Synthesis of natural compounds via the cycloolefin cometathesis with α-olefins

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Abstract

Cometathesis of cycloolefins with α-olefins has been studied in the presence of a $MoCl_5/SiO_2$–$SnMe_4$ catalyst. Three types of polyenes were observed in the products of this reaction: polyenes without any terminal double bond and those having one or two such bonds. It was shown that stereoselectivity of the cometathesis depends on cycloolefin ring size and reaction conditions. In some cases, the content of *cis*-isomers of $1,\Delta$-dienes in final mixture reached 63–70%. The obtained polyenes were functionalized via a selective hydroboration of terminal double bonds. A technologically prospective strategy has been developed for the preparation of great variety of natural biologically active compounds (insect sex pheromones, growth regulators, fragrant composition components) on the basis of the cometathesis and hydroboration. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Cometathesis; Hydroboration; Cycloolefins; Natural compounds; Pheromone components; Growth stimulators; Fragrance components

1. Introduction

Long chain linear or macrocyclic mono- or bifunctional derivatives are known to be widespread constituents of naturally occurring compounds of both animal and vegetable origin [1].

For example, monounsaturated C_{10}–C_{16} linear acetates, alcohols, or aldehydes, having *cis*- or *trans*-double bonds in 5–11 positions are abundant in many insect sex pheromones of *Lepidoptera* [2,3]. Natural waxes contain frequently long chain alcohols C_{20}–C_{46} or their esters many of which show an extremely high biological activity. Thus, triacontanol *n*-$C_{30}H_{61}OH$, a component of waxes covering the alfalfa leaves, is an effective growth stimulator for such popular vegetables as tomatoes, cucumber, asparagus, etc. [4].

Another type of biologically active compounds are alarm substances emitted by mammals which consist of macrocyclic ketones, e.g., muscone (3-methylcyclopentadecanone), the active component of a musk produced by inquinal glands of musk deer males. Muscone is a necessary ingredient of commercial perfume formulation [5].

In this paper, we would like to discuss some main synthetic approaches, both traditional and metathetical, to the preparation of above-men-

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tioned natural compounds. The majority of scientific and patent publications in this field are devoted to the synthesis of insect pheromones. To date, the pheromone compositions belonging to more than 600 insect species were identified. Many insects are harmful for agriculture, forestry, warehouses, etc. [2]. Therefore, application of the pheromones as ecologically pure insecticides has a great commercial and environmental value.

Among the laboratory and technological methods of synthesis of long chain olefins containing functional groups, the most popular ones are so-called 'acetylenic' route and approaches based on the Wittig reaction utilizing phosphoranes [2,3]. Both of them involve many technologically uneasy stages and demand of the expensive starting materials.

Olefin metathesis reactions open a new approach to assembling of unsaturated long chain compounds, which are precursors of many natural compounds, including pheromone components. The literature and our data show that the use of these reactions as a key step for the synthesis of natural compounds allows to substantially reduce a number of stages, and utilize cheap raw materials as well as technologically prospective heterogeneous catalysts. In principle, there are two variants of this metathetical strategy: based on the participation of either functionalized olefins or purely hydrocarbon initial olefins. Until recently, the most popular version of metathetical route was cometathesis with the participation of functionalized olefins especially esters having terminal or internal double bond [6–11]. The apparent simplicity of this variant is complicated by a range of limitations. The functional groups interact with active centers poisoning catalyst systems. Therefore, the syntheses of this kind share such well known imperfection of functionalized olefin metathesis as a limited number of available catalysts, their low stability and activity resulting in extremely low turnover. Besides, the commercial accessibility of monoenic functional derivatives is rather confined. Only esters of oleic or 10-unde-

cenoic acids may be assigned to relatively accessible raw materials. This makes the use of functionalized olefin metathesis practically impossible for commercial goals. The other trouble lies in the fact that catalysts are unable to provide effective stereo control in metathesis processes of linear olefins or their functional derivatives. Therefore, the content of final reaction mixtures is close to thermodynamic equilibrium by their stereo content, i.e., they contain preferently *trans*-isomers. At the same time, biological activity of many natural compounds including pheromone components depends dramatically on their stereoisomer content, while in many cases, only pure *cis*-isomers or the mixtures containing the latter as a predominant component have the necessary high activity [2].

