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Preparation of 3-Bromomethyl-3-butenal Diethylacetal and Its Conversion into Isoprenoid Aldehydes Derivatives

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Abstract—The cyclopropanation of ethyl 3,3-diethoxypropionate with alkoxytitanacyclopropane reagents followed by the cleavage of the three-membered carbocycle in the formed cyclopropyl mesylate provided in a good yield 3-bromomethyl-3-butenal diethylacetal. The latter was brought into reactions of aldehyde allylation and cross-coupling with allyl halides in the intermediate stages at the generation of carbanionic intermediates. The conversion of compounds obtained into the corresponding β,γ- or α,β-unsaturated aldehydes demonstrated the opportunity of applying 3-bromomethyl-3-butenal diethylacetal as a C_5-isoprenoid building block.

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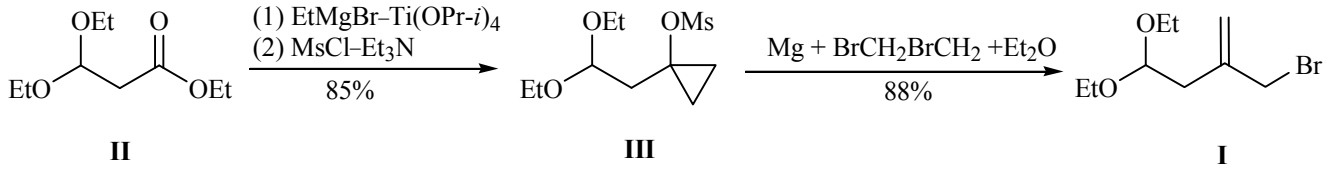
We recently developed a convenient method of the preparation of methyl 3-bromomethyl-3-butenoate and the procedure for its application to the allylation of electrophiles in the presence of zinc in a water-organic medium [1]. The use of this compound as a nucleophilic C_5-isoprenoid building block made it possible to obtain the corresponding esters both with the methylene- and the methyl-substituted carbon skeleton [1–3]. In this study an analogous approach was extended to the preparation of 3-bromomethyl-3-butenal diethylacetal (**I**) by the cyclopropanation of an available ethyl 3,3-diethoxypropionate (**II**) with ethylmagnesium bromide in the presence of titanium(IV) isopropoxide [4, 5] followed by subsequent mesylation and by the treatment of obtained mesylate **III** with magnesium bromide in anhydrous ethyl ether [1, 6] (Scheme 1).

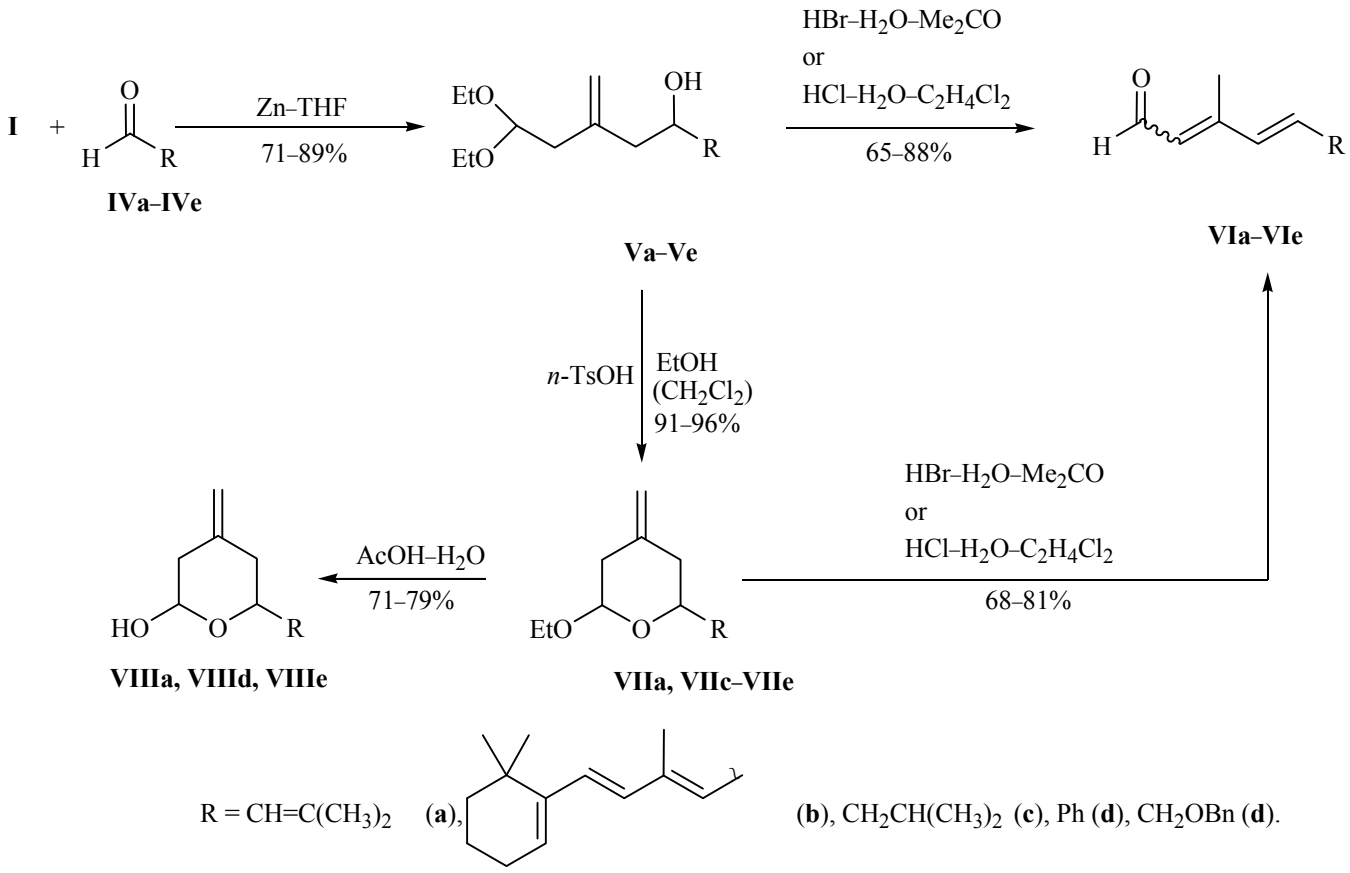
Allyl bromide **I** readily condensed with aldehydes **IVa–IVe** under the treatment with zinc activated with dibromoethane in tetrahydrofuran forming the corresponding aldol acetals **Va–Ve** (Scheme 2). The hydrolysis of the latter with the hydrobromic acid in acetone [7] or in a two-phase system hydrochloric acid–dichloroethane [8] is accompanied by the dehydration leading to the formation of mixtures similar in the stereoisomers composition containing *cis*- and *trans*-dehydrocitrals **VIa** and retinals **VIb** with the content of the *trans*-isomers not exceeding 75%. The hydrolysis with the hydrochloric acid of cyclic acetal **VIIa** which cleanly formed by keeping hydroxyacetal **Va** in the presence of *p*-toluenesulfonic acid resulted in *trans*-dehydrocitral **VIa** [9–16] with 90% diastereoselectivity. Under the same conditions the relative content of *trans*-retinal **VIb** in the hydrolysis products of precursor **Vb** did not essentially increase. Inasmuch as an efficient procedure for the conversion of a mixture of *cis*- and *trans*-retinals **VIb** into a pure trans-isomer was published [7], we did not attempt to improve the stereoselectivity of its formation from compound **Vb**. The hydrolysis of cyclic acetals **VIIa, VIIc–VIIe** without dehydration and the shift of the multiple bond cleanly occurred in aqueous

Scheme 1.



II **III** **I**

Scheme 2.



acetic acid [17], whereas acyclic hydroxyacetals **Va–Ve** under these conditions were converted into complex mixtures of compounds.

The reductive elimination by treating with sodium in ethanol [18] of the arenesulfonyl group of compound **IX** obtained by the alkylation of sulfone **X** with prenyl bromide afforded an acetals mixture of β,γ-unsaturated aldehydes **XI** and **XII** in a ratio 1:4 (Scheme 3). In the hydrolysis of the mixture in the presence of pyridinium *p*-tolyenesulfonate [19] the corresponding trienals formed in approximately the same stereoisomers ratio, whereas the treatment of the acetals mixture **XI** and **XII** with the aqueous formic acid in petroleum ether [20] provided an aldehyde with nonconjugated *trans*-trisubstituted double bond **XIII** that was isolated in an individual state by column chromatography.

