ELECTROPHILIC CYCLIZATION OF α-SERIES MONOTERPENE ω-DERIVATIVES

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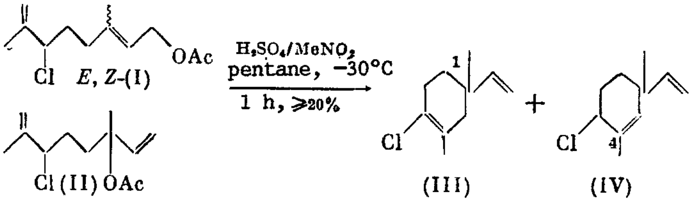
New information is discussed concerning the protic and Lewis acid-initiated electrophilic cyclization reaction of α-monoterpenols and their acetates; the distinguishing feature of these reactions is their termination by isopropenyl residues in these molecules. The reactions have been found to be general in nature, given additional functionalization of the terminator by chloro-, sulfonyl, sulfonylmethyl, or ester substituents. Cyclization of these linear substrates has also been shown to provide a convenient method for the synthesis of dimethylvinylcyclohexene derivatives and related cyclohexanediols, which are not readily available by other methods.

We have recently shown that α-geraniol, α-nerol, and α-linalool are capable, under specific conditions, of undergoing electrophilic cyclization (EC) via a scheme in which the ω-isopropenyl fragment in these molecules acts as the reaction terminator, leading to the formation of a rarely seen monoterpene skeleton [1]. In the present paper we discuss a new approach to the synthesis of compounds having this same skeleton, namely functionalized 1-vinyl-1,3-dimethylcyclohexanes, starting from corresponding ω-derivatives of the above-mentioned α-monoterpenols, either readily available derivatives or specially prepared ones.

Low temperature treatment of the known allyl chloride acetates (I) and (II) [2] with a series of protic and Lewis acids leads, in a reaction independent of the nature of the diene starting material, to a limited yield of the labile vinyl chloride (III), in addition to a small (~5%) amount of its allylic (stereo)isomers (IV).* The latter compounds did not withstand chromatographic purification on either SiO_2 or Al_2O_3, but were detected based on the presence in the PMR spectra of the reaction mixtures of a broad singlet signal for the olefinic proton at approximately δ 5.1 and 5.3 ppm. The best results in this reaction were achieved with ~7 mole equiv. 100% H_2SO_4 in $MeNO_2$–pentane emulsion at −30°C. The structure of the main product (III) was established based on the results of spectral and elemental analysis.



The regioisomeric E-(I) allyl chloride (VI) necessary for further study was prepared in measured yield by chlorination of α-geranyl acetate (V) [3] with SO_2Cl_2, in accordance with our previously developed procedure [2] modified somewhat by the addition of ~20 mole % $LiClO_4$ to the reaction mixture. In the absence of the latter additive substantial amounts of other mono- and dichlorides are formed (based on PMR data), which are difficult to separate using conventional methods and which are also present together with (VI) under the modified reaction conditions. The structure of (VI), which like E-(I) is a thermally and chromatographically labile compound (cf. [2]), was reliably inferred based on the presence in its PMR spectrum of broad singlet signals for the chloroisopropenyl fragment at δ 4.04 (CH_2Cl), and 4.97

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*A mixture of roughly equal amounts of diastereomers (according to PMR data).

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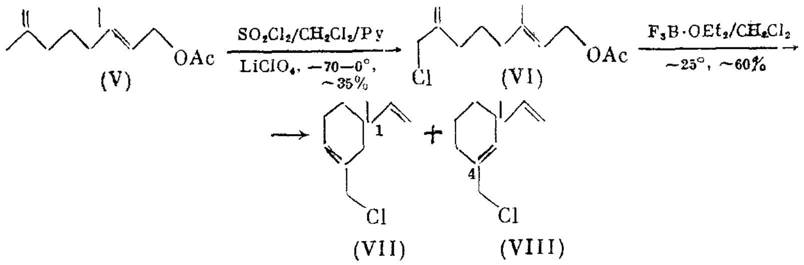
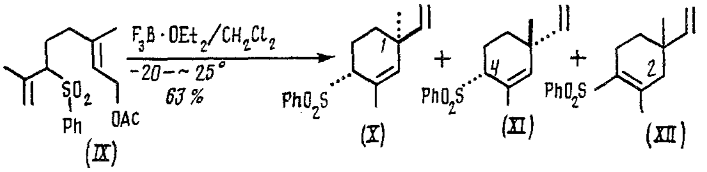


and 5.14 ppm ($H_2C{=}C$). The relative integrated intensity ratio (IIR) of these signals served as the criterion for determining the concentration of (VI) in the mixture of products arising from the chlorination of (V).

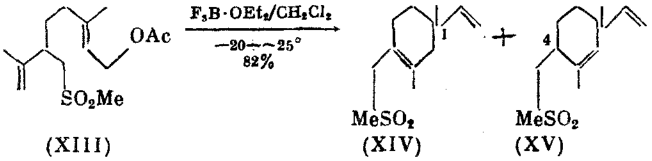
The most successful variation of this EC reaction of the above mixture rich in allyl chloride (VI) was obtained with an excess of $F_3B \cdot OEt_2$ in CH_2Cl_2 medium at ~25°C. The mixture of (VII)/(VIII) ≈ 4:1 which was readily obtained using this procedure was characterized based on the results of elemental and spectral analysis; the relative IIR of the CH_3 singlet signals (δ 1.04 and 1.09 ppm, respectively) provided the basis for estimating the ratio of regioisomers.

