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Reductive Ethylation of Homoallyl Alcohols with a Disubstituted Double Bond with Ethylmagnesium Bromide in the Presence of Titanium(IV) Isopropoxide

O.G. Kulinkovich, T.A. Shevchuk, V.E. Isakov, and K.N. Prokhorevich

Belarussian State University, Minsk, 220050 Belarus
e-mail: kulinkovich@bsu.by

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Abstract—Homoallyl and bishomoallyl alcohols with a disubstituted double bond treated with ethylmagnesium bromide in the presence of titanium(IV) isopropoxide are converted into the products of a reductive ethylation of the olefin fragment. Under similar conditions esters of β,γ-unsaturated carboxylic acids undergo a successive cyclopropanation of the ester group and reductive ethylation of the double carbon–carbon bond and yield 1-(3-ethylalkyl)cyclopropanols. The features of the observed reactions are explained in the framework of the carbometallation mechanism of the double carbon–carbon bond by the action of dialkoxytitanacyclopropane reagents.

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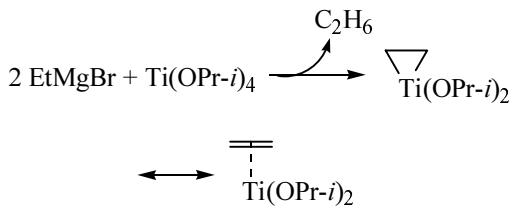
The reaction of titanium(IV) isopropoxide with ethylmagnesium bromide proceeds through a stage of diethyldiisopropoxytitanium which under common conditions suffers disproportionation into ethane and a labile diisopropoxytitanacyclopropane (**I**) [1] (Scheme 1). Reagent **I** is capable of behaving as an equivalent of a 1,2-dicarbanion in reactions with derivatives of carboxylic acids and some other electrophilic substrates, or it acts as an equivalent of an ethyl carbanion [2]. Thus reagent **I** generated in situ transformed the esters of carboxylic acids into 1-substituted cyclopropanols [1], whereas allyl alcohols under similar conditions suffered S_N2' substitution of the hydroxyl by an ethyl group [3]. The latter process is an analog of olefins carbomethallation (Dzhemilev reaction) [4], and it occurs through generation of the corresponding titanacyclopentane intermediates [3, 5].

Titanacyclopropane **I** is also able to show the property of a titanium-ethylene complex and can take part in the ligand exchange with olefins [6]. In reactions with homoallyl and bishomoallyl alcohols with a terminal double bond these processes induce formation of products of the substrate reductive dimerization by the "head-to-head" type [7]. We report here on the alternative route of the reaction between titanacyclopropane reagents **I** with homoallyl **IIa** and **IIb** and bishomoallyl **IIc–IIe** alcohols with a disubstituted double bond.

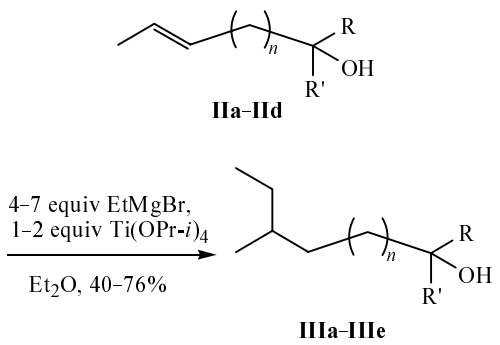
Scheme 1.



The addition of 4 equiv of ethylmagnesium bromide to an ether solution of equimolar quantities of compounds **IIa–IIe** and titanium(IV) isopropoxide at room temperature afforded as the main products mixtures of saturated and unsaturated monohydric alcohols (see the table) that were separated from the other components of the reaction mixture by column chromatography. According to the NMR and GC=MS data the isolated fractions of monohydric alcohols with the close values of the chromatographic mobility contained from 66 to 98% of the product of reductive ethylation of the double carbon-carbon bond **IIIa–IIIe** (Scheme 2).