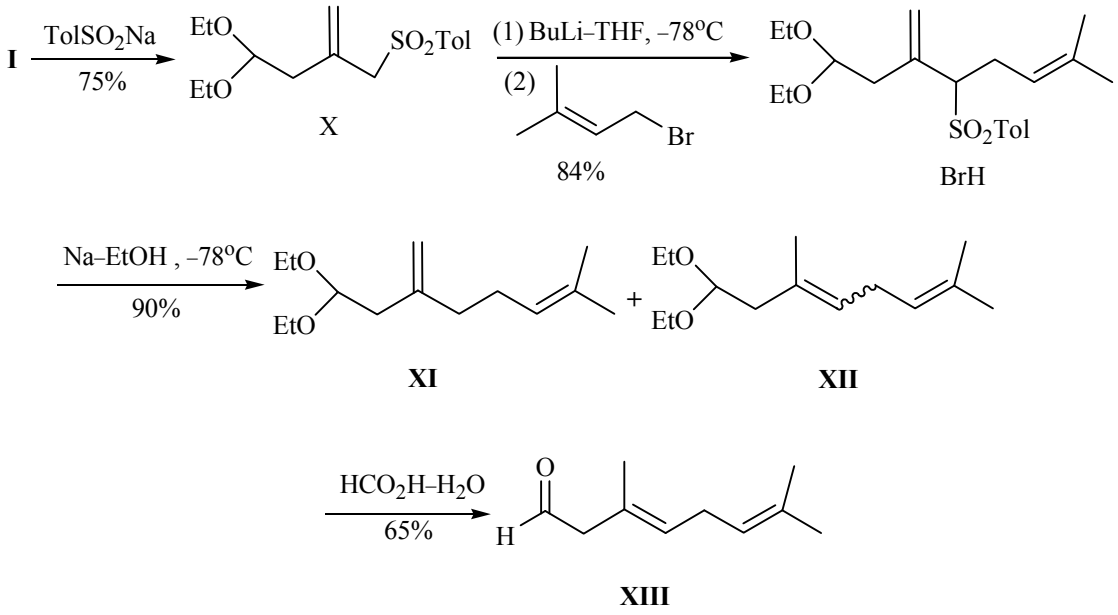
In addition to the above described conversions functionally substituted allyl bromide **I** was brought into reactions of carbon-carbon bonds formation as an electrophilic substrate. Its reaction with allylmagnesium chloride or prenylmagnesium chloride in the presnce of copper iodide [21] gave quantitatively the corresponding acetals of β-methylene-substituted aldehydes **XI** and **XIV** (Scheme 4). The condensation of compound **I** with allyl sulfone **XV** in the presence of lithium diisopropylamide at low temperature resulted in a moderate yield of acetal **XVI**, whereas at the use as a base of potassium *tert*-butylate and the reaction performance in the boiling benzene the elimination of tolyl sulfinate occurred with the formation of compound **XVII** whose hydrolysis gave rise to a mixture of *cis*- and *trans*-dehydrocitrals **VIa** in a ratio 1:5.

The studied reactions of 3-bromomethyl-3-butenal diethylacetal (**I**) leading to the formation of carbon-carbon bonds and the stereoselective conversions of the formed compounds demonstrate the versatile opportunities of its application as a C_5-isoprenoid building block that we plan to use in the preparation of naturally occurring compounds of more complex structures.

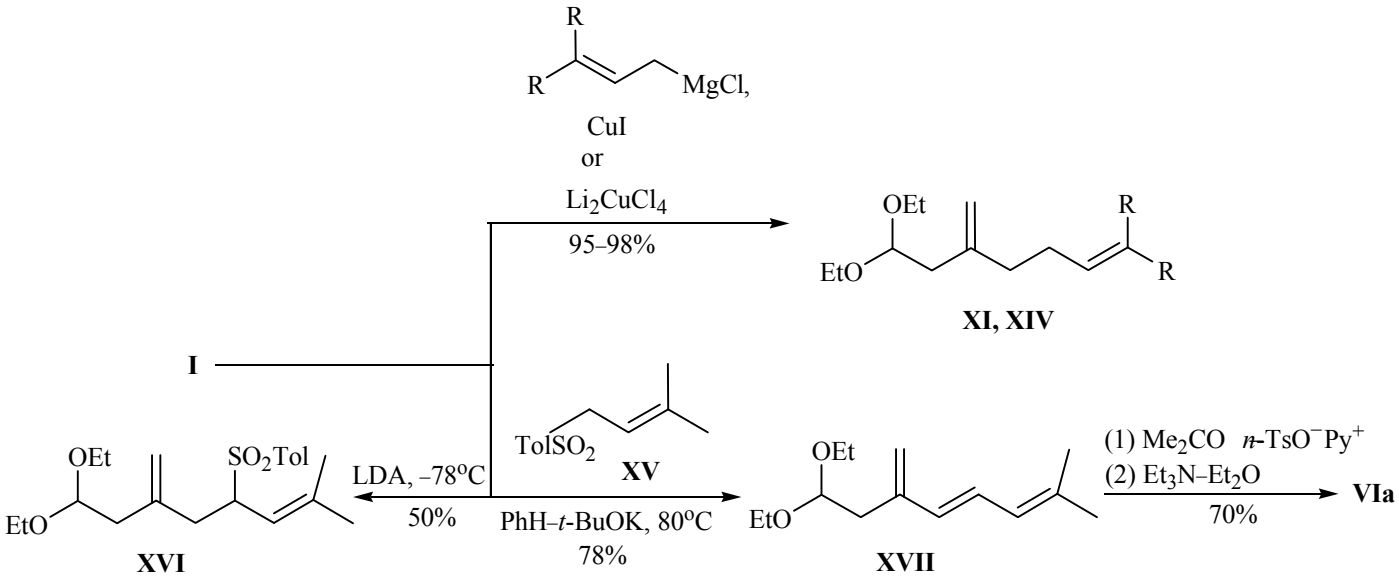
EXPERIMENTAL

^1H and ^{13}C NMR spectra were registered on a spec-

Scheme 3.



Scheme 4.



trometer Bruker AC 400 at operating frequencies 400 and 100 MHz respectively from solutions in deuterochloro-form. IR spectra were recorded on spectrophotometers Specord 75IR and Vertex 70 from solutions of compounds in CCl_4. The isolation of individual substances was carried out by column chromatography on silica gel (70–230 mesh). All solvents before use were purified and distilled by standard procedures. The elemental analysis was performed by semimicro method.

3-Bromomethyl-3-butenal diethylacetal (I). To a solution of $MgBr_2$ obtained from 2.90 g (120 mmol) of magnesium turnings and 10.4 ml of 1,2-dibromoethane in 60 ml of anhydrous ethyl ether was added dropwise at stirring a solution of 16.92 g (60 mmol) of cyclopropyl mesylate **III** [1] in 100 ml of the same solvent. On completion of the reaction (TLC monitoring) was added at cooling 100 ml of water, the organic layer was separated, the water layer was extracted with ethyl ether

(3×50 ml). The combined organic solutions were washed with a saturated water solution of $NaHCO_3$ (3 × 25 ml), NaCl (25 ml), and it was dried with $MgSO_4$. On removing the solvent at a reduced pressure and on the separation of the reaction product by column chromatography (eluent benzene) we obtained 12.48 g (88%) of substituted acetal **I** as an oily fluid quickly yellowing on storage. IR spectrum, ν, cm^{-1}: 1208 (C–O), 1124 (C–O), 1064 (C–O). ^1H NMR spectrum, δ, ppm: 1.19 t (6H, 2 CH_3CH_2O, *J* 7.0 Hz), 2.52 d (2H, CH_2CH, *J* 5.6 Hz), 3.46–3.54 m (2H, CH_3CH_2O), 3.62–3.70 m (2H, CH_3CH_2O), 4.04 br.s (2H, CH_2Br), 4.62 t (1H, OCHO, *J* 5.6 Hz), 5.06 br.s (1H, CH_2=), 5.25 br.s (1H, CH_2=). ^{13}C NMR spectrum, δ, ppm: 15.20 (2 CH_3), 37.36 (CH_2Br), 37.49 (CH_2), 61.31 (2 CH_2), 101.83 (CH), 117.81 (CH_2=), 141.38 (C). Found, %: C 43.35; H 6.27. $C_9H_{17}BrO_2$. Calculated, %: C 43.26; H 6.35.

Condensation of 3-bromomethyl-3-butenal diethylacetal (I) with aldehydes IVa–IVe. To a mixture of 1.82 g (7.7 mmol) of compound **I** in 5 ml of THF and 7.7 mmol of aldehyde **IVa–IVe** was added 0.55 g (8.46 mmol) of zinc, several drops of dibromoethane, and the reaction mixture was heated at stirring for 30 min. After treating with water (20 ml) the organic layer was separated, the water layer was extracted with ethyl ether (3×15 ml), the combined organic solutions were dried with Na_2SO_4. On removing the solvent at a reduced pressure and on the separation of the reaction product by column chromatography (eluent petroleum ether–ethyl acetate, 10:1) we obtained aldol acetates **Va–Ve** as colorless oily fluids.

2-Methyl-6-methylene-8,8-diethoxyoct-2-en-4-ol (Va). Yield 1.49 g (80%). IR spectrum, ν, cm^{-1}: 3617 (OH), 3473 (OH), 1127 (C–O), 1058 (C–O). ^1H NMR spectrum, δ, ppm: 1.19 t (6H, 2 CH_3CH_2O, *J* 6.9 Hz), 1.68 br.s (3H, CH_3), 1.71 br.s (3H, CH_3), 2.15–2.29 m (3H, CH_2CHOH, OH), 2.37 d.d (1H, CH_2C, J_1 15.6, J_2 5.6 Hz), 2.41 d.d (1H, CH_2C, J_1 15.6, J_2 5.9 Hz), 3.45–3.53 m (2H, CH_3CH_2O), 3.61–3.69 m (2H, CH_3CH_2O), 4.49 d.t (1H, CHOH, J_1 8.2, J_2 4.9 Hz), 4.62 t (1H, OCHO, *J* 5.9 Hz), 4.56 br.s (1H, CH_2=), 4.97 br.s (1H, CH_2=), 5.17 d (1H, CH=, *J* 8.2 Hz). ^{13}C NMR spectrum, δ, ppm: 15.14 (CH_3), 15.17 (CH_3), 18.19 (CH_3), 25.68 (CH_3), 39.85 (CH_2), 45.37 (CH_2), 61.25 (CH_2), 61.46 (CH_2), 66.34 (CH), 102.39 (CH), 115.53 (CH_2=), 127.37 (CH=), 134.75 (C), 141.93 (C). Found, %: C 69.92; H 10.72. $C_{14}H_{26}O_3$. Calculated, %: C 69.83; H 10.81.

