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Dedicated to Full Member of the Russian Academy of Sciences I. P. Beletskaya on occasion of her jubilee

Ethylation of 2-Alkenyltetrahydrofurans and 2-Alkenyltetrahydropyrans Catalyzed by Titaniun(IV) Isoprpopoxide. Supplement to the Synthesis of Pheromones of Lesser Plum Worm and Tea Leaf Roller Moth

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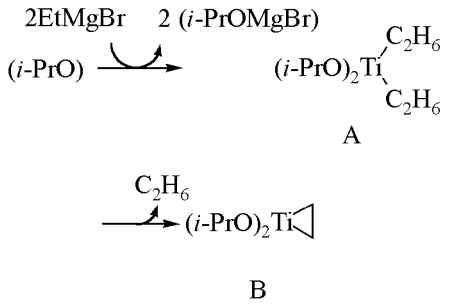
Abstract—Reaction of 2-vinyltetrahydrofuran and 2-vinyltetrahydropyran with ethylmagnesium bromude in the presence ot titanium(IV) isopropoxide afforded in moderate selectivity *trans*-4-octen-1-ol and *trans*-5-nonen-1-ol respectively. Best yields and high stereochemical purity of products were obtained in ethylation under these conditions of 2-(*cis*-1-propenyl)tetrahydrofuran, 2-(*cis*-1-proprnyl)- and 2-(*trans*-1-propenyl)-tetrahydropyran. It is assumed that the key organometallic intermediate formed was diisopropoxy-titanacycloprpopane, and direction of its addition to the doubel bond governed the streochemistry of the resulting product. The obtained *trans*-4-octen-1-ol and *trans*-7-methyl-5-nonen-1-ol were applied as initial products in the synthesis of sex pheromones of lesser plum worm (*Grafolita funebrana*) and tea leaf roller moth (*Adoxophyes sp*).

Several years ago our research team developed an efficient and experimentally simple cyclopropanation method for carboxylic acids esters by treating them with ethylmagnesium bromide in the presence of titanium(IV) isopropoxide [1, 2]. It was assumed that the reaction proceeded via formation of thermally unstable diethyltitanium intermediate A which suffered β-elimination giving ethane and diisopropoxy-titanacyclopropane B (Scheme 1). The latter acted in reactions with esters as an equivalent of 1,2-ethylene dicarbanion affording the corresponding cyclopropanols.

Scheme 1.



It was established later that the dialkoxytitanacyclopropane reagent B took part in ligand exchange with olefins [3, 4], in alkylation of *N*,*N*-dialkylamides [5] and carboxilic acids nitriles [6] furnishing the corresponding aminocyclopropanes, and also effected some other synthetically useful reactions [2, 7, 8]. In particular, we recently found that reaction of EtMgBr with magnesium alcoholates of allyl alcohols in the presence of Ti(*i*-PrO)$_4$ afforded products of formal $S_{N}2'$ substitution of a hydroxy group by ethyl [9]. Similarly react also ethers of allyl alcohols; therewith the corresponding olefins with the best *trans*-, *cis*-selectivity form from tetrahydropyranyl ethers [9].

In this study we investigated titanium-catalyzed ethylation of allyl ethers whose oxygen atom is located in a saturated heteroring. The process is a convenient way to unsaturated alcohols. A reaction of 2-vinyltetrahydrofuran (**Ia**) with 2.5 equiv of EtMgBr in the presence of 0.1 equiv of Ti(*i*-PrO)$_4$ afforded in a moderate yield *cis*- and *trans*-isomeric octanols **IIa** in 1 : 3 ratio (Scheme 2, table, run no. 1). At the use of twice less relative amount of EtMgBr 2-vinyltetrahydrofuran (**Ia**) reacted incompletely, and also the yield of compound **IIa** decreased in about the same proportion (table, run no. 2). The increased stereoselectivity [up to 90% of the *trans*-4-octen-1-ol (**IIa**)] was achieved at lower temperature, but in this case the complete conversion of substrate was reached at the use of 3 equiv of EtMgBr per 1 equiv of Ti(*i*-PrO)$_4$ (table, run no. 3).

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Reactions of alkenyltetrahydrofurans **Ia, c** and alkenyltetrahydropyrans **Ib, d** with ethylmagnesium bromide in the presence of titanium(IV) isopropoxide

Run no.	Substrate	EtMgBr (equiv)	Ti(*i*-PrO)$_4$ (equiv)	*T*, °C	Reaction product	*trans*-/*cis*-ratio	Yield, %[a]
1	**Ia**	2.5	0.1	20	**IIa**	75/25	55
2	**Ia**	1.3	0.1	20	**IIa**	Not determined	35
3	**Ia**	3.0	1.0	–65–20	**IIa**	90/10	50
4	**Ib**	2.5	0.1	20	**IIb**	70/30	63
5	**Ib**	3.0	1.0	–65–20	**IIb**	80/20	57
6	*cis*-**Ic**	2.5	0.1	20	**IIc**	95/5	55
7	*cis*-**Id**	2.5	0.2	20	**IId**	95/5	67
8	*trans*-**Id**	2.5	0.2	20	**IId**	95/5	85
9	*trans*-**Id**	3.0	1.0	–65–20	**IId**	98/2	81

[a] Yield of isolated product.