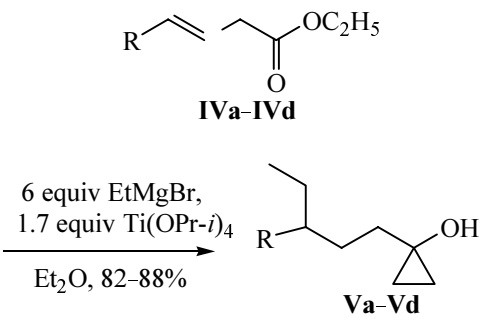
The application of relatively large amounts of ethylmagnesium bromide and titanium(IV) isopropoxide somewhat increased the yield of ethylation products, but therewith the substrate conversion did not notably grow (see table, runs nos. *3–5*, *7*, *9*). Even in reaction of tertiary alcohol **IIb** with 10 equiv of ethylmagnesium

Scheme 2.



$n = 1$, R = R' = H (**a**), CH_3 (**b**); $n = 2$, R = R' = H (**c**), CH_3 (**e**); R = H, R' = CH_3 (**d**).

Scheme 3.



R = CH_3 (**a**), C_2H_5 (**b**), C_3H_7 (**c**), C_5H_{11} (**d**).

Conversion of unsaturated alcohols **II** and yield of reductive ethylation products **III** in reaction with ethylmagnesium bromide in the presence of titanium(IV) isopropoxide

Run no.	Compd. no.	$Ti(OPr\text{-}i)_4$, equiv	EtMgBr, equiv	Conversion of compd. **II**, %[a]	Yield of compd. **III**, %[b]
1	**IIa**	1	4	96	41
2	**IIb**	1	4	75	65
3	**IIb**	1	6	77	64
4	**IIb**	2	7	84	74
5	**IIb**	3	10	85	76
6	**IIc**	1	4	62	58
7	**IIc**	2	7	70	71
8	**IId**	1	4	92	40
9	**IId**	2	7	92	53
10	**IIe**	1	4	65	63

[a] Conversion and yield were estimated from the data of GC-MS and ^1H NMR spectra of the reaction mixture.

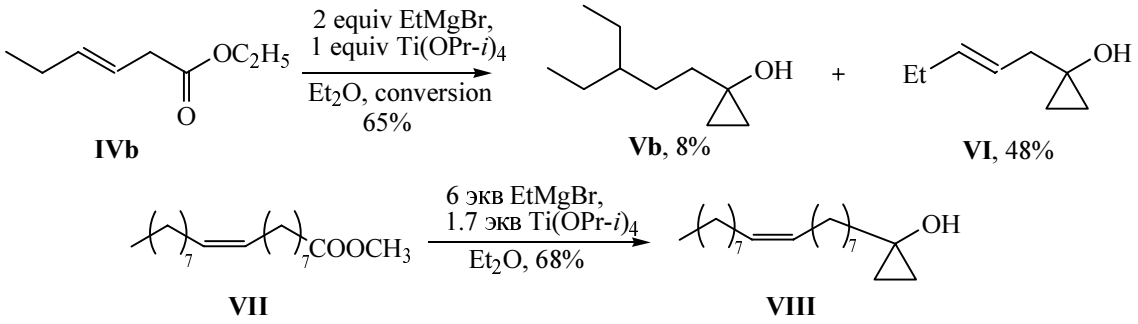
[b] Yield calculated on the reacted alkenol **II**.

bromide and 3 equiv of titanium(IV) isopropoxide about 15% of the initial compounds was recovered unchanged (run no. *5*). The variation of concentration of the reactants and of reaction temperature also did not significantly raised the yield of compound **IIIb** or the conversion of the substrate. At the same time primary alcohol **IIa** and secondary alcohol **IId** under the given conditions were nearly totally consumed (runs nos. *1*, *8*), but significant amounts of side products of low chromatographic mobility were obtained.

Considering the above mentioned ability of reagent **I** to convert esters of carboxylic acids into 1-substituted cyclopropanols [1] we studied also the reactions of ethylmagnesium bromide and titanium(IV) isopropoxide with esters of β,γ-unsaturated carboxylic acids **IVa–IVd**. The treatment of esters **IVa–IVd** with 6 equiv of ethylmagnesium bromide and 1.7 equiv of titanium(IV) isopropoxide afforded in 82–88% yields the corresponding saturated cyclopropanols **Va–Vd** (Scheme 3). Under the applied reaction conditions a complete conversion of alkenoates **IVa–IVd** was observed, and the yields of compounds **Va–Vd** originating from a two-stage process of ester group cyclopropanation and reductive ethylation of the double carbon-carbon bond were to our surprise considerably higher than those of the products of the one-stage reductive ethylation of tertiary unsaturated alcohols **IIb** and **IIe**.