We already mentioned above that saturated long chain alcohols are of interest as natural, biologically active compounds, especially relates to triacontanol(n-$C_{30}H_{61}OH$). It can be prepared from 1-morpholino-1-cyclohexene in five [12] or seven [13] steps by fine organic chemistry approach or via the metathetical methods. Metathesis of 1-hexadecene to give 15-triacontene was the key step in the triacontanol syntheses reported in Refs. [14,15]. Hydroboration [14] or hydrozirconation [15] of the latter olefin was followed by isomerisation and oxidation of the respective trialkylborane or alkylzirconocene chloride. In both cases, triacontanol mixtures with secondary C_{30} alcohols were obtained, which diminishes the usefulness of these synthetic procedures. Another approach to triacontanol synthesis is based on cometathesis of unsaturated fatty acid esters with olefins. Cometathesis of methyl oleate with cyclodecene, methyl erucate with cyclooctene [16], or methyl erucate with 1-octadecene [17] gave unsaturated C_{30} fatty acid esters which were then reduced to triacontanol. All these methods have obvious drawbacks such as the necessity of many stages, deficient selectivity, and the use of expensive raw materials.

For many years, muscone remains as an attractive object for the chemists working in the

field of fine organic synthesis. A key semiproduct in the majority of already realized methods is 2,15-hexadecanedione which undergoes the ring-closing condensation [18]. This diketone was prepared by various techniques, e.g., from 3,8-nonadiene by oxidation of terminal double bond and hydrogenation of internal double bond with following electrolysis of the salt of non-aketo acid [19]. Warwel has profitably used ethenolysis of cycloheptene for preparation 1,8,15-hexadecatriene. The latter was oxidized via both terminal double bonds followed by cyclysation and than hydrogenated into target muscone [20]. The only disadvantage of this way is relative inaccessibility of starting cycloheptene.

We believed that the problems of the synthesis of pheromones and other above-mentioned compounds can be solved by a cometathesis of cycloolefins with α-olefins. Previously, only several publications [21–25] were related to the synthesis of pheromone components via this pathway. These works do not contain practically

any information about general selectivity and stereoselectivity dependence on the reaction conditions and the structure of initial substrates.

2. Results and discussion

2.1. Cometathesis of cycloolefins with α-olefins

We have observed that cometathesis of cycloolefins with α-olefins under the influence of $MoCl_5/SiO_2$–$SnMe_4$ catalyst [26] leads to the formation of three types of polyenes; (a) with two terminal double bonds, (b) with one terminal double bond, (c) without terminal double bonds. Besides, a competitive homometathesis of α-olefins produced corresponding symmetrical internal olefin and ethylene (Scheme 1).

A comprehensive GLC analysis of the reaction mixtures at various substrate conversions showed that all theoretically expected processes are realized under the reaction condition em-

n=1,3,4;   m=1-3   X=1,2,3 ...
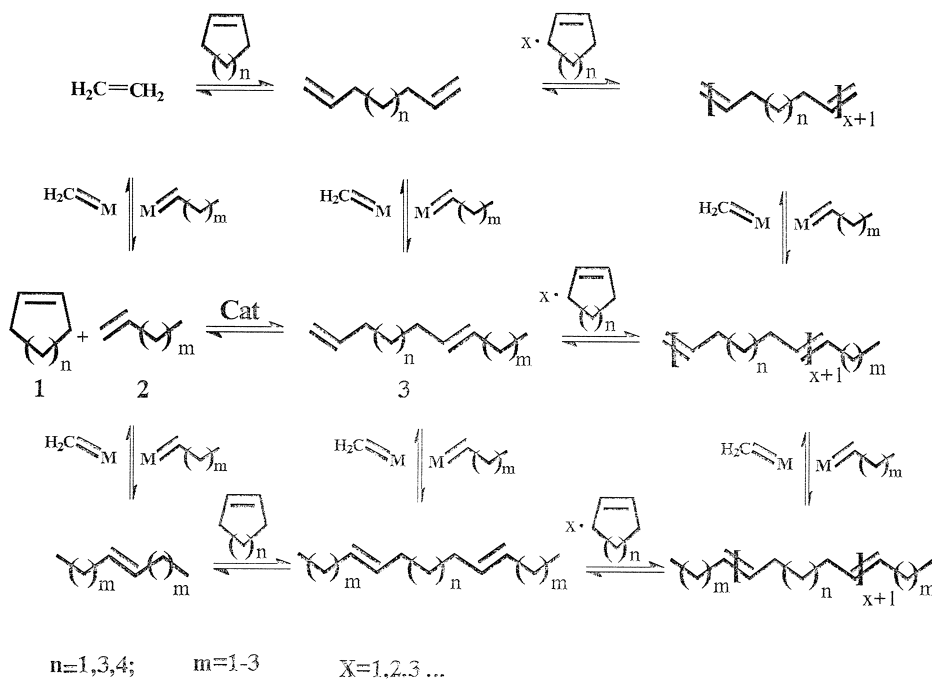
Scheme 1.

