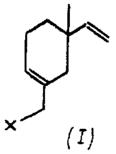
3-SUBSTITUTED 1-VINYL-1-METHYLCYCLOHEX-3-ENES – PRECURSORS OF TRICYCLIC DITERPENOIDS OF THE PIMARANE/ROSANE GROUP

V. A. Dragan, V. V. Veselovskii, E. D. Daeva,
and A. M. Moiseenkov

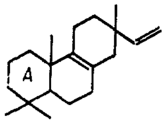
UDC 542.91:547.592.2

The synthesis of 1-vinyl-1-methyl-3-chloromethylcyclohex-3-ene from 3-vinyl-3-methylcyclohexanone and the corresponding exomethylene derivative has been optimized and related allylsulfones prepared. By a standard combination of these compounds with the appropriate (cyclo)geranyl block synthones a series of regular functionalized diterpenoids has been prepared which are considered as likely precursors of the natural compounds indicated in the title.

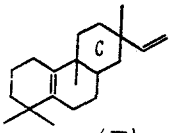
We recently showed that Lewis-acid initiated electrophilic cylization of derivatives of α-monoterpenols, including representatives of the class functionalized on the ω-sidechain, opens up a simple route to dimethylvinylcyclohexenes (I) [1]. An attractive feature of the ten-carbon skeleton of the latter consists in the fact that it is a characteristic structural fragment of the tricyclic diterpenes of the pimarane/rosane group [2] which are widely distributed in nature; for example, pimaradienes (II) and the rosadienes (III) [3] which are easily obtained from them. From this one can foresee the possibility of employing the monoterpenoids (I) in a complete synthesis of such diterpenes. In this connection we consider, in the present communication, the preparation of a series of these likely A/B precursors.



(I)

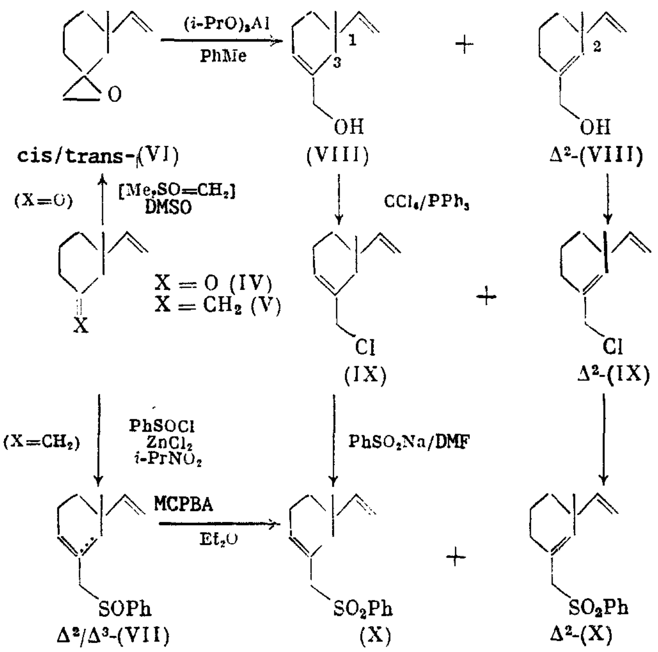


(II)



(III)

Scheme 1



N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 857-862, April, 1991. Original article submitted May 30, 1990.

0568-5230/91/4004-0754$12.50 © 1991 Plenum Publishing Corporation

Synthesis of the structures selected and discussed in the summing up was undertaken on the basis of the allylchloride (IX) and the sulfone (X) (Scheme 1). First, however, it was necessary to develop a method of preparing the chloride (IX) alternative to the available method which leads to the formation of ~25% of the undesirable Δ^2-regioisomer [1]. The vinyl ketone (IV) [4] which was chosen as an accessible starting material for this purpose was first smoothly converted by the method of Cory and Chaykovsky [5] to the oxide (VI); this proved to be a 2:1 mixture of trans and cis isomers which could be separated with some difficulty by adsorption chromatography. The structure of the minor isomer was assigned on the basis of the interaction, recorded by means of the nuclear Overhauser effect, of the OCH_2 and CH_3 axial groups and the appearance in its PMR spectrum of a W constant, $^4J = 1.3$, resulting from spin–spin interaction of OCH_2 protons with neighboring equatorial protons which is not possible in the case of the trans isomer of (VI).