EC of the known α-geranyl acetoxysulfone (IX) [4] proved to be most efficient in the presence of ~2 mole equiv. $Et_2O \cdot BF_3$ (instead of H_2SO_4, CF_3CO_2H, or HCO_2H) in CH_2Cl_2 medium in the temperature range −20 to 25°C. Under these conditions a good overall yield of a mixture of epimeric allyl sulfones (X)/(XI) ≈ 3:2 is formed, containing <5% vinyl sulfone (XII), based on the IIR for the CH_3 singlet signals at δ 0.89, 0.99, and 0.95 ppm, corresponding to the above-mentioned components in the PMR spectrum of the mixture. The concentration of (XII) can be increased to ~30% relative yield by equilibration of the combined product mixture (X)-(XII) with MeONa in MeOH.



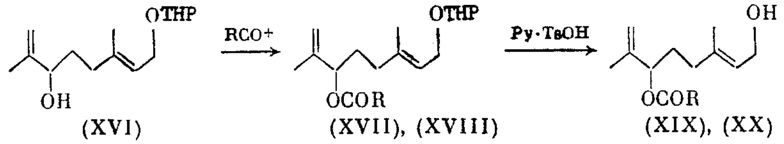
Nuclear Overhauser effect (NOE) data for (X) suggest the possibility of steric or spatial proximity of the HC^4 and $\underline{H}C{=}CH_2$ protons in this compound, which indicates in turn a cis relationship or orientation of the HC^4 and vinyl groups in this molecule, i.e., a transoid orientation of the $PhSO_2$ and $CH{=}CH_2$ substituents. Analysis of the ^3J spin–spin coupling constants (SSCC) for the HC^4 proton with the adjacent protons on C^5 [6.1 and 2.1 Hz for (X), 5.6 Hz for both protons in (XI)] further reveals that in both of these compounds the sulfonyl group occupies a pseudoaxial position in the predominant conformer, which is consistent with known observations [5].

The EC conditions developed for (IX) also proved to be optimum in the case of the known [6] methyl sulfone (XIII), which is converted in high yield to a mixture of vinylcyclohexenes (XIV)/(XV) ≈ 9:1; crystalline (XIV) was isolated in pure form from this mixture and its structure was established based on the results of elemental and spectral analysis. The ratio of regioisomers noted above was determined by measuring the IIR for the singlet CH_3 signals in the δ 1.02-1.05 ppm region in the PMR spectrum of the mixture, although it was not possible using this method to obtain an accurate estimate of the stereoisomer composition for (XV).



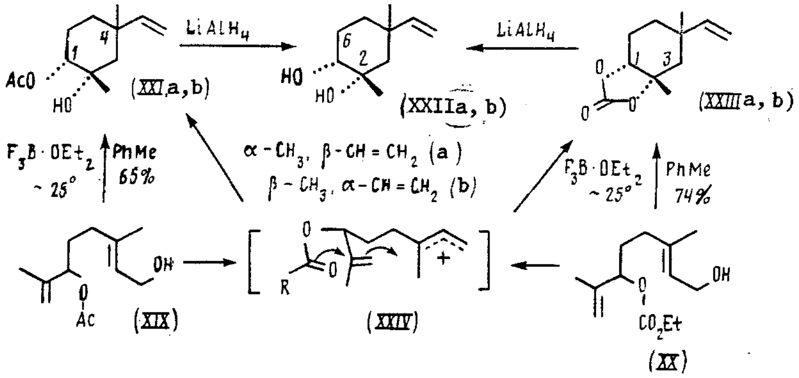
In this way, therefore, functionalization of the carbon site adjacent to the C=C double bond does not substantially affect or alter the reactivity of the isopropenyl fragment as a terminator in EC reactions involving chloro- and sulfonyl derivatives of α-monoterpenyl acetates. It was thus of interest to us to carry out this reaction with their related O-acyl derivatives, which would offer a promising and direct route to various substituted cis-cyclohexanediols.

The acetate (XIX) and carbonate (XX) derivatives of α-geraniol were selected for this purpose; they were prepared in almost quantitative yield from the readily available [7] monoether (XVI) after selective removal of the THP-protecting group in the corresponding diesters (XVII) and (XVIII). The structures of (XVII)-(XX), of which only the acetate (XIX) had been known previously [8], were reliably ascertained based on their spectral analysis data.



R = Me (XVII), (XIX); R = OEt (XVIII), (XX); THP = 2-tetrahydropyranyl.