Table 1
The influence of the cycloolefin ring size on the ratio of cometathesis/homometathesis products

No.	Cycloolefin	Mass of cometathesis products/mass of 5-decene	Cycloolefin conversion (%)
1	Cyclopentene	12.3	57
2	Cyclohexene	0.01	1
3	Cycloheptene	2.2	85
4	Cyclooctene	2.3	85

$T = 20°C$; Cycloolefin:1-hexene:Mo:Sn = 200:400:1:4.

ployed. However, main reaction pathways are determined by the ring size of starting cycloolefins and practically do not depend on the length of α-olefins chain. The ratios of products formed by co- and homometathesis of various cycloolefins with 1-hexene at the nearly equilibrium of cycloolefin conversions are listed in Table 1. It is noteworthy that practically no evolution of ethylene was observed during the reaction with cyclopentene, although reactions with other cycloolefins occurred with evaluation of ethylene. This difference is apparently related to the stability of π-metallocarbenes of type a, which determines the equilibrium concentra-

tions of active centers of types a and b (Scheme 2).

Thus, in the case of cyclohexene, the equilibrium is shifted far towards the formation of the cycloolefin and carbene centers of type b, so that practically only homometathesis of α-olefins occurs.

For cyclopentene, the equilibrium is shifted towards the formation of π-metallocarbene, which is likely to have a thermodynamically advantageous pseudocyclohexane structure, so that the cometathesis reaction prevails. For cycloheptene and cyclooctene, the concentrations of the active centers of type a and b are compa-
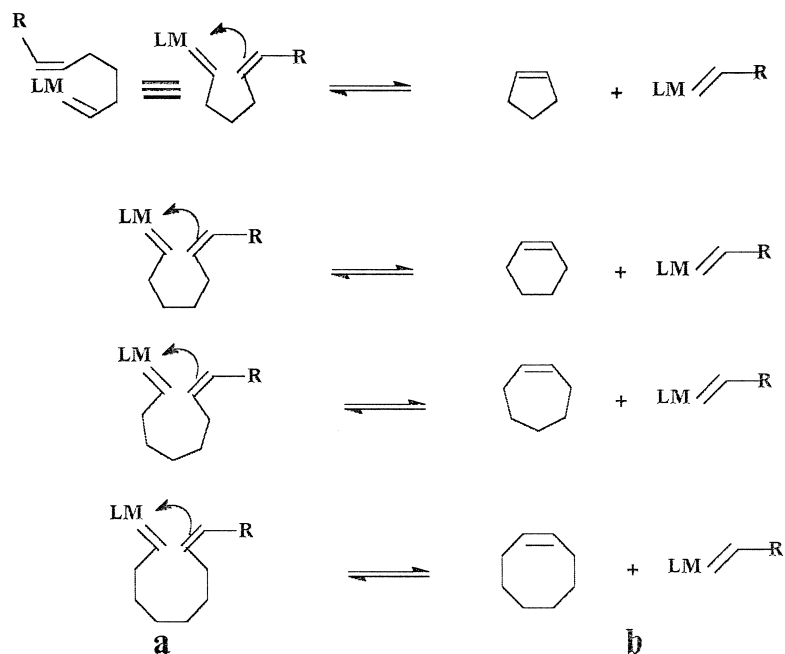
Scheme 2.

rable, which determines the ratio of products formed by homo- and cometathesis.