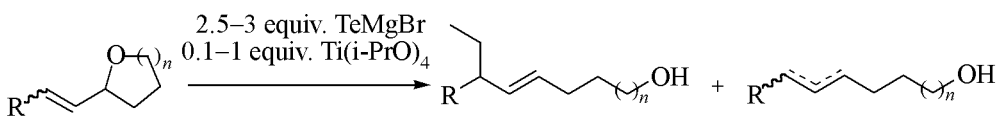
Reactions with vinyltetrahydropyran (**Ib**) under the same conditions gave similar results (Scheme 2, table, runs nos. 4, 5). In reaction of compounds **Ia** and **Ib** with EtMgBr in the presence of Ti(*i*-PrO)$_4$ formed about 20–30% of side products arising from reductive elimination of the hydroxy group [8]; these were mixtures of hexenols **IIIa** and heptenols **IIIb** respectively. We did not determine the isomeric composition of compounds **IIIa** and **IIIb** and separated them from the main products **IIa, b** by fractional distillation in a vacuum.

The ethylation 2-(*cis*-1-propenyl)tetrahydrofuran (**Ic**) and 2-(*cis*-1-propenyl)tetrahydropyran (**Id**) also furnished the target products in a moderate yield, but the stereoselectivity of the reaction was considerably higher, and the *cis*-isomer content in the arising *trans*-alkenols **IIc, d** did not exceed 5% (tanle, runs nos. 6, 7). Here also formed unsaturated alcohols **IIIc, d** as side products (about 15%). The most cleanly occurred the ethylation with ethylmagnesium bromide in the presence of catalytic amounts of Ti(*i*-PrO)$_4$ when 2-(*trans*-1-propenyl)-tetrahydropyran (**Id**) was used as substrate. The resulting *trans*-7-methyl-5-nonen-1-ol (**IId**) was obtained in over 80% yield and of stereochemical purity up to 98(table, runs nos. 7, 8).

The ethylation mechanism of compounds **Ia–d** similar to previously assumed ethylation mechanism of allyl alcohols [9] is presented in Scheme 3. The coordination of initial compounds **Ia–d** to the titanacyclopropane imtermediate B results in complex C. Therewith the approach of bulky reagent B to the double bond of substrate **Ia–d** located in syn-position to oxygen [10] becomes less sterically hindered and occurs from the less sterically loaded *exo*-side. The addition of ethylmagnesium bromide to the arising complex C furnishes titancyclopentane at-complex D [7] followed by intramolecular anti-elimination of the titanium alkoxide, and formation of a *trans* double carbon–carbon bond. Thus formed dialkylated titanium derivatives E undergo disproportionation into titanacyclopropane B and magnesium alcoholates of unsaturated alcohols (**IIa–d**). Therewith the highest stereoselectivity of the reaction with substrate **Id** originates apparently from lesser tendency of *trans*-disubstituted double bond to π-complexing with metal atoms; thus increases the directing influence of the oxygen atom on the stereochemistry of titanacyclo= propane complex B addition to the double bond resulting in complex C formation.

The appearance of side products resulting from reductive elimination of hydroxy group **IIIa–d** is due

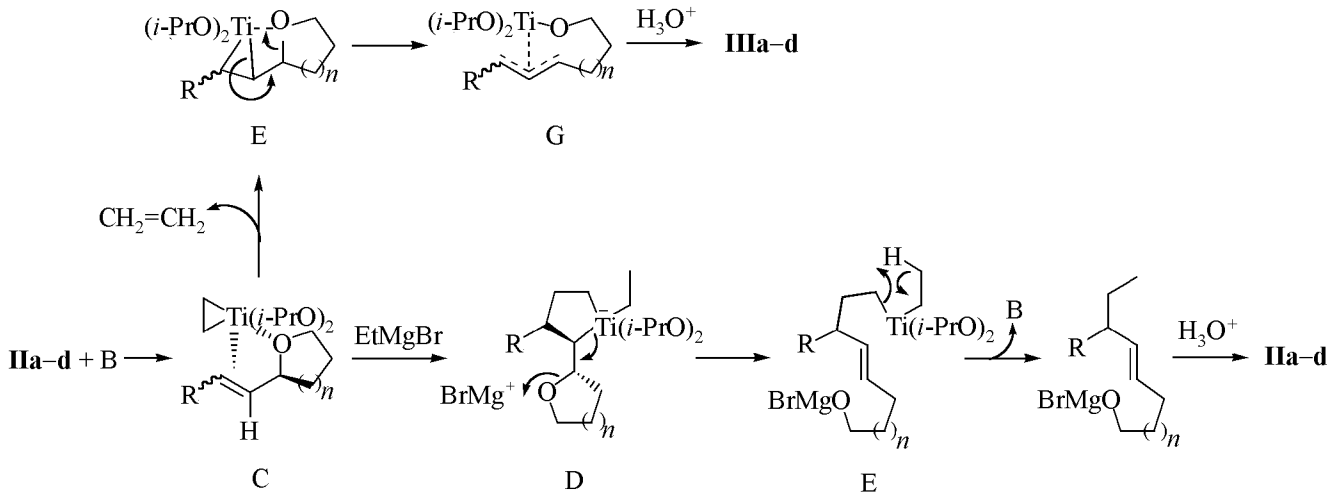
Scheme 2.



Ia–d **IIa–d** 50–85% **IIIa–d** 6–30%

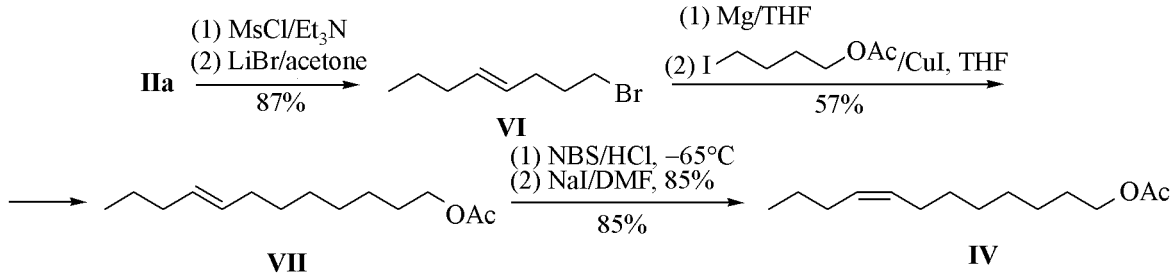
Ia–**IIIa**, R = H, *n* = 1; **Ib**–**IIIb**, R = H, *n* = 2; **Ic**–**IIIc**, R = CH_3, *n* = 1; **Id**–**IIId**, R = CH_3, *n* = 2.

