cyclohexyl benzenesulfenate [(–)menthyl benzenesulfenate] (**4**) (0.73 g, 2.25 mmol), methyl vinyl ketone (1.93 g, 27.5 mmol) and tributyltin hydride (0.80 g, 2.75 mmol) in benzene (220 ml) in an argon atmosphere was irradiated, at room temperature using a 125 W high pressure mercury lamp during 2 h. The benzene was evaporated under reduced pressure and the residual oil dissolved in ether (100 ml) and the resulting solution was treated with 7.5 % aqueous solution of sodium fluoride (20 ml) and stirred overnight. The mixture was filtered, the ethereal solution was separated and the water solution was extracted with ether (3×20 ml). The combined solutions were dried over anhydrous Na_2SO_4. The ether was evaporated and the oily residue was purified by chromatography on a silica gel column using petroleum ether, petroleum ether/acetone 95 : 5, and petroleum ether/acetone 9 : 1, successively. 6-[(1*S*,2*R*,4*R*)-2-hydroxy-4-methylcyclohexyl]-heptan-2-one (**5**) was obtained in 32 % yield (0.2 g) as a yellow-green oil containing a mixture of two diastereoisomers 6*R* and 6*S* in the ratio 1 : 3.5. IR (neat, cm^{-1}): 3420, 1713, 1456, 1411, 1363, 1262, 1226, 1170, 1103, 1080, 1044, 991,969, 922. ^{1}H-NMR (200 MHz) δ: 0.80 (*d*, *J* = 7.0 Hz, 3H), [0.91 (*d*, *J* = 6.4 Hz), 0.92 (*d*, *J* = 7.0 Hz), 3H], 0.86–1.71 (*m*, 9H), 1.22 (*q*, *J* = 7.8 Hz, 2H), 1.90–2.06 (*m*, 2H), 2.14 (*s*, 3H), 2.43 (*t*, *J* = 7.4 Hz, 2H), 3.43 (*td*, J_{aa} = 10.0 Hz, J_{ae} = 4.0 Hz, 1H). ^{13}C-NMR (50 MHz) δ: 209.53, 70.75, 70.54, 50.30, 48.10, 44.84, 43.76, 43.60, 34.52, 34.30, 31.42, 30.98, 30.22, 29.68, 24.26, 22.85, 22.15, 22.04, 21.77, 17.53, 13.60. MS (CI): 209 ($M^+ + 1$) 100 %, 191 [($M^+ + 1$) – H_2O] 25 %.

*6-[(1S,2S,4R)-2-(p-Nitrophenylcarbonyloxy)-4-methylcyclohexyl]-heptan-2-one (**6**)*

To a solution of 6-[(1*S*,2*R*,4*R*)-2-hydroxy-4-methylcyclohexyl]-heptan-2-one (**5**) (0.163 g, 0.72 mmol), triphenylphosphine (1.13 g, 4.31 mmol) and *p*-nitrobenzoic acid (0.72 g, 4.31 mmol) in benzene (14 ml) was added slowly with stirring diethyl azodicarboxylate (0.75 g, 0.67 ml, 4.31 mmol) at room temperature and in an argon atmosphere. The esterification was completed in 6 h; silica gel (3 g) was added to the mixture and from the resulting suspension the benzene was evaporated. The residual powder was transferred onto a silica gel column and eluted with petroleum ether, petroleum ether/acetone 95 : 5, successively. The title compound **6** was obtaind in 82 % yield (0.22 g) as an oily mixture of two (6*R* and 6*S*) diastereoisomers in the ratio of 1 : 3.5. IR (neat, cm^{-1}): 2000–1600, 1718, 1609, 1530, 1457, 1411, 1352, 1320, 1273, 1166, 1116, 1104, 1015, 921, 875, 839, 785, 722. ^{1}H-NMR (200 MHz) δ: 0.88 (*d*, *J* = 6.4 Hz, 3H), 0.91 (*d*, *J* = 4.8 Hz, 3H), 0.98–1.89 (*m*, 12H), 2.03–2.10 (*m*, 1H), 2.07 and 2.12 (*s*, 3H), 2.35 (*t*, *J* = 7.2 Hz, 2H), 5.48 (*s*, *broad*, 1H), 8.26 (AB *q*, $\Delta\delta_{AB}$ = 0.11, J_{AB} = 8.6 Hz, 4H), ^{13}C-NMR (50 MHz) δ: 208.90, 163.97, 150.43, 136.26, 130.56, 123.55, 73.32, 72.99, 44.59, 43.81, 39.13, 34.67, 34.19, 34.03, 33.43, 29.77, 26.84, 24.76, 22.01, 20.52, 16.95.