2.2. Synthesis of monoene sex pheromone components of Lepidoptera

By varying the starting cycloolefin and α-olefins, as well as their molar ratio, polyenes of predetermined length can be synthesized. The ring size dictates a position of double bond in the target $1,\Delta$-dienes. This position is a number of endo-cyclic C-atoms plus one. The length of these dienes is a sum of C-atoms in both initial hydrocarbons namely cycloolefin ring and α-olefin chain. At mole excess of α-olefins predominantly $1,\Delta$-dienes are formed. We used them for preparation of sex pheromone components of *Lepidoptera*.

For example, the selectivities of $1,\Delta$-dienes formation as high as 57–86% has been achieved (Table 2, Runs 1–4), when the reaction was carried out at 4°C, with five-fold excess of α-olefins and at cycloolefin conversions of $\leq$ 85%. Cometathesis products contain up to 79% of Z-isomers. Selectivities of all type drop when the cycloolefin conversion increases. At higher temperature (23°C) and lower olefin to catalyst ratio, the reaction is carried out very fast with lower selectivity even in chlorobenzene solution, the equilibrium is achieved for 14 min (Table 2, Run 5). $1,\Delta$-Dienes listed in Table 2 were isolated from final mixtures with purity $\geq$ 99% and were used for pheromone syntheses (Scheme 3).

Synthesis of monoenic alcohols **4 a**–**c** having double bond in 8- and 9-positions was realized with the help of highly regioselective hydroboration reaction using 9-BBN [27]. The letter provides addition of B-atom precisely to terminal double bond of dienes retaining internal double bond intact. This allows to prepare the target monoenic alcohols of high purity. They can be easy transformed into corresponding acetates and aldehydes, widespread pheromone components. It should be noted that components with double bond in 8- or 9-positions are con-

stituents of natural pheromone composition peculiar to a great number of insects which are harmful for agriculture [2]. For example, Z- and E-9-dodecenyl acetates are constituents of more than 30 insect species and Z- and E-9-tetradecenyl acetates—of more than 50 ones [2].

We have already mentioned that cyclohexene is practically incapable to be involved in cometathesis with α-olefins. Therefore, this way is not practical for preparation of 1,7-dienes, which are precursors for preparation of widespread 7-monoene pheromone components (e.g., Z- and E-7-dodecenyl acetates are compounds of pheromone composition emitted by more than 40 insect species). For their synthesis, we have used cyclopentene as initial cycloolefin. Its cometathesis with 1-hexene gave 1,6-undecadiene, that was then hydroborated followed by carbonylation [28]. The latter operation lengthened the hydrocarbon chain by one C-atom placing the double bond in the target 7-position (Scheme 3).

The same approach can be used for preparation of pheromone components with double bond in the 10-position. Direct synthesis of the structures of this type require the cometathesis stage with the use of cyclononene which is rather expensive and not an easily accessible product. The more prospective scheme consists of the cometathesis of cyclooctene with a convenient α-olefin followed by hydroboration–carbonylation of 1,9-dienes.

Cyclodecene did not display any tendency to form the dienes having predominantly *cis* double bonds. Even at a low cycloolefin conversion, a content of Z-11-dienes did not exceed 18%, that is close to thermodynamically equilibrium value typical for metathesis and cometathesis of linear olefins [10]. At the same time, there are a great number of commercially important pheromones containing structures with *cis* double bond in 11-position as main component. Among them, there is the sex attractant of the Omnivorous Leafroller (*Archips podana*) which is a mixture of Z- and E-11-tetradecenyl acetates with the ratio from 50/50 [29] to 63/37