Scheme 3.



R = H, CH_3; *n* = 1, 2.

Scheme 4.

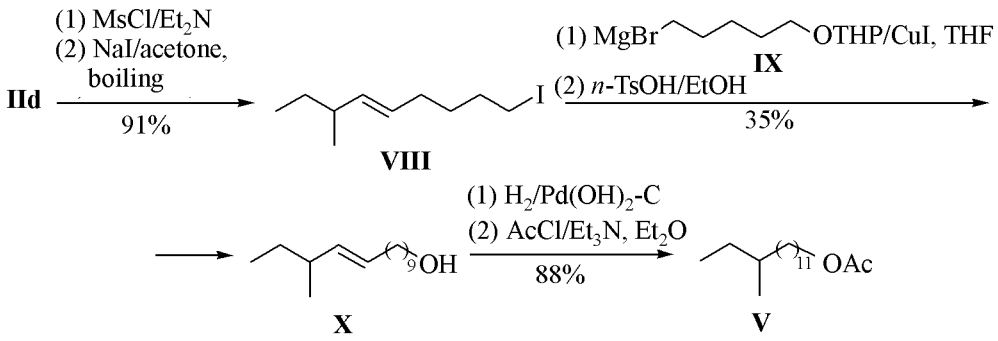


to ejection of ethylene from C intermediate giving rise to tetrahydrofuryl- and tetrahydropyranyl-substituted titanacyclopropane intermediates F. The subsequent intramolecular 1,2-elimination of titanium alkoxide affords allyltitanium alcoholates G which on hydrolysis furnish linear unsaturated alcohols **IIIa–d**. Therewith the contribution of this side reaction to the overall ethylation product falls in the series **Ia** ~ **Ib** > **Ic** > **Id** in compliance with decrease in the double carbon–carbon bond ability to form complexes with titanium in the series CH_2=CH > *cis*-CH_3CH=CH > *trans*-CH_3CH=CH.

We applied the ethylation of 2-alkenyl-substituted oxygen-containing heterocycles to the synthesis of *cis*-8-dodecen-1-yl acetate (**IV**) [11] (Scheme 4) that constituted the main component of pheromone compositions of lesser plum worm (*Grafolita funebrana*) [12, 13] and some other insects from order of *Lepidoptera* [12, 14, 15], and also to preparation of racemic form of 12-methyltetradecan-1-yl acetate (**V**) (Scheme 5), a component of pheromone of tea leaf roller moth (*Adoxophyes sp*) [16].

Compound **IV**, a strong inhibitor of the attractive effect of codlemone (sex pheromone of lesser apple worm *Laspeyresia pomonella L* [17]) was synthesized from *trans*-4-octen-1-ol (**IIa**), prepared in its turn by ethylating tetrahydrofuran **Ia** with ethylmagnesium bromide at low temperature (see the table, run no. 3). The unsaturated alcohol **IIa** containing no more than 10% of *cis*-isomer was converted into the corresponding bromide **VI** via methylsulfonate. The building-up of the carbon–carbon backbone was carried out by cross-coupling of alkylmagnesium bromide obtained from bromide **VI** with 4-iodobutyl acetate in the presence of copper(I) iodide [18]. Thus in a moderate yield was obtained *trans*-8-dodecen-1-yl acetate (**VII**) which in its turn was a component of a pheromone composition of a false lesser apple worm (*Cryptophlebia leucotreta*) [19]. The method of configuration change applied to this compound was described earlier [20]. It consists in alternating bromochlorination stages effected by *N*-bromosuccinimide in the presence of hydrogen chloride with dehalogenation of the product obtained with sodium

Scheme 5.



iodide in dimethylformamide. The content of the *trans*-isomer in the target *cis*-8-dodecen-1-yl acetate (**IV**) was about 15%, close to the amount of the minor isomer in the ethylation product obtained from vinyltetrahydrofuran **Ia**.

12-Methyltetradecan-1-yl acetate (**V**) was synhesized from unsaturated alcohol **IId** (see the table, run no. 7) that by a common procedure was converted into the corresponding iodide **VIII**. Cross-coupling of the latter in the presence of copper(I) iodide with a Grignard reagent **IX** prepared from 2-(5-bromopentyloxy)tetrahydro-2*H*-pyran afforded after removing the tetrahydropyranyl protection unsaturated alcohol **X**. The catalytic hydrogenation of compound **X** followed by acetylation furnished the target pheromone **V** in 28% overall yield (Scheme 5).

Thus in the present paper we have reported on a useful application of titanium-catalyzed alkylation of allyl ethers with ethylmagnesium bromide to preparation of 4- and 5-alken-1-ols. The latter were used in syntheses of pheromones of lesser plum worm and tea leaf roller moth.

EXPERIMENTAL

^{1}H NMR spectra were registered on spectrometers Bruker AC-200 (operating frequency 200 MHz) and Bruker Avance 400 (operating frequency 400 MHz) from 4% solutions of compounds in $CDCl_3$ (as internal reference served residual protons of the solvent). ^{13}C NMR spectra were measured on the same instruments at operating frequencies 50 and 100.6 MHz respectively from solutions in $CDCl_3$. IR spectra were recorded on spectrophotometer Specord 75IR from solutions in CCl_4. Chromatographic analysis and measurement of mass spectra was performed on a Hewlett Packard GC-MS 5890/5972 instrument, ionizing electrons energy 70 eV.