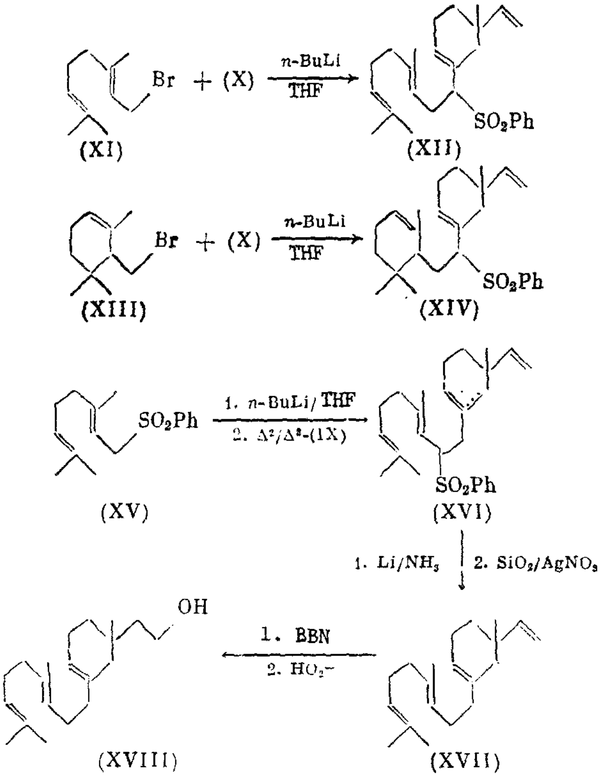
Isomerization of (VI) under the action of $(i\text{-PrO})_3Al$ in boiling toluene gave an almost quantitative yield of a mixture of allyl alcohols (VIII), $\Delta^3/\Delta^2 \approx 85:15$ which, although difficult to separate by chromatography, was smoothly converted into the labile allyl chlorides (IX) with the same ratio of regioisomers. This ratio was also retained for the mixture of allyl sulfones (X) formed in high yield by treatment of (IX) with $PhSO_2Na$ and readily separated into the individual products by flash chromatography on SiO_2.

A shorter synthesis of the sulfones (X) in the form of a mixture of regioisomers, $\Delta^3/\Delta^2 \approx 1:1$, was effected by selective oxidation, by means of m-chloroperbenzoic acid (MCPBA), of the labile allylsulfoxides (VII) which were in their turn prepared by a method which we developed [6] – the $ZnCl_2$-catalyzed ene-type reaction of PhSOCl with the known [7] methylenocyclohexane (V).

The structure of the previously unreported diasteromeric sulfoxides (VII) together with that of the isomeric oxides (VI), alcohols (VIII), and sulfones (X) was reliably confirmed from the results of their spectroscopic and elemental analysis. The ratios of stereo- (VI) and regioisomers (VII)-(X) mentioned above were found from the relative integral intensities of the diagnostic CH_3 signals in their high-resolution PMR spectra, δ 0.9-1.1 ppm, and additionally supported, in the case of (VI)-(IX), by the results of GLC analysis.

The three-stage synthesis given for allyl chloride (IX) from (IV) proved to be more acceptable overall than its preparation from the α-geranyl precursor of [1] because of the lower content (~15%) of the undesirable impurity Δ^2-(IX) thereby achieved. The two-stage synthesis of allyl sulfone (X) from (V), which was developed simultaneously, opened up a

Scheme 2



real possibility of a preparative yield of the intended diterpenoid objectives from monoterpenoid block synthones (Scheme 2).

Thus, a standard combination of (X), deprotonated by a strong base, with geranyl bromide (XI) gives a 90% yield of the diterpenoid sulfone (XII). Similarly, from (X) and α-cyclogeranylbromide (XIII) one can obtain the bicyclic derivative (XIV), and from geranyl sulfone (XV) and the allyl chloride (IX) a mixture of Δ^2/Δ^3-tetraenes (XVI). Reductive desulfonylation of (XVI), which was accompanied by partial allyl shift (5-7% from GLC and PMR results) leading to the formation of a $\Delta^{2'}$ impurity (cf. [8]), required careful purification of the mixture of olefins obtained, and this was carried out by adsorption chromatography on silvered SiO_2. The individual diterpenoids (XVII) thus separated in ~70% yield were further smoothly converted into the primary alcohls (XVIII) by anti-Markovnikov hydroxylation by means of 9-borabicyclononane (BBN).

