(3H, OMe), 3.90 m (1H, J = 7, OCHMe₂), 5.50 br.s and 5.57 br.s (1H total, ~15:85 intensity ratio, 2-<u>H</u>), 6.01 m (2H, 4-<u>H</u> and 5-<u>H</u> signals in major isomer and 5-<u>H</u> in minor isomer), 7.60 d (~0.15H, J = 16, 4-H in minor isomer).

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EFFECTIVE SYNTHESIS OF 7-KETONOR- α -GERANIOL, 7-KETONOR- α -NEROL,

AND 6,8-DIOXABICYCLOOCTANES FROM THEM

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A simple synthesis of 7-ketonor- α -nerol and -geraniol has been developed. It was shown that epoxidation of these allyl alcohols or the silyl ether of the latter proceeds stereospecifically, possibly via the stage of the corresponding unstable epoxides, and results in the formation of derivatives of 6,8-dioxabicyclo]3,2,1]octane.

It has recently been shown in [1] that the trans-ketoepoxide (I; R = H) readily cyclizes in the presence of a weak organic acid into a derivative (II; R = H) having a bisnorgrandisane skeleton (Scheme 1). Suzuki et al. [1] believe that this transformation, clearly pro-



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ceeding with the participation of the methyl-substituted epoxide (I; R = Me) and via the key stage of a semiketal (II; R = Me), ensures ready access to the monoterpenoid grandisol (III), a component of sex pheromone of cotton weevil, <u>Authonomus grandis</u>, the existing methods of a total synthesis of which are very laborious [2, 3]. The attractiveness of this approach is, however, to a great extent lessened due to the well-known high lability of the disubstituted cis- and trans-ketoxides (IV)[closely related to (I)], which readily transform, respectively, into exo- and endo-6,8-dioxabicyclo[3.2.1]octanes (V) [3, 4] (Scheme 1), the first of which, exo-brevicomin, is included in the composition of the aggregation pheromone of the weevil beetle Dendroctonus brevicomis. With these considerations in mind, we attempted to prepare the stereoisomeric ketoepoxides of the series of (I: R = Me), which is the main subject of the present article.

The 7-ketonor- α -geraniol E-(IX) and 7-ketonor- α -nerol Z-(IX) required for the realization of our aim and previously described in [5] without specification of detailed characteristics, were found to be fairly difficultly obtainable compounds and, therefore, we have developed their preparative synthesis, whereby isomer E-(IX) was prepared by two separate methods (Scheme 2). According to the first of these, by selective epoxidation according to Scharpless [7], the known [6] geranyl derivative E-(VI) was converted first into oxide E-(VII), which was in turn reduced by LiAlH₄ into triol E-(VIII), and then, by periodate splitting of the vicinal diol fragment in E-(VIII) the desired hydroxy-ketone E-(IX) was obtained in an overall yield of >55% for the three above-described stages.

The other, also a three-step but somewhat less effective synthesis of the above isomer, consists in a preliminary alkylation of the E-hydroxy-sulfone (X) by 3-butenyl bromide into an intermediate sulfone (XI) which, in contrast to the closely related structures (cf. [8]), under the reductive splitting conditions of the C-S bond according to Birch, converts into hydroxy-diene (XII) with a minimal (<5%, according to PMR data) allylic shift of the neighboring C=C bond. By selective oxidation according to Walker-Tsuji under the conditions of [9], the ketoolefin E-(IX) was obtained, and, from the latter, the silyl ether E-(IXa).

As in the case of E-(VI), from the nerol derivative Z-(VI) [6], via the stage of previously not described epoxide Z-(VII) and triol Z-(VIII), the hydroxy-ketone Z-(IX) was prepared in a high overall yield (Scheme 2). The structure of compounds (VII)-(IX), as well as that of the unknown alcohol (XI), its acetate (XIa) and hydroxy-diene (XII) was confirmed by combination of their spectral and elemental analysis data.



The thus readily available normonoterpene olefins (IX) were then subjected to epoxidation under maximally mild and neutral conditions in order to isolate the corresponding ketooxides (Ia) (Scheme 3). However, as a result, it was found that during the oxidation of the allyl alcohol E-(IX) according to Scharpless only the bicyclic hydroxyketal endo-(XIII) was obtained, while from alcohol Z-(IX) - its stereoisomer - exo-(XIII) was obtained. These Scheme 3



compounds are clearly formed by intramolecular cyclization of trans- and cis-(Ia) epoxides, respectively, initially generated from olefins (IX) and unstable under the conditions used. The trans- and cis-(Ia) epoxides, as well as the bicyclic semiacetals of type (II; R = Me) could not be recorded by analysis of the reaction mixture by the PMR method after their purification by flash chromatography on SiO₂. An indirect indication of the formation of (Ia) is the fact that in the unpurified reaction mixtures considerable amounts of an intermediate product were detected by TLC (Silufol), which is more polar than the initial E- and Z-(IX), and which disappears on completion of the reaction and formation of the final bicyclic compound.

