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Synthesis of Aryl-Containing Isoprenoids from 1,5-Dimethylcycloocta-1,5-diene

O. S. Kukovinets[a], A. G. Kukovinets[a], V. G. Kasradze[b], E. V. Salimova[b], and M. I. Abdullin[a]

[a] *Bashkir State University, Ufa, Bashkortostan, Russia*

[b] *Institute of Organic Chemistry, Ufa Research Center, Russian Academy of Sciences, pr. Oktyabrya 71, Ufa, 450054 Bashkortostan, Russia*
e-mail: salimovaev@mail.ru

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Abstract—A procedure has been developed for the synthesis of Pro-Drone homo analogs from the ozonolysis products of 1,5-dimethylcycloocta-1,5-diene and 1,5-dimethylcyclooctene.

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The most important methods for the protection of warm-blooded animals and agricultural products from deleterious effects, including those produced by causative organisms and insect vectors, are based on integral approaches with the use of hormones controlling behavioral response (pheromones) and insecticides [1], growth and development regulators (juvenoids) and drugs [2], etc. Here, each component should be nontoxic and species-specific. Pro-Drone (I) and its nor and homo analogs are among means ensuring successful control over various dipteran pests at poultry and fur farms [3].

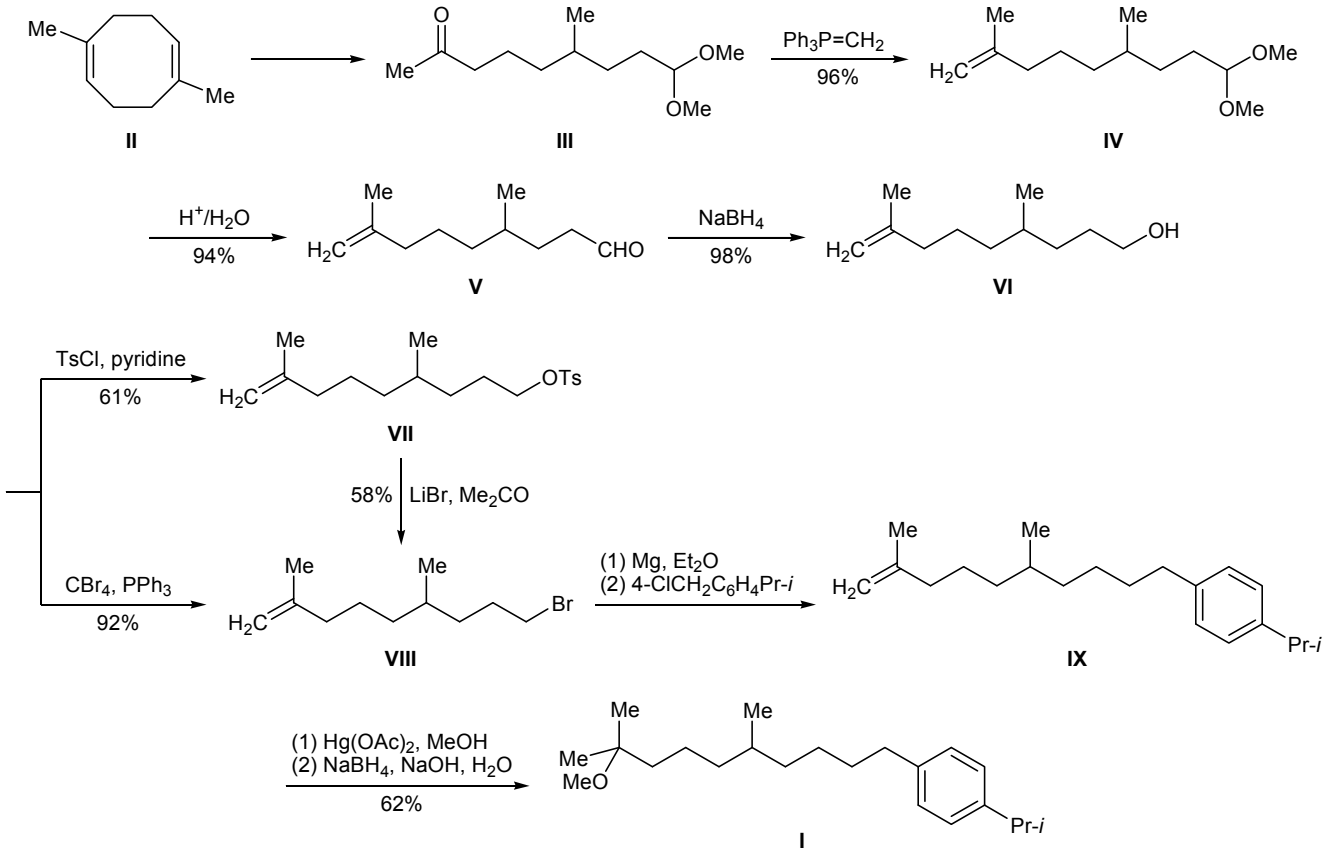
Retrosynthetic analysis has shown that a convenient synthon for compound **I** is keto acetal **III** obtained previously from 1,5-dimethylcycloocta-1,5-diene (**II**) [4]. By Wittig olefination of the oxo group in **III** with methylidene(triphenyl)phosphorane and subsequent removal of the dimethyl acetal protection we obtained 4,8-dimethylnon-8-enal (**V**) which displayed in the IR spectrum absorption bands at 940, 1640, 3080 (terminal methylene group) and 1725 cm^{-1} (CHO); the ^1H NMR spectrum of **V** contained a broadened singlet at δ 9.6 ppm.

Unsaturated aldehyde **V** was then used to synthesize Pro-Drone (**I**) homo analog. For this purpose, the aldehyde group in **V** was reduced to hydroxymethyl with sodium tetrahydridoborate, and alcohol **VI** thus formed was converted into bromide **VIII** through intermediate *p*-toluenesulfonate **VII**. Alkylation of *p*-isopropylbenzyl chloride with the Grignard compound derived from bromide **VIII** gave 2,6-dimethyl-10-(4-isopropylphenyl)dec-1-ene (**IX**). In the ^1H NMR spectrum of **IX** we observed two doublets at δ 1.09 and 1.28 ppm and a singlet at δ 1.70 ppm with an intensity ratio of 1:2:1 from the methyl groups, multiplets from methylene and methine protons (δ 1.45–1.56 ppm), and an unresolved signal at δ 7.20 ppm from aromatic protons. Introduction of a methoxy group into molecule **IX** according to the procedure described in [5] afforded target 1-(4-isopropylphenyl)-9-methoxy-5,9-dimethyldecane (**I**) (Scheme 1). The IR spectrum of **I** lacked absorption bands assignable to terminal double bond, and its ^1H and ^{13}C NMR spectra contained signals typical of a methoxy group (δ 3.03, δ_C 52.40 ppm) together with signals belonging to aromatic ring. These data confirmed the formation of homo-Pro-Drone (**I**) whose overall yield was 8%, calculated on the initial compound **III**. We succeeded in raising the yield of **I** to 21% following an alternative procedure for the replacement of the hydroxy group in alcohol **VI** by bromine (using CBr_4/PPh_3).