The structure of the previously unknown compounds (XII)-(XVIII) was reliably confirmed from spectroscopic and elemental analyses. Information on the electrophilic cyclization of the sulfones (XII), (XIV), and the alcohol (XVIII) into rosadienes (III) will be published separately.

EXPERIMENTAL

IR spectra were obtained on a UR-20 instrument in solution in CCl_4. NMR spectra of solutions in $CDCl_3$ were run on Bruker WM-250 and Bruker AM-300 instruments. Mass spectra were obtained on a Varian MAT CH-6 spectrometer at 70 eV. Values of R_f are given for a fixed layer of Silufol SiO_2. GLC was effected on an LKhM-80 chromatograph with a column 2 m × 3 mm with 15% Carbowax-20M on Chromaton N-AW-HMDS.

cis/trans-5-Vinyl-5-methyloxaspiro[2,5]octanes (VI). A suspension of 3.4 g (0.14 mole) NaH and 31.5 g (0.14 mole) trimethyloxosulfonium iodide [5] in 250 ml DMSO was stirred (Ar) at ~25°C until hydrogen evolution ceased (~15 min) and further treated over ~15 min with a solution of 15 g (0.11 mole) (IV) [4] in 40 ml DMSO. The reaction mixture was heated for ~15 min up to 60°C and held at this temperature for 45 min and then diluted with 100 ml water and poured into 500 ml pentane. The organic layer was washed with water and dried over $MgSO_4$. The residue (15.6 g) after removal of the solvent was distilled to yield 14.7 g (88%) (VI) in the form of a colorless liquid, bp 52-53°C/3 mm, n_D^{20} 1.4695. For the ≈2:1 trans/cis mixture of (VI): Found: IR spectrum (ν, cm^{-1}): 920, 1000, 1105, 1150, 1375, 1400, 1415, 1455, 1485, 1640, 1725, 1830, 2870, 2935, 3035, 3085. PMR spectrum for the trans isomer (δ, ppm; J, Hz): 1.11 s (3H, CH_3), 1.2-1.9 m (8H, CH_2), 2.62 AB (2H, CH_2, J_{AB} = 5, Δδ = 0.05 ppm, ^4J = 1.3), 4.94, AB part of ABM spectrum, (2H, $H_2C{=}C$, J_{AM} = 17.5, J_{BM} = 11.3, J_{AB} = 1.4), 5.84, M part of ABM spectrum (1H, HC=C, J_{AM} = 17.5, J_{BM} = 11.3). PMR spectrum for cis isomer (δ, ppm; J, Hz): 1.05 s (3H, CH_3), 1.2-1.9 m (8H, CH_2), 2.56 AB spectrum (2H, H_2C^2, J_{AB} = 5, Δδ = 0.02 ppm), 4.97, AB part of ABM spectrum (2H, $H_2C{=}C$, J_{AM} = 17.5, J_{BM} = 11.0, J_{AB} = 1.4), 5.93, M part of ABM spectrum (1H, HC=C, J_{AM} = 17.5, J_{BM} = 11.0).

For the mixture (VI): Found, %: C 78.94, H 10.71. M^+ 152. $C_{10}H_{16}O$. Calculated, %: C 78.90, H 10.59; mol. wt. 152.2.