As expected, treatment of (XIX) with an equimolar amount of $F_3B·OEt_2$ in toluene at ~25°C gave a mixture of approximately equal amounts of epimeric at C^4 thermodynamically favored secondary (and not tertiary [9]) monoacetates (XXIa, b). The latter were in turn easily converted via hydride reduction to an equivalent mixture of epimeric glycols (XXIIa, b), which like their precursors could not be resolved chromatographically. On the other hand, EC of (XX) initiated by ~8 mole equiv. $Et_2O·BF_3$ led in high yield to a mixture of cyclocarbonates (XXIII) in an a/b ratio ≈ 7:4, as determined after their separation by flash chormatography



on SiO_2. Hydride reduction of the pure isomers (XXIIIa) and (XXIIIb) gave crystalline compounds (XXIIa) and (XXIIb), respectively; the relative cis configuration of the diol fragment was inferred from the most probable mechanism for EC of the ester starting materials (XIX) and (XX), involving formation of a carbonium ion intermediate such as (XXIV). The relative configuration at the C^4 site in these conformationally labile glycols (XXII), and by implication their esters (XXI) and (XXIII), was assigned based on analysis of their high resolution PMR spectra, which allowed us in part to isolate in the spectra of (XXII) the signal multiplet for the $H_a{-}C^6$ proton, δ 1.5-1.7 ppm, and to distinguish using the NOE method its steric proximity to the method (δ 1.14 ppm) [in the case of (XXIIa)] or vinyl $HC{=}CH_2$ (δ 6.00 ppm) [in the case of (XXIIB)] protons.

In conclusion, EC of α-geraniol derivatives containing ω-ester substituents provides a satisfactorily efficient method for the preparation of functionalized cis-cyclohexanediols.

EXPERIMENTAL

Melting points were measured using a Koffler block and were not corrected. IR spectra of solutions in $CHCl_3$ were recorded on a Specord M-80 spectrophotometer. PMR spectra were obtained on Bruker WM-250 and Bruker AM-300 spectrometers using $CDCl_3$ solutions versus TMS. Mass spectra were measured on a Varian MAT CH-6 spectrometer at 70 eV. Values of R_f are given for Silufol plates impregnated with a layer of SiO_2.

<u>1-Vinyl-1,3-dimethyl-4-chlorocyclohex-3-ene (III) and 1-Vinyl-1,3-dimethyl-4-chlorocyclohex-2-enes (IV).</u> An emulsion containing 0.55 g (2.38 mmoles) E-(I) [2] and 1.83 g

(18.7 mmoles) 100% H_2SO_4 in 10 ml pentane and 3 ml $MeNO_2$ was stirred vigorously at −30°C under Ar for 1 h; the lower layer was separated and extracted with pentane. The combined pentane solution was washed with H_2O, neutralized with $NaHCO_3$, dried with $MgSO_4$, and evaporated under vacuum; the residue (~0.3 g) was then chromatographed on 15 g SiO_2. Elution with pentane gave 90 mg (22%) of a mixture of (III)/(IV) ≈ 95:5 (based on PMR analysis) in the form of a colorless liquid, bp 77-78°C (10 mm Hg), n_D^{20} 1.4920. IR spectrum (ν, cm^{-1}): 985, 1005, 1040, 1160, 1235, 1380, 1440, 1640, 2860, 2930, 3090. For (III), PMR spectrum (δ, ppm, J, Hz): 1.02 s (3H, $CH_3{-}C^1$), 1.6 m (2H, HC^6), 1.77 br. s (3H, $CH_3{-}C^3$), 2.02 AB (2H, HC^2, J_{AB} = 18, Δδ 0.18), 2.3 m (2H, HC^5), 4.95 m (2H, $H_2C{=}C$), 5.79 dd (1H, HC=C, J = 18 and 11). Found, %: C 70.49; H 8.96; Cl 20.62; M^+ 170. $C_{10}H_{15}Cl$. Calculated, %: C 70.37; H 8.86; Cl 20.77; mol. wt. 170.7. For (IV), PMR spectrum (δ, ppm, J, Hz): 1.06 s (3H, $CH_3{-}C^1$), 1.4-2.0 m (4H, CH_2), 1.82 and 1.86 br. s (3H, $CH_3{-}C^3$), 4.4 and 4.65 m (1H, HCCl), 4.8-5.1 m (2H, $H_2C{=}C$), 5.11 and 5.30 br. s (1H, HC^2), 5.8 m (1H, HC=C).

In an analogous manner, reaction of 2.7 g (11.7 mmoles) Z-(I) [2] and 2.66 g (27.7 mmoles) 100% H_2SO_4 in 30 ml pentane and 10 ml $MeNO_2$ gave 0.39 g (20%) of a mixture of (III)/(IV) ≈ 95:5, which was practically identical to the sample obtained above in terms of its PMR spectrum.

Also, treatment of 0.63 g (2.73 mmoles) (II) [2] and 1.83 g (18.7 mmoles) 100% H_2SO_4 in 10 ml pentane and 5 ml $MeNO_2$ gave 0.15 g (24%) of a mixture of (III)/(IV) ≈ 95:5, again practically identical in terms of its PMR spectrum to the sample described above.