Compound **XIV** was synthesized via olefination of the oxo group in **III** with ethylidene(triphenyl)phosphorane and subsequent transformations which were analogous to those described above for the synthesis of compound **I** (Scheme 2).

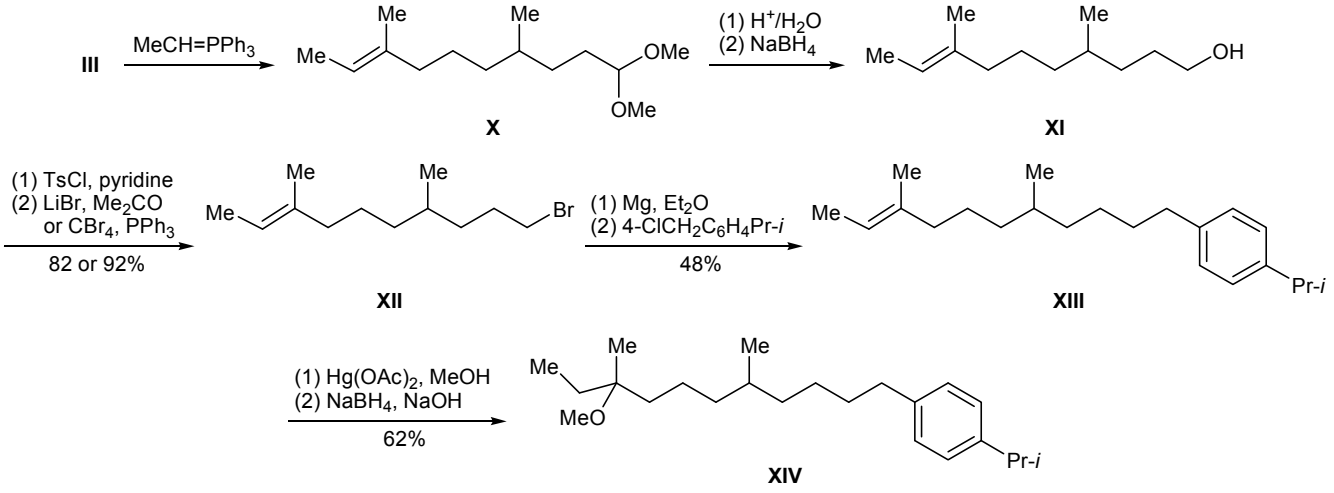
Pro-Drone homo analogs **XV** and **XVI** having a double bond at the 4- or 5-position of the isoprenoid chain were synthesized from 9,9-dimethoxy-6-methylnon-5-en-2-one (**XVII**); the latter was obtained by

Scheme 1.

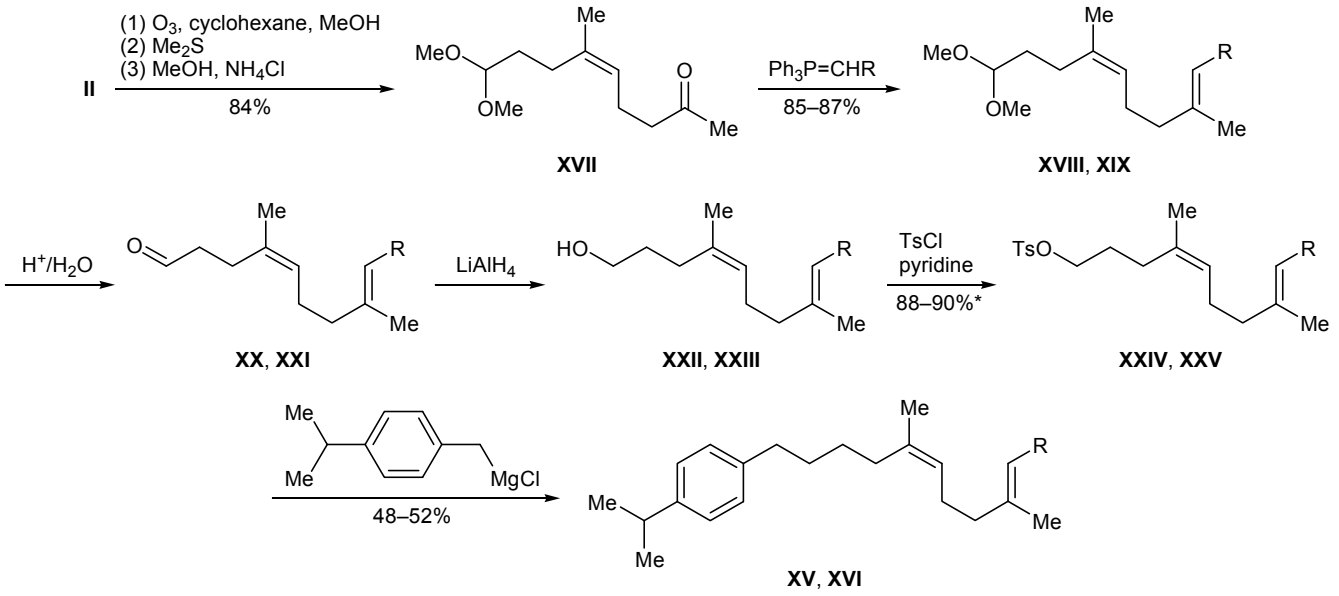


partial ozonolysis of 1,5-dimethylcycloocta-1,5-diene (**II**) [4]. Olefination of **XVII** with ethylidene- or methylidene(triphenyl)phosphorane, removal of the dimethyl acetal protection, reduction of the aldehyde group, and treatment of alcohols **XXII** and **XXIII** with *p*-toluenesulfonyl chloride in the presence of pyridine gave 4,8-dimethylnona-4,8-dien-1-yl *p*-toluenesulfonate (**XXIV**) or 4,8-dimethyldeca-4,8-dien-1-yl *p*-toluenesulfonate (**XXV**), respectively. By alkylation of **XXIV** and **XXV** with the Grignard compound derived from *p*-isopropylbenzylmagnesium chloride we obtained homo analogs **XV** and **XVI** (Scheme 3). Compounds **XV** and **XVI** can be obtained in higher yields when alcohols **XXII** and **XXIII** were preliminarily

Scheme 2.



Scheme 3.



XV, **XVIII**, **XX**, **XXII**, **XXIV**, R = H; **XVI**, **XIX**, **XXI**, **XXIII**, **XXV**, R = Me.

converted into bromides **XXVI** and **XXVII** and Grignard compounds derived from the latter were subjected to coupling with more reactive *p*-isopropylbenzyl chloride (Scheme 4).