Table 2
Results of cometathesis of some cycloolefins with α-olefins

Runs Cycloolefin + α-olefins	Cycloolefin conversion %	Time (min)	Selectivity 1,Δ-dienes % mass	Yield of 1,Δ-diene to initial cyclo-olefins % mass	Yield of 1,Δ-diene to initial cyclo-olefins % mole	Stereoselectivity 1,Z-Δ-diene
1			1,9-Tetradecadiene			
Z-Cyclooctene + 1-Hexene						
($n=4$; $m=3$)	3	3.5	86	4.5	2.5	73
	8	9.0	84	11.8	6.7	72
	35	37.5	74	45.6	25.8	72
	58	60.0	66	67.4	38.2	69
	70	80.0	62	76.4	43.3	68
2			1,8-Dodecadiene			
Cycloheptene + 1-Pentene						
($n=3$; $m=2$)	8	2.0	77	10.6	6.4	79
	22	4.5	75	28.5	17.2	78
	30	7.0	71	36.8	22.2	78
	61	17.5	66	69.4	41.9	74
	82	47.0	60	85.1	51.3	67
	85	60.0	57	83.8	50.5	64
3			1,6-Undecadiene			
Cyclopentene + 1-Hexene						
($n=1$; $m=3$)	7	2.5	83	12.9	5.8	59
	25	10.0	81	45.1	20.0	57
	49	18.0	77	84.1	37.7	49
	69	50.0	65	100.0	44.8	39
4			1,9-Dodecadiene			
Z-Cyclooctene + 1-Butene						
($n=4$; $m=1$)	11	3.6	79	13.1	8.7	72
	26	10.2	75	29.1	19.2	71
	48	19.2	73	52.9	35.0	69
	64	27.0	70	67.6	44.8	68
	77	42.0	65	75.5	50.0	65
	80	60.0	60	72.4	48.0	63
5			1,9-Tetradecadiene			
Z-Cyclooctene + 1-Hexene						
($n=4$; $m=3$)	57	0.5	53	53.3	30.2	61
	71	1	44	55.1	31.2	44
	81	2	37	52.9	30.0	27
	95	7	36	60.3	34.2	22
	96	14	36	63.5	36.0	16

Runs 1–4; Cycloolefin:α-olefin:Mo:Sn = 200:1000:1:4; T = 4°C. Run 5; mole ratio = 70:210:1:4; T°C = 23; 15% solution of COE + 1-hexene in chlorobenzene.
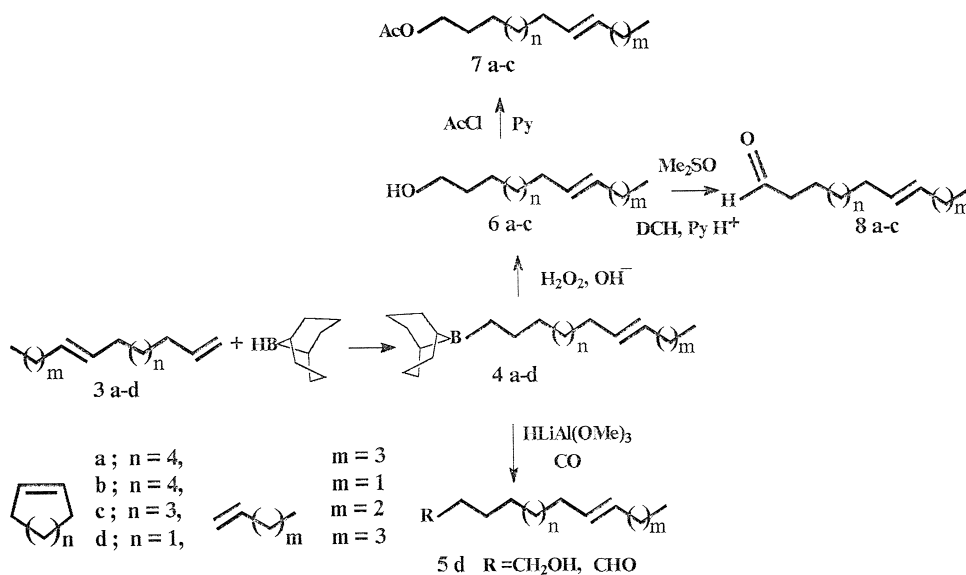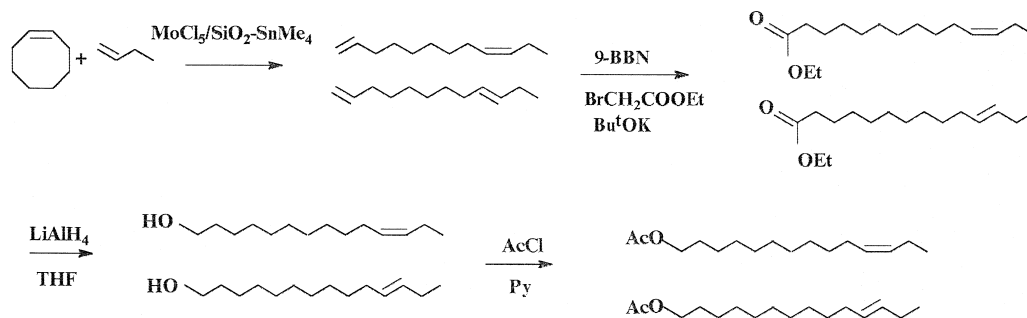
Scheme 3.