3-Methyl-7-chloromethylocta-2E,7-dien-1-ol Acetate (VI). To a stirred suspension under Ar at −70°C of 1.43 g (7.3 mmoles) (V) [3], 0.15 g (1.4 mmoles) $LiClO_4$, and 0.75 g (9.5 mmoles) pyridine in 10 ml CH_2Cl_2 was added after 5 min a solution of 1.28 g (9.5 mmoles) SO_2Cl_2 in 5 ml CH_2Cl_2. After 10 min the reaction mixture was warmed to 0°C, diluted twofold with hexane, and neutralized with saturated aqueous $NaHCO_3$ solution; the aqueous layer was then extracted with hexane. This was followed by conventional workup of the combined organic solution to give 1.8 g of a substance, which was chromatographed on 50 g SiO_2. Gradient elution from hexane to ether (up to 10% of the latter) gave 1.24 g of a colorless liquid, bp 73-77°C (0.05 mm), n_D^{20} 1.4800, containing ~0.5 g (~40%) monoallyl chloride (VI) (based on PMR data). IR spectrum (ν, cm^{-1}): 960, 1025, 1230, 1370, 1385, 1445, 1650, 1675, 1740, 2950, 3090. PMR spectrum (δ, ppm, J, Hz): 1.6-2.2 m (6H, CH_2), 1.87 br. s (3H, CH_3), 2.04 s (3H, CH_3CO), 4.04 br. s (2H, CH_2Cl), 4.55 br. d (2H, CH_2O, J = 7), 4.97 and 5.14 br. s (2H, $H_2C{=}C$), 5.39 br. t (1H, HC^2, J = 7).

1-Vinyl-1-methyl-3-chloromethylcyclohex-3-ene (VII) and 1-Vinyl-1-methyl-3-chloromethylcyclohex-2-ene (VIII). A solution of 14.8 g of the mixture prepared as described above, containing (PMR data) ~5.9 g (~26 mmoles) (VI), and 27.3 g (0.19 mole) $F_3B{\cdot}OEt_2$ in 270 ml CH_2Cl_2 was stirred under Ar at ~25°C for 2 h, then diluted with hexane, and neutralized with saturated aqueous $NaHCO_3$ solution; the aqueous layer was also extracted with hexane. Conventional workup of the combined organic layer gave 2.64 g (~60%) of a mixture of (VII)/(VIII) ≈ 4:1 (based on PMR analysis) in the form of a colorless liquid, bp 83-85°C (11 mm Hg), n_D^{20} 1.4971. IR spectrum (ν, cm^{-1}): 915, 1000, 1260, 1345, 1410, 1440, 1500, 1660, 2860, 2960, 3080. For (VII), PMR spectrum (δ, ppm, J, Hz): 1.04 s (3H, CH_3), 1.45 m (2H, HC^6), 2.04 AB (2H, HC^2, J_{AB} = 17.5, Δδ = 0.22), 2.1 m (2H, HC^5), 4.03 br. s (2H, CH_2Cl), 5.0 m (2H, $H_2C{=}C$), 5.79 dd (1H, $\underline{H}C{=}CH_2$, J = 17.5 and 7), 5.8 m (1H, HC^4). For (VIII), PMR spectrum (δ, ppm, J, Hz): 1.09 s (3H, CH_3), 1.6-2.1 m (6H, CH_2), 4.02 br. s (2H, CH_2Cl), 5.0 m (2H, $H_2C{=}C$), 5.5 br. s (1H, HC^2), 5.76 dd (1H, $\underline{H}C{=}CH_2$, J = 17.5 and 7). Found, %: C 70.33; H 9.31; Cl 20.99. $C_{10}H_{15}Cl$. Calculated, %: C 70.37; H 8.86; Cl 20.77.

1β-Vinyl-1α,3-dimethyl-4α-phenylsulfonylcyclohex-2-ene (X), 1α-Vinyl-1β,3-dimethyl-4α-phenylsulfonylcyclohex-2-ene (XI), and 1-Vinyl-1,3-dimethyl-4-phenylsulfonylcyclohex-3-ene (XII). To a stirred solution of 1.17 g (3.48 mmoles) (IX) [4] in 10 ml CH_2Cl_2 under Ar at −20°C was added in one portion 1 g (7.05 mmoles) $F_3B{\cdot}OEt_2$. The reaction mixture was warmed to ~25°C after 10 min, maintained at room temperature for 30 min, then diluted with ether and neutralized with saturated aqueous $NaHCO_3$ solution; the aqueous layer was also extracted with ether. Conventional workup of the combined organic layer gave ~0.8 g of a substance which was chromatographed on 50 g SiO_2. Gradient elution from hexane to ether (up to 20% of the latter) gave 0.61 g (63%) of a mixture of (X)/(XI) ≈ 3:2, containing as well ~5% (XII) (according to PMR data) in the form of a colorless oil, R_f 0.54 (ether/hexane, 1:1). IR spectrum (ν, cm^{-1}): 920, 1000, 1090, 1150, 1315, 1450, 1640, 2870, 2930, 2960, 3080. Found, %: C 69.91; H 7.62; S 11.40; M^+ 276. $C_{16}H_{20}O_2S$. Calculated, %: C 69.53; H 7.29; S 11.60; mol. wt. 276.4.