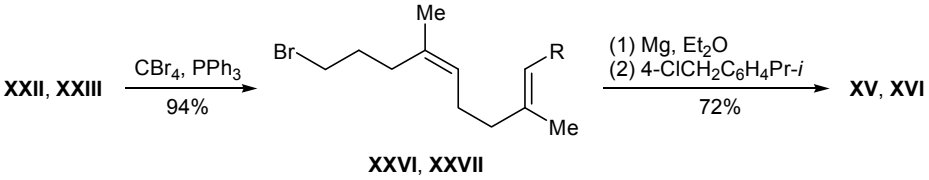
An alternative route to *p*-toluenesulfonates **XXIV** and **XXV** is based on ozonolysis of 1,5-dimethylcycloocta-1,5-diene (**II**) to obtain keto acid **XXVIII** which is then converted into methyl ester **XXIX**. The subsequent Wittig olefination of the oxo group with methylidene- or ethylidene(triphenyl)phosphorane, reduction of esters **XXX** and **XXXI** with lithium tetrahydridoaluminate, and treatment of alcohols **XXII** and **XXIII** with *p*-toluenesulfonyl chloride in pyridine gave *p*-toluenesulfonates **XXIV** and **XXV** in an overall yield of 57–62% (Scheme 5).

EXPERIMENTAL

The IR spectra in the range from 400 to 4000 cm^{-1} were recorded from thin films on a Specord M-80 spectrometer. The ^1H and ^{13}C NMR spectra were measured on a Bruker AM-300 spectrometer at 300 and 75.46 MHz, respectively using $CDCl_3$ as solvent; the chemical shifts are given relative to tetramethylsilane. GLC analysis was performed on a Chrom-5 chromatograph; 1200×3-mm column, stationary phase 5% of SE-30 on Chromaton N-AW-DMCS (grain size 0.16–0.20 mm); oven temperature 50–300°C; carrier gas helium.

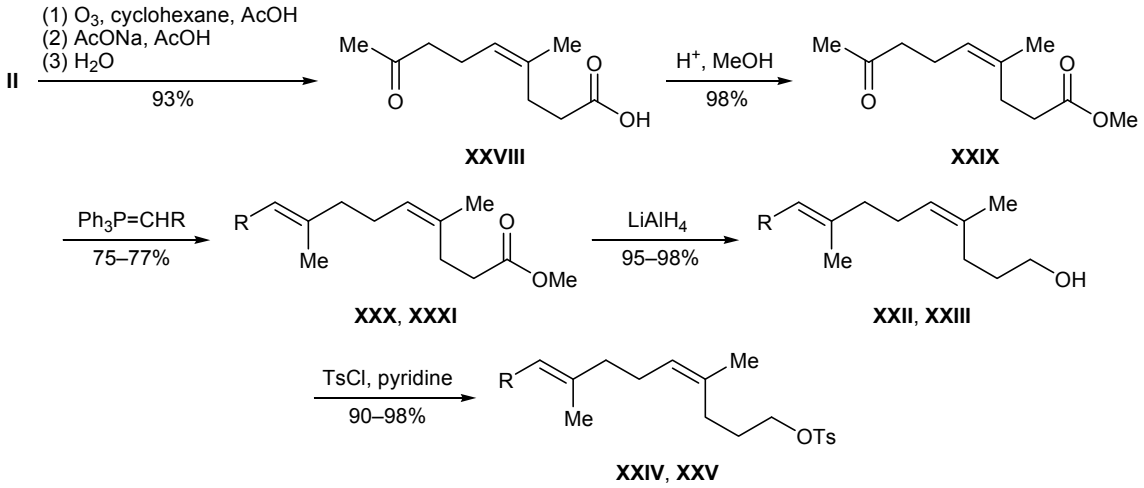
1-(4-Isopropylphenyl)-9-methoxy-5,9-dimethyldecane (I). Compound **IX**, 0.6 g (2.1 mmol), was dissolved in 9 ml of anhydrous methanol, the solution was cooled to 5°C, and 0.80 g $Hg(OAc)_2$ was added under argon. The mixture was stirred for 1 h, allowed to warm up to 20°C, kept for 24 h, and cooled to 0°C, and a mixture of 0.33 g $NaBH_4$, 0.92 g of sodium hydroxide, and 1.13 ml of water was added dropwise under stirring. The mixture was kept for 1 h at 0°C and for 2 h at 20°C, poured into water, and extracted with ethyl acetate. The extract was washed with a saturated solution of sodium chloride, dried over $MgSO_4$, and filtered, the solvent was distilled off, and the residue

Scheme 4.



XV, **XXII**, **XXVI**, R = H; **XVI**, **XXIII**, **XXVII**, R = Me.

Scheme 5.



XXII, **XXIV**, **XXX**, R = H; **XXIII**, **XXV**, **XXXI**, R = Me.

was purified by chromatography on silica gel using petroleum ether–ethyl acetate (9:1) as eluent. Yield 0.41 g (62%). Light yellow oily substance. IR spectrum, ν, cm^{-1}: 3080 w, 1600 m, 1105 s, 1005 s. ^1H NMR spectrum, δ, ppm: 1.06 d (3H, 5-CH_3, J = 6.0 Hz), 1.23 s and 1.25 s (3H each, 9-CH_3, $C^{10}H_3$), 1.28 d [6H, $(CH_3)_2CH$, J = 6.0 Hz], 1.40–1.56 m (13H, CH_2, CH), 2.32 m [3H, C^1H_2, $(CH_3)_2CH$], 3.03 s (3H, OCH_3), 7.20 br.s (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 18.34 q (5-CH_3), 20.98 t (C^7), 23.45 q (CH_3CH), 28.03 t (C^3), 30.53 q (C^{10}, 9-CH_3), 31.18 t (C^2), 31.24 d (C^5), 33.70 d (C_6H_4CH), 35.61 t (C^1), 36.84 t (C^6), 37.33 t (C^4), 44.08 t (C^8), 51.14 q (OCH_3), 60.84 s (C^9), 127.50 and 127.67 d (C^o, C^m), 141.13 s (C^i), 148.94 s (C^p). Found, %: C 82.64; H 12.46. $C_{22}H_{38}O$. Calculated, %: C 83.02; H 11.95.

9,9-Dimethoxy-6-methylnonan-2-one (III) was synthesized as described in [4].

2,6-Dimethyl-9,9-dimethoxynon-1-ene (IV). A suspension of 7.29 g (20 mmol) of methyl(triphenyl)-phosphonium bromide in 40 ml of anhydrous tetrahydrofuran was cooled to –70°C, and 10.6 ml of a 3.3 M solution of *n*-butyllithium in hexane diluted with 10 ml of anhydrous THF was added dropwise under argon, maintaining the temperature at –60 to –70°C. The mixture was stirred until it became bright red (ylide formation, ~1 h) and allowed to slowly warm up to –30°C, 4 g (18.5 mmol) of keto acetal **III** was added, and the mixture was stirred for 1 h at –30°C and left to stand for 12 h at 20°C. The mixture was then diluted with 150 ml of hexane, stirred, and filtered through a small layer of silica gel, the solvent was distilled off, and the residue was subjected to chromatography on silica gel using hexane as eluent. Yield 3.8 g (96%). IR spectrum, ν, cm^{-1}: 1640 m, 1135 s, 1080 s, 1020 m, 910 m. ^1H NMR spectrum, δ, ppm: 0.89 d (3H, CH_3, J = 7.0 Hz), 1.25–1.50 m (7H, CH, CH_2), 1.60 m (2H, 8-H), 1.68 s (3H, 2-CH_3), 2.26 t (2H, 3-H, J = 6.5 Hz), 3.15 s (6H, OCH_3), 4.25 t (1H, 9-H, J = 5.5 Hz), 4.80 br.s (2H, 1-H). Found, %: C 72.61; H 12.45. $C_{13}H_{26}O_2$. Calculated, %: C 72.90; H 12.15.