Decreasing the relative amount of titanium(IV) isopropoxide from 1.7 to 1.3 equiv in the reaction of compound **IVb** with 6 equiv of ethylmagnesium bromide resulted in formation in a 62% yield of a mixture of 1-(3-ethylpentyl)cyclopropanol **Vb** and 1-(3-pentenyl)cyclopropanol **VIb** in a ratio 85:15. Compound **VI** turned out to be the main product in reaction of ester **IVb** with 2 equiv of ethylmagnesium bromide in the presence of 1 equiv of titanium(IV) isopropoxide; therewith we failed to detect in the reaction mixture any products of the double carbon-carbon bond alkylation in compound **IVb** which retained the ester function (Scheme 4). These data indicate the comparable activity of titanacyclopropane **I** with respect to the ester group of compounds **IV** and the double carbon-carbon bond of alkenylcyclopropanols **VI**. At the same time we did not find any notable amounts of products originating from the reductive ethylation of the double carbon-carbon bond in a reaction of methyl oleate (**VII**) with ethylmagnesium bromide in the presence of titanium(IV) isopropoxide under standard conditions: The only product isolated from the reaction mixture was unsaturated cyclopropanol **VIII** (Scheme 4). The

Scheme 4.



IVb **Vb**, 8% **VI**, 48%

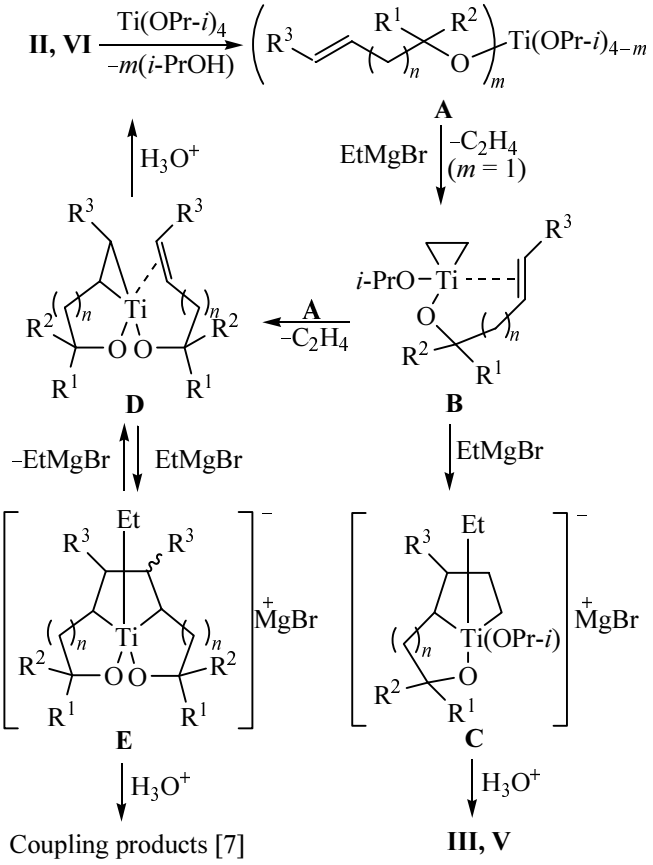
VII **VIII**

retention of the multiple bond in compound **VIII** was not obviously due to its *cis*-configuration, but to the remote position of the hydroxy and olefin groups, since a special experiment of cyclopropanation under the same conditions of a *cis*-*trans* isomer mixture of compound **IVb** (*cis*:*trans* ratio was 60 : 40) gave the saturated cyclopropanol **Vb** in a high yield.