(1*E*,3*E*)-3-Methyl-7-methylene-1-(2,6,6-trimethyl-cyclohex-1-enyl)-9,9-diethoxynona-1,3-dien-5-ol (Vb). Yield 2.06 g (71%). IR spectrum, ν, cm^{-1}: 3617 (OH), 3466 (OH), 1127 (C–O), 1058 (C–O). ^1H NMR spectrum, δ, ppm: 0.98 br.s (3H, CH_3), 0.99 br.s (3H, CH_3), 1.20 t (6H, 2 CH_3CH_2O, *J* 6.9 Hz), 1.42–1.47 m [2H, $CH_2C(CH_3)_2$], 1.56–1.62 m (2H, $CH_2CH_2CH_2$), 1.67 br.s (3H, CH_3), 1.85 br.s (3H, CH_3), 1.97–2.00 m (2H, CH_2CCH_3), 2.25–2.37 m (3H, CH_2CHOH, OH), 2.39–2.43 m (2H, CCH_2CH), 3.48–3.56 m (2H, CH_3CH_2O), 3.63–3.71 m (2H, CH_3CH_2O), 4.60–4.68 m (1H, CHCHOH), 4.64 t (1H, OCHO, *J* 5.9 Hz), 4.99 br.s (1H, CH_2=), 5.00 br.s (1H, CH_2=), 5.40 d (1H, CHCHOH, *J* 8.5 Hz), 5.99 d (1H, CCHCH, *J* 16.1 Hz), 6.09 d (1H, CCHCH, *J* 16.1 Hz). ^{13}C NMR spectrum, δ, ppm: 12.81 (CH_3), 15.16 (CH_3), 15.21 (CH_3), 19.24 (CH_2), 21.56 (CH_3), 28.84 (CH_3), 32.86 (CH_2), 34.16 (C), 39.50 (CH_2), 39.95 (CH_2), 45.38 (CH_2), 61.34 (CH_2), 61.53 (CH_2), 66.45 (CH), 102.51 (CH), 115.81 (CH_2=), 126.66 (CH=), 128.84 (C), 132.16 (CH=), 135.68 (C), 137.15 (CH=), 137.57 (C), 141.81 (C). Found, %: C 83.76; H 6.97. $C_{24}H_{40}O_3$. Calculated, %: C 83.69; H 7.02.

2-Methyl-6-methylene-8,8-diethoxyoctan-4-ol (Vc). Yield 1.41 g (75%). IR spectrum, ν, cm^{-1}: 3485 (OH), 1127 (C–O), 1062 (C–O). ^1H NMR spectrum, δ, ppm: 0.86–0.88 m [6H, 2 $CH(CH_3)_2$], 1.13–1.17 m [7H, 2 CH_3CH_2O, $CH_2CH(CH_3)_2$], 1.34–1.42 m [1H, $CH_2CH(CH_3)_2$], 1.71–1.79 m [1H, $CH(CH_3)_2$], 2.03 d.d (1H, CH_2CHOH, J_1 13.5, J_2 9.5 Hz), 2.22–2.29 m (1H, CH_2CHOH), 2.30 br.s (1H, OH), 2.33–2.35 m (2H, CH_2C), 3.42–3.49 m (2H, CH_3CH_2O), 3.58–3.65 m (2H, CH_3CH_2O), 3.73–3.79 m (1H, CHOH), 4.60 t (1H, OCHO, *J* 5.8 Hz), 4.90 br.s (1H, CH_2=), 4.93 br.s (1H, CH_2=). ^{13}C NMR spectrum, δ, ppm: 15.07 (CH_3), 15.09 (CH_3), 22.06 (CH_3), 23.27 (CH_3), 24.55 (CH), 39.77 (CH_2), 45.82 (CH_2), 46.25 (CH_2), 61.10 (CH_2), 61.37 (CH_2), 67.02 (CH), 102.38 (CH), 115.27 (CH_2=), 142.41 (C). Found, %: C 68.90; H 11.43. $C_{14}H_{28}O_3$. Calculated, %: C 68.81; H 11.55.

3-Methylene-5,5-diethoxy-1-phenylpentan-1-ol (Vd). Yield 1.81 g (89%). IR spectrum, ν, cm^{-1}: 3540 (OH), 3492 (OH), 1127 (C–O), 1059 (C–O). ^1H NMR spectrum, δ, ppm: 1.22 t (6H, 2 CH_3CH_2O, *J* 7.0 Hz), 2.42 d.d (1H, CH_2CHOH, J_1 14.1, J_2 9.7 Hz), 2.46 d (2H, CH_2C, *J* 5.9 Hz), 2.55 d.d (1H, CH_2CHOH, J_1 14.1, J_2 3.1 Hz), 2.80 br.s (1H, OH), 3.48–3.56 m (2H, CH_3CH_2O), 3.65–3.73 m (2H, CH_3CH_2O), 4.66 t (1H, OCHO, *J* 5.9 Hz), 4.85 d.d (1H, CHOH, J_1 9.7, J_2 3.3 Hz), 5.04 br.s (2H, CH_2=), 7.24–7.39 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 15.16 (2 CH_3), 39.70 (CH_2), 47.63

(CH_2), 61.30 (CH_2), 61.60 (CH_2), 71.78 (CH), 102.46 (CH), 116.12 (CH_2=), 125.70 ($C^{2,6}$arom), 127.28 ($C^{3,5}$ arom), 128.31 (C^4 arom), 142.01 (C^1 arom), 144.14 (C). Found, %: C 72.78; H 9.07. $C_{16}H_{24}O_3$. Calculated, %: C 72.69; H 9.15.

1-(Benzyloxy)-4-methylene-6,6-diethoxyhexan-2-ol (Ve). Yield 1.80 g (76%). IR spectrum, ν, cm^{-1}: 3591 (OH), 3510 (OH), 1160 (C–O), 1116 (C–O). ^1H NMR spectrum, δ, ppm: 1.18 t (3H, CH_3CH_2O, *J* 6.9 Hz), 1.19 t (3H, CH_3CH_2O, *J* 6.9 Hz), 1.83 br.s (0.3H, OH), 2.23 d.d (1H, CCH_2CH, J_1 14.1, J_2 8.5 Hz), 2.30 d.d (1H, CCH_2CH, J_1 14.1, J_2 4.6 Hz), 2.40 d (2H, CH_2C, *J* 5.9 Hz), 2.69 br.s (0.7H, OH), 3.40 d.d (1H, CH_2OBn, J_1 9.5, J_2 6.9 Hz), 3.46–3.53 m (3H, CH_2OBn, CH_3CH_2O), 3.61–3.69 m (2H, CH_3CH_2O), 3.97–4.03 m (1H, CHOH), 4.56 br.s (2H, CH_2Ph), 4.63 t (1H, OCHO, *J* 5.9 Hz), 4.96 br.s (1H, CH_2=), 4.97 br.s (1H, CH_2=), 7.27–7.36 m (5H, CH_2Ph). ^{13}C NMR spectrum, δ, ppm: 15.16 (2 CH_3), 39.89 (CH_2), 40.94 (CH_2), 61.13 (CH_2), 61.26 (CH_2), 68.48 (CH), 73.30 (CH_2), 74.08 (CH_2), 102.19 (CH), 115.29 (CH_2=), 127.66 ($C^{2,4,6}$arom), 128.35 ($C^{3,5}$ arom), 137.99 (C^1 arom), 141.63 (C). Found, %: C 70.14; H 9.06. $C_{18}H_{28}O_4$. Calculated, %: C 70.10; H 9.15.

Unsaturated aldehydes VIa–VIc, VIe. *a*. To a solution of 2 mmol of aldol acetal **Va–Ve** in 20 ml of boiling acetone was added 1 ml of water and 0.5 ml of 48% hydrobromic acid. After 1 h the reaction mixture was treated with a saturated solution of $NaHCO_3$ (10 ml), the reaction product was extracted into dichloromethane (3×15 ml), the combined extracts were dried with $MgSO_4$. On removing the solvent at a reduced pressure and on the separation of the reaction product by column chromatography (eluent petroleum ether–ethyl acetate, 40:1) we obtained the corresponding unsaturated aldehydes **VIa–VIc, VIe** as a mixture of *cis*- and *trans*-isomers, 1:3.