1-Vinyl-1-methyl-3-phenylsulfinylmethylcyclohex-2-ene (VII) and Its Δ^3 Isomer. To a vigorously stirred (Ar) solution of 0.18 g (1.32 mmoles) (V) [7] in 1.8 ml $i\text{-}PrNO_2$ at −30°C was added 0.27 g (1.98 mmoles) $ZnCl_2$ and then 0.32 g (1.99 mmoles) PhSOCl. The reaction mixture was stirred 20 min at −20°C and then decomposed at −50°C by a solution of 0.32 g (4 mmoles) Py in 1 ml ether and treated at 0°C with 10 ml ether and 2 ml water. The aqueous layer was separated and extracted with ether and the combined organic layer washed with water, dried over $MgSO_4$ and evaporated in vacuum. The residue (0.24 g) was chromatographed on 50 g SiO_2 at 0°C. Gradient elution from hexane to ether (up to 60% of the latter) gave 0.22 g (64%) of a mixture (VII) Δ^2/Δ^3 ≃ 1:1, in the form of a colorless oil, R_f 0.35 (2:1 ether–hexane). For the mixture of diasteromeric regioisomers (VII), IR spectrum (ν, cm^{-1}): 915, 1000, 1025, 1050, 1070, 1090, 1310, 1370, 1380, 1450, 1480, 1640, 2880, 2930, 2960, 3060, 3080.

For Δ^3-(VII), PMR spectrum (δ, ppm; J, Hz): 0.97 s (3H, CH_3), 1.2-2.2 m (6H, CH_2), 3.42 AB (2H, CH_2S, J_{AB} = 5, Δδ = 0.023), 4.93, AB part of ABM spectrum (2H, $H_2C{=}C$, J_{AM} = 17.5, J_{BM} = 11.7, J_{AB} = 1.5), 5.48 m (1H, HC^4), 5.75, M part of ABM spectrum (1H, HC=C, J_{AM} = 17.5, J_{BM} = 11.7), 7.4-7.7 m (5H, C_6H_5).

For Δ^2-(VII), PMR spectrum (δ, ppm; J, Hz): 0.92 s (3H, CH_3), 1.2-2.2 m (6H, CH_2), 3.50 AB (2H, CH_2S, J_{AB} = 4, Δδ = 0.017), 4.73 d.d (1H, trans-$H_2C{=}C$, J_1 = 17.5, J_2 = 1.5), 4.82 d.d (1H, cis-H_2C=C, J_1 = 11.7, J_2 = 1.5), 5.15 m (1H, HC^2), 5.62 d.d (1H, HC=C, J_1 = 17.5, J_2 = 11.7), 7.4-7.7 m (5H, C_6H_5).

For the mixture of sulfoxides (VII): Found: M^+ 260. Calculated for $C_{16}H_{20}OS$, mol. wt. 260.4.

1-Vinyl-1-methyl-3-hydroxymethylcyclohex-3-ene (VIII) and Its Δ^2 Isomer. A solution of 8.1 g (53.2 mmoles) (VI) and 16.3 g (80 mmoles) $(i\text{-}PrO)_3Al$ in 300 ml toluene was heated at bp (Ar) for 8 h. The reaction mixture was cooled to ~25°C and treated with a 9:9:1 mixture of Celite-NH_4Cl-H_2O. After stirring vigorously for 30 min, the deposit was filtered off and the filtrate evaporated. The residue (8.2 g) was chromatographed on 200 g silica. Gradient elution from hexane to ether (up to 20% of the latter) gave 6.8 g (84%) (VIII), $\Delta^2/\Delta^3 \simeq$ 15:85, and 1.2 g (15%) starting material (VI), trans/cis ≃ 1:1.

The allyl alcohol (VIII) was a colorless liquid, bp 46-47°C/2 mm, n_D^{20} 1.4939; IR spectrum (ν, cm^{-1}): 910, 995, 1040, 1170, 1370, 1410, 1435, 1450, 1635, 1670, 1825, 2870, 2920, 2955, 3080, 3330, 3620. PMR spectrum (VIII) (δ, ppm; J, Hz): 1.02 s (3H, CH_3), 1.3-2.2 m (6H, CH_2), 4.00 br.s (2H, CH_2O), 4.900, AB part of ABM spectrum (2H, H_2C=C, J_{AM} = 16.8, J_{BM} = 10.7, J_{AB} = 1.8), 5.65 m (1H, HC^4), 5.82, M part of ABM spectrum (1H, HC=C, J_{AM} = 16.8, J_{BM} = 10.7). Found, %: C 78.40, H 10.65; M^+ 152. $C_{10}H_{16}O$. Calculated, %: C 78.90, H 10.60; mol. wt. 152.2.