A solution of the above mixture of sulfones (X)-(XII) (0.13 g, 0.47 mmole) in 2 ml 3 M MeONa in MeOH (6 mmoles) was diluted with 0.2 ml MeOH and allowed to stand at ~25°C for 3 h. The reaction mixture was worked up with H_2O (5 ml) and ether (20 ml), and the aqueous layer was subsequently separated, neutralized with 50% H_2SO_4, and extracted with ether. The combined organic layer was washed with H_2O, dried over $MgSO_4$, and evaporated under vacuum; the residue (0.13 g) was chromatographed on 20 g SiO_2. Gradient elution from hexane to ether (up to 10% of the latter) gave, in order of their elution, 10 mg (X), 75 mg of a mixture of (X)/(XI)/(XII) ≈ 65:15:20, and 40 mg of a mixture of (XI)/(XII) ≈ 1:1 (according to PMR data).

For (X), PMR spectrum (δ, ppm, J, Hz): 0.89 s (3H, CH_3), 1.3-2.0 m (4H, CH_2), 2.05 br. s (3H, CH_3), 3.61 dd (1H, HC^4, J = 6.1 and 2.1), 4.58 dd (1H, E-HC=C, J = 17.3 and 1.4), 4.93 dd (1H, Z-HC=C, J = 10.7 and 1.4), 5.56 br. s (1H, HC^2), 5.60 dd (1H, $HC{=}CH_2$, J = 17.3 and 10.7), 7.5-8.0 m (5H, C_6H_5).

For (XI), PMR spectrum (δ, ppm, J, Hz): 0.99 s (3H, CH_3), 1.1-2.0 m (4H, CH_2), 2.04 br. s (3H, CH_3), 3.66 br. t (1H, HC^4, J = 5.6), 4.76 dd (1H, E-HC=C, J = 15.9 and 1.1), 4.89 dd (1H, Z-HC=C, J = 9.8 and 1.1), 5.47 dd (1H, $HC{=}CH_2$, J = 15.9 and 9.8), 5.49 br. s (1H, HC^2), 7.5-7.9 m (5H, C_6H_5).

For (XII), PMR spectrum (δ, ppm, J, Hz): 0.95 s (3H, CH_3), 1.4-1.6 m (2H, HC^2), 2.13 br. s (3H, CH_3), 4.6-4.8 m (2H, $H_2C{=}C$), 5.65 m (1H, HC=C), 7.4-7.9 m (5H, C_6H_5).

1-Vinyl-1,3-dimethyl-4-methylsulfonylcyclohex-3-ene (XIV) and 1-Vinyl-1,3-dimethyl-4-methylsulfonylcyclohex-2-enes (XV). To a stirred solution of 0.63 g (2.18 mmoles) (XIII) [6] in 10 ml CH_2Cl_2 under Ar at −20°C was added in one portion 0.62 g (4.37 mmoles) $Et_2O\cdot BF_3$. The reaction mixture was warmed to ~25°C after 30 min, then diluted with ether and neutralized with saturated aqueous $NaHCO_3$ solution; the aqueous layer was also extracted with ether. Conventional workup of the combined organic extracts gave ~0.6 g of a substance which was chromatographed on 30 g SiO_2. Gradient elution from hexane to 20% ether gave 0.41 g (82%) of a mixture of sulfones (XIV)/(XV) ≈ 9:1 (PMR data), in the form of colorless crystals, mp 75-77°C. An analytical sample of (XIV) gave mp 77-78°C (ether–hexane). IR spectrum, (ν, cm^{-1}): 960, 1000, 1145, 1250, 1325, 1415, 1455, 1640, 2880, 2960, 3080. PMR spectrum (δ, ppm, J, Hz): 1.02 s (3H, CH_3), 1.5 m (2H, HC^6), 1.77 br. s (3H, CH_3), 2.02 AB (2H, HC^2, J_{AB} = 17.5, Δδ 0.18), 2.25 m (2H, HC^5), 2.83 s (3H, CH_3), 3.77 AB (2H, CH_2S, J_{AB} = 13, Δδ 0.06), 4.8-5.0 m (2H, $H_2C{=}C$), 5.77 dd (1H, HC=C, J = 18 and 10.4). Found, %: C 63.41; H 8.78; S 13.73; M^+ 228. $C_{12}H_{20}O_2S$. Calculated, %: C 63.12; H 8.83; S 14.04; mol. wt. 228.4. For (XV), PMR spectrum (δ, ppm, J, Hz): 1.04 and 1.05 s (3H, CH_3), 1.4-1.8 m (4H, CH_2), 1.71 and 1.73 br. s (3H, CH_3), 2.6 m (1H, HC^4), 2.9 m (2H, CH_2S), 2.94 s (3H, CH_3), 4.9 m (2H, $H_2C{=}C$), 5.25 m (1H, HC^2), 5.70 dd (1H, HC=C, J = 18 and 10).