(2*EZ*,4*E*)-3,7-Dimethylocta-2,4,6-trienal (VIa). Light-yellow oily fluid with a pleasant grass odor. Yield 0.24 g (80%). IR spectrum, ν, cm^{-1}: 1640 (C=O). ^1H NMR spectrum, δ, ppm: 1.87 br.s [6H, $CH=C(CH_3)_2$], 2.29 br.s [3H, $CHC(CH_3)$], 5.94 d (1H, CCHCO, *J* 8.5 Hz), 5.99 d [1H, $CH=C(CH_3)_2$, *J* 11.3 Hz], 6.23 d (1H, CCHCH, *J* 15.1 Hz), 6.96 d.d (1H, CHCHCH, J_1 15.1, J_2 11.3 Hz), 10.09 d (1H, CHO, *J* 8.5 Hz). ^{13}C NMR spectrum, δ, ppm: 13.06 (CH_3), 18.87 (CH_3), 26.51 (CH_3), 125.39 (CH=), 128.67 (CH=), 132.52 (CH=), 132.62 (CH=), 142.46 (C), 155.17 (C), 191.11 (C). Found, %: C 79.99; H 9.24. $C_{10}H_{14}O$. Calculated, %: C 79.96; H 9.39.

(2*EZ*,4*E*,6*E*,8*E*)-3,7-Dimethyl-9-(2,6,6-trimethyl-1-cyclohexenyl)-2,4,6,8-nonatetraenal (retinal) (VIb). Yield 0.34 g (60%). The spectral characteristics of the obtained isomers mixture are consistent with those described in [22].

(2*E*,4*E*)-3,7-Dimethylocta-2,4-dienal (VIc). Light-yellow oily fluid with a pleasant grass odor. Yield 0.25 g (88%). IR spectrum, ν, cm^{-1}: 1672 (C=O), 1633 (C=C), 1206 (C–O), 1116 (C–O). ^1H NMR spectrum, δ, ppm: 0.89 br.s [3H, $CH(CH_3)_2$], 0.90 br.s [3H, $CH(CH_3)_2$], 1.67–1.76 m [1H, $CH(CH_3)_2$], 2.04–2.12 m [2H, $CH_2CH(CH_3)_2$], 2.23 s (3H, CH_3C), 5.86 d (1H, CHCO, *J* 8.2 Hz), 6.16 d (1H, CCHCH, *J* 16.1 Hz), 6.24 t (1H, CH_2CHCH, *J* 7.2 Hz), 10.08 d (1H, CHO, *J* 8.2 Hz). ^{13}C NMR spectrum, δ, ppm: 13.04 (CH_3), 22.29 (2 CH_3), 28.32 (CH), 42.43 (CH_2), 128.36 (CH=), 134.40 (CH=), 138.46 (CH=), 154.74 (C), 191.41 (C). Found, %: C 78.96; H 10.43. $C_{10}H_{16}O$. Calculated, %: C 78.90; H 10.59.

(2*EZ*,4*E*)-6-(Benzyloxy)-3-methylhexa-2,4-dienal (VIe). Light-yellow oily fluid. Yield 0.28 g (80%). IR spectrum, ν, cm^{-1}: 1673 (C=O), 1640 (C=C), 1240 (C–O), 1206 (C–O), 1106 (C–O). ^1H NMR spectrum, δ, ppm: 2.17 br.s (3H, CH_3), 4.08 d (2H, CH_2OBn, *J* 5.1 Hz), 4.49 br.s (2H, CH_2Ph), 5.86 d (1H, CHCO, *J* 7.9 Hz), 6.24 d.t (1H, $CHCH_2OBn$, J_1 15.9, J_2 5.1 Hz), 6.35 d (1H, $CHCHCH_2$, *J* 15.9 Hz), 7.21–7.27 m (5H, Ph), 10.02 d (1H, CHO, *J* 7.9 Hz). ^{13}C NMR spectrum, δ, ppm: 12.99 (CH_3), 69.94 (CH_2), 72.73 (CH_2), 126.04 (C^2 arom), 127.73 ($C^{4,6}$ arom), 127.80 (C^3 arom), 128.45 (C^5 arom), 129.76 (CH_2=), 134.08 (CH=), 134.16 (CH=), 137.73 (C^1 arom), 153.55 (C), 191.40 (CO). Found, %: C 77.83; H 7.37. $C_{14}H_{16}O_2$. Calculated, %: C 77.75; H 7.46.

Preparation of unsaturated aldehydes VIa and VId at treatment with hydrochloric acid. *b*. To a solution of 1 mmol of aldol acetal **Va** or **Vd** in 4 ml of dichloroethane was added 4 ml of 10% HCl, and the mixture was vigorously stirred for 12 h. The reaction mixture was diluted with 30 ml of dichloromethane, washed with the saturated water solution of $NaHCO_3$ (15 ml), and dried with $MgSO_4$. On removing the solvent at a reduced pressure and on the separation of the reaction product by column chromatography (eluent petroleum ether–ethyl acetate, 30:1) we obtained the target aldehydes **VIa and VId** as a mixture of *cis*- and *trans*-isomers, 1:3. Compound **VIa**. Yield 0.11 g (73%).

(2*EZ*,4*E*)-3-Methyl-5-phenylpenta-2,4-dienal (VId). Bright yellow oily fluid. Yield 0.11 g (65%). IR spectrum, ν, cm^{-1}: 1671 (C=O), 1616 (C=C), 1250 (C–O). ^1H NMR spectrum, δ, ppm: 2.40 br.s (3H, CH_3),

6.09 d (1H, CHCHO, *J* 7.9 Hz), 6.91 d (1H, CHPh, *J* 16.1 Hz), 7.08 d [1H, CHC(CH_3), *J* 16.1 Hz], 7.33–7.40 m (3H, $H^{3,4,5}$ arom), 7.51 d (2H, $H^{2,6}$ arom, *J* 7.2 Hz), 10.17 d (1H, CHO, *J* 7.9 Hz). ^{13}C NMR spectrum, δ, ppm: 13.07 (CH_3), 127.34 ($C^{2,6}$ arom), 128.88 ($C^{3,5}$ arom), 129.21 (C^4 arom), 130.07 (CH), 131.31 (CH), 135.68 (CH), 135.85 (C^1 arom), 154.19 (C), 191.22 (C). Found, %: C 83.76; H 6.97. $C_{12}H_{12}O$. Calculated, %: C 83.69; H 7.02.

Ethylacetals VIIa–VIIe. To 1 mmol of aldol acetal **Va–Ve** in 2 ml of ethanol (or dichloromethane) was added at stirring 0.01 g (0.05 mmol) of *p*-TsOH·$2H_2O$. On completion of the reaction (TLC monitoring) the reaction mixture was treated with water (10 ml), the reaction product was extracted into dichloromethane (3 × 15 ml), the combined extracts were dried with Na_2SO_4. On removing the solvent at a reduced pressure acetals **VIIa–VIIe** were isolated by column chromatography (eluent petroleum ether–ethyl acetate, 30 : 1) as a mixture of diastereomers.

4-Methylene-6-(2-methylprop-1-enyl)-2-ethoxytetrahydro-2*H*-pyran (VIIa). Colorless oily fluid with a pleasant flower odor. Yield 0.16 g (91%), isomers ratio 2 : 3. IR spectrum, ν, cm^{-1}: 1123 (C–O), 1046 (C–O). ^1H NMR spectrum, δ, ppm: 1.20 t (1.2H, CH_3CH_2O, *J* 7.0 Hz), 1.21 t (1.8H, CH_3CH_2O, *J* 7.0 Hz), 1.67 br.s [1.2H, CH=C(CH_3)$_2$], 1.69 br.s [1.8H, CH=C(CH_3)$_2$], 1.73 br.s [3H, CH=C(CH_3)$_2$], 2.00–2.22 m (2H, CH_2CHCH), 2.27–2.43 m (2H, CH_2CHO), 3.47–3.56 m (1H, CH_3CH_2O), 3.69–3.77 m (0.6H, CH_3CH_2O), 3.91–3.97 m (0.4H, CH_3CH_2O), 4.01 d.d.d (0.4H, CH_2CHO, J_1 11.0, J_2 8.2, J_3 2.6 Hz), 4.37 d.d (0.4H, $CHOCH_2$, J_1 9.5, J_2 2.3 Hz), 4.49 d.d.d (0.6H, CH_2CHO, J_1 11.3, J_2 8.7, J_3 2.8 Hz), 4.76–4.80 m (1.8H, CH_2CHO, CH_2=), 4.94 br.s (0.4H, CH_2=), 4.95 br.s (0.4H, CH_2=), 5.19 d (0.6H, CH=, *J* 8.5 Hz), 5.25 d (0.4H, CH=, *J* 7.9 Hz). ^{13}C NMR spectrum, δ, ppm: 14.99 (CH_3), 15.12 (CH_3), 18.22 (CH_3), 18.39 (CH_3), 38.83 (CH_2), 40.28 (2 CH_2), 40.80 (CH_2), 62.53 (CH_2), 64.24 (CH_2), 66.56 (CH), 72.48 (CH), 97.24 (CH), 101.50 (CH), 110.41 (2 CH_2=), 125.13 (CH=), 125.30 (CH=), 135.79 (C), 136.41 (C), 140.65 (C), 142.71 (C). Found, %: C 73.49; H 10.14. $C_{12}H_{20}O_2$. Calculated, %: C 73.43; H 10.27.