The above findings also fully apply to the result of the epoxidation by m-chloroperbenzoic acid (MCPBA) of silyl ether E-(IXa), which converts stereospecifically, also under the conditions adopted in [1], into the bicyclic product endo-(XIIIa), which by standard desilylation gives the previously mentioned primary alcohol, endo-(XIII).

The presence of the hydroxymethyl group in the molecules of ketals (XIII) was proved chemically by their conversion into trimethyldioxabicyclooctanes exo/endo-(XIV) structurally related to brevicomins (V), via the stage of a hydride reduction of the corresponding tosylates, which can be isolated in a pure state. Further confirmation of the structure of the previously unknown bicyclic compounds (XIII) and (XIV) was obtained from their elemental and spectral analysis.

In particular, in accordance with the structure of epimers (XIV), the experimental data on nuclear Overhauser effect (NOE) revealed for the endo-(XIV) a steric convergence of one of the methylene protons at C³ of the hydropyran fragment of this molecule with the methyl protons of the CH_3-C^7 fragment. Moreover, the HC⁷ signal found in the PMR spectrum of this epimer has, in contrast to the quartet signal for exo-(XIV), a doublet of quartets (d.q) form with a smaller constant J = 1.5 Hz, due to the presence of a distant hyperfine interaction (HFI) of this proton with the exo-methylene HC², which is impossible in the molecule of exo-(XIV), none of the protons of which, removed by four bonds from HC⁷, being able to form a planar W-fragment.

Thus, in accordance with the available data (cf. [4]), direct epoxidation of linear olefins (IX) is accompanied by a ready intramolecular opening of the intermediate ketoxides (Ia) with the formation of bicyclic structures (XIII).

EXPERIMENTAL

The IR spectra (in $CHCl_3$) were run on the UR-20 spectrophotometer. The PMR spectra of the solutions in $CDCl_3$ were run on a Bruker WM-250 spectrometer. The mass spectra were obtained on a Varian MAT CH-6 spectrometer at 70 eV. The R_f values are given for a stationary Silufol-type SiO₂ layer.

<u>trans-6,7-Epoxy-3,7-dimethyl-8-hydroxyoct-2E-en-1-ol Acetate E-(VII).</u> A 1.5-ml portion of a 2.14 M solution of t-BuO₂H in toluene (3.21 mmoles) was added in the course of 5 min to a suspension of 0.65 g (3.06 mmoles) of E-(VI) [6] and 35 mg (0.13 mmole) of VO(acac)₂ in 2 ml of benzene stirred at 10°C (Ar). The reaction mixture was heated in the course of 20

min to 15°C, then was diluted by ether, and treated with a saturated solution of $Na_2S_2O_3$. The aqueous layer was separated and extracted with ether. The combined organic layer was washed with a saturated NaCl solution, dried over Na_2SO_4 , evaporated under vacuum, and the residue (~0.7 g) was chromatographed on 25 g of SiO₂. Gradient elution from hexane to ether gave 0.61 g (87%) of E-(VII) in the form of a yellow oil. R_f 0.49 (ether). IR spectrum (ν , cm⁻¹): 870, 950, 1025, 1060, 1230, 1370, 1385, 1495, 1640, 1730, 2930, 3000, 3500. PMR spectrum (δ , ppm, J, Hz): 1.27 s (3H, CH₃-C⁷), 1.6-2.3 m (4H, CH₂), 1.71 br.s (3H, CH₃-C³), 2.03 s (3H, CH₃CO). 2.98 t (1H, HC⁶, J = 6.5), 3.6 m (2H, HC⁸), 4.56 br.d (2H, HC¹, J = 7), 5.36 br.t (1H, HC², J = 7). Found, %: C 63.53, H 9.03. $C_{12}H_{20}O_4$. Calculated, %: C 63.13, H 8.83.