2,6-Dimethyl-3-acetoxy-8-(2-tetrahydropyranyloxy)octa-1,6E-diene (XVII). A solution of 1.25 g (4.9 mmoles) (XVI) [7], 0.65 ml (8.1 mmoles) pyridine, and 0.55 g (5.4 mmoles) Ac_2O in 30 ml ether was stirred at ~25°C for 3 h, then diluted with ether and washed with 3% HCl, followed by saturated NaCl solution; the organic layer was dried over $MgSO_4$, evaporated, and the residue (1.6 g) chromatographed on 80 g SiO_2. Gradient elution from hexane to 20% ether gave 1.4 g (96%) (XVII), R_f 0.55 (hexane/ether, 3:2). IR spectrum (ν, cm^{-1}): 640, 820, 850, 870, 915, 975, 1030, 1060, 1080, 1120, 1135, 1160, 1190, 1205, 1255, 1325, 1380, 1445, 1460, 1475, 1660, 1735, 2665, 2740, 2855, 2870, 2930, 2950, 3015, 3085, 3450. PMR spectrum (δ, ppm, J, Hz): 1.5-1.9 m (8H, CH_2), 1.68 and 1.72 s (6H, CH_3), 2.0-2.1 m (2H, HC^5), 2.07 s (3H, CH_3CO), 3.51 and 3.88 m (2H, OCH_2), 4.13 AB portion of ABX spectrum (2H, HC^8, δ_A = 4.02, δ_B = 4.23, J_{AB} = 12, J_{AX} = 7.5, J_{BX} = 6.5), 4.62 br. t (1H, OCHO, J = 3.5), 4.89 and 4.94 br. s (2H, HC^1), 5.14 t (1H, HC^3, J = 7), 5.36 br. t (1H, HC^7, J = 7). Mass spectrum, m/e (%): 254 (1), 237 (3), 236 (6), 212 (5), 195 (25), 194 (20), 168 (15), 163 (10), 155 (20), 153 (100), 152 (90), 145 (10), 137 (30), 136 (50), 135 (100), 134 (100), 123 (30), 121 (50), 113 (25), 109 (50), 108 (75), 107 (100), 105 (50), 101 (75), 95 (50). Found, %: C 69.03; H 9.56. $C_{17}H_{28}O_4$. Calculated, %: C 68.87; H 9.54.

2,6-Dimethyl-3-ethoxycarbonyl-8-(2-tetrahydropyranyloxy)octa-1,6E-diene (XVIII). A solution of 0.4 g (1.6 mmoles) (XVI), 0.62 ml (7.7 mmoles) pyridine, 19 mg 4-dimethylaminopyridine, and 0.34 g (3.1 mmoles) $ClCO_2Et$ in 15 ml ether was refluxed for 4 h, then worked up as in the preceding experiment, and the isolated product (0.55 g) was chromatographed on 50 g SiO_2. Gradient elution from hexane to ether (up to 10% of the latter) gave 0.49 g (95%) of (XVIII) in the form of a colorless oil, R_f 0.30 (hexane/ether, 4:1).

IR spectrum (ν, cm^{-1}): 810, 865, 905, 945, 1005, 1020, 1035, 1050, 1075, 1115, 1155, 1180, 1210, 1265, 1375, 1440, 1465, 1655, 1740, 2850, 2950, 3005, 3080. PMR spectrum (δ, ppm, J, Hz): 1.29 t (3H, CH_3, J = 7), 1.5-1.9 m (8H, CH_2), 1.66 and 1.72 s (6H, CH_3), 2.0-2.1 m (2H, HC^5), 3.49 and 3.87 m (2H, OCH_2), 4.0 and 4.2 m (2H, HC^8), 4.16 q (2H, CO_2CH_2, J = 7), 4.60 br. t (1H, OCHO, J = 3.5), 4.9-5.0 m (3H, HC^1, HC^3), 5.35 br. t (1H, HC^7, J = 7). Mass spectrum, m/e (%): M^+ 326 (1), 311 (1), 243 (5), 242 (10), 236 (10), 225 (25), 224 (25), 175 (10), 174 (25), 168 (25), 153 (50), 152 (100), 151 (25), 137 (30), 136 (50), 135 (100), 134 (100), 121 (50), 119 (75), 117 (20), 115 (20). Found, %: C 66.63; H 9.35. $C_{18}H_{30}O_5$. Calculated, %: C 66.23; H 9.26.

Acetoxyalcohol (XIX). A solution of 1.25 g (4.2 mmoles) (XVII) and 0.11 g (0.4 mmole) TsOH·Py in 40 ml EtOH was heated at 50-55°C for 4 h, then evaporated under vacuum; the residue (1.2 g) was chromatographed on 50 g SiO_2. Gradient elution from hexane to ether (up to 20% of the latter) gave 0.86 g (96%) of (XIX) [8], in the form of a colorless oil, R_f 0.27 (hexane–ether, 1:4). PMR spectrum (δ, ppm; J, Hz): 1.6-1.8 m (2H, HC^5), 1.67 and 1.72 s (6H, CH_3), 2.01 br. t (2H, HC^4, J = 7), 2.07 s (3H, CH_3CO), 4.14 d (2H, HC^1, J = 7), 4.89 and 4.94 br. s (2H, HC^8), 5.14 t (1H, HC^6, J = 7), 5.39 br. t (1H, HC^2, J = 7).