Chlorides (IX). A solution of 6.5 g (42.7 mmoles) of the mixture (VIII) mentioned above and 14.6 g (55.7 mmoles) PPh_3 in 17 ml CCl_4 was heated at bp (Ar) for 20 min, cooled, diluted with 200 ml pentane, the deposit filtered off and the filtrate evaporated. Distillation of the residue (7.0 g) yielded 6.1 g (84%) of mixture (IX), $\Delta^2/\Delta^3 \simeq$ 15:85, as a colorless liquid, bp 48-49°C/4 mm, n_D^{20} 1.4958 (cf. [1]).

1-Vinyl-1-methyl-3-phenylsulfonylmethylcyclohex-3-ene (X) and Its Δ^2 Isomer. To a solution of 2.64 g (15.5 mmoles) chlorides (IX) ($\Delta^2/\Delta^3 \simeq$ 15:85) in 30 ml DMF, stirred (Ar) at ~25°C was added, in portions over a period of 30 min, 3.31 g (20.2 mmoles) $PhSO_2Na$. The reaction mixture was held at 40°C for ~2 h and then treated with ether and water. The organic layer was separated, washed with water, and dried over $MgSO_4$. The residue (3.4 g) after removal of the solvent was chromatographed on 200 g SiO_2. Gradient elution from hexane to ether (up to 20% of the latter) gave 0.5 g (12%) Δ^2-(X) and 2.8 g (65%) (X) as a viscous colorless oil with R_f 0.53 and 0.48, respectively (here and below, the eluent was 1:1 ether–hexane).

IR spectrum of (X) (ν, cm^{-1}): 915, 1000, 1025, 1085, 1155, 1245, 1290, 1310, 1325, 1375, 1400, 1450, 1587, 1640, 2875, 2925, 2965, 3075, 3085. PMR spectrum (δ, ppm; J, Hz): 0.97 s (3H, CH_3), 1.2-2.2 m (6H, CH_2), 3.71 br.s (2H, CH_2S), 4.96, AB part of ABM spectrum (2H, H_2C=C, J_{AM} = 17.8, J_{BM} = 10.9, J_{AB} = 1.6), 5.36 m (1H, HC^4), 5.76, M part of ABM spectrum (1H, $\underline{H}C$=CH_2, J_{AM} = 17.8, J_{BM} = 10.9), 7.5-7.9 m (5H, C_6H_5); ^{13}C NMR spectrum (δ, ppm): 23.24 (C^6), 25.76 (C^9), 32.42 (C^5), 35.25 (C^1), 39.93 (C^2), 64.52 (C^{10}), 110.85 (C^8), 124.50 (C^3), 128.39 (m-C_6H_5), 128.86 (o-C_6H_5), 131.80 (C^4), 133.51 (p-C_6H_5), 138.55 (CS, C_6H_5), 147.67 (C^7).

For Δ^2-(X), IR spectrum (ν, cm^{-1}): 910, 995, 1025, 1085, 1160, 1245, 1310, 1325, 1365, 1400, 1450, 1585, 1635, 2870, 2930, 2960, 3070, 3085. PMR spectrum (δ, ppm; J, Hz): 0.87 s (3H, CH_3), 1.2-2.1 m (6H, CH_2), 3.73 br.s (2H, CH_2S), 4.67 d.d (1H, trans-H_2C=C, J_1 = 18.0, J_2 = 1.6), 4.85 d.d (1H, cis-H_2C=CH, J = 10.8, J_2 = 1.6), 5.07 m (1H, HC^2), 5.55 d.d (1H, $\underline{H}C$=CH_2, J_1 = 18.0, J_2 = 10.8), 7.5-7.9 m (5H, C_6H_5); ^{13}C NMR spectrum (δ, ppm): 19.19 (C^6), 27.53 (C^9), 28.80 (C^5), 34.85 (C^4), 39.00 (C^1), 64.90 (C^{10}), 112.32 (C^8), 126.10 (C^3), 128.66 (m-C_6H_5), 129.05 (o-C_6H_5), 133.54 (p-C_6H_5), 138.80 (CS, C_6H_5), 139.45 (C^2), 146.37 (C^7).

For the mixture of sulfones (X): Found, %: C 69.70, H 7.72, S 11.18. M^+ 276. $C_{16}H_{20}O_2S$. Calculated, %: C 69.53, H 7.29, S 11.60. Mol. wt. 276.4.