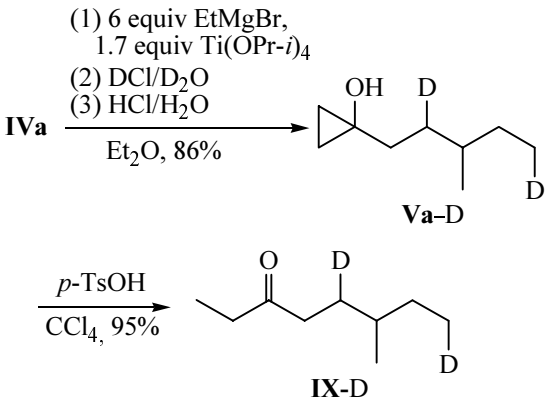
The experimental data obtained may be interpreted in the framework of the mechanism we have previously suggested of allyl ethylation [3] and reductive coupling of unsaturated alcohols under the action of dialkoxytitanacyclopropane reagents [7]. Titanium alcoholates **A** originating from the *trans*-etherification of the titanium(IV) isopropoxide (we do not consider for the sake of simplicity the possible participation in the reactions of the magnesium alcoholates) treated with ethylmagnesium bromide are converted into the corresponding titanacyclopropane derivatives **B** (Scheme 5). The addition to the latter of ethylmagnesium bromide induces [5] the formation of titanacyclopentane at-complexes **C** which are the direct precursors of compounds **III** and **V**. We believe that the easier occurrence of the reductive ethylation of the 1-alkenyl-substituted cyclopropanolates **A** ($R^1 + R^2 = CH_2CH_2$) is caused by the enhanced values of the bond angles between the geminal exocyclic bonds in the cyclopropane compounds [8]. These differences may stabilize cyclopropane-containing at-complexes **C** ($R^1 + R^2 = CH_2CH_2$) owing to the reduced internal strain in the oxatitanacyclopentane ring and may destabilize the leading to side products titanium-olefin complexes **D** by hampering the coordination of the multiple bond to the metal. In its turn the observed growing yields of reductive ethylation products in the presence of excess titanium(IV) isopropoxide is due to the increased equilibrium concentration of monoalkenyl cyclopropanolates **A** (at $m = 1$) compared with those formed at the deeper *trans*-etherification of titanium(IV) isopropoxide with alcoholates **A** (at $m > 1$) where a higher rate of conversion into intermediates **D** should be expected.

When the reaction mixture prepared under above described conditions from compound **I** and substrate **IVa** was treated with DCl in D_2O formed 1-(2,5-dideutero-3-methylpentyl)cyclopropanol (**Va**-D). This fact is in agreement with the assumption that the reaction proceeds via titanacyclopentane intermediates **C**. The deuterium content in positions *2* and *5* of compound **Va**-D, and also in the product obtained thereof by an acid-catalyzed ring

Scheme 5.



Scheme 6.



opening, 5,8-dideutero-6-methyloctan-3-one (**IX**-D), exceeded 95% according to the data of ^{1}H NMR spectroscopy (Scheme 6).

The involvement of complex **B** into the concurrent process of the ethylene ligand displacement with titanium alcoholates **A** present in excess in the initial stages of the ethylation furnishes titanium(II)-bisolefin complexes **D** which add ethylmagnesium bromide to transform into tricyclic titanacyclopentane at-complexes **E**. The hydrolytic cleavage of intermediates **D** and **E** at the workup of the reaction mixture leads respectively to recovery of initial unsaturated alcohols **II** and to formation of the products of their reductive coupling. The latter process prevails in reactions of homoallyl alcohols with the less sterically hindered terminal double bond [7]. Thus complexes **D** can play the role of certain vessels for conservation of alkoholates of the unsaturated alcohols; this fact explains the unsuccessful attempts to increase the conversion of initial compounds **II** even at application of a considerable excess of organometallic reagents (see above).

Considering the ability of cyclopropanols to opening of the three-membered ring under mild conditions [9] the approach developed in this study to preparation of these compounds with a branched carbon-carbon skeleton from the esters of β,γ-unsaturated acids may be of interest from synthetic viewpoint. In particular, nondeuterated 6-methyloctan-3-one (**IX**) is a component of the anxiety pheromone of ants from the *Genus Crema-togaster* [10].

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer Specord 75IR from solutions in CCl_4. ^{1}H and ^{13}C NMR spectra were registered from 5–10% solutions of compounds under study in $CDCl_3$ using TMS as internal reference on spectrometers Bruker AvanCe-400 at operating frequencies 400 (^{1}H), 100 MHz (^{13}C), and Brucker AC-200 at operating frequency 200 MHz (^{1}H). GC-MS measurements were performed on a Hewlett Packard GC MS 5890/5972 instrument (electron impact energy 70 eV).