6-Isobutyl-4-methylene-2-ethoxytetrahydro-2*H*-pyran (VIIc). Colorless oily fluid with a pleasant flower odor. Yield 0.18 g (93%), isomers ratio 1.2:1. IR spectrum, ν, cm^{-1}: 1123 (C–O), 1059 (C–O). ^1H NMR spectrum, δ, ppm: 0.89 br.s [3H, CH(CH_3)$_2$], 0.91 br.s [6.6H, CH(CH_3)$_2$], 0.92 br.s [3.6H, CH(CH_3)$_2$], 1.20 t (3.6H, CH_3CH_2O, *J* 7.2 Hz), 1.24 t (3H, CH_3CH_2O, *J* 6.9 Hz), 1.45–1.52 m [1H, $CH_2CH(CH_3)_2$], 1.57–1.64 m [1.2H, $CH_2CH(CH_3)_2$], 1.77–1.89 m [2H, $CH(CH_3)_2$, $CH_2CH(CH_3)_2$], 1.92–2.00 m [2.4H, $CH(CH_3)_2$, $CH_2CH(CH_3)_2$], 2.10–2.14 m (2H, CH_2CHCH_2), 2.19–2.23 m (2H, $CHCH_2C$), 2.28–2.35 m (2.4H, CH_2CHCH_2), 2.38–2.43 m (2.4H, $CHCH_2C$), 3.30–3.37 m (1H, CH_2CHCH_2), 3.44–3.57 m (2.2H, CH_3CH_2O), 3.66–3.74 m (1.2H, CH_3CH_2O), 3.79–3.85 m (1.2H, CH_2CHCH_2), 3.91–3.99 m (1H, CH_3CH_2O), 4.31 d.d (1H, $CHOCH_2$, J_1 9.5, J_2 2.3 Hz), 4.75–4.78 m (3.6H, $CHOCH_2$, CH_2=), 4.92 br.s (1H, CH_2=), 4.93 br.s (1H, CH_2=). ^{13}C NMR spectrum, δ, ppm: 14.55 (CH_3), 15.20 (CH_3), 22.06 (CH_3), 22.21 (CH_3), 23.22 (CH_3), 23.41 (CH_3), 24.27 (CH), 24.74 (CH), 39.10 (CH_2), 39.33 (CH_2), 40.69 (CH_2), 41.03 (CH_2), 44.74 (CH_2), 45.34 (CH_2), 62.34 (CH_2), 64.24 (CH_2), 67.49 (CH), 73.42 (CH), 97.09 (CH), 101.85 (CH), 110.17 (CH_2=), 110.21 (CH_2=), 141.08 (C). Found, %: C 72.74; H 11.09. $C_{12}H_{22}O_2$. Calculated, %: C 72.68; H 11.18.

4-Methylene-6-phenyl-2-ethoxytetrahydro-2*H*-pyran (VIId). Colorless oily fluid. Yield 0.21 g (96%), isomers ratio 0.6:1. IR spectrum, ν, cm^{-1}: 1128 (C–O), 1058 (C–O), 1045 (C–O). ^1H NMR spectrum, δ, ppm: 1.24 t (1.8H, CH_3CH_2O, *J* 7.1 Hz), 1.27 t (3H, CH_3CH_2O, *J* 6.9 Hz), 2.22–2.35 m (2H, CH_2CHPh, CH_2CHO), 2.38–2.59 m (4.4H, CH_2CHPh, CH_2CHO), 3.50–3.65 m (1.6H, CH_3CH_2O), 3.72–3.79 m (0.6H, CH_3CH_2O), 3.98–4.06 m (1H, CH_3CH_2O), 4.39 d.d (1H, OCHPh, J_1 11.5, J_2 2.3 Hz), 4.54 d.d (1H, $CHOCH_2$, J_1 9.7, J_2 2.6 Hz), 4.81 d.d (0.6H, OCHPh, J_1 11.5, J_2 2.3 Hz), 4.88–4.90 m (3.2H, CH_2=), 5.11 d (0.6H, $CHOCH_2$, *J* 3.8 Hz), 7.30–7.44 m (8H, Ph). ^{13}C NMR spectrum, δ, ppm: 15.00 (CH_3), 15.19 (CH_3), 38.79 (CH_2), 40.76 (CH_2), 41.93 (CH_2), 42.24 (CH_2), 62.63 (CH_2), 64.39 (CH_2), 71.43 (CH), 76.99 (CH), 97.54 (CH), 102.09 (CH), 110.87 (2 CH_2=), 125.80 ($C^{2,6}$ arom), 126.07 ($C^{2,6}$ arom), 127.45 (C^4 arom), 127.56 (C^4 arom), 128.27 ($C^{3,5}$ arom), 128.37 ($C^{3,5}$ arom), 140.61 (C^1 arom), 141.56 (C^1 arom), 142.00 (C), 142.52 (C). Found, %: C 77.11; H 8.24. $C_{14}H_{18}O_2$. Calculated, %: C 77.03; H 8.31.

2-[(Benzyloxy)methyl]-4-methylene-6-ethoxytetrahydro-2*H*-pyran (VIIe). Colorless oily fluid. Yield 0.24 g (91%), isomers ratio 0.3:1. IR spectrum, ν, cm^{-1}: 1126 (C–O), 1070 (C–O). ^1H NMR spectrum, δ, ppm: 1.21 t (0.9H, CH_3CH_2O), 1.25 t (3H, CH_3CH_2O), 1.89–1.95 m (0.6H, CH_2CHCH_2), 2.06–2.17 m (2.6H, CH_2CHCH_2, CH_2CHO), 2.22–2.25 m (1H, CH_2CHO),

2.33–2.38 m (1H, CH_2CHO), 3.39–3.56 m (4.6H, CH_2OBn, CH_3CH_2O, $CHCH_2OBn$), 3.60–3.68 m (0.6H, CH_3CH_2O), 3.86–3.94 m (1.3H, CH_3CH_2O, $CHCH_2OBn$), 4.31 d.d (1H, $CHOCH_2CH_3$, J_1 9.5, J_2 2.6 Hz), 4.47–4.55 m (2.6H, CH_2Ph), 4.72 br.s (2.3H, $CHOCH_2CH_3$, CH_2=), 4.92 br.s (0.3H, CH_2=), 4.93 br.s (0.3H, CH_2=), 7.19–7.29 m (6.5H, Ph). ^{13}C NMR spectrum, δ, ppm: 14.98 (CH_3), 15.17 (CH_3), 36.37 (CH_2), 36.80 (CH_2), 38.83 (CH_2), 40.87 (CH_2), 62.47 (CH_2), 64.34 (CH_2), 68.53 (CH), 72.87 (CH_2), 73.27 (CH_2), 73.43 (2 CH_2), 74.50 (CH), 97.22 (CH), 100.69 (CH), 110.81 (CH_2=), 110.94 (CH_2=), 127.52 ($C^{2,4,6}$ arom), 127.57 ($C^{2,4,6}$ arom), 127.62 ($C^{3,5}$ arom), 128.32 ($C^{3,5}$ arom), 138.23 (2 C^{1} arom), 140.22 (C), 141.88 (C). Found, %: C 73.32; H 8.34. $C_{16}H_{22}O_3$. Calculated, %: C 73.25; H 8.45.

Unsaturated aldehydes VIa, VIc, VId. The hydrolysis of cyclic acetals **VIIa, VIIc, VIId** was performed with hydrobromic acid in acetone (method *a*) or in a two-phase system hydrochloric acid–dichloroethane (method *b*) as described above for the hydrolysis of acyclic acetals **Va, Vc, Vd**. Aldehyde **VIa**: yield 75%, *Z*/*E* = 1:3 (*a*); 70%, *Z*/*E* = 1:10 (*b*). Aldehyde **VIc**: yield 81%, *Z*/*E* = 1:3 (*a*). Aldehyde **VId**: yield 68%, *Z*/*E* = 1:10.

Lactols VIIIa, VIIId, VIIIe. Ethylacetals **VIIa, VIId, VIIe** (2.5 mmol) were vigorously stirred at heating with 4 ml of 50% acetic acid for 1 h. The reaction mixture was diluted with 30 ml of dichloromethane, washed with a saturated water solution of $NaHCO_3$ (30 ml), and dried with $MgSO_4$. On removing the solvent at a reduced pressure and on the separation of the reaction product by column chromatography (eluent petroleum ether–ethyl acetate, 10:1) we obtained the corresponding mixtures of lactols diastereomers **VIIIa, VIIId, VIIIe** as colorless oily fluids.