Ethyl ether and tetrahydrofuran were dried and distilled over sodium.

Ethylation of 2-alkenyltetrahydrofurans Ia, c and 2-alkenyltetrahydropyrans Ib, d. (a) Reaction at room temperature (see the table, runs nos. 1, 2, 4, 6–8). To a stirred solution of 100 mmol of compounds **Ia–d** [21] and 3–6 ml (10–20 mmol) of Ti(*i*-PrO)$_4$ in anhydrous ether (60 ml) was added dropwise 2 M solution of ethylmagnesium bromide in ether (125 ml) within 2 h at room temperature. After stirring fot 3 h the black reaction mixture was cautiously poured into a mixture of 30 ml of concn. sulfuric acid and 300 g of ice. The organic layer was separated, the water layer was extracted with ether (3×30 ml). The combined organic solutions were washed in succession with saturated solutions of $NaHCO_3$ and NaCl. The resulting organic phase was dried on Na_2SO_4, the solvent was distilled off at the atmospheric pressure, and the unsaturated alcohols **IIa–d** were distilled in a vacuum.

(b) Reaction at low temperature (see the table, runs nos. 3, 5, 9). To a stirred solution of 50 mmol of compounds **Ia, b, d** [21] and 14.9 ml (50 mmol) of Ti(*i*-PrO)$_4$ in anhydrous ether (30 ml) at cooling to –75°C was added dropwise 2 M solution of ethylmagnesium bromide in ether (75 ml) at a rate permitting to maintain the temperature of the reaction mixture below –65°C. After completing the addition the reaction mixture was stirred for 3 h while gradually warming to room temperature, and the stirring at room temperature was continued for another 2 h. Then the work-up was performed as described above. Unsaturated alcohols **IIa, b, d** were distilled in a vacuum.

***trans*-4-Octen-1-ol (IIa).** Bp 85–90°C (12 mm Hg) {86–88°C (11 mm Hg) [22]}. IR spectrum, cm^{-1}: 3613 (ν_{OH}). 1H NMR spectrum (200 MHz) (identical to publ. [22]), δ, ppm: 0.90 t, (3H, *J* 7 Hz), 1.28–

1.46 m (2H), 1.56–1.70 m (2H), 1.86 s (1H), 1.90–2.16 m (4H), 3.64 t (2H, *J* 7 Hz), 5.36–5.50 m (2H). ^{13}C NMR spectrum (50 MHz), δ, ppm: 13.6, 22.6, 28.8, 32.4, 34.6, 62.4, 129.5, 130.9. Mass spectrum, *m/z*: 29, 41, 55, 67, 81, 95, 110, 128 $[M]^+$. Found, %: C 73.51; H 12.01. C8H16O. Calculated, %: C 74.94; H 12.58.

***trans*-5-Nonen-1-ol (IIb).** Bp 95–100°C (12 mm Hg) {107°C (17.5 mm Hg) [23]}. IR spectrum, cm^{-1}: 3615 (ν_{OH}). ^{1}H NMR spectrum (200 MHz), δ, ppm: 0.86 t (3H, *J* 7 Hz), 1.26–1.48 m (4H), 1.48–1.58 m (2H), 1.88–2.16 m (5H), 3.62 t (2H, *J* 6.5 Hz), 5.30–5.50 m (2H). Mass spectrum, *m/z*: 29, 41, 55, 67, 81, 95, 109, 124, 142 $[M]^+$. Found, %: C 75.32; H 12.37. $C_9H_{18}O$. Calculated, %: C 76.00; H 12.75.

***trans*-6-Methyl-4-octen-1-ol (IIc).** Bp 55–60°C (3 mm Hg) {94–95°C (10 mm Hg) [24]}. IR spectrum, cm^{-1}: 3633 (ν_{OH}). ^{1}H NMR spectrum (200 MHz), δ, ppm: 0.85 t (3H, *J* 7 Hz), 0.95 d (3H, *J* 6.5 Hz), 1.20–1.34 m (2H), 1.56–1.75 m (2H), 1.96–2.16 m (4H), 3.63 t (2H, *J* 6.5 Hz), 5.30–5.48 m (2H). ^{13}C NMR spectrum (50 MHz), δ, ppm: 12.0, 20.9, 29.6, 30.5, 33.3, 39.2, 62.5, 128.4, 137.3. Mass spectrum, *m/z*: 29, 41, 55, 67, 81, 95, 109, 142 $[M]^+$. Found, %: C 74.73; H 11.92. $C_9H_{18}O$. Calculated, %: C 75.99; H 12.75.

***trans*-7-Methyl-5-nonen-1-ol (IId).** Bp 80–85°C (3 mm Hg). IR spectrum, cm^{-1}: 3633 (ν_{OH}). ^{1}H NMR spectrum (200 MHz), δ, ppm: 0.84 t (3H, *J* 7 Hz), 0.94 d (3H, *J* 6.5 Hz), 1.18–1.65 m (6H), 1.95–2.16 m (4H), 3.64 t (2H, 7 Hz), 4.88–5.44 m (2H). ^{13}C NMR spectrum (50 MHz), δ, ppm: 11.9, 20.4, 25.8, 27.3, 30.4, 32.1, 38.3, 62.4, 128.3, 136.8. Mass spectrum, *m/z*: 29, 41, 55, 67, 81, 95, 109, 123, 128, 138, 156 $[M]^+$. Found, %: C 75.40; H 11.61. $C_{10}H_{20}O$. Calculated, %: C 76.86; H 12.90 (publ.: [25]).