[30], the latter composition being most active. Its synthesis was realized via the cometathesis of cyclooctene with 1-hexene according to the Scheme 4.

The condition of cometathesis which allowed to achieve a mixture of 1,9-dodecadiene containing the 'ideal' ratio Z/E = 63/37 are shown in Table 2, Run 4. For the purpose of assembling the hydrocarbon chain containing 14 carbon atoms, the stage of hydroboration was combined with the chain elongation by two C-atoms in the reaction with ethyl bromoacetate [31]. The subsequent transformation of the obtained esters in the (63% Z, 37% E)-11-tetradecenyl acetates, the sex pheromone of the Omnivorous Leafroller, was realized according to well known techniques of traditional organic synthesis. It should be noted that a sample of this pheromone composition has been successfully tested in orchards of the Moscow Area [32].

2.3. Synthesis of long chain alcohols: a new synthesis of triacontanol

The known methods for preparation of higher alcohols include syntheses from organoaluminum compounds; oxo synthesis; paraffin oxidation; and reduction of fats, oils, and fatty acid esters. These methods can give only the alco-

Scheme 4.

Table 3

Products of homo- and cometathesis of cycloolefins and α-olefins (% mass)

Cyclopentene + 1-pentene ($n = 1$; $m = 2$)

Products	% Mass	Products	% Mass
4-octene	trace	1,6,11,16,21-pentacosapentaene	10.1
1,6-decadiene	19.3	C_{30} and higher	20.6
1,6,11-pentadecatriene	21.4	other products	12.1
1,6,11,16-eicosatetraene	16.5		

Cyclooctene + 1-hexene ($n = 4$; $m = 3$)

Products	% Mass	Products	% Mass
5-decene	1.8	hexacosatri- and tetraenes	9.3
1,9-decadiene	1.8	1,9,17,25-triacontatetraene	10.9
1,9-tetradecadiene	5.6	tetratriacontatetraene	7.8
5,13-octadecadiene	3.1	C_{38} and higher	25.4
1,9,17-octadecatriene	2.5	other products	25.4
1,9,17-docosatriene	9.4		

$T = 20°C$; mole ratio Mo:cycloolefin:α-olefin:Sn = 1:500:100:4; cyclopentene conversion 44% (60 min); cyclooctene conversion 80% (6 min).

hols with backbone chains no longer than 20 carbon atoms.

We propose to use the cometathesis of cycloolefins with α-olefins as a key reaction for synthesis of linear primary alcohols having more than 20 C-atoms in the chain. At proper multiple excess of cycloolefins, polyenes with one terminal double bond are formed as main products, whereas, α-olefins homometathesis products are practically absent in the reaction mixture (Table 3).

Polyenes presented in Table 3 was isolated by distillation of reaction mixtures and then utilized for preparation of long chain primary alcohols according to Scheme 5. Unsaturated alcohols can be hydrogenated smoothly to corresponding saturated strictly linear alcohols bearing terminal hydroxyl group. Thus, we used the product of three-fold insertion of cyclooctene into 1-hexene, 1,9,17,25-triaconta-

tetraene, for the synthesis of triacontanol. This polyene has been hydroborated by 9-BBN in combination with oxidation by hydrogen peroxide. The obtained 9,17,25-triacontatrienol has been hydrogenated in the presence of Pd-catalyst at 100°C and 10 atm of H_2 for 6 h, with practically quantitative yield of triacontanol (Scheme 5).

2.4. Synthesis of bifunctional derivatives: a new synthesis of muscone

Polyenes having two terminal double bonds (Scheme 1) can be used for the synthesis of various α,ω-bifunctional derivatives such as oxyacids, diols, ketoacids, diacids, diketones, etc. (Scheme 6).