Sulfones (X). To a solution of 0.16 g (0.61 mmole) sulfoxides (VIII; $\Delta^2/\Delta^3 \simeq$ 1:1) in 2 ml ether, stirred (Ar) at –40°C, was added, over a period of ~10 min, 0.13 g (0.75 mmole) MCPBA. The reaction mixture was warmed to 0°C over 30 min and then treated with 0.2 g (2.6 mmoles) DMSO, 0.05 g (0.89 mmole) KOH, and 0.5 ml water. The usual treatment of the organic layer yielded 0.17 g of material which was chromatographed on 15 g SiO_2. Gradient elution from hexane to ether (up to 20% of the latter) gave 165 mg (98%) (X) as a 1:1 mixture of Δ^2/Δ^3 isomers the PMR spectrum of which was the sum of the spectra quoted above for these compounds.

1-Vinyl-1-methyl-3-(4',8'-dimethyl-1'-phenylsulfonyl-3'E,7'-nonadienyl)cyclohex-3-ene (XII). To a solution of 1.45 g (5.2 mmoles) (X) in 20 ml THF and 1.5 ml HMPA, stirred (Ar) at −78°C was added over ~10 min 2.86 ml (5.72 mmoles) of a 2M solution of n-BuLi in hexane, and over 5 min, a solution of 1.36 g (6.3 mmoles) freshly prepared geranyl bromide [9] in 10 ml THF. The reaction mixture was warmed to 25°C over ~30 min and treated with ether (100 ml) and saturated NH_4Cl solution. Subsequent normal treatment of the organic layer yielded 2.4 g of product which was chromatographed on 150 g SiO_2. Gradient elution from hexane to ether (up to 15% of the latter) gave 1.9 g (88%) (XII) as a colorless oil with R_f 0.57.

For the mixture of diastereomers of (XII), IR spectrum (ν, cm^{-1}): 1000, 1085, 1150, 1207, 1310, 1320, 1377, 1450, 1640, 2860, 2930, 2970, 3070. PMR spectrum (δ, ppm; J, Hz): 0.89 and 0.98 s (3H, CH_3), 1.2-2.2 m (10H, CH_2), 1.59 and 1.68 br.s (9H, CH_3), 2.5-2.9 m (2H, $H_2C^{2'}$), 3.45 m (1H, CHS), 4.8-5.1 m (4H, $H_2C{=}C$, $HC^{3'}$, $HC^{7'}$), 5.47 m (1H, HC^4), 5.73 m (1H, $\underline{H}C{=}CH_2$), 7.4-7.9 m (5H, C_6H_5). Found, %: S 7.67 ($M^+ - SO_2Ph$) 271. $C_{26}H_{36}O_2S$. Calculated, %: S 7.77; mol. wt. 412.6.

1-Vinyl-1-methyl-3-[1'-phenylsulfonyl-2'-(2",6",6"-trimethylcyclohex-2"-enyl)ethyl]-cyclohex-3-ene (XIV). To a solution of 0.32 g (1.2 mmoles) (X) in 6 ml THF and 0.5 ml HMPA, stirred (Ar) and cooled to −78°C, was added over ~10 min 1.6 ml of 1.75 M n-BuLi in hexane and after 5 min a solution of 0.6 g (2.8 mmoles) freshly prepared (XIII) [10] in 1 ml THF was added at −30°C. The reaction mixture was warmed to ~25°C over 20 min, held at this temperature for ~1 h, and treated with ether and saturated NH_4Cl solution. The usual treatment of the organic layer yielded 0.82 g product which was chromatographed on 30 g SiO_2. Gradient elution from hexane to ether (up to 20% of the latter) gave, in order of isolation, 0.28 g bromide starting material (XIII), 0.16 g (33%) (XIV), and 0.19 g sulfone starting material (X).

Bicyclic sulfone (XIV), viscous oil with R_f 0.71. IR spectrum (ν, cm^{-1}): 915, 970, 1090, 1100, 1150, 1250, 1310, 1320, 1400, 1450, 1540, 1640, 2365, 2875, 2925, 2970. PMR spectrum (δ, ppm; J, Hz), 0.81, 0.85, 0.87, 0.95, and 0.97 s (9H, CH_3), 0.9-2.2 m (13H, CH_2, CH), 1.54 and 1.66 br.s (3H, CH_3), 3.65 m (1H, CHS), 4.93 m (2H, $H_2C{=}C$), 5.27, 5.46, and 5.72 m (3H, HC=C), 7.4-7.9 m (5H, C_6H_5). Found, %: S 7.53; M^+ 412. $C_{26}H_{36}O_2S$. Calculated, %: S 7.77; mol wt. 412.6.