3,7-Dimethyl-6-ethoxycarbonylocta-2E,7-dien-1-ol (XX). In an analogous manner, 0.54 g (1.65 mmoles) (XVIII) and 40 mg (0.16 mmole) TsOH·Py in 20 ml EtOH gave after 4 h 0.45 g of product, which was chromatographed on 25 g SiO_2. Gradient elution from hexane to ether (up to 50% of the latter) gave 0.39 g (98%) (XX) in the form of a colorless oil, R_f 0.34 (hexane–ether, 2:3). IR spectrum (ν, cm^{-1}): 875, 910, 945, 1005, 1045, 1265, 1375, 1145, 1465, 1480, 1655, 1740, 2940, 2980, 3005, 3080, 3610. PMR spectrum (δ, ppm, J, Hz): 1.30 t (3H, CH_3, J = 7), 1.66 and 1.72 s (6H, CH_3), 1.7-1.9 m (2H, HC^5), 2.04 br. t (2H, HC^4, J = 7), 4.12 br. d (2H, HC^1, J = 7), 4.17 q (2H, CO_2CH_2, J = 7), 4.9-5.0 m (3H, HC^6, HC^8), 5.39 br. t (1H, HC^2, J = 7). Mass spectrum, m/e (%): M^+ 242 (1), 224 (2), 205 (5), 196 (5), 195 (5), 174 (15), 152 (25); 143 (15), 137 (25), 135 (50), 134 (75), 121 (50), 119 (100), 117 (20), 115 (25), 109 (30), 107 (30), 97 (30), 95 (30), 94 (50), 93 (100), 91 (50). Found, %: C 64.01; H 9.01. $C_{13}H_{22}O_4$. Calculated, %: C 64.43; H 9.15.

1α-Acetoxy-2β,4α/β-dimethyl-4α/β-vinylcyclohexanes (XXIa, b). To a stirred solution of 0.83 g (3.9 mmoles) (XIX) in 250 ml PhMe under Ar at ~25°C was added within 5 min 0.48 ml (3.9 mmoles) $F_3B{\cdot}OEt_2$. After 1 h the mixture was neutralized at 0°C with 5% aqueous $NaHCO_3$ solution, washed with saturated NaCl solution, dried over $MgSO_4$, and evaporated under vacuum; the residue (0.64 g) was chromatographed on 25 g SiO_2. Gradient elution from hexane to ether (up to 25% of the latter) gave 0.54 g (65%) of a mixture of (XXIa)/(XXIb) ≈ 1:1 (PMR data) in the form of a colorless oil, R_f 0.27 (hexane–ether, 3:2). IR spectrum (ν, cm^{-1}): 800, 845, 870, 920, 960, 1000, 1010, 1045, 1130, 1260, 1340, 1380, 1420, 1460, 1645, 1735, 2375, 2470, 2880, 2930, 2970, 3025, 3090, 3460, 3560, 3595, 3675. PMR spectrum (δ, ppm, J, Hz): 0.97, 1.12, 1.17, and 1.21 s (6H, CH_3), 1.4-2.0 m (6H, CH_2), 2.10 and 2.12 s (3H, CH_3CO), 4.6-4.7 m (1H, HC^1), 4.88 and 5.08 d (1H, Z-HC=C, J = 11), 4.92 and 5.11 d (1H, E-HC=C, J = 17.5), 5.73 and 6.08 dd (1H, $\underline{H}C{=}CH_2$, J = 17.5 and 11). Mass spectrum, m/e (%): M^+ 212 (1), 197 (10), 170 (15), 169 (10), 155 (20), 153 (25), 152 (100), 137 (100), 135 (25), 134 (100), 127 (20), 125 (40), 124 (45), 123 (75), 119 (100), 112 (100), 111 (100), 110 (75), 109 (100), 108 (90), 107 (50), 105 (40), 97 (75), 96 (75). Found, %: C 67.83; H 9.56. $C_{12}H_{20}O_3$. Calculated, %: C 67.89; H 9.50.

2β,4α-Dimethyl-4β-vinylcyclohexane-1α,2α-diol Cyclocarbonate (XXIIIa) and 2β,4β-Dimethyl-4α-vinylcyclohexane-1α,2α-diol Cyclocarbonate (XXIIIb). In an analogous manner, reaction of 0.91 g (3.76 mmoles) (XX) and 3.7 ml (30.1 mmoles) $F_3B{\cdot}OEt_2$ in 300 ml PhMe gave after 1 h 0.9 g of product, which was chromatographed on 50 g SiO_2. Gradient elution from hexane to 45% ether gave, in order of their elution, 0.35 g (47%) (XXIIIa) and 0.20 g (27%) (XXIIIb) in the form of colorless oils. For (XXIIIa), R_f 0.38 (hexane–ether, 1:1). IR spectrum (ν, cm^{-1}): 660, 725, 885, 920, 960, 1000, 1030, 1040, 1060, 1100, 1155, 1205, 1265, 1295, 1315, 1350, 1370, 1390, 1455, 1640, 1740, 1790, 2400, 2885, 2910, 2960, 3010, 3080. PMR spectrum (δ, ppm, J, Hz): 1.09 s and 1.48 s (6H, CH_3), 1.5-2.1 m (6H, CH_2), 4.32 t (1H, HC^1, J = 4), 5.00 d (1H, E-HC=C, J = 17.5), 5.07 d (1H, Z-HC=C, J = 11), 5.72 dd (1H, $\underline{H}C{=}CH_2$, J = 17.5 and 11). Mass spectrum, m/e (%): M^+ 196 (1), 153 (2), 152 (15), 137 (45), 134 (90), 119 (50), 111 (100), 109 (75), 106 (35), 105 (30), 95 (50), 93 (75), 92 (35), 91 (40).