4-Methylene-6-(2-methylprop-1-enyl)tetrahydro-2*H*-pyran-2-ol (VIIIa). Yield 0.33 g (78%), (isomers ratio 0.7:1). IR spectrum, ν, cm^{-1}: 3608 (OH), 1095 (C–O), 1048 (C–O). ^1H NMR spectrum, δ, ppm: 1.64 br.s [2.1H, $CH=C(CH_3)_2$], 1.66 br.s [2.1H, $CH=C(CH_3)_2$], 1.70 br.s [6H, $CH=C(CH_3)_2$], 1.97–2.11 m (3.4H, CH_2CHCH), 2.19–2.31 m (1.7H, CH_2CHOH), 2.39–2.47 m (1.7H, CH_2CHOH), 3.37–3.48 m (1H, OH), 4.03–4.14 m (1.4H, OH, CHCHO), 4.64–4.69 m (1.4H, CHCHO, CHOH), 4.79 br.s (2H, CH_2=), 4.83 br.s (0.7H, CH_2=), 4.86 br.s (0.7H, CH_2=), 5.16 d [1H, $CH=C(CH_3)_2$, *J* 9.2 Hz], 5.20 d [0.7H, $CH=C(CH_3)_2$, *J* 9.2 Hz], 5.34 br.s (1H, CHOH). ^{13}C NMR spectrum, δ, ppm: 18.26 (CH_3), 18.31 (CH_3), 25.57 (CH_3), 25.59 (CH_3), 39.34 (CH_2), 39.93 (CH_2), 40.33 (CH_2), 41.93 (CH_2), 67.08 (CH), 72.76 (CH), 91.98 (CH), 95.98 (CH), 110.66 (CH_2=), 111.40 (CH_2=), 124.53 (CH=), 124.82 (CH=), 136.08 (C), 136.43 (C), 140.04 (C), 142.16 (C). Found, %: C 71.46; H 9.48. $C_{10}H_{16}O_2$. Calculated, %: C 71.39; H 9.59.

4-Methylene-6-phenyltetrahydro-2*H*-pyran-2-ol (VIIId). Yield 0.38 g (79%), diastereomers ratio 1:1. IR spectrum, ν, cm^{-1}: 3608 (OH), 3426 (OH), 1118 (C–O), 1113 (C–O), 1052 (C–O), 1047 (C–O). ^1H NMR spectrum, δ, ppm: 2.16–2.29 m (2H, CH_2CHPh), 2.34–2.43 m (3H, CH_2CHPh, CH_2CHO), 2.48–2.58 m (3H, CH_2CHO), 3.16 br.s (1H, OH), 3.72 br.s (1H, OH), 4.38 d.d (1H, CHPh, J_1 11.5, J_2 2.3 Hz), 4.77–4.80 m (1H, CHOH), 4.88 br.s (1H, CH_2=), 4.89 br.s (1H, CH_2=), 4.93 br.s (1H, CH_2=), 4.97 br.s (1H, CH_2=), 5.00 d.d (1H, CHPh, J_1 11.5, J_2 2.6 Hz), 5.51 br.s (1H, CHOH), 7.29–7.41 m (10H, Ph). ^{13}C NMR spectrum, δ, ppm: 39.30 (CH_2), 41.90 ($2CH_2$), 42.44 (CH_2), 72.05 (CH), 77.63 (CH), 92.40 (CH), 96.59 (CH), 111.18 (CH_2=), 111.87 (CH_2=), 125.94 (C^{2} arom), 126.04 (C^{6} arom), 127.65 (C^{4} arom), 127.73 (C^{3} arom), 128.40 (C^{5} arom), 140.01 (C^{1} arom), 141.07 (C^{1} arom), 141.71 (C), 141.98 (C). Found, %: C 75.85; H 7.37. $C_{12}H_{14}O_2$. Calculated, %: C 75.76; H 7.42.

6-[(Benzyloxy)methyl]-4-methylenetetrahydro-2*H*-pyran-2-ol (VIIIe). Yield 0.42 d (71%), diastereomers ratio 1 : 1. IR spectrum, ν, cm^{-1}: 3608 (OH), 3439 (OH), 1241 (C–O), 1094 (C–O), 1050 (C–O), 1012 (C–O). ^1H NMR spectrum, δ, ppm: 1.85–2.18 m (5H, CH_2CHCH_2, CH_2CHOH), 2.21–2.25 m (1H, CH_2CHOH), 2.33–2.39 m (2H, CH_2CHOH), 3.34 br.s (1H, OH), 3.37–3.57 m (5H, OH, CH_2OBn), 3.95 br.s (1H, CHOH), 4.08–4.14 m (1H, $CHCH_2OBn$), 4.45–4.53 m (4H, CH_2Ph), 4.57–4.60 m (1H, $CHCH_2OBn$), 4.72 br.s (1H, CH_2=), 4.74 br.s (1H, CH_2=), 4.78 br.s (1H, CH_2=), 4.82 br.s (1H, CH_2=), 5.32 br.s (1H, CHOH), 7.19–7.27 m (10H, Ph). ^{13}C NMR spectrum, δ, ppm: 36.22 (CH_2), 36.49 (CH_2), 39.47 (CH_2), 41.95 (CH_2), 68.90 (CH), 72.68 (CH_2), 72.80 (CH_2), 73.34 (CH_2), 73.41 (CH_2), 74.46 (CH), 92.05 (CH), 96.19 (CH), 111.13 (CH_2=), 111.82 (CH_2=), 127.62 (C^{4} arom), 127.63 ($C^{2,6}$ arom), 128.32 ($C^{3,5}$ arom), 137.94 ($2C^{1}$ arom), 139.61 (C), 141.52 (C). Found, %: C 71.84; H 7.68. $C_{14}H_{18}O_3$. Calculated, %: C 71.77; H 7.74.

4-Methyl-1-[(2-methylene-4,4-diethoxybutyl)-sulfonyl]benzene (X). To a dispersion of 6.9 g (32.6 mmol) of sodium sulfinate dihydrate in 26 ml of

DMF was added at vigorous stirring 6.19 g (26.1 mmol) of substituted allyl bromide **I**. On completion of the reaction (TLC monitoring) the reaction mixture was treated with water (100 ml). The organic layer was separated, the water layer was extracted with dichloromethane (3×30 ml), the combined organic solutions were washed with a saturated water solution of NaCl (50 ml), and dried with $MgSO_4$. On removing the solvent at a reduced pressure the reaction product was purified by column chromatography (eluent petroleum ether–ethyl acetate, 20:1–5:1). Yield 6.1 g (75%). Colorless oily fluid. IR spectrum, ν, cm^{-1}: 1326 (SO_2), 1154 (SO_2), 1144 (SO_2), 1089 (C–O), 1061 (C–O). ^1H NMR spectrum, δ, ppm: 1.08 t (6H, $2CH_3CH_2O$, *J* 7 Hz), 2.34 br.s (3H, CH_3Ph), 2.37 d (2H, CCH_2CH, *J* 5.4 Hz), 3.33–3.41 m (2H, CH_3CH_2O), 3.49–3.57 m (2H, CH_3CH_2O), 3.80 br.s (2H, CH_2SO_2Tol), 4.44 t (1H, OCHO, *J* 5.4 Hz), 4.77 br.s (1H, CH_2=), 5.04 br.s (1H, CH_2=), 7.22 d (2H, $H^{3,5}$ arom, *J* 8 Hz), 7.64 d (2H, $H^{2,6}$ arom, *J* 8 Hz). ^{13}C NMR spectrum, δ, ppm: 15.17 (2 CH_3), 21.56 ($PhCH_3$), 39.45 (CH_2), 61.45 (2 CH_2), 63.00 (CH_2), 102.28 (CH), 122.61 (CH_2=), 128.27 (C^4 arom), 128.48 ($C^{2,6}$ arom), 129.54 ($C^{3,5}$ arom), 133.37 (C), 144.52 (C^1 arom). Found, %: C 61.54; H 7.70. $C_{16}H_{24}O_4S$. Calculated, %: C 61.51; H 7.74.

4-Methyl-4-[(1-methylene-3,3-diethoxypropyl)-pent-3-en-1-ylsulfonyl]benzene (IX). To a solution of 0.31 g (1 mmol) of sulfone **X** in 10 ml of THF cooled to –78°C was added 1.4 ml (1.5 mmol) of 1.1 M butyllithium solution in hexane, the reaction mixture was maintained at this temperature for 1.5 h. Then 0.15 g (1.05 mmol) of prenyl bromide in 1 ml of THF was added, and the mixture was stirred for 3 h at –78°C. The reaction mixture was treated with water (15 ml), the organic layer was separated, the water layer was extracted with ethyl ether (3×15 ml), the combined organic solutions were washed with a saturated water solution of $NaHCO_3$ (10 ml), and dried with $MgSO_4$. On removing the solvent at a reduced pressure the reaction product was isolated by column chromatography (eluent petroleum ether–ethylacetate, 30:1–6:1). Yield 0.32 g (84%). Colorless oily fluid. IR spectrum, ν, cm^{-1}: 1364 (SO_2), 1344 (SO_2), 1304 (SO_2), 1131 (SO_2), 1105 (SO_2), 1078 (C–O). ^1H NMR spectrum, δ, ppm: 1.16 t (3H, CH_3CH_2O, *J* 7 Hz), 1.17 t (3H, CH_3CH_2O, *J* 7 Hz), 1.53 br.s [3H, $CH=C(CH_3)_2$], 1.61 br.s [3H, $CH=C(CH_3)_2$], 2.29–2.44 m (3H, CH_2CHSO_2Tol, CCH_2CH), 2.43 br.s (3H, CH_3Ph), 2.69–2.76 m (1H, CH_2CHSO_2Tol), 3.37–3.49 m (2H, CH_3CH_2O), 3.51–3.58 m (1H, CH_3CH_2O), 3.58–3.66 m (1H, CH_3CH_2O), 3.74 d.d (1H, $CHSO_2Tol$, J_1 11.3, J_2 4.1 Hz), 4.47 t (1H, OCHO, *J* 5.4 Hz), 4.91 t [1H, $CH=C(CH_3)_2$, *J* 8.7 Hz], 5.04 br.s (1H, CH_2=), 5.29 br.s (1H, CH_2=), 7.30 d (2H, $H^{3,5}$ arom, *J* 8.2 Hz), 7.71 d (2H, $H^{2,6}$ arom, *J* 8.2 Hz). ^{13}C NMR spectrum, δ, ppm: 15.12 (CH_3), 15.20 (CH_3), 17.76 (CH_3), 21.52 (CH_3), 25.55 (CH_3), 26.67 (CH_2), 40.27 (CH_2), 60.47 (CH_2), 61.33 (CH_2), 69.95 (CH), 101.94 (CH), 118.98 (CH=), 120.34 (CH_2=), 129.28 ($C^{2,3,5,6}$ arom), 134.31 (C), 134.66 (C^1 arom), 136.79 (C), 144.35 (C^4 arom). Found, %: C 66.34; H 8.41. $C_{21}H_{32}O_4S$. Calculated, %: C 66.28; H 8.48.