1-Vinyl-1-methyl-3-(4',8'-dimethyl-2'-phenylsulfonyl-3'E,7'-nonadienyl)cyclohex-3-ene (XVI). T a solution of 2.35 g (8.4 mmoles) geranyl sulfone [9] in 25 ml THF and 3 ml HMPA was added over a period of ~10 min, 4.4 ml (8.4 mmoles) of 1.9 M n-BuLi in hexane under stirred Ar and cooled to −78°C, and after 5 min a solution of 1.3 g (7.6 mmoles) mixed chlorides (IX; $\Delta^3/\Delta^2 \approx 85{:}15$) in 5 ml THF was added over ~10 min. The reaction mixture was warmed over ~30 min to ~25°C and treated with ether and saturated NH_4Cl solution. Subsequent normal treatment of the organic layer yielded 3.3 g product which was chromatographed on 150 g SiO_2. Gradient elution from hexane to ether (up to 15% of the latter) gave 2.64 g (99%) mixed diastereomers (XVI) as a colorless oil with R_f 0.58. IR spectrum (ν, cm^{-1}): 910, 1000, 1085, 1150, 1310, 1320, 1380, 1450, 1635, 2850, 2920, 2960, 3070. PMR spectrum (δ, ppm; J, Hz): 0.87 and 0.96 s (3H, CH_3), 1.14 br.s (3H, $CH_3{-}C^{4'}$), 1.2-1.5 m (2H, HC^6), 1.60 and 1.69 s (6H, $CH_3{-}C^{8'}$), 1.7-2.1 m (8H, CH_2), 2.31 and 2.85 m (2H, $HC^{1'}$), 3.88 m (1H, CHS), 4.8-5.1 m (4H, HC=C, $H_2C{=}C$),. 5.41 m (1H, HC^4), 5.6-5.9 m (1H, $\underline{H}C{=}CH_2$), 7.4-7.9 m (5H, C_6H_5). Found, %: C 75.24, H 8.72, S 7.48; M^+ 412. $C_{26}H_{36}O_2S$. Calculated, %: C 75.68, H 8.79, S 7.77; mol. wt. 412.6.

1-Vinyl-1-methyl-3-(4',8'-dimethyl-3'E,7'-nonadienyl)cyclohex-3-ene (XVII). To a vigorously stirred Ar solution of 0.75 g (108.6 mg-atom) Li in 100 ml NH_3 at −78°C was added over 10 min a solution of 2.6 g (6.3 mmoles) (XVI) in 10 ml THF. The reaction mixture was kept for 15 min and then decomposed with an excess of NH_4Cl, the NH_3 evaporated, and the residue treated with hexane and water. The organic layer was separated, washed with water, dried over $MgSO_4$, evaporated in vacuum, and the residue (1.5 g) chromatographed on 150 g SiO_2 impregnated with 10% $AgNO_3$ [11]. Gradient elution from hexane to benzene and then to ether (up to 10% of the latter) gave 1.17 g (68%) (XVII) as a colorless liquid with bp 99-100°C/0.04 mm, n_D^{20} 1.4948. IR spectrum (ν, cm^{-1}): 910, 1000, 1105, 1145, 1210, 1375, 1435, 1450, 1635, 1670, 1825, 2850, 2920, 2970, 3080. PMR spectrum (δ, ppm; J, Hz): 1.01 s (3H, CH_3), 1.3-1.6 m (2H, HC^6), 1.62 and 1.70 br.s (9H, CH_3), 1.7-2.2 m (12H, CH_2), 4.94, AB part of ABM spectrum (2H, $H_2C{=}C$, J_{AM} = 17.8, J_{BM} = 11.5, J_{AB} = 2.0), 5.12 m (2H, HC=C), 5.38 m (1H, HC^4), 5.84, M part of ABM spectrum (1H, $\underline{H}C{=}CH_2$, J_{AM} = 17.8, J_{BM} = 11.5). Found, %: C 88.40, H 11.50; M^+ 272. $C_{20}H_{32}$. Calculated, %: C 88.16, H 11.84; mol. wt. 272.5.