Only polyenes of this type are formed by ethenolysis of cycloolefins. It should be mentioned that α,ω-dienes are always formed in the

n=1,4; m=2,3; x=1-5
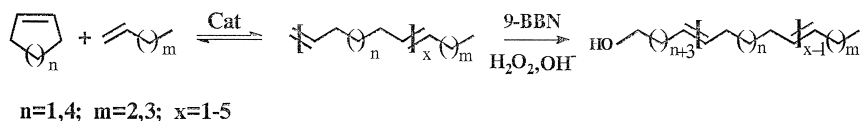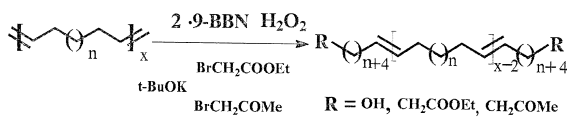
Scheme 5.

Scheme 6.

cometathesis of cycloolefins with α-olefins when the excess of the latter is used. Thus, 1,9-decadiene is present in cometathesis mixtures of cyclooctene. In the case of cometathesis of cyclooctene with 1-butene at five-fold excess of this α-olefin 1,9-decadiene content in the cometathesis products achieved 35% at 10°C and cyclooctene conversion 71%. Easily separated 1,9-decadiene was used for preparation of 2,14-hexadecadione, key semiproduct in the synthesis of muscone (Scheme 7).

Here, we propose a technologically prospective synthetic approach to the preparation of linear long chain or macrocyclic mono- and bifunctional derivatives including naturally occurring substances. The method is based on cometathesis of accessible cycloolefins and α-olefins in combination with hydroboration–oxidation or hydroboration–homologation reactions.

3. Experimental

NMR spectra were recorded with a Bruker MSL-300 and a Bruker WP-200 (200.13 MHz) instrument in CCl_4 using TMS as the internal standard. IR spectra were taken in thin layers with a Specord IR-75 instrument. Ms spectra were recorded using a Kratos MS-80 mass spec-

trometer (electron energy 70 or 12 eV). GLC analysis were performed with a LKhM8 MD chromatograph fitted with a flame ionization detector (25 m × 0.16 mm column packed with SE-30 on silica or 50 m × 0.2 mm with SKTFP; He was used as carrier gas).

Reaction products were isolated by distillation or by using a Pye Unicam preparative chromatograph (2 m × 8 mm column packed with 10% SE-30 on Chromaton N-AW). The *cis/trans*-isomer ratios were calculated from NMR and GLC data.

The starting materials were purified over Na, CaH_2, or 5 A molecular sieves under argon atmosphere.

3.1. Cometathesis of cycloolefins with α-olefins

Cometathesis of cycloolefins **1** with α-olefins **2** (Scheme 1) was carried out in a reactor equipped with a magnetic stirrer, pressure gauge and a device for charging reagents and sampling the reaction mixture. Prior to the experiment, the necessary quantities of $MoCl_5/SiO_2$ and α-olefins have been thermostated in the reactor at the desired temperature. The tetramethyltin solution in cycloolefin was then introduced into the reactor. This instant was considered as the zero reaction time. When the reaction was completed, the products were separated from catalyst and distilled to obtain the target polyenes.

3.2. Hydroboration–oxidation [27]

Hydroboration–oxidation of target polyenes was carried out by addition of an equimolar
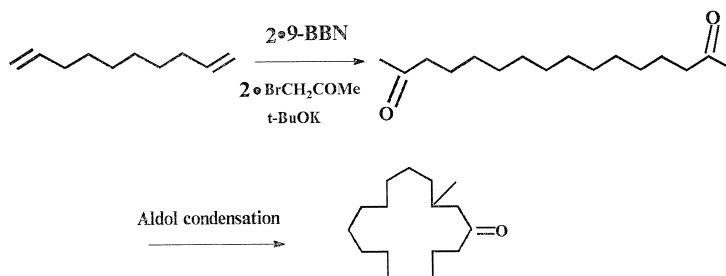
Scheme 7.

amount of 9-BBN in dry THF to polyenes. The mixture was stirred under argon for 1 h at 8°C and 1 h at 25°C and cooled to 8°C. Then, the equal volumes of methanol and 3-M sodium hydroxide were added to the solution. Oxidation was carried out by the dropwise addition of 30% hydrogen peroxide while keeping the temperature below 20°C. Polyenes alcohols were obtained with 90–96% yield.