***trans*-4-Octenylmethanesulfonate.** To a solution of 4.35 g (34 mmol) of *trans*-4-octen-1-ol and 6.17 g (61 mmol) of triethylamine in 50 ml of anhydrous ethyl ether at cooling with an ice bath was added dropwise while stirring 5.15 g (45 mmol) of methanesulfonyl chloride. After completing the addition the reaction mixture was stirred for 1 h, then 50 ml of water was added. The organic layer was separated, the water layer was extracted with ether (2 × 20 ml). The combined organic solutions were washed in succession with 5% solution of HCl (30 ml), water (30 ml), saturated solution of $NaHCO_3$ (30 ml), and saturated solution of NaCl (50 ml). The organic phase was dried over Na_2SO_4, and the solvent was distilled off in a vacuum. The *trans*-4-octen-1-yl methanesulfonate was used further without additional purification. Yield 6.93 g (99%). ^{1}H NMR spectrum (400 MHz), δ, ppm: 0.87 t (3H, *J* 7.4 Hz), 1.36 sextet (2H, *J* 7.4 Hz), 1.80 quintet (2H, *J* 6.8 Hz), 1.95 q.d (2H, *J* 6.8, 1.2 Hz), 2.11 q.d (2H, *J* 6.8, 1.2 Hz), 2.98 s (3H), 4.21 t (2H, *J* 6.8 Hz), 5.35 d.t.t (1H, *J* 15.6, 6.8, 1.2 Hz), 5.46 d.t.t (1H, *J* 15.6, 6.8, 1.2 Hz). 13C NMR spectrum (100.6 MHz), δ, ppm: 13.53, 22.51, 28.21, 28.89, 34.54, 37.30, 69.40, 127.92, 132.12.

***trans*-1-Bromo-4-octene (VI).** A solution of 6.80 g (33 mmol) of *trans*-4-octenyl methanesulfonate and 5.65 g (65 mmol) of anhydrous LiBr in 100 ml of anhydrous acetone was heated under reflux for 3 h. On cooling the solvent was distilled off under reduced pressure. To the residue was added 100 ml of water and 50 ml of ethyl ether. The organic layer was separated, the water layer was extracted with ether (2 × 20 ml). The combined organic solutions were washed with water (30 ml), with saturated NaCl solution (50 ml), and dried with Na_2SO_4. On removing the solvent the residue was distilled in a vacuum. Yield of bromide **VI** 5.55 g (88%), bp 74–80°C (12 mm Hg) {82–85°C (5 mm Hg) [26]}. ^{1}H NMR spectrum (400 MHz), δ, ppm: 0.88 t (3H, *J* 7.2 Hz), 1.32–1.43 m (2H), 1.87–2.01 m (4H), 2.10–2.18 m (2H), 3.40 t (2H, *J* 7.0 Hz), 5.30–5.41 m (1H), 5.43–5.53 m (1H). ^{13}C NMR spectrum (100.6 MHz), δ, ppm: 13.57, 22.58, 30.86, 30.50, 33.22, 34.62, 128.05, 131.98.

***trans*-8-Dodecenyl acetate (VII).** Into a three-neck flask of 100 ml capacity equipped with a stirrer, low-temperature thermometer, and flushed with dry argon was charged 5.57 g (23 mmol) 4-iodobut-1-yl acetate, 0.28 g (1.47 mmol) of anhydrous CuI, and 5 ml of tetrahydrofuran. The mixture was cooled to –80°C, and thereto was gradually added under argon atmosphere at stirring a solution of Grignard reagent prepared from 5.54 g (29 mmol) of 1-bromo-4-octene (**VI**) and 0.70 g (29 mmol) of magnesium turnings in 22 ml of THF. The rate of addition was so controlled as to maintain the temperature of the reaction mixture below –70°C. After completing the addition the reaction mixture was stirred for 3 h while gradually warming to room temperature, and then it was slowly within 1.5 h heated to boiling. Then the mixture was refluxed for 1.5 h and on cooling it was treated with a saturated NH_4Cl solution (30 ml). The organic layer was separated, the water layer was extracted with ether (3 × 5 ml). The combined organic solutions were washed with water (2 × 30 ml), with

saturated NaCl solution (40 ml), and dried with Na_2SO_4. Then the solvent was distilled off, and the residue was subjected to fractional distillation in a vacuum collecting the fraction with bp 114–122°C (3 mm Hg) {69–71°C (0.04 mm Hg) [27]}. The substance obtained (3.72 g) was additionally purified by column chromatography on silica gel (eluent cyclohexane ethyl acetate, 20 : 1) to get 2.98 g of acetate **VII** as a mixture of geometric isomer [*trans*-/*cis*-, 88 : 12 (GC-MS)]. Yield 57% (with respect to 4-iodobut-1-yl acetate). IR spectrum, cm^{-1}: 1716 (ν_{CO}). ^1H NMR spectrum (400 MHz), δ, ppm: 0.86 t (3H, *J* 7.5 Hz), 1.29–1.37 m (10H), 1.56–1.61 m (2H), 1.92–2.01 m (4H), 2.01 s (3H), 4.04 t (2H, *J* 6.9 Hz), 5.35-5.39 m (2H). ^{13}C NMR spectrum (100.6 MHz), δ, ppm: 13.53, 20.86, 22.66, 25.81, 28.55, 28.90, 29.04, 29.46, 32.46, 34.63, 64.53, 130.16, 130.34, 171.08. Mass spectrum, *m/z*: 43, 55, 67, 82, 96, 109, 110, 166.