4,8-Dimethylnon-8-en-1-ol (VI). Acetal **IV**, 2.74 g (12.8 mmol), was dissolved in 100 ml of purified acetone, 2.74 ml of water and 0.74 g of pyridinium *p*-toluenesulfonate were added, and the mixture was heated for 2 h under reflux. The solvent was distilled off, the residue was dissolved in ethyl acetate, and the solution was washed in succession with saturated solutions of $NaHCO_3$ and NaCl, dried over $MgSO_4$, filtered, and evaporated to obtain 2.02 g (94%) of aldehyde **V** (IR spectrum, ν, cm^{-1}: 3050 w, 2750 m, 1725 s, 1645 s, 1180 s, 1120 m, 900 m). The latter (without additional purification) was dissolved in 25 ml of anhydrous methanol, 0.74 g of sodium tetrahydridoborate was added in portions, and the resulting suspension was stirred for 1 h and left to stand for 12 h. The mixture was treated under stirring with 12 ml of a 5% solution of acetic acid in water and stirred for 30 min, methanol was distilled off under reduced pressure, the residue was extracted with ethyl acetate, the extract was dried over $MgSO_4$ and filtered, and the solvent was distilled off to obtain 2.09 g of a viscous oily substance which was purified by chromatography on silica gel using petroleum ether–ethyl acetate (3:1) as eluent. Yield 2.0 g (98%).

IR spectrum, ν, cm^{-1}: 3200–3560 br.s, 3030 w, 1645 m, 905 m. ^1H NMR spectrum, δ, ppm: 0.98 d (3H, 4-CH_3, J = 6.0 Hz), 1.52–1.59 m (9H, CH, CH_2), 1.72 s (3H, 8-CH_3), 2.21 t (2H, 7-H, J = 7.5 Hz), 3.82 t (2H, 1-H, J = 7.0 Hz), 4.93 br.s (2H, 9-H), 5.04 br.s (1H, OH). Found, %: C 77.38; H 13.02. $C_{11}H_{22}O$. Calculated, %: C 77.65; H 12.94.

9-Bromo-2,6-dimethylnon-1-ene (VIII). *a*. Alcohol **VI**, 2.0 g (11.8 mmol), was dissolved in 26 ml of anhydrous pyridine, the solution was cooled to 0°C, 2.3 g of *p*-toluenesulfonyl chloride was added under stirring, and the mixture was stirred for 3 h at 0°C and left to stand for 12 h at 5°C. The mixture was then poured into 40 g of an ice–water mixture and extracted with methylene chloride. The extract was washed in succession with 1 N hydrochloric acid and saturated solutions of $NaHCO_3$ and NaCl, dried over $MgSO_4$, and evaporated. The residue was 2.10 g (61%) of *p*-toluenesulfonate **VII**; IR spectrum, ν, cm^{-1}: 3080 w, 1645 m, 1600 m, 1505 m, 900 m. Lithium bromide, 0.9 g (10.3 mmol), was dispersed in 60 ml of anhydrous acetone, 2.80 g (9.6 mmol) of compound **VII** was added under stirring in an argon atmosphere, and the mixture was stirred until compound **VII** disappeared completely (TLC; petroleum ether–ethyl acetate, 6:3). The solvent was distilled off, the residue was diluted with diethyl ether, the resulting solution was washed in succession with saturated solutions of $NaHCO_3$ and NaCl and dried over $MgSO_4$, the solvent was distilled off, and the residue was subjected to chromatography on silica gel using petroleum ether–ethyl acetate (19:1) as eluent. Yield 1.14 g (58%), yellow viscous oily liquid. IR spectrum, ν, cm^{-1}: 3030 w, 1655 m, 1030 m, 905 m, 690 m. ^1H NMR spectrum, δ, ppm: 0.98 d (3H, 6-CH_3, J = 6.5 Hz), 1.45–1.60 m (9H, CH_2, CH), 1.72 s (3H, 2-CH_3), 1.90 t (2H, 3-H, J = 7.0 Hz), 3.37 t (2H, CH_2Br, J = 7.0 Hz), 4.87 br.s (2H, 1-H). Found, %: C 56.31; H 9.23; Br 34.44. $C_{11}H_{21}Br$. Calculated, %: C 56.65; H 9.01; Br 34.33.

b. Carbon tetrabromide, 1.35 g (4.06 mmol), was added at 20°C to a solution of 0.5 g (2.9 mmol) of alcohol **VI** and 1.02 g (3.90 mmol) of triphenylphosphine in 5 ml of anhydrous methylene chloride. The mixture was stirred for 2 h at 20°C, 30 ml of ethyl acetate was added, and the mixture was washed in succession with saturated solutions of $NaHCO_3$ and NaCl and dried over $MgSO_4$. The solvent was distilled off, the residue was diluted with hexane, the precipitate was filtered off, and the filtrate was evaporated. Yield 0.63 g (92%). Samples of **VIII** obtained by the two methods (*a* and *b*) were identical.

10-(*p*-Isopropylphenyl)-2,6-dimethyldec-1-ene (IX). A solution of Grignard compound prepared from 1.5 g (6.4 mmol) of bromide **VIII** and 0.15 g of magnesium in 20 ml of anhydrous THF was heated to the boiling point, a solution of 1.34 g (8.0 mmol) of *p*-isopropylbenzyl chloride in 15 ml of anhydrous THF was added dropwise, and the mixture was heated under reflux until compound **VIII** disappeared completely (TLC, silica gel, eluent hexane). The mixture was cooled, washed with a saturated solution of sodium chloride, and dried over $MgSO_4$, the drying agent was filtered off, the solvent was distilled off, and the residue was subjected to chromatography on silica gel using hexane as eluent. Yield 0.77 g (42%), light yellow oily substance. IR spectrum, ν, cm^{-1}: 3080 w, 1660 m, 1600 w, 1510 m, 910 m. ^1H NMR spectrum, δ, ppm: 1.09 d (3H, 6-CH_3, J = 6.0 Hz), 1.28 d [6H, $(CH_3)_2CH$, J = 6.0 Hz], 1.45–1.56 m (11H, CH_2, CH), 1.70 s (3H, 2-CH_3), 2.03 br.s (2H, 3-H), 2.28 and 2.36 m [10-H, $(CH_3)_2CH$], 4.85 br.s (2H, 1-H), 7.20 m (4H, H_{arom}). Found, %: C 88.27; H 11.91. $C_{21}H_{34}$. Calculated, %: C 88.11; H 11.89.