Reductive ethylation of unsaturated alcohols IIa–IIe with ethylmagnesium bromide in the presence of titanium(IV) isopropoxide. To a stirred solution of 2.5 mmol of unsaturated alcohol **II** and 2.5–5.0 mmol of Ti(OPr-*i*)$_4$ in 7–15 ml of anhydrous ethyl ether was added within 0.5 h 10–17.5 mmol of EtMgBr as a 1.0–1.4 M solution in the same solvent. On completion of the addition the reaction mixture was stirred for 0.5 h and then was treated with 10% H_2SO_4 at 0°C. The organic layer was separated, the reaction products from the water layer were extracted into ether (4×10 ml). The combined ether solutions were washed in succession with saturated solutions of $NaHCO_3$ and NaCl, dried with $MgSO_4$, evaporated, and the residue was subjected to column chromatography on silica gel (eluent petroleum ether–dichloromethane). The yields of compounds were estimated from the ratio of the integral intensity of the upfield signals of methyl groups and of the areas of the chromatographic peaks. The spectral characteristics of compounds **IIIa** and **IIIc** (content in the isolated fractions about 70%) were consistent with those published in [11, 12].

2,5-Dimethylheptan-2-ol (IIIb) (content in the isolated fraction 98%). IR spectrum, cm^{-1}: 3609, 3453. ^{1}H NMR spectrum (400 MHz), δ, ppm: 0.81 t (3H, *J* 7.3 Hz), 0.81 d (3H, *J* 6.4 Hz), 1.03–1.48 m (7H), 1.14 s (6H), 1.84 br.s (1H). ^{13}C NMR spectrum (100 MHz), δ, ppm: 11.19, 19.06, 29.06, 29.27, 30.82, 34.72, 41.22, 70.91. Mass spectrum, *m/z*: 29, 43, 55, 59 (100%), 69, 74, 81, 85, 91, 97, 111, 125, 129.

6-Methyloctan-2-ol (IIId) (content in the isolated fraction 74%). IR spectrum, cm^{-1}: 3613, 3393. ^{1}H NMR spectrum (400 MHz), δ, ppm: 0.82 d (3H, *J* 6.4 Hz), 0.82 t (3H, *J* 7.1 Hz), 1.02–1.18 m (2H), 1.14 d (3H, *J* 6.1 Hz), 1.18–1.61 m (7H), 2.07 br.s (1H), 3.75 sextet (1H, *J* 5.7 Hz). ^{13}C NMR spectrum (100 MHz), δ, ppm: 11.25, 19.05, 23.17, 23.32, 29.35, 34.30, 36.52, 39.61, 68.00. Mass spectrum, *m/z*: 29, 45 (100%), 55, 69, 84, 97, 111, 129, 143 $[M-1]^+$.

2,6-Dimethyloctan-2-ol (IIIe) (content in the isolated fraction 82%). IR spectrum, cm^{-1}: 3607, 3400. ^{1}H NMR spectrum (400 MHz), δ, ppm: 0.82 d (3H, *J* 6.4 Hz),

0.82 t (3H, *J* 7.2 Hz), 1.00–1.43 m (9H), 1.16 s (6H), 1.79 br.s (1H). ^{13}C NMR spectrum (100 MHz), δ, ppm: 11.27, 19.08, 21.75, 29.06, 29.39, 34.32, 37.07, 44.22, 71.00. Mass spectrum, *m/z*: 29, 43, 59 (100%), 69, 83, 95, 102, 111, 125, 143.

1-(3-Ethylalkyl)-substituted cyclopropanol from esters of 3-alkenoic acids IVa–IVd. To a stirred solution of 10 mmol of 3-alkenoate and 17 mmol of Ti(OPr-*i*)$_4$ in 30 ml of anhydrous ethyl ether was added within 2 h 60 mmol of EtMgBr as a 1M solution in the same solvent. On completion of the addition the reaction mixture was stirred for 0.5 h and then was treated with 5% H_2SO_4 at 0°C. The products were extracted from the water layer into ether (3×30 ml). The combined ether solutions were washed in succession with saturated solutions of $NaHCO_3$ and NaCl, dried with $MgSO_4$, evaporated, and the residue was subjected to column chromatography on silica gel to isolate compounds **Va–Vd** (eluent cyclohexane– ethyl acetate).