***cis*-8-Dodecenyl acetate (IV).** Through a solution of 1.10 g (4.9 mmol) of *trans*-8-dodecenyl acetate in 11 ml of anhydrous dichloromethane cooled to –70°C was passed for 15 min a flow of dry hydrogen chloride till saturation. Then at the same temperature was added by portions at stirring 1.03 g (5.8 mmol) of powdered *N*-bromosuccinimide. In 20 min after completion of addition the reaction mixture was cautiously poured into 20 ml of cooled 10% solution of sodium sulfite, the organic layer was separated, the water layer was extracted with dichloromethane (3 × 10 ml), the combined organic solutions were washed with water (2 10 ml), with saturated solution of $NaHCO_3$ (20 ml), and dried over Na_2SO_4. On removing the solvent under reduced pressure we obtained 1.30 g of product that was added to a solution of 13.0 g (86.7 mmol) of anhydrous NaI in 65 ml of dry DMF. The mixture was heated at stirring to 85°C for 20 h, then the hot reaction mixture was poured into 150 ml of water, sodium sulfite was added till the color of iodine disappeared, and the reaction products were extracted into cyclohexane (4 × 25 ml). The combined organic solutions were washed with water (2 × 20 ml), with saturated NaCl solution (40 ml), and dried with Na_2SO_4. On removing the solvent under reduced pressure we obtained 0.81 g (94%) of compound **IV** as a mixture of isomers [*trans*- and *cis*-isomers, 15 : 85 (GC-MS)]. IR spectrum, cm^{-1}: 1716 (ν_{CO}). ^1H NMR spectrum (400 MHz), δ, ppm: 0.88 t (3H, *J* 7.5 Hz), 1.30–1.42 m (10H), 1.60–1.70 m (2H), 1.97–2.04 m (4H), 2.02 s (3H), 4.03 t (2H, *J* 6.6 Hz), 5.37–5.44 m (2H). ^{13}C NMR spectrum (100.6 MHz), δ, ppm: 13.69, 20.87, 22.81, 25.82, 27.09, 28.55, 29.07, 29.22, 29.57, 64.53, 129.66, 129.85, 171.03. Mass spectrum, *m/z*: 43, 55, 67, 82, 96, 109, 110, 166 (publ.: [11]).

***trans*-9-Iodo-3-methyl-4-nonene (VIII).** To a solution of 5.77 g (37 mmol) of *trans*-7-methyl-4-nonen-1-ol and 6.78 g (67 mmol) of triethylamine in 50 ml of anhydrous ethyl ether was added dropwise while stirring and cooling with ice bath 5.50 g (48 mmol) of methanesulfonyl chloride. The reaction mixture was stirred for 1 h, and then 50 ml of water was added. The organic layer was separated, the water layer was extracted with ether (2 × 20 ml). The combined organic solutions were washed in succession with 5% solution of HCl (30 ml), water (30 ml), saturated solution of $NaHCO_3$ (30 ml), and saturated solution of NaCl (50 ml). The organic phase was dried over Na_2SO_4, and the solvent was distilled off in a vacuum. Then to the residue (8.64 g) was added 11.10 g (74 mmol) of anhydrous NaI in 70 ml of anhydrous acetone. The mixture was boiled for 2 h, the solvent was removed under reduced pressure, and 120 ml of water and 60 ml of ethyl ether was added to the residue. The organic layer was separated, the water layer was extracted with ether (2 × 20 ml). The combined organic solutions were washed with water (30 ml), with saturated NaCl solution (50 ml), and dried with Na_2SO_4. On distilling off the solvent under reduced pressure we obtained 9.15 g (93%) of iodide **VIII**. ^1H NMR spectrum (400 MHz), δ, ppm: 0.84 t (3H, *J* 7.2 Hz), 0.95 d (3H, *J* 6.4 Hz), 1.22–1.34 m (2H), 1.41–1.52 m (2H), 1.78–1.89 m (2H), 1.92–2.10 m (3H), 3.18 t (2H, *J* 7.2 Hz), 5.23–5.37 m (2H). ^{13}C NMR spectrum (100.6 MHz), δ, ppm: 6.84, 11.72, 20.35, 29.79, 30.43, 31.41, 32.96, 38.32, 127.55, 137.01.

***trans*-12-Methyl-10-tetradecen-1-ol (X).** A mixture of 1.86 g (7 mmol) of *trans*-9-iodo-3-methyl-4-nonene (**VIII**), 84 mg (0.44 mmol) of anhydrous CuI and 4 ml of THF under argon atmosphere was cooled to –90°C, and at stirring was slowly added a solution of Grignard reagent prepared from 2.17 g (8.7 mmol) of 2-(5-bromopentyloxy)tetrahydro-2*H*-pyran and 0.21 g (8.7 mmol) of magnesium turnings in 9 ml of THF. The rate of addition was so controlled that the temperature of the reaction mixture was below –70°C. After addition the mixture within 2 h was warmed at stirring to room temperature, and then it was gradually within 1.5 h heated to boiling. Then the mixture was refluxed for 1 h. The solvent was removed at reduced pressure, and to the residue was added a saturated NH_4Cl solution (15 ml) and ether (15 ml). The organic layer was separated, the water layer was extracted with ether (3 × 15 ml). The combined