10,10-Dimethoxy-3,7-dimethyldec-2-ene (X). A solution of 2.7 g (12.5 mmol) of acetal **III** in 20 ml of anhydrous THF was added to a solution of phosphorus ylide prepared from 5.2 g (14 mmol) of ethyl(triphenyl)phosphonium bromide and 17 ml of a 1.4 M solution of *n*-BuLi in hexane at –70°C under argon in 45 ml of THF, as described above in the synthesis of compound **IV**. When the reaction was complete, the product was isolated in a similar way. Yield 2.02 g (71%), light yellow oily liquid. IR spectrum, ν, cm^{-1}: 1650 w, 1135 s, 1070 s, 1060 s, 890 m. ^1H NMR spectrum, δ, ppm: 0.89 d (3H, 7-H, J = 7.0 Hz), 1.40–1.55 m (9H, CH, CH_2), 1.68 d (3H, 1-H, J = 6.5 Hz), 1.72 s (3H, 3-CH_3), 2.03 t (2H, 4-H, J = 6.5 Hz), 3.18 s (6H, OCH_3), 4.25 t (1H, 10-H, J = 5.5 Hz), 5.06 q (1H, 2-H, J = 7.0 Hz). Found, %: C 73.84; H 12.18. $C_{14}H_{28}O_2$. Calculated, %: C 73.68; H 12.28.

4,8-Dimethyldec-8-en-1-ol (XI). Following the procedure described above for the synthesis of compound **V**, treatment of 2 g (8.8 mmol) of acetal **X** with 2 ml of water and 0.70 g of pyridinium *p*-toluenesulfonate in 90 ml of anhydrous acetone gave the corresponding aldehyde which (without additional purification) was reduced with 0.70 g of $NaBH_4$ in 22 ml of anhydrous methanol. The mixture was treated with 8.2 ml of a 5% solution of acetic acid in water as

described above for the synthesis of **VI**. Yield 1.29 g (80%), light yellow oily liquid. IR spectrum, ν, cm^{-1}: 3400 br.s, 1645 m, 905 m. The product was used in the synthesis of bromide **XII** without additional purification.

10-Bromo-3,7-dimethyldec-2-ene (XII). *a*. A solution of 0.24 g (1.3 mmol) of alcohol **XI** in 3 ml of anhydrous pyridine was cooled to 0°C, 0.27 g of *p*-toluenesulfonyl chloride was added, and the mixture was stirred for 2 h at 0°C and left to stand for 8 h at 5°C. The mixture was poured into an ice–water mixture, and the product was extracted into diethyl ether. The extracts were combined, washed in succession with 1 N hydrochloric acid and saturated solutions of NaCl, $NaHCO_3$, and NaCl again, dried over $MgSO_4$, filtered, and evaporated. The residue was 0.42 g of 4,8-dimethyldec-8-en-1-yl *p*-toluenesulfonate which was added while stirring under argon to a suspension of 0.12 g of lithium bromide in 15 ml of anhydrous acetone. The mixture was stirred until 4,8-dimethyldec-8-en-1-yl *p*-toluenesulfonate disappeared (TLC, silica gel, petroleum ether–diethyl ether, 1 : 1), the solvent was distilled off, the residue was diluted with diethyl ether, and the resulting solution was washed in succession with saturated solutions of $Na_2S_2O_3$ and NaCl and dried over $MgSO_4$. The drying agent was filtered off, and the solvent was distilled off under reduced pressure to isolate 0.31 g of crude bromide **XII** which was purified by column chromatography on silica gel using petroleum ether as eluent. Yield 0.26 g (82%, calculated on alcohol **XI**), light yellow oily substance. IR spectrum, ν, cm^{-1}: 1640 m, 780 m, 690 m. ^{1}H NMR spectrum, δ, ppm: 0.93 d (3H, 7-CH_3, J = 6.5 Hz), 1.40–1.56 m (9H, CH, CH_2), 1.62 d (3H, 1-H, J = 7.0 Hz), 1.68 s (3H, 3-CH_3), 2.28 t (2H, 4-H, J = 7.0 Hz), 3.19 t (2H, CH_2Br, J = 7.5 Hz), 5.12 q (1H, 2-H, J = 7.0 Hz). Found, %: C 58.43; H 9.18; Br 32.68. $C_{12}H_{23}Br$. Calculated, %: C 58.30; H 9.31; Br 32.39.

b. Carbon tetrabromide, 0.48 g (1.4 mmol), was added at room temperature to a solution of 0.24 g (1.3 mmol) of alcohol **XI** and 0.35 g (1.3 mmol) of triphenylphosphine in 2 ml of methylene chloride, and the mixture was stirred for 2 h at room temperature and diluted with ethyl acetate. The organic solution was washed in succession with saturated solutions of $NaHCO_3$ and NaCl, dried over $MgSO_4$, filtered, and evaporated, the residue was diluted with hexane, and the precipitate was filtered off. The filtrate was evaporated, and the residue was purified by chromatography as described above in *a*. Yield 0.30 g (92%). Samples of **XII** obtained by the two methods (*a* and *b*) were identical in spectral parameters.

11-(*p*-Isopropylphenyl)-3,7-dimethylundec-2-ene (XIII) was synthesized as described above for compound **IX** by heating a mixture of 1.68 g (10.0 mmol) of *p*-isopropylbenzyl chloride and Grignard compound prepared from 2.0 g (8.1 mmol) of bromide **XII** and 0.19 g of magnesium. The product was isolated by column chromatography on silica gel using hexane as eluent. Yield 1.17 g (48%). IR spectrum, ν, cm^{-1}: 3080 w, 1655 m, 1600 w, 980 m. ^{1}H NMR spectrum, δ, ppm: 0.88 d (3H, 7-CH_3, J = 6.0 Hz), 1.21 d [6H, $(CH_3)_2CH$, J = 6.0 Hz], 1.40–1.50 m (11H, CH_2, CH), 1.62 d (3H, 1-H, J = 6.5 Hz), 1.69 s (3H, 3-CH_3), 1.95 t (2H, 4-H, J = 6.5 Hz), 2.35 t (2H, 11-H, J = 6.5 Hz), 2.41 m [1H, $(CH_3)_2CH$], 7.20–7.35 br.s (4H, H_{arom}). Found, %: C 88.08; H 12.06. $C_{22}H_{36}$. Calculated, %: C 88.00; H 12.00.

1-(*p*-Isopropylphenyl)-9-methoxy-5,9-dimethylundecane (XIV) was synthesized as described above for compound **I** by treatment of 0.6 g (2 mmol) of compound **XIII** with 0.45 g of mercury(II) acetate, followed by reduction of intermediate organomercury compound with 0.33 g of $NaBH_4$ in alkaline medium. The product was purified by chromatography on silica gel using petroleum ether–ethyl acetate (9:1) as eluent. Yield 0.41 g (62%), light yellow viscous oily substance. IR spectrum, ν, cm^{-1}: 2950 br.s, 1600 w, 1505 m, 1105 s. ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, $C^{11}H_3$, J = 6.5 Hz), 1.04 d (3H, 5-CH_3, J = 7.0 Hz), 1.22 d [6H, $(CH_3)_2CH$, J = 6.0 Hz], 1.28 s (3H, 9-CH_3), 1.40–1.52 m (15H, CH, CH_2), 2.43 m [3H, $(CH_3)_2CH$, 1-H], 3.16 s (3H, OCH_3), 7.20–7.40 m (4H, H_{arom}). Found, %: C 88.04; H 11.81. $C_{23}H_{40}O$. Calculated, %: C 88.13; H 12.05.