1-(3-Methylpentyl)cyclopropanol (Va). Yield 88%. IR spectrum, cm^{-1}: 3593, 3073. ^{1}H NMR spectrum (400 MHz), δ, ppm: 0.44 d.d (2H, J_1 6.0, J_2 4.5 Hz), 0.74 d.d (2H, J_1 6.0, J_2 4.5 Hz), 0.87 d (3H, *J* 5.5 Hz), 0.88 t (3H, *J* 7.0 Hz), 1.08–1.20 m (1H), 1.22–1.40 m (3H), 1.42–1.58 m (3H), 1.87 br.s (1H). ^{13}C NMR spectrum (100 MHz), δ, ppm: 11.29, 13.39, 13.48, 19.15, 29.40, 32.49, 34.33, 35.75, 56.00. Mass spectrum, *m/z*: 27, 29, 41, 43 (100%), 55, 57, 72, 85, 95, 142 [*M*]$^+$. Found, %: C 75.62; H 12.35. $C_9H_{18}O$. Calculated, %: C 76.00; H 12.76.

1-(2,5-Dideutero-3-methylpentyl)cyclopropanol (Va-D) was obtained by the similar procedure from ethyl 3-pentenoate. The reaction mixture was treated with DCl in D_2O. Yield 86%. ^{1}H NMR spectrum (400 MHz), δ, ppm: 0.44 d.d (2H, J_1 6.0, J_2 4.5 Hz), 0.74 d.d (2H, J_1 6.0, J_2 4.5 Hz), 0.82–0.92 m (5H), 1.09–1.23 m (1H), 1.24–1.42 m (2H), 1.46–1.63 m (3H), 1.80 br.s (1H).

1-(3-Ethylpentyl)cyclopropanol (Vb). Yield 85%. IR spectrum, cm^{-1}: 3593, 3073. ^{1}H NMR spectrum (400 MHz), δ, ppm: 0.43 d.d (2H, J_1 6.3, J_2 5.0 Hz), 0.73 d.d (2H, J_1 6.3, J_2 5.0 Hz), 0.84 t (6H, *J* 7.4 Hz), 1.16–1.26 m (1H), 1.27 quintet (2H, *J* 7.0 Hz), 1.29 quintet (2H, *J* 7.0 Hz), 1.42–1.55 m (4H), 1.78 br.s (1H). ^{13}C NMR spectrum (100 MHz), δ, ppm: 10.83, 13.46, 25.38, 28.60, 35.37, 40.25, 56.07. Mass spectrum, *m/z*: 27, 29, 41, 43 (100%), 55, 57, 69, 72, 84, 85, 109, 156 [*M*]$^+$. Found, %: C 76.38; H 12.54. $C_{10}H_{20}O$. Calculated, %: C 76.86; H 12.90.

1-(3-Ethylhexyl)cyclopropanol (Vc). Yield 87%. IR spectrum, cm^{-1}: 3595, 3075. ^{1}H NMR spectrum (400 MHz), δ, ppm: 0.43 d.d (2H, J_1 6.3, J_2 5.1 Hz), 0.73 d.d (2H, J_1 6.3, J_2 5.1 Hz), 0.84 t (3H, *J* 7.4 Hz), 0.88 t (3H, *J* 6.6 Hz), 1.17–1.33 m (7H), 1.41–1.55 m (4H), 1.73 br.s (1H). ^{13}C NMR spectrum (100 MHz), δ, ppm: 10.76, 13.40, 14.42, 19.79, 25.84, 29.01, 35.30, 35.53, 38.50, 56.01. Found, %: C 77.09; H 12.75. $C_{11}H_{22}O$. Calculated, %: C 77.58; H 13.02.