*6-[(1S,2S,4R)-2-Hydroxy-4-methylcyclohexyl]-heptan-2-one (**7**)*

6-[(1*S*,2*S*,4*R*)-2-(*p*-Nitrophenylcarbonyloxy)-4-methylcyclohexyl]-heptan-2-one (**6**) (0.21 g, 0.57 mmol) was dissolved in methanol (1.1 ml) and tetrahydrofuran (0.25 ml) and then an aqueous solution of potassium hydroxide (0.13 g, 2.3 mmol in 0.2 ml of water) was added. The mixture was stirred at room temperature for 30 h. Ether (150 ml) was added to the reaction mixture and washed with 2 M hydrochloric acid, saturated aqueous sodium chloride and the resulting solution was dried over anhydrous Na_2SO_4. The ether was evaporated and the residual oil was purified by dry flash chromatography on a silica gel column using petroleum ether/acetone 95 : 5. The isomerized hydroxy ketone **7** was obtained in 97 % yield (0.125 g) as a colorless oil containing the 6*R* and 6*S* diastereosisomers in the ratio of 1 : 3.5. IR (neat, cm^{-1}): 3492, 1713, 1531, 1456, 1410, 1363, 1258, 1167, 1129, 1031, 962, 936, 722. ^{1}H-NMR (200 MHz) δ: 0.87 (*d*, *J* = 6.6 Hz, 3H), 0.90 (*d*, *J* = 7.0 Hz, 3H), 0.95–1.88 (*m*, 13H), 2.14 (*s*, 3H), 2.42 (*t*, *J* = 7.0 Hz, 2H), 4.08 (*s*, broad, 1H). ^{13}C-NMR (50 MHz) δ: 209.67, 67.82, 45.70, 45.56, 44.05, 43.90, 42.63, 35.01, 33.85, 33.69, 33.54, 33.19, 29.84, 29.63, 25.87, 24.07, 23.82, 22.27, 20.85, 20.69, 17.17, 16.83.

*6-[(1S,2S,4R)-2-Methanesulfonyl-4-methylcyclohexyl]-heptan-2-one (**8**)*

To the solution of hydroxy ketone **7** (45 mg, 0.20 mmol) and pyridine (0.114 g, 1.4 mmol) in dichloromethane (2 ml), cooled to 0 ºC, methanesulfonyl chloride (91.3 mg, 0.79 mmol) was added dropwise during 3 min. The mixture was stirred for 15 h at room temperature to complete the reaction. The solvent was evaporated and the residue was dissolved in ether (150 ml). The solution was washed successively with water, 1.5 M hydrochloric acid, saturated aqueous solution of sodium bicarbonate and water and dried over anhydrous Na_2SO_4. The ether was removed by evaporation to give the pure title compound **8** as a viscous oil in quantitative yield (61 mg). The mesylate **8** was obtained as a mixture of the 6*R* and 6*S* diastereoisomers in the ratio of 1 : 5. IR (neat, cm^{-1}): 1714, 1457, 1413, 1348, 1223, 1173, 1085, 1007, 974, 952, 911, 896, 840, 796. ^{1}H-NMR (200 MHz) δ: 0.90 (*d*, *J* = 6.6 Hz, 6H), 0.94–1.82 (*m*, 12H), 2.14 (*s*, 3H), 2.44 (*t*, *J* = 7.0 Hz, 2H), 3.02 (*s*, 3H), 5.11 (*s*, *broad*, 1H). ^{13}C-NMR (50 MHz) δ: 209.31, 81.19, 45.31, 45.04, 43.81, 43.67, 40.01, 39.13, 39.01, 34.33, 33.44, 33.24, 32.88, 29.78, 25.97, 24.03, 23.70, 21.83, 20.50, 20.28, 16.72, 16.52.

*{(1S,4R,6R,7R,10R+10S)-4,10-Dimethylbicyclo[4.4.0]dec-7-yl}ethanone (**1**). Tetrahydrokhusitone*