10-(*p*-Isopropylphenyl)-2,6-dimethyldeca-1,5-diene (XV). *a*. A solution of Grignard compound prepared from 6 g (35.6 mmol) of *p*-isopropylbenzyl chloride and 1 g (41.7 mmol) of magnesium in 30 ml of anhydrous diethyl ether was cooled to –30°C, a solution of 2 g (6.2 mmol) of *p*-toluenesulfonate **XXIV** in 12 ml of anhydrous THF was added dropwise, the mixture was cooled to –70°C, 3.1 ml of a 0.1 M solution of Li_2CuCl_4 in anhydrous THF was added dropwise, and the mixture was kept for 1.5 h at –70°C, allowed to slowly warm up to 20°C, and left to stand for 12 h at 20°C. The mixture was then cooled to 5–10°C, 100 ml of 10% hydrochloric acid was added, and the mixture was extracted with methylene chloride. The extract was dried over $MgSO_4$ and filtered,

the solvent was distilled off, and the residue was subjected to chromatography on silica gel using hexane as eluent. Yield 0.92 g (52%), yellow oily liquid. IR spectrum, ν, cm^{-1}: 3080 w, 3020 w, 1640 m, 1605 w, 1500 m, 920 m. ^1H NMR spectrum, δ, ppm: 1.24 d (6H, CH_3, J = 6.0 Hz), 1.38 m (4H, CH_2), 1.68 s and 1.72 s (3H each, 2-CH_3, 6-CH_3), 2.06 m (6H, CH_2), 2.34 t (2H, 10-H, J = 6.8 Hz), 2.44 m (1H, $C_6H_4C\mathbf{H}$), 4.8 br.s (2H, 1-H), 5.19 t (1H, 5-H, J = 7.0 Hz), 7.28–7.36 m (4H, C_6H_4). Found, %: C 88.54; H 11.31. $C_{21}H_{32}$. Calculated, %: C 88.73; H 11.27.

b. A solution of 0.18 g of *p*-isopropylbenzyl chloride in 15 ml of anhydrous THF was added dropwise to a solution of Grignard compound prepared from 1.2 g (5.2 mmol) of bromide **XXVI** and 0.12 g of magnesium in 20 ml of anhydrous THF. The mixture was heated under reflux until the reactant disappeared completely (TLC, silica gel, hexane) and was treated as described above for compound **IX**. Yield 1.06 g (72%). Samples of **XV** synthesized by the two methods (*a* and *b*) were identical in spectral parameters.

11-(*p*-Isopropylphenyl)-3,7-dimethylundeca-2,6-diene (XVI). *a*. Compound **XVI** was synthesized as described above for diene **XV** by reaction of 2 g (6.0 mmol) of *p*-toluenesulfonate **XXV** with cuprate prepared from 2.9 ml of a 0.1 M solution of Li_2CuCl_4 and Grignard compound prepared from 5.8 g of *p*-isopropylbenzyl chloride and 0.97 g of magnesium. Yield 0.92 g (52%). IR spectrum, ν, cm^{-1}: 3020 w, 1640 m, 1600 m, 1505 m. ^1H NMR spectrum, δ, ppm: 1.23 d (6H, CH_3, J = 6.0 Hz), 1.30 m (4H, CH_2), 1.57 d (3H, C^1H_3, J = 6.5 Hz), 1.68 s and 1.72 s (3H each, 3-CH_3, 7-CH_3), 2.03 m (6H, CH_2), 2.35 t (2H, 11-H, J = 6.8 Hz), 2.43 m (1H, $C_6H_4C\mathbf{H}$), 5.2–5.4 m (2H, 2-H, 5-H), 7.28 br.s (4H, H_{arom}). Found, %: C 88.44; H 11.53. $C_{22}H_{34}$. Calculated, %: C 88.59; H 11.41.

b. As described above for compound **XV**, the reaction of 0.26 g of *p*-isopropylbenzyl chloride with Grignard compound prepared from 1.8 g (7.3 mmol) of bromide **XXVII** and 0.17 g of magnesium gave 1.73 g (79%) of **XVI**. Samples of **XVI** synthesized by the two methods (*a* and *b*) were identical in spectral parameters.

9,9-Dimethoxy-6-methylnon-5-en-2-one (XVII) was synthesized according to the procedure described in [4].

9,9-Dimethoxy-2,6-dimethylnona-1,5-diene (XVIII) was synthesized as described above for compound **IV** from 3.54 g (10.0 mmol) of methyl(triphenyl)phosphonium bromide, 4.12 g of hexamethyldisilazane sodium salt, and 2 g (9.3 mmol) of keto acetal **XVII** in 68.8 ml of anhydrous THF. Yield 1.72 g (87%), light yellow viscous oily substance. IR spectrum, ν, cm^{-1}: 3080 w, 1660 m, 1645 m, 1020 s, 910 m. ^1H NMR spectrum, δ, ppm: 1.48 m (2H, 8-H), 1.57 s and 1.62 s (3H each, 2-CH_3, 6-CH_3), 1.98 m (6H, CH_2C=), 3.04 s (6H, OCH_3), 4.25 t (1H, 9-H, J = 5.5 Hz), 4.8 br.s (2H, 1-H), 5.18 t (1H, 5-H, J = 6.0 Hz). Found, %: C 73.12; H 11.81. $C_{13}H_{24}O_2$. Calculated, %: C 73.58; H 11.32.

10,10-Dimethoxy-3,7-dimethyldeca-2,6-diene (XIX) was synthesized as described above for compound **IV** from 3.68 g (10.3 mmol) of ethyl(triphenyl)-phosphonium bromide, 4.12 g of hexamethyldisilazane sodium salt, and 2 g (9.3 mmol) of keto acetal **XVII** in 68.8 ml of anhydrous THF. Yield 1.8 g (85%), light yellow viscous oily substance. IR spectrum, ν, cm^{-1}: 1660 m, 1650 m, 1020 s. ^1H NMR spectrum, δ, ppm: 1.48 m (2H, 9-H), 1.52 s and 1.57 s (3H each, 3-CH_3, 7-CH_3), 1.62 d (3H, C^1H_3), 1.98 m (6H, CH_2C=), 3.04 s (6H, OCH_3), 4.25 t (1H, 10-H, J = 5.5 Hz), 5.10 t (1H, 6-H, J = 7.0 Hz), 5.28 q (1H, 2-H, J = 7.0 Hz). Found, %: C 74.12; H 11.31. $C_{14}H_{26}O_2$. Calculated, %: C 74.34; H 11.50.