2-Methyl-6-methylene-8,8-diethoxyoct-2-ene (XI), (5*EZ*)-2,6-dimethyl-8,8-diethoxy-2,5-octadiene (XII). To 0.38 g (1 mmol) of sulfone **IX** dissolved in a cooled to –78°C mixture of 4 ml of THF, 4 ml of Et_2O, and 1 ml of petroleum ether [23] was added in succession at vigorous stirring by small pieces 0.27 g (12 mmol) of sodium and 2.5 ml of ethanol. On completion of the reaction (TLC monitoring) the reaction mixture was treated with water (25 ml) and warmed to the room temperature. The organic layer was separated, the water layer was extracted with ethyl ether (3×15 ml), the combined organic solutions were washed with a saturated water solution of NaCl (25 ml), and dried with $MgSO_4$. On removing the solvent at a reduced pressure and on the separation of the reaction products by column chromatography (eluent petroleum ether–ethyl-acetate, 80:1) we obtained 0.20 g (90%) of a mixture of isomeric acetals **XI** and **XII** as a colorless oily fluid with a pleasant flower odor. IR spectrum, ν, cm^{-1}: 1131 (C–O), 1118 (C–O). ^1H NMR spectrum, δ, ppm: 1.16–1.21 m (6H, CH_3CH_2O), 1.60 br.s (0.6H, CH_3), 1.62 br.s (1.8H, CH_3), 1.68 br.s (4.2H, CH_3), 1.75 br.s (0.6H, CH_3), 2.06–2.16 m (0.8H, CH_2CH_2CH), 2.28 d (1.2H, CCH_2CH, *J* 5.5 Hz), 2.34 d (0.4H, $CHCH_2C$, *J* 5.9 Hz), 2.37 d (0.4H, CCH_2CH, *J* 5.8 Hz), 2.66–2.72 m (1.6H, $CHCH_2CH$), 3.45–3.53 m (2H, CH_3CH_2O), 3.60–3.68 m (2H, CH_3CH_2O), 4.50–4.63 m (1H, OCHO), 4.83 br.s (0.4H, CH_2=), 5.06–5.10 m (1H, CH=), 5.17–5.20 m (0.8H, CH=).

(3*E*)-3,7-Dimethyl-3,6-octadienal (XIII). To 0.42 g (1.86 mmol) of the mixture of acetals **XI** and **XII** in 2.5 ml of petroleum ether was added at vigorous stirring 1 ml of 85% formic acid. On completion of the reaction (TLC monitoring) the reaction mixture was treated with water (10 ml). The organic layer was separated, the water layer was extracted with petroleum ether (3 × 10 ml), the combined organic solutions were washed with

a saturated water solution of $NaHCO_3$ (20 ml), and dried with Na_2SO_4. On removing the solvent at a reduced pressure the reaction product was isolated by column chromatography (eluent benzene). Yield 0.18 g (65%), fluid with a pleasant flower odor. IR spectrum, ν, cm^{-1}: 1728 (C=O), 1465 (C=C). ^1H NMR spectrum, δ, ppm: 1.63 br.s [3H, $CH=C(CH_3)_2$], 1.69 br.s [6H, $CH=C(CH_3)_2$, CH_2CCH_3], 2.75 t (2H, $CHCH_2CH$, *J* 2.5 Hz), 3.03 d (2H, CH_2CHO, *J* 2.0 Hz), 5.09 t (1H, $CHCCH_3$, *J* 7.0 Hz), 5.29 t [1H, $CH=C(CH_3)_2$, *J* 6.0 Hz], 9.61 t (1H, CHO, *J* 2.5 Hz). ^{13}C NMR spectrum, δ, ppm: 16.79 (CH_3), 17.63 (CH_3), 25.57 (CH_3), 27.24 (CH_2), 54.15 (CH_2), 122.20 (CH=), 126.09 (C), 129.62 (CH=), 132.07 (C), 200.35 (CO). Found, %: C 78.93; H 10.54. $C_{10}H_{16}O$. Calculated, %: C 78.90; H 10.59.

Allyl-allyl coupling. To a solution of 2.37 g (10 mmol) of substituted allyl bromide **I** in 20 ml of THF at –78°C was added in succession within 10 min 0.1 g (0.5 mmol) of CuI and 20 ml (20 mmol) of 1 M solution of allyl- or prenylmagnesium chloride. The reaction mixture was stirred at the same temperature for 1 h, then it was treated with 25 ml of saturated water solution of NH_4Cl, extracted with ethyl ether (3 × 20 ml), and the combined extracts were dried with Na_2SO_4. On removing the solvent at a reduced pressure and on the separation of the reaction product by column chromatography (eluent petroleum ether–ethyl acetate, 80:1) we obtained hemiacetals **XI** and **XIV** as colorless fluids with a pleasant flower odor.

2-Methyl-6-methylene-8,8-diethoxyoct-2-ene (XI). Yield 2.21 g (98%). IR spectrum, ν, cm^{-1}: 1128 (C–O), 1059 (C–O). ^1H NMR spectrum, δ, ppm: 1.19 t (6H, $2CH_3CH_2O$, *J* 6.9 Hz), 1.60 br.s [3H, $CH=C(CH_3)_2$], 1.67 br.s [3H, $CH=C(CH_3)_2$], 2.04–2.12 m (4H, $CHCH_2CH_2$), 2.34 d (2H, $CHCH_2C$, *J* 5.9 Hz), 3.46–3.52 m (2H, CH_3CH_2O), 3.60–3.68 m (2H, CH_3CH_2O), 4.61 t (1H, OCHO, *J* 5.9 Hz), 4.83 br.s (2H, $CH_2=$), 5.10 t [1H, $CH=C(CH_3)_2$, *J* 6.7 Hz]. ^{13}C NMR spectrum, δ, ppm: 15.25 (2 CH_3), 17.67 (CH_3), 25.65 (CH_3), 26.28 (CH_2), 36.34 (CH_2), 40.27 (CH_2), 61.02 (2 CH_2), 102.05 (CH), 111.65 ($CH_2=$), 124.01 (CH=), 131.57 (C), 145.13 (C). Found, %: C 74.33; H 11.46. $C_{14}H_{26}O_2$. Calculated, %: C 74.29; H 11.59.

5-Methylene-7,7-diethoxyhept-1-ene (XIV). Yield 1.88 g (95%). IR spectrum, ν, cm^{-1}: 1129 (C–O), 1060 (C–O). ^1H NMR spectrum, δ, ppm: 1.19 t (6H, $2CH_3CH_2O$, *J* 7 Hz), 2.12–2.20 m (4H, $CHCH_2CH_2$), 2.34 d (2H, $CHCH_2C$, *J* 5.6 Hz), 3.45–3.53 m (2H, CH_3CH_2O), 3.60–3.68 m (2H, CH_3CH_2O), 4.60 t (1H, OCHO, *J* 5.6 Hz), 4.82 br.s (1H, $CH_2=$), 4.84 br.s (1H, $CH_2=$), 4.94 d (1H, $CH_2=CH$, *J* 10.2 Hz), 5.01 d (1H, $CH_2=CH$, *J* 17.2 Hz), 5.81 d.d.t (1H, $CH_2=CHCH_2$, J_1 10.2, J_2 6.6, J_3 6.2 Hz). ^{13}C NMR spectrum, δ, ppm: 15.23 (2 CH_3), 31.85 (CH_2), 35.84 (CH_2), 40.30 (CH_2), 61.03 (2 CH_2), 102.13 (CH), 111.92 ($CH_2=$), 114.48 ($CH_2=$), 138.30 (CH=), 144.66 (C). Found, %: C 72.74; H 11.12. $C_{12}H_{22}O_2$. Calculated, %: C 72.68; H 11.18.