organic solutions were washed with water (2 × 15 ml), with saturated NaCl solution (30 ml), and dried with Na_2SO_4. Then the solvent was distilled off, to the residue obtained (3.0 g) was added 25 ml of 96% ethanol, 0.1 g of *p*-toluenesulfonic acid, and the mixture was boiled for 1 h. On cooling to the reaction mixture was added 4 ml of saturated $NaHCO_3$ solution, the solvent was distilled off at reduced pressure, and to the residue was added 15 ml of water and 15 ml of ether. The organic layer was separated, the water layer was extracted with ether (3 × 15 ml). The combined organic solutions were washed with saturated NaCl solution and dried on Na_2SO_4. On removing the solvent the product was purified by column chromatography on silica gel (eluent ethyl acetate–cyclohexane, 1 : 5). Yield of *trans*-12-methyl-10-tetradecen-1-ol (**X**) 0.55 g (35%). IR spectrum, cm^{-1}: 3627 (ν_{OH}). ^1H NMR spectrum (200 MHz), δ, ppm: 0.86 t (3H, *J* 7.0 Hz), 0.95 d (3H, *J* 6.5 Hz), 1.32 br.s (14H), 1.50–1.63 m (2H), 1.88 s (1H), 1.92-2.06 m (3H), 3.62 t (2H, *J* 7.0 Hz), 5.04–5.44 m (2H). Mass spectrum , m/z: 29, 41, 55, 70, 83, 95, 109, 123, 137, 151, 179, 197, 208, 226 $[M]^+$ (publ.: [28]).

12-Methyltetradecan-1-ol. A mixture of 0.20 g (0.88 mmol) of *trans*-12-methyl-10-tetradecen-1-ol (**X**), 20 mg of catalyst (10% palladium hydroxide on carbon [29]), and 2 ml of anhydrous methanol was stirred under hydrogen atmosphere at room temperature for 2 h. The catalyst was filtered off and washed with 2 ml of methanol. On removing the solvent in a vacuum we obtained 0.18 g (90%) of 12-methyltetradecan-1-ol as colorless oily fluid. IR spectrum, cm^{-1}: 3607 (ν_{OH}). 1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 0.80–0.92 m (6H), 1.05–1.20 m (2H), 1.26 br.s (19H), 1.52–1.66 m (3H), 3.63 t (2H, *J* 6.7 Hz). ^{13}C NMR spectrum (100.6 MHz), δ, ppm: 11.35, 19.19, 25.72, 27.08, 29.40, 29.47, 29.58, 29.63, 29.68, 30.00, 32.79, 34.38, 36.62, 63.04. Mass spectrum , m/z: 29, 41, 55, 70, 83, 97, 111, 125, 139, 153, 181, 195, 210 (publ: [30]).

12-Methyltetradecyl acetate (V). To a solution of 0.08 g (0.35 mmol) of 12-methyltetradecen-1-ol and 0.07 g (0.09 ml, 0.70 mmol) of triethylamine in 3 ml of anhydrous ethyl ether while cooling with ice and stirring was added dropwise a solution of 0.04 g (0.52 mmol) of acetyl chloride in 1 ml of anhydrous ether. After completion of addition the mixture was stirred for 1 h, the 5% solution of HCl was added, the organic layer was separated, and the water layer was extracted with ether (2–5 ml). The combined organic solutions were washed in succession with saturated $NaHCO_3$ solution (5 ml), saturated NaCl solution (10 ml), and dried over Na_2SO_4. On removing the solvent under reduced pressure the product was purified by column chromatography on silica gel (eluent ethyl acetate–cyclohexane, 1 : 10). Yield 95 mg (95%). IR spectrum, cm^{-1}: 1722 (ν_{CO}). ^1H NMR spectrum (400 MHz, CDCl3), δ, ppm: 0.82–0.95 m (6H), 1.05–1.20 m (2H), 1.26 br.s (19H), 1.58–1.70 m (2H), 2.04 s (3H), 4.05 t (2H, *J* 7.0 Hz). ^{13}C NMR spectrum (100.6 MHz), δ, ppm: 11.36, 19.19, 20.96, 25.90, 27.09, 28.60, 29.24, 29.49, 29.55, 29.62, 29.68, 30.00, 34.39, 36.63, 64.64, 171.00. Mass spectrum, *m/z*: 29, 43, 55, 70, 83, 97, 111, 125, 140, 153, 181, 199, 210, 255 (publ.: [16, 28]).

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REFERENCES

1. Kulinkovich, O.G., Sviridov, S.V., Vasilevskii, D.A., and Pritytskaya, T.S., *Zh. Org. Khim.*, 1989, vol. 25, p. 2244; Kulinkovich, O.G., Vasilevskii, D.A., Savchenko, A.I., and Sviridov, S.V., *Zh. Org. Khim.*, 1991, vol. 27, p. 1428; Kulinkovich, O.G., Sviridov, S.V. and Vasilevskii, D.A., *Synthesis*, 1991, p. 234.
2. Kulinkovich, O.G. and De Meijere, A., *Chem. Rev.*, 2000, vol. 100, p. 2789.
3. Kulinkovich, O.G., Savchenko, A.I., Sviridov, S.V., and Vasilevsky, D.A., *Mendeleev Commun.*, 1993, no. 6, p. 230; Epstein, O.L., Savchenko, A.I., and Kulinkovich, O.G., *Tetrahedron Lett.*, 1999, vol. 40, p. 5935.
4. Kasatkin, A. and Sato, F., *Tetrahedron Lett.*, 1995, vol. 36, p. 6079; Kang, C.H., Kim, H., and Cha, K., *J. Am. Chem. Soc.*, 1996, vol. 118, p. 291; Lee, J., Kim, H., and Cha, K., *J. Am. Chem. Soc.*, 1996, vol. 118, p. 4198.
5. Chaplinski, V. and de Meijere, A., *Angew. Chem. Int. Ed.*, 1996, vol. 35, p. 413; Chaplinski, V., Winsel, H., Kordes, M., and de Meijere, A., *Synlett.*, 1997, p. 111; Lee, J. and Cha, J.K., *J. Org. Chem.*, 1997, vol. 62, p. 1584.
6. Bertus, P. and Szymoniak, J., *Chem. Commun.*, 2001, 1792; Bertus, P. and Szymoniak, J., *J. Org. Chem.*, 2002, vol. 67, p. 3965.
7. Kulinkovich, O.G., *Pure Appl. Chem.*, 2000, vol. 72, p. 1715.
8. Sato, F., Urabe, H., and Okamoto, S., *Chem. Rev.*, 2000, vol. 100, p. 2835.
9. Kulinkovich, O.G., Epstein, O.L., Isakov, V.E., and