1-(2-Hydroxyethyl)-1-methyl-3-(4',8'-dimethyl-3'E,7'-nonadienyl)cyclohex-3-ene (XVIII). To a solution of 1.14 g (4.2 mmoles) (XVII) in 10 ml THF, vigorously stirred (Ar) at 0°C was added in portions 1.53 g (12.5 mmoles) BBN. The reaction mixture was warmed to ~25°C over 20 min, held there for 1 h, and then, at 0°C, treated successively with 6 ml 15% NaOH and 5 ml 30% H_2O_2 and stirred at ~25°C for a further 3 h. The aqueous layer was neutralized with 50% H_2SO_4 and extracted with ether. Subsequent normal treatment of the organic layer yielded 1.4 g product, chromatography of which on 80 g SiO_2 with 4:1 hexane–ether, yielded 0.78 g (64%) (XVIII) as a colorless oil with R_f 0.34. IR spectrum (ν, cm^{-1}): 980, 1010, 1025, 1055, 1105, 1145, 1210, 1375, 1435, 1445, 1665, 1735, 2850, 2920, 2960, 3630. PMR spectrum (δ, ppm; J, Hz): 0.91 s (3H, CH_3), 1.34 t (2H, $\underline{H}_2CCH_2O$, J = 7.8), 1.55 m (2H, HC^6), 1.60 and 1.69 s (9H, CH_3), 1.6-2.1 m (12H, CH_2), 3.72 t (2H, CH_2O, J = 7.8), 5.10 m (2H, HC=C), 5.37 m (1H, HC^4). Found, %: C 82.53, H 11.83; M^+ 290. $C_{20}H_{34}O$. Calculated, %: C 82.70, H 11.80; mol. wt. 290.5.

LITERATURE CITED

1. V. V. Veselovskii (Veselovsky), V. A. Dragan, and A. M. Moiseenkov, Tetrahedron Lett., 31, No. 8, 1187 (1990); A. M. Moiseenkov, V. V. Veselovskii, V. A. Dragan, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 6, 1368 (1990); A. M. Moiseenkov, V. A. Dragan, V. V. Veselovskii, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 6, 1361 (1990).
2. R. M. Coates, Prog. Chem. Org. Nat. Prod., 33, 74 (1976); P. F. Vlad, Izv. Akad. Nauk Mold SSR, Ser. Biol. Khim. Nauk, No. 1, 67 (1977); D. E. Cane, Tetrahedron, 36, No. 9, 1109 (1980).
3. T. McCreadie and K. H. Overton, J. Chem. Soc. (C), No. 2, 312 (1971).
4. J. W. ApSimon, S. Badripersaund, J. W. Hooper, et al., Can. J. Chem., 56, No. 16, 2139 (1978).
5. E. J. Corey and M. Chaykovsky, J. Am. Chem. Soc., 87, No. 6, 1353 (1965).
6. A. M. Moiseenkov, V. A. Dragan, V. A. Koptenkova, and V. V. Veselovskii (Veselovsky), Synthesis, No. 9, 814 (1987); V. V. Veselovskii, V. A. Dragan, and A. M. Moiseenkov, Izv. Akad. Nauk SSSR. Ser. Khim., No. 12, 2787 (1987).
7. R. M. Coates and H.-Y. Kang, J. Chem. Soc., Chem. Commun., No. 4, 232 (1987).
8. A. M. Moiseenkov and E. V. Polunin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 7, 1368 (1983); M. A. Novikova, A. V. Lozanova, V. V. Veselovskii, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 2, 356 (1987).
9. R. V. M. Campbell, L. Crombie, D. A. R. Findley, et al., J. Chem. Soc., Perkin Trans. 1, No. 10, 897 (1975).
10. M. Stoll, P. Bolle, and L.Ruzicka, Helv. Chim. Acta, 33, No. 6, 1510 (1950).
11. T. Norin and L. Westfelt, Acta Chem. Scand., 17, 1828 (1963).