3.3. Hydroboration–carbonylation [28]

For carbonylation of boranes **4** (Scheme 3) the equimolar volume of 0.7-M lithium trimethoxyaluminium hydride in dry THF was added dropwise at 8°C. The reaction proceeded for 2 h under carbon monoxide atmosphere. To obtain alcohol **5d**, the same volume of 2-M potassium hydroxide in methanol was added to the borane derivatives and the solution was stirred for 4 h at 70°C. To prepare aldehyde **5d**, equimolar volume 3-M sodium acetate were added to the solution of the borane derivative and then, in both cases, oxidation was carried out as described above. After distillation, the desired alcohol or aldehyde were obtained with 70–80% yield.

3.4. Hydroboration–homologation by ethyl bromoacetate [31]

Hydroboration of **3b** (Scheme 3) was carried out as described above. THF was removed in vacuo, and equimolar amount of ethyl bromoacetate was added. Then, equimolar amount of 1 M solution of Bu^{t}OK in Bu^{t}OH was added dropwise while keeping the temperature below 20°C. The mixture was stirred for 2 h, and then the oxidation was carried out as described above. Bu^{t}OH and water were removed in vacuo, and the residue was extracted with hexane. The extract was washed with water and dried with MgSO$_4$, and hexane was removed. After distillation, ethyl Z,E-11-tetradecenoate was obtained with 60% yield.

3.5. Reduction of ethyl Z,E-11-tetradecenoate by lithium aluminum hydride

LiAlH$_4$ (1.9 g, 0.05 mol) and anhydrous THF (25 ml) were placed in a flask with a stirrer, reflux condenser, and dropping funnel. Then a solution of ethyl Z,E-11-tetradecenoate (4.2 g, 0.0165 mol) in THF (10 ml) was added dropwise with stirring to the suspension. The mixture was heated to 50°C and stirred for 1 h. Then, excess LiAlH$_4$ was decomposed with HCl (7 ml) in water (14 ml). THF was removed in vacuo, and the residue was extracted with hexane. The extract was washed with water and dried with MgSO$_4$. After removal of hexane, Z,E-11-tetradecenol (3.3 g) was obtained with 94% yield.

3.6. Acetylation of alcohols by acetyl chloride / pyridine

For acetylation of alcohols **5,6** (Scheme 3), a solution of AcCl in dry hexane was added dropwise to a mixture of alcohol, pyridine and hexane while keeping the temperature below 20°C. The 1.2–2 molar excesses of AcCl and Py were used. The mixture was stirred for 2 h, then the reaction mass was treated with water, and the acetates were extracted with hexane. The extract was washed with water and dried with MgSO$_4$. After removal of hexane, acetates **7** were obtained with 95–98% yields.

3.7. Oxidation of alcohols by dimethyl sulfoxide / dicyclohexylcarbodiimide (DCH) and pyridinium trifluoroacetate as a catalyst [33]

For the preparation of aldehydes **8** (Scheme 3), a solution of pyridinium trifluoroacetate (10% mass) in DMSO was added to a mixture of equimolar amounts alcohol, DMSO and DCH in dry toluene. The mixture was stirred for 2 h, then the reaction mass was diluted with equivalent amount of water. The toluene layer was separated, washed with water and dried with

MgSO$_4$. After removal of toluene aldehydes **8** were obtained with 90–95% yields.

3.8. *Hydroboration–homologation by bromoacetone [31]*

A solution of 1.9-decadiene (10 g, 0.072 mol) and 9-BBN (17.7 g, 0.072 mol) in 100-ml dry THF was stirred at 25°C 2 h, and cooled to −60°C, then, Bu^{t}OK (16.1 g, 0.144 mol) was added. Bromoacetone (19.7 g, 0.144 mol) was added dropwise with stirring to the suspension, while keeping the temperature below −60°C. Then, the temperature was increased up to 8°C during 8 h, and oxidation was carried out as described above. After removal of liquid products, the residue was extracted with Et$_2$O. The extract was washed with water and dried with MgSO$_4$. After removal of Et$_2$O, and recrystallisation, 2,15-hexadecadione (2.7 g) was obtained with 15% yield.

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