The mesylate **8** (30 mg, 0.098 mmol) was dissolved in dimethoxy ethane (1.5 ml) and then clean sodium hydride (9.4 mg, 0.39 mmol) was added at room temperature in an argon atmosphere. The mixture was stirred and heated to 80 ºC during 20 h. After the reaction was completed, ethanol was added to react with the excess sodium hydride. Water (2 ml) was added to the mixture and extracted with ether (3× 25 ml). The combined ethereal solutions were washed with saturated aqueous sodium chloride and dried over anhydrous Na_2SO_4. The ether was evaporated and the oily residue purified by preparative TLC chromatography using petroleum ether/acetone 97.5 : 2.5 as the eluent. *Tetrahydrokhusitone* **1** was obtained (10.9 mg) in 53 % yield as a viscous oil. IR (neat, cm^{-1}): 1701, 1595, 1453, 1355, 1178, 935. ^{1}H-NMR (200 MHz) δ: 0.50–0.67 (*m*, 1H), 0.82 (*d*, *J* = 6.4 Hz, 3H), 0.88 (*d*, *J* = 6.0 Hz, 3H), 0.90–1.81 (*m*, 12H), 1.96 (*dt*, J_1 = 9.0 Hz, J_2 = 3.2 Hz, 1H), 2.12 (*s*, 3H),

2.19 (*td*, J_{aa} = 12.8 Hz, J_{ae} = 4.0 Hz, 1H). ^{13}C-NMR (50 MHz) δ: 212.67 C, (58.11, 47.67, 43.32) CH, 40.21 CH_2, 36.77 CH, (35.13, 34.88) CH_2, 32.25 CH, (30.08, 29.67) CH_2, (29.47, 22.53, 19.72) CH_3.

In addition to the tetrahydrokhusitone **1** as the cyclization product, 7 mg (34 % yield) of 6*R* and 6*S* [(4*R*)-4-methyl-1-cyclohexenyl]-heptan-2-one **14** was isolated as a colorless oil. These olefinic compounds are a product of the elimination reaction and have the same ^{1}H-NMR spectra as the product obtained in the reaction of the tosylate **12** with sodium hydride.

*6-[(1*S*,2*R*,4*R*)-2-p-Toluenesulfonyl-4-methylcyclohexyl]-heptan-2-one (***12***)*

To a solution of 6-[(1*S*, 2*R*, 4*R*)-2-hydroxy-4-methylcyclohexyl]-heptan-2-one (162 mg, 0.72 mmol) in dichloromethane (2 ml) and pyridine (160 mg, 2.1 mmol), *p*-toluenesulfonyl chloride (163 mg, 0.72 mmol) was added. The reaction mixture was stirred at room temperature for 12 h after which time the reaction was completed. The mixture was worked up by the standard procedure, the solvents were evaporated and the oily residue purified by chromatography on a silica gel column using petroleum ether/acetone 95 : 5 as the eluent. The title tosylate **12** was obtained in 82 % yield (220 mg).

*6-[(4*R*)-4-Methyl-1-cyclohexenyl]-heptan-2-one (***14***)*

The tosylate **12** (0.2 g) was dissolved in dimethoxy ethane (3 ml) and then a clean solution of sodium hydride (45 mg) was added at room temperature under an argon atmosphere. The mixture was stirred and heated to 80 ºC for 20 h.Ethanol was added to react with the excess sodium hydride. Water (5 ml) was added to the mixture and extracted with ether (3 × 30 ml). The combined ethereal solutions were washed with saturated aqueous sodium chloride and dried over anhydrous Na_2SO_4. The ether was evaporated and the oily residue purified by preparative TLC using petroleum ether/acetone 97.5 : 2.5 as the eluent. The unsaturated ketone **14** was isolated as the only reaction product and identified by ^{1}H-NMR (200 MHz) δ: 0.83 and 0.96 (*d*, *J* = 6.6 Hz, 3H), 0.88 and 0.93 (*d*, *J* = 5.5 Hz, 3H), 1.12–1.72 (*m*, 9H), 1.89–2.08 (*m*, 3H), 2.12 (*s*, 3H), 2.39 (*t*, *J* = 7.4 Hz, 2H), 5.34–5.68 (*m*, 1H).

ИЗВОД

СИНТЕЗА ТЕТРАХИДРОКУСИТОНА. АНЕЛАЦИЈА ЦИКЛОХЕКСАНОВОГ ПРСТЕНА СЛОБОДНОРАДИКАЛСКОМ И КАРБАНЈОНСКОМ СЕКВЕНЦОМ РЕАКЦИЈА

ГОРАН ПЕТРОВИЋ и ЖИВОРАД ЧЕКОВИЋ

Хемијски факултет, Универзитет у Београду, Студентски трг 16, п. пр. 158 и Центар за хемију, Институт за хемију, технологију и металургију, Његошева 12, 11000 Београд

Извршена је синтеза норкадинанског сесквитерпена тетрахидрокуситона **1** новом методом анелације циклохексановог прстена која обухвата следећу секвенцу реакција: слободно-радикалско δ-алкиловање неактивираног угљениковог атома и интрамолекулско карбанјонско алкиловање. (–)-Ментол је употребљен као полазно једињење.

(Примљено 16. децембра 2002)

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