1-Methyl-4-[3-methyl-1-(2-methylene-3,3-diethoxybutyl)but-2-enylsulfonyl]benzene (XVI). To a solution of 0.16 g (1.5 mmol) of diisopropylamine in 3 ml of tetrahydrofuran cooled to –50°C was added 1.5 ml (1.5 mmol) of 1M butyllithium solution in hexane, and the mixture was warmed to –30°C. After the addition of 0.23 g (1 mmol) of prenyl tolyl sulfone (**XV**) in 3 ml of THF the reaction mixture was cooled to –78°C, 0.24 g (1 mmol) of substituted allyl bromide **I** was added, and within 1 h the mixture was warmed to –20°C. The mixture was treated with water (10 ml), the organic layer was separated, the water layer was extract-ed with ethyl ether (3 × 15 ml), the combined organic solutions were washed with a saturated water solution of $NaHCO_3$ (20 ml), and dried with $MgSO_4$. On removing the solvent at a reduced pressure the reaction product was isolated by column chromatography (eluent petroleum ether–ethyl acetate, 15 : 1). Yield 0.19 g (50%). Colorless oily fluid. IR spectrum, ν, cm^{-1}: 1145 (C–O), 1086 (C–O). ^1H NMR spectrum, δ, ppm: 1.16 t (3H, CH_3CH_2O, *J* 6.9 Hz), 1.17 t (3H, CH_3CH_2O, *J* 6.9 Hz), 1.18 br.s [3H, $CH=C(CH_3)_2$], 1.64 br.s [3H, $CH=C(CH_3)_2$], 2.18 d.d (1H, CH_2CHSO_2Tol, J_1 14.6, J_2 5.9 Hz), 2.25 d.d (1H, CH_2CHSO_2Tol, J_1 14.6, J_2 5.4 Hz), 2.35 d.d (1H, $CHCH_2C$, J_1 14.1, J_2 11.5 Hz), 2.42 br.s (3H, CH_3Ph), 2.91–2.95 m (1H, $CHCH_2C$), 3.41–3.49 m (2H, CH_3CH_2O), 3.54–3.64 m (2H, CH_3CH_2O), 3.93 d.d.d (1H, CH_2CHSO_2Tol, J_1 13.3, J_2 10.2, J_3 3.1 Hz), 4.51 t (1H, OCHO, *J* 5.6 Hz), 4.78 br.s (1H, $CH_2=$), 4.86 br.s (1H, $CH_2=$), 4.88 d (1H, CH=, *J* 3.1 Hz), 7.29 d (2H, $H^{3,5}$ arom, *J* 8.2 Hz), 7.68 d (2H, $H^{2,6}$ arom, *J* 8.2 Hz). ^{13}C NMR spectrum, δ, ppm: 16.25 (2 CH_3), 18.83 (CH_3), 22.56 (CH_3), 26.62 (CH_3), 27.68 (CH_2), 41.31 (CH_2), 62.37 (CH_2), 70.95 (CH), 102.97 (CH), 119.98 ($CH_2=$), 121.41 (CH=), 130.52 ($C^{2,6}$ arom), 130.77 ($C^{3,5}$ arom), 135.39 (C), 137.80 (C^1 arom), 142.15 (C^4 arom), 149.68 (C). Found, %: C 66.34; H 8.41. $C_{21}H_{32}O_4S$. Calculated, %: C 66.28; H 8.48.

(4*E*)-2-Methyl-6-methylene-8,8-diethoxyocta-2,4-diene (XVII). To a boiling solution of 0.90 g (4 mmol) of prenyl tolyl sulfone (**XV**) in 20 ml of anhydrous benzene was added in one portion 0.67 g

(6 mmol) of potassium *tert*-butylate, and after 2 min, 0.47 g (2 mmol) of substituted allyl bromide **I** in 2 ml of benzene, and the reaction mixture was heated at reflux for 2 h. After treating with water (25 ml) and extraction with benzene (3 × 20 ml) the combined organic solutions were washed with 15 ml of a saturated water solution of NH_4Cl, and dried with Na_2SO_4. The solvent was removed at a reduced pressure; the reaction product was isolated by column chromatography (eluent petroleum ether–ethyl acetate, 80 : 1). Yield 0.35 g (78%). Colorless oily fluid with a pleasant odor. IR spectrum, ν, cm^{-1}: 1126 (C–O), 1060 (C–O). ^1H NMR spectrum, δ, ppm: 1.20 t (6H, $2CH_3CH_2O$, *J* 7.0 Hz), 1.79 br.s [3H, $CH=C(CH_3)_2$], 1.80 br.s [3H, $CH=C(CH_3)_2$], 2.57 d (2H, CCH_2CH, *J* 5.4 Hz), 3.47–3.54 m (2H, CH_3CH_2O), 3.63–3.70 m (2H, CH_3CH_2O), 4.66 t (1H, OCHO, *J* 5.4 Hz), 5.04 br.s (1H, $CH_2=$), 5.07 br.s (1H, $CH_2=$), 5.86 br.d [1H, $CH=C(CH_3)_2$, *J* 11.0 Hz], 6.15 d (1H, CCHCH, *J* 15.4 Hz), 6.49 d.d (1H, CHCHCH, J_1 15.4, J_2 11.0 Hz). ^{13}C NMR spectrum, δ, ppm: 15.27 (2 CH_3), 18.50 (CH_3), 26.15 (CH_3), 37.08 (CH_2), 61.55 (CH_2), 102.01 (CH), 116.71 ($CH_2=$), 125.40 (CH=), 125.51 (CH=), 132.11 (CH=), 136.17 (C), 141.90 (C). Found, %: C 74.98; H 10.72. $C_{10}H_{24}O_2$. Calculated, %: C 74.95; H 10.78.

Conversion of trienal diethylacetal XVII into dehydrocitral VIa. To a solution of 0.44 g (2 mmol) of trienal diethylacetal in 3 ml of acetone was added 0.05 g (0.1 mmol) of pyridinium *p*-tosylate, and the mixture was boiled for 1 h. The mixture was treated with water (20 ml), the organic layer was separated, the water layer was extracted with dichloromethane (3×15 ml), the combined organic solutions were washed with a saturated water solution of $NaHCO_3$ (20 ml), and dried with $MgSO_4$. On removing the solvent the reaction product was dissolved in 1.5 ml of ethyl ether, 0.1 ml of triethylamine was added, and the mixture was left overnight at room temperature. The reaction mixture was treated with water (20 ml), extracted with ethyl ether (3×10 ml), the combined organic solutions were washed with 15 ml of a saturated water solution of NH_4Cl, and dried with Na_2SO_4. The solvent was removed at a reduced pressure; the reaction product was isolated by column chromatography (eluent petroleum ether–ethyl acetate, 45:1). Yield 0.21 g (70%), isomers ratio 10:1.

REFERENCES

1. Mineeva, I.V. and Kulinkovich, O.G., *Zh. Org. Khim.,* 2008, vol. 44, p. 1277.
2. Keck, G.E. and Yu, T., *Org. Lett*., 1999, vol. 1, p. 289.
3. Sanchez, C.C. and Keck, G.E., *Org. Lett*., 2005, vol. 7, p. 3053.
4. Kulinkovich, O.G., Sviridov, S.V., Vasilevskii, D.A., and Prityts kaya, T.S., *Zh. Org. Khim.,* 1989, vol. 25, p. 2244.
5. Kulinkovich, O.G., Sviridov, S.V., and Vasilevskii. D.A., *Synthesis*., 1991, p. 234.
6. Kozyrkov, Yu.Yu. and Kulinkovich, O.G., *Synlett*., 2002, p. 443.
7. Bienayme, H. and Yezeguelian, C., *Tetrahedron*, 1994, vol. 50, p. 3389.
8. Cahard, D., Duhamel, L., Lecomte, S., and Poirier, J.-M., *Synlett*., 1998, p. 1399.
9. Makin, S.M., *Pure Appl.Chem*., 1976, vol. 47, p. 173.
10. Duhamel, L., Duhamel, P., and Lecouve, J.P., *Tetrahedron*, 1987, vol. 43, p. 4339.
11. Duhamel, L., Duhamel, P., and Lecouve, J.P., *Tetrahedron*, 1987, vol. 43, p. 4349.
12. Kann, N., Rein, T., Akermark, B., and Helquist, P., *J. Org. Chem.,* 1990, vol. 55, p. 5312.
13. Duhamel, L. and Angel, J.-E., *Tetrahedron*, 1992, vol. 48, p. 9237.
14. Bienayme, H., *Tetrahedron Lett*., 1994, vol. 35, p. 7383.
15. Fodil-Si, M., Ferreira, H., Gralak, J., and Duhamel, L., *Tetrahedron Lett*., 1998, vol. 39, p. 7093.
16. Cahard, D., Poirier, J.-M., and Duhamel, L. *Tetrahedron, Lett*., 1998, vol. 39, p. 8975.
17. Rama, Rao, A.V., Jadav, G.S., Srinivas, Rao, C.S., and Chandrasekhar, S., *J. Chem. Soc., Perkin, Trans. I*, 1990, p. 1211.
18. Masaki, Y., Nagata, K., Serizawa, Y., and Kaji, K., *Tetrahedron, Lett*., 1982, vol. 23, p. 5553.
19. Greene, A.E., Teixeira, M.A., Barreiro, E., Cruz, A., and Crabbe, P., *J. Org. Chem*., 1982, vol. 47, p. 2552.
20. Barbot, F. and Miginiac, P., *Synthesis.,* 1983, p. 651.
21. Derguini-Boumechal, F., Lorne, R., and Linstrumelle, G., *Tetrahedron Lett*., 1977, vol. 18, p. 1181.
22. Cardillo, G., Contento, M., Sandri, S., and Panunzio, M., *J. Chem. Soc., Perkin Trans. I,* 1979, p. 1729.
23. Wakefield, B.J., *Organolithium methods*, London: Academic Press, 1988.