4,8-Dimethylnona-4,8-dien-1-ol (XXII). A suspension of 0.24 g (6.3 mmol) of $LiAlH_4$ in 15 ml of anhydrous diethyl ether was cooled to 10°C, 0.96 g (4.9 mmol) of ester **XXX** in 15 ml of anhydrous diethyl ether was added dropwise under stirring, and the mixture was stirred for 0.5 h at 10°C, allowed to warm up to 20°C, and left to stand for 12 h. The mixture was then treated with 0.28 ml of water, the organic phase was separated, and the product was extracted into diethyl ether (2×10 ml). The combined organic extracts were dried over $MgSO_4$, the drying agent was filtered off, the solvent was distilled off, and the residue, 0.93 g, was subjected to column chromatography on silica gel using petroleum ether–ethyl acetate (3:2) as eluent. Yield 0.78 g (95%), light yellow oily substance. IR spectrum, ν, cm^{-1}: 3510 br.s, 3050 w, 1642 w, 1638 m, 915 m. ^1H NMR spectrum, δ, ppm: 1.38 m (2H, 2-H), 1.64 s and 1.68 s (3H each, 4-CH_3, 8-CH_3), 1.94–1.98 m (6H, CH_2C=), 3.36 t (2H, $C\mathbf{H}_2OH$, J = 7.0 Hz), 4.87 br.s (2H, 9-H), 5.12 t (1H, 5-H, J = 6.5 Hz), 5.36 s (1H, OH). Found, %: C 78.69; H 11.76. $C_{11}H_{20}O$. Calculated, %: C 78.57; H 11.90.

4,8-Dimethyldeca-4,8-dien-1-ol (XXIII) was synthesized as described above for compound **XXII** by reduction of 1.32 g (6.3 mmol) of ester **XXXI** with 0.24 g of $LiAlH_4$. Yield 1.12 g (98%). IR spectrum, ν,

cm^{-1}: 3460 br.s, 1645 m, 1630 m. ^1H NMR spectrum, δ, ppm: 1.34 m (2H, 2-H), 1.60 d (3H, $C^{10}H_3$, J = 7.0 Hz), 1.64 s and 1.71 s (3H each, 4-CH_3, 8-CH_3), 1.90–1.95 m (6H, CH_2C=), 3.38 t (2H, C**H**$_2$OH, J = 7.0 Hz), 5.15 t (1H, 5-H, J = 6.5 Hz), 5.39 q (1H, 9-H, J = 7.0 Hz), 5.34 br.s (1H, OH). Found, %: C 79.28; H 12.03. $C_{12}H_{22}O$. Calculated, %: C 79.12; H 12.09.

4,8-Dimethylnona-4,8-dien-1-yl *p*-toluenesulfonate (XXIV). Acetal **XVIII**, 1.04 g (4.9 mmol), was dissolved in 58 ml of anhydrous acetone, 11 ml of water and 0.32 g of pyridinium *p*-toluenesulfonate were added, the mixture was heated for 3 h under reflux, and aldehyde **XX** was isolated as described above for compound **V**. Yield of **XX** 0.69 g (IR spectrum, ν, cm^{-1}: 2750 m, 1725 s). The product was dissolved in 15 ml of anhydrous diethyl ether, the solution was cooled to 10°C and added dropwise to a suspension of 0.2 g of $LiAlH_4$ in 10 ml of anhydrous diethyl ether, and the mixture was stirred for 2 h at 10°C and carefully decomposed by adding 0.25 ml of water. The organic phase was separated, and the residue was washed with diethyl ether. The combined extracts were dried over $MgSO_4$, filtered, and evaporated to isolate 0.67 g of alcohol **XXII** (IR spectrum, ν, cm^{-1}: 3510 br.s, 3050 m). Compound **XXII** without preliminary purification was dissolved in 11.5 ml of anhydrous pyridine, the solution was cooled to 0°C, and 1 g of *p*-toluenesulfonyl chloride was added. The mixture was then treated as described above for compound **VII** to isolate 1.58 g of crude product **XXIV** which was purified by chromatography on silica gel using petroleum ether–ethyl acetate (3:2) as eluent. Yield 1.16 g (90%, calculated on alcohol **XXII**. IR spectrum, ν, cm^{-1}: 3080 m, 3020 w, 1665 m, 1605 w, 1530 m, 930 m. ^1H NMR spectrum, δ, ppm: 1.46 m (2H, 2-H), 1.62 s and 1.68 s (3H each, 4-CH_3, 8-CH_3), 2.08 m (6H, CH_2C=), 2.30 s (3H, C**H**$_3C_6H_4$), 3.69 t (2H, CH_2O, J = 7.0 Hz), 4.88 br.s (2H, 9-H), 5.21 t (1H, 5-H, J = 77.0 Hz), 7.29 d (2H, *m*-H, J = 8.8 Hz), 8.02 d (2H, *o*-H, J = 8.8 Hz). Found, %: C 67.24; H 8.14; S 9.49. $C_{18}H_{26}O_3S$. Calculated, %: C 67.08; H 8.07; S 9.94.

4,8-Dimethyldeca-4,8-dien-1-yl *p*-toluenesulfonate (XXV). A solution of 0.74 g (4.1 mmol) of aldehyde **XXI** (prepared from compound **XIX** according to the procedure described above for the synthesis of **XX**) in 15 ml of anhydrous diethyl ether was cooled to 10°C and added dropwise to a suspension of 0.2 g of $LiAlH_4$ in 10 ml of anhydrous diethyl ether. The mixture was stirred for 2 h at 10°C and carefully treated with 0.6 ml of water. The organic phase was separated, dried over $MgSO_4$, filtered, and evaporated. The residue was 0.7 g of alcohol **XXIII** (IR spectrum, ν, cm^{-1}: 3510 br.s, 1640 m) which was dissolved in 11.7 ml of anhydrous pyridine. The solution was cooled to 0°C, 1.0 g of *p*-toluenesulfonyl chloride was added under stirring, and the mixture was treated as described above for compound **VII** to isolate 1.8 g of crude compound **XXV** which was purified by column chromatography on silica gel using petroleum ether–ethyl acetate (3:2) as eluent. Yield 1.14 g (88%, calculated on alcohol **XXIII**), light yellow oily substance. IR spectrum, ν, cm^{-1}: 3080 w, 1665 w, 1605 m, 1595 m. ^1H NMR spectrum, δ, ppm: 1.46 m (2H, 2-H), 1.60 d (3H, $C^{10}H_3$, J = 6.5 Hz), 1.62 s and 1.68 s (6H, 4-CH_3, 8-CH_3), 2.0 m (6H, CH_2), 2.30 s (3H, C**H**$_3C_6H_4$), 3.69 t (2H, CH_2O, J = 7.0 Hz), 5.10 t (1H, 5-H, J = 7.0 Hz), 5.21 q (1H, 9-H, J = 6.5 Hz), 7.29 d (2H, *m*-H, J = 8.8 Hz), 8.02 d (2H, *o*-H, J = 8.8 Hz). Found, %: C 67.94; H 8.25; S 9.04. $C_{19}H_{28}O_3S$. Calculated, %: C 67.86; H 8.33; S 9.52.