Khmel'nitskaya, E.A., *Synlett.*, 2001, p. 49.
10. Kahn, S.D. and Hehre, W.J., *J. Am. Chem. Soc.*, 1987, vol. 109, p. 666; Gung, B.W., Melnick, J.P., Wolf, M.A., and King, A., *J. Org. Chem.*, 1995, vol. 60, p. 1947.
11. Horiike, M., Tanouchi, M., and Hirano, Ch., *Agric. Biol. Chem.*, 1980, vol. 44, p. 257; Ranganathan, S., Maniktala, V., Kuvar, R., and Singh, P., *Indian J. of Chem.*, 1984, vol. 23B, p. 1197; Aukrust, A., Rongred, P., and Skattebshl, L., *Acta Chem. Scand. B*, 1985, vol. 39, p. 267; Schlosser, M., Tuong, H.B., and Schaub, B., *Tetrahedron Lett.*, 1985, vol. 26, p. 311; Vinczer, P., Juvancz, Z., Novbk, L., and Szbntay, C., *Acta Chim. Hung.*, 1987, vol. 124, p. 737; Odinokov, V.N., Ishmuratov, G.Yu., Galeeva, R.I., Kharisov, R.Ya., Sokol'skaya, O.V., Mukhametzyanova, R.S., Kargapol'tseva, T.A., Tolstikov, G.A., *Zh. Org. Khim.*, 1988, vol. 24, p. 719; Odinokov, V.N., Akhmatova, V.R., Khasanov, Kh.D., Abduvakhabov, A.A., Tolstikov, G.A., and Panasenko, A., *Khim. Polim. Soed.*, 1989, p. 276; Ishmuratov, G.Yu., Ishmuratova, N.M., Odinokov, V N., and Tolstikov, G.A., *Khim. Polim. Soed.*, 1997, p. 34.
12. Roelofs, W.L., Comeau, A., and Selle, R., *Nature*, 1969, vol. 224, p. 723.
13. Carde, A.M., Baker, T.C., and Carde, R.T., *J. Chem. Ecol.*, 1979, vol. 5, p. 423.
14. Gentry, C.R., Beroza, M., Blythe, J.L., and Bierl, B.A., *Environ. Entomol.*, 1975, vol. 4, p. 822; *Chem. Abstr.*, 1976, vol. 84, 55284k.
15. Gentry, C.R., Beroza, M., and he, J.L., *Environ. Entomol.*, 1975, vol. 4, p. 227; *Chem. Abstr.*, 1976, vol. 83, 73422n.
16. Bestmann, H.J., Frighetto, R.T.S., Frighetto, N., and Vostrowsky, O., *Liebigs Ann.*, 1990, 829; Tamaki, Y., Noguchi, H., Sugie, H., Sato, R., and Kariya, A., *Appl. Entomol. Zool.*, 1979, vol. 14, p. 101; *Chem. Abstr.*, 1979, vol. 91, p. 53072k.
17. Arn, N., Schwarz, C., Limacher, H., and Mani, E., *Experientia*, 1974, vol. 30, p. 1142.
18. Stowell, J.C. and King, B.T., *Synthesis*, 1984, no. 3, p. 278.
19. Angelini, A., Descoins, C., Le, Rumeur, C., and Lhoste, J., *Coton Fibres, Trop.*, 1980, vol. 35, p. 277; *Chem. Abstr.*, 1981, vol. 94, 115953w.
20. Sonnet, Ph.E. and Oliver, J.E., *J. Org. Chem.*, 1976, vol. 41, p. 3284.
21. Ficini, J., *Bull. Soc. Chim.*, 1956, p. 119.
22. Crombie, L. and Harper, S.H., *J. Chem. Soc.*, 1950, p. 1707.
23. Crombie, L., *J. Chem. Soc.*, 1952, p. 2997.
24. Crombie, L. and Harper, S.H., *J. Chem. Soc.*, 1950, p. 2685.
25. Albores, M., Bestmann, H.J., Doehla, B., Hirsch, H.-L., Roesel, P., and Vostrowsky, O., *Liebigs Ann.*, 1993, p. 231.
26. Jacobson, M., Keiser, I., Chambers, D.L., Miyashita, D.H., and Harding, Ch., *J. Med. Chem.*, 1971, vol. 14, p. 236.
27. Kovaleva, A.S., Borisov, N.N., Tsyban', A.V., Ivanov, L.L., Pyatnova, Yu.B., and Evstigneeva, R.P., *Zh. Org. Khim.*, 1972, vol. 8, p. 2474.
28. Horiike, M., Hirano, Ch., and Tamaki, Y., *Agric. Biol. Chem.*, 1982, vol. 46, p. 1925.
29. Fieser, L.F. and Fieser, M., *Natural Products Related to Phenanthrene*, New York: Reinhold, 1949.
30. Helmich, O., Streibl, M., Filip, J., and Hradec, J., *J. Labelled Compd. Radiopharm.*, 1985, vol. 22, p. 917; *Chem. Abstr.*, 1985, vol. 105, 23929k.