1-(3-Ethyloctyl)cyclopropanol (Vd). Yield 87%. IR spectrum, cm^{-1}: 3595, 3073. ^{1}H NMR spectrum (400 MHz), δ, ppm: 0.43 d.d (2H, J_1 6.0, J_2 5.0 Hz), 0.73 d.d (2H, J_1 6.0, J_2 5.0 Hz), 0.84 t (3H, *J* 7.0 Hz), 0.88 t (3H, *J* 6.8 Hz), 1.17–1.34 m (11H), 1.40–1.55 m (4H), 1.80 br.s (1H). ^{13}C NMR spectrum (100 MHz), δ, ppm: 10.75, 13.32, 14.03, 22.64, 25.78, 26.32, 29.00, 32.29, 33.04, 35.28, 38.72, 55.91. Found, %: C 78.44; H 12.88. $C_{13}H_{26}O$. Calculated, %: C 78.72; H 13.21.

1-(2-Pentenyl)cyclopropanol (VI) containing 15% of compound **Vb** was obtained by the similar procedure from ethyl 3-hexenoate using 6 equiv of EtMgBr and 0.2 equiv of Ti(OPr-*i*)$_4$. Yield 61%. IR spectrum, cm^{-1}: 3580, 3066, 1466. ^{1}H NMR spectrum (200 MHz), δ, ppm: 0.50 d.d (2H, J_1 7.0, J_2 5.0 Hz), 0.76 d.d (2H, J_1 7.0, J_2 5.0 Hz), 0.98 t (3H, *J* 7.0 Hz), 1.66 br.s (1H), 2.07 quintet (2H, *J* 7.0 Hz), 2.36 br.d (2H, *J* 7.0 Hz), 5.47 d.t (1H, J_1 11.0, J_2 7.0 Hz), 5.61 d.t (1H, J_1 11.0, J_2 7.0 Hz).

1-(8-Heptadecenyl)cyclopropanol (VIII). Yield 68%. IR spectrum, cm^{-1}: 3595, 3071. ^{1}H NMR spectrum (200 MHz), δ, ppm: 0.42 d.d (2H, J_1 5.0, J_2 6.5 Hz), 0.72 d.d (2H, J_1 5.0, J_2 6.5 Hz), 0.89 t (3H, *J* 6.5 Hz), 1.12–1.44 m (22H), 1.52 br.s (2H), 1.90–2.10 m (4H), 2.66 br.s (1H), 5.35 t (2H, *J* 5.0 Hz). Found, %: C 81.15; H 12.54. $C_{20}H_{38}O$. Calculated, %: C 81.56; H 13.01.

6-Methyloctan-3-one (IX). To a solution of 0.71 g (0.5 mmol) of 1-(3-methylpentyl)cyclopropanol (**Va**) in 10 ml of tetrachloromethane was added 0.02 g (0.1 mmol) of *p*-toluenesulsonic acid. The reaction mixture was boiled for 10 min cooled to room temperature, and passed through a bed of aluminum oxide (5 g). The solvent was evaporated, and the residue was subjected to column chromatography on silica gel (eluent cyclohexane–ethyl acetate). Yield 0.68 g (95%). ^{1}H NMR spectrum is consistent with that published in [13]. IR spectrum, cm^{-1}: 1720. ^{13}C NMR spectrum (100 MHz), δ, ppm: 7.76, 11.16, 18.82, 29.14, 30.38, 34.01, 35.70, 40.08, 212.00. Mass spectrum, *m/z*: 29, 43, 57 (100%), 72, 85, 95, 113, 142 [*M*]$^+$.

5,8-Dideutero-6-methyloctan-3-one (IX-D) was obtained in the same way from 1-(2,5-dideutero-3-

methylpentyl)cyclopropanol (**Va**-D). Yield 95%. IR spectrum, cm^{-1}: 1720. ^1H NMR spectrum (400 MHz), δ, ppm: 0.85 d (3H, *J* 6.3 Hz), 0.82–0.87 m (2H), 1.05 t (3H, *J* 7.3 Hz), 1.08–1.19 m (1H), 1.25–1.39 m (2H), 1.55–1.62 m (1H), 2.35–2.42 m (2H), 2.42 q (2H, *J* 7.3 Hz). ^{13}C NMR spectrum (100 MHz), δ, ppm: 7.74, 10.85 t (*J* 19.0 Hz), 18.78, 29.00, 29.98 t (*J* 19.0 Hz), 33.88, 35.68, 39.97, 211.88. Mass spectrum, *m/z*: 29, 44, 57 (100%), 72, 86, 97, 115, 144 $[M]^+$.

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