9-Bromo-2,6-dimethylnona-1,5-diene (XXVI). Carbon tetrabromide, 2.9 g (8.7 mmol), was added at 20°C to a solution of 1.0 g (6.0 mmol) of alcohol **XXII** and 2.07 g (7.90 mmol) of triphenylphosphine in 15 ml of methylene chloride, and the mixture was stirred for 2 h at 20°C and diluted with ethyl acetate. The organic phase was washed with saturated solutions of $NaHCO_3$ and NaCl and dried over $MgSO_4$, the drying agent was filtered off, the solvent was distilled off, the residue was diluted with hexane, the precipitate was filtered off, and the filtrate was evaporated to isolate 1.64 g of crude product **XXVI** which was purified by column chromatography on silica gel using hexane as eluent. Yield 1.29 g (94%), light yellow oily liquid. IR spectrum, ν, cm^{-1}: 3030 w, 1645 m, 1015 m, 905 m, 685 m. ^1H NMR spectrum, δ, ppm: 1.60 m (2H, 8-H), 1.68 s and 1.74 s (6H, 2-CH_3, 6-CH_3), 1.94–2.06 m (6H, CH_2), 3.35 t (2H, CH_2Br, J = 7.0 Hz), 4.91 br.s (2H, 1-H), 5.13 t (1H, 5-H, J = 6.5 Hz). Found, %: C 57.06; H 8.34; Br 34.91. $C_{11}H_{19}Br$. Calculated, %: C 57.14; H 8.23; Br 34.63.

10-Bromo-3,7-dimethyldeca-2,6-diene (XXVII) was synthesized from 1.1 g (6.0 mmol) of alcohol **XXIII** and 2.9 g (8.70 mmol) of carbon tetrabromide in 18 ml of anhydrous methylene chloride in the presence of 2.07 g (7.90 mmol) of triphenylphosphine. The product was isolated and purified as described above for compound **XXVI**. Yield 1.41 g (94%), light yellow oily substance. IR spectrum, ν, cm^{-1}: 1650 m, 1020 m, 680 m. ^1H NMR spectrum, δ, ppm: 1.36 m (2H, 9-H), 1.59 d (3H, C^1H_3, J = 6.5 Hz), 1.65 s and 1.72 s (6H,

3-CH_3, 7-CH_3), 1.94–2.06 m (6H, CH_2), 3.38 t (2H, CH_2Br, J = 7.0 Hz), 5.2–5.3 m (2H, 6-H). Found, %: C 58.93; H 8.39; Br 32.71. $C_{12}H_{21}Br$. Calculated, %: C 58.78; H 8.57; Br 32.65.

4-Methyl-8-oxonon-4-enoic acid (XXVIII). An ozone–oxygen mixture was passed through a solution of 5 g (36.8 mmol) of 1,5-cycloocta-1,5-diene (**II**) in a mixture of 50 ml of cyclohexane and 2.7 ml of acetic acid under continuous stirring at 0–5°C until ozone appeared at the outlet of the reactor (iodine–starch test). The mixture was purged with argon, cyclohexane was separated from the oily material by decanting, and 8.3 ml of acetic anhydride was added to the residue (peroxide product) under stirring at 5°C. The mixture was allowed to warm up to 15°C, a mixture of 3.6 g (57.8 mmol) of sodium acetate and 17 ml of acetic acid was added under stirring, the mixture was stirred for 30 min at 15°C, 8.3 ml of water was added, and the mixture was heated for 30 min at the boiling point, cooled to 20°C, and kept for 12 h at that temperature. Acetic acid was distilled off under reduced pressure, 190 ml of a 1:1 benzene–diethyl ether mixture was added to the residue, and the precipitate was filtered off. The filtrate was washed with a saturated solution of sodium chloride and dried over $MgSO_4$. The drying agent was filtered off, the solvent was distilled off, and the residue was subjected to chromatography on silica gel using petroleum ether–ethyl acetate (3:1) as eluent. Yield 6.29 g (93%), colorless amorphous substance. IR spectrum, ν, cm^{-1}: 2400–3200 br.s, 1715 s, 1700 s, 1640 m, 900 s. ^1H NMR spectrum, δ, ppm: 1.62 s (3H, 4-CH_3), 2.08 s (3H, C^9H_3), 1.9–2.6 m (8H, CH_2), 5.12 t (1H, 6-H, J = 7.0 Hz), 10.9 s (1H, COOH). Found, %: C 65.34; H 8.56. $C_{10}H_{16}O_3$. Calculated, %: C 65.22; H 8.70.

Methyl 4,8-dimethylnona-4,8-dienoate (XXX) was synthesized by reaction of 1.5 g (7.8 mmol) of oxo ester **XXIX** with methylidene(triphenyl)phosphorane generated from 2.85 g (8.0 mmol) of methyl(triphenyl)-phosphonium bromide and 3.32 g of hexamethyldisilazane sodium salt in 55 ml of anhydrous THF as described above for compound **IV**. Yield 1.14 g (77%), colorless viscous oily substance. IR spectrum, ν, cm^{-1}: 3080 w, 1745 s, 1645 w, 1640 m, 915 m. ^1H NMR spectrum, δ, ppm: 1.64 s and 1.72 s (3H each, 4-CH_3, 8-CH_3), 1.98–2.45 m (8H, CH_2), 3.59 s (3H, OCH_3), 4.87 br.s (2H, 9-H), 5.24 t (1H, 6-H, J = 7.0 Hz). Found, %: C 73.64; H 10.06. $C_{12}H_{20}O_2$. Calculated, %: C 73.47; H 10.20.

Methyl 4,8-dimethyldeca-4,8-dienoate (XXXI) was synthesized by reaction of 2.0 g (10.1 mmol) of oxo ester **XXIX** with ethylidene(triphenyl)phosphorane [generated from 3.95 g (10.6 mmol) of ethyl(triphenyl)phosphonium bromide and 13 ml of a 1.4 M solution of *n*-BuLi in hexane] at –70°C in 40 ml of anhydrous THF under argon. The product was isolated as described above for compound **IV**. Yield 1.59 g (75%), colorless viscous oily substance. IR spectrum, ν, cm^{-1}: 1745 s, 1645 w, 1640 m. ^1H NMR spectrum, δ, ppm: 1.64 d (3H, $C^{10}H_3$, J = 6.5 Hz), 1.68 s and 1.72 s (3H each, 4-CH_3, 8-CH_3), 1.9–2.0 m (6H, CH_2), 2.42 t (2H, 2-H, J = 7.0 Hz), 3.61 s (3H, OCH_3), 5.13 t (1H, 5-H, J = 7.0 Hz), 5.26 q (1H, 9-H, J = 6.5 Hz). Found, %: C 74.41; H 10.36. $C_{13}H_{22}O_2$. Calculated, %: C 74.29; H 10.48.

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