For (XXIIIb), R_f 0.30 (hexane–ether, 1:1). IR spectrum (ν, cm^{-1}): 660, 725, 860, 885, 915, 945, 960, 1010, 1045, 1065, 1090, 1110, 1140, 1160, 1175, 1205, 1265, 1320, 1375, 1455, 1465, 1640, 1740, 1795, 2400, 2870, 2930, 2960, 3010, 3080. PMR spectrum (δ, ppm, J, Hz):

1.04 s (3H, CH_3–C^4), 1.2-1.4 m (2H, HC^5), 1.50 s (3H, CH_3–C^2), 1.5-2.1 m (4H, CH_2), 4.37 t (1H, HC^1, J = 4.5), 4.98 d (1H, Z-HC=C, J = 11), 5.00 d (1H, E-HC=C, J = 17.5), 5.84 dd (1H, HC=CH_2, J = 17.5 and 11). Mass spectrum, m/e (%): 153 (10), 152 (50), 137 (80), 134 (90), 119 (40), 111 (100), 109 (100), 107 (25), 97 (30), 96 (30), 95 (75), 93 (75), 91 (50).

For the mixture of (XXIIIa) and (XXIIIb): Found, %: C 67.67; H 8.47. $C_{11}H_{16}O_3$. Calculated, %: C 67.32; H 8.21.

2β,4α-Dimethyl-4β-vinylcyclohexane-1α,2α-diol (XXIIa). To a stirred suspension of 12 mg (0.3 mmoles) $LiAlH_4$ in 5 ml ether under Ar at 0°C was added within 5 min a solution of 50 mg (0.25 mmole) (XXIIIa) in 1 ml ether. After 0.5 h the reaction mixture was worked up with a mixture of celite and $Na_2SO_4 \cdot 10H_2O$ [10], then filtered and the filtrate evaporated; the residue (~50 mg) was chromatographed on 5 g SiO_2. Gradient elution from hexane to 50% ether gave 26 mg (60%) of (XXIIa) in the form of colorless crystals, mp 64.5-65.5°C (from hexane). IR spectrum (ν, cm^{-1}): 860, 875, 895, 930, 950, 990, 1025, 1045, 1070, 1135, 1255, 1295, 1385, 1460, 1640, 1740, 2470, 2875, 2935, 2970, 3025, 3090, 3560, 3620. PMR spectrum (δ, ppm, J, Hz): 1.14 and 1.23 s (6H, CH_3), 1.4-1.9 m (6H, CH_2), 3.41 dd (1H, HC^1, J = 9 and 4), 4.89 d (1H, Z-HC=C, J = 11), 4.92 d (1H, E-HC=C, J = 17.5), 5.73 dd (1H, HC=CH_2, J = 17.5 and 11). Mass spectrum, m/e (%): M^+ 170 (10), 155 (75), 153 (40), 152 (100), 137 (100), 134 (50), 127 (50), 126 (40), 125 (40), 124 (60), 123 (90), 122 (50), 119 (75), 112 (90), 111 (100), 110 (90), 109 (100), 108 (90), 107 (40), 97 (70), 96 (100), 95 (75), 94 (75), 93 (75), 91 (75).

2β,4β-Dimethyl-4α-vinylcyclohexane-1α,2α-diol (XXIIb). Analogously, reaction of 50 mg (0.25 mmole) (XXIIIb) and 12 mg (0.3 mmole) $LiAlH_4$ gave 30 mg (70%) of (XXIIb), mp 65.5-66.5°C (from hexane). IR spectrum (ν, cm^{-1}): 840, 870, 930, 960, 985, 1020, 1060, 1120, 1160, 1255, 1300, 1355, 1380, 1420, 1460, 1640, 1735, 1865, 2470, 2875, 2940, 2960, 3020, 3090, 3560, 3620. PMR spectrum (δ, ppm, J, Hz): 0.95 and 1.21 s (6H, CH_3), 1.3-2.0 m (6H, CH_2), 3.28 dd (1H, HC^1, J = 11.5 and 5), 5.12 d (1H, Z-HC=C, J = 11), 5.16 d (1H, E-HC=C, J = 18), 6.00 dd (1H, HC=CH_2, J = 18 and 11). Mass spectrum, m/e (%): M^+ 170 (25), 155 (50), 153 (50), 152 (100), 150 (50), 149 (40), 140 (50), 139 (50), 138 (100), 137 (100), 135 (75), 134 (100), 127 (75), 125 (70), 124 (90), 123 (100), 122 (90), 121 (95), 119 (95), 119 (75), 117 (60), 113 (60), 111 (75), 110 (80), 109 (95), 108 (100), 105 (75), 101 (75), 98 (50), 92 (60).

Also, reaction of 60 mg (0.28 mmole) of the acetate mixture (XXIa, b) described above with 16 mg (0.42 mmole) $LiAlH_4$ in 6 ml ether gave 40 mg (84%) of a mixture of diols (XXIIa)/(XXIIb) ≈ 1:1 (PMR data), mp 42.5-44.5°C. The PMR spectrum of this mixture contained the same signals as reported above for the pure isomers. Found, %: C 70.69; H 10.90. $C_{10}H_{18}O_2$. Calculated, %: C 70.55; H 10.66.

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