 $\frac{\text{trans-6,7-Epoxy-3,7-dimethyl-8-hydroxyoct-2Z-en-1-ol Acetate Z-(VII).}{\text{from 0.65 g (3.06 mmoles) of Z-(VI) [6], 50 mg (0.19 mmole) of VO(acac)_2 in 2 ml of benzene, and 1.5 ml of a 2.14 M solution of t-BuO_2H in toluene (3.21 mmoles), 0.54 g (77%) of Z-(VII) was obtained in the form of a yellow oil. Rf 0.51 (ether). IR spectrum (v, cm⁻¹): 865, 990, 1025, 1060, 1230, 1370, 1385, 1455, 1630, 1730, 2940, 3000, 3500. PMR spectrum (<math>\delta$, ppm, J, Hz): 1.30 s (3H, CH₃-C⁷), 1.7 m (2H, HC⁵), 1.80 br.s (3H, CH₃-C³), 2.06 s (3H, CH₃CO), 2.28 br.t (2H, HC⁴, J = 8), 3.03 t (1H, HC⁶, J = 6.5), 3.65 m (2H, HC⁸), 4.60 br.d (2H, HC¹, J = 7.5), 5.42 br.t (1H, HC², J = 7.5). Found, %: C 63.15, H 8.99. C₁₂H₂₀O₄. Calculated, %: C 63.13, H 8.83.

<u>3,7-Dimethyloct-2E-ene-1,7,8-triol E-(VIII).</u> A solution of 3.06 g (13.4 mmoles) of E-(VII) in 15 ml of THF was added in the course of 1 h to a suspension of 0.8 g (21.1 mmoles) of LiAlH₄ in 120 ml of THF vigorously stirred at 30°C (Ar). After 20 min, the reaction mixture was decomposed according to [10] (0.8 ml of H₂O, 0.8 ml of 15% NaOH, 2.4 ml of H₂O). The precipitate was filtered off, washed on the filter with ether, the filtrate was evaporated under vacuum and the residue (~2 g) was chromatographed on 50 g of SiO₂. Gradient elution from hexane to ether and then to methanol (up to 4% of the latter) gave 1.94 g (77%) of E-(VIII) in the form of a colorless oil, R_f 0.25 (ether-acetone, 4:1). IR spectrum (v, cm⁻¹): 930, 1020, 1120, 1230, 1380, 1450, 1660, 2940, 2980, 3400, 3600. PMR spectrum (δ , ppm, J, Hz): 1.11 s (3H, CH₃-C⁷), 1.2-1.6 m (4H, HC⁵, HC⁶), 1.64 br.s (3H, CH₃-C³), 2.0 m (2H, HC⁴), 3.4 m (2H, HC⁸), 4.10 br.d (2H, HC¹, J = 7), 5.37 br.t (1H, HC², J = 7). Found, %: C 63.68, H 10.63. C₁₀H₂₀O₃. Calculated, %: C 3.80, H 10.71.

 $\frac{3,7-\text{Dimethyloct-}2Z-\text{ene}-1,7,8-\text{triol}\ Z-(\text{VIII}). \text{ In a similar way, from 0.65 g (2.85 mmoles)} of Z-(\text{VII}) and 0.17 g (4.48 mmoles) of LiAlH₄ in 25 ml of THF, 0.45 g (84%) of Z-(\text{VIII}) was obtained in the form of a colorless oil, R_f 0.23 (ether-acetone, 4:1). IR spectrum (<math>\nu$, cm⁻¹): 910, 1040, 1120, 1210, 1380, 1450, 2880, 2940, 3000, 3400, 3600. PMR spectrum (δ , ppm, J, Hz): 1.13 s (3H, CH₃-C⁷), 1.3-1.7 m (4H, HC⁵, HC⁶), 1.75 br.s (3H, CH₃-C³), 2.1 m (2H, HC⁴), 3.4 m (2H, HC⁸), 4.10 br.d (2H, HC¹, J = 8), 5.44 br.t (1H, HC², J = 8). Found, %: C 63.39, H 10.66. C₁₀H₂₀O₃. Calculated, %: C 63.80, H 10.71.

<u>3-Methyl-4-phenylsulfonylocta-2E,7-dien-1-ol (XI).</u> A 3.5 ml portion of a 1.37 M solution of n-BuLi in hexane (4.8 mmoles) was added in the course of 5 min to a solution of 0.5 g (2.21 mmoles) of (X) [11] in 10 ml of THF and 0.8 ml of DMF stirred at -70° C (Ar) and then, after 10 min, a solution of 0.38 g (2.81 mmoles) of 4-bromobutene in 2 ml of THF was added in the course of 5 min. The reaction mixture was allowed to stand at -50° C for 30 min, and then was heated to 20°C in the course of 30 min, and decomposed by a saturated solution of NH₄Cl. The aqueous layer was separated and extracted with ether. The combined organic layer was washed with a saturated NaCl solution, dried over MgSO₄, evaporated under vacuum, and the residue (~0.7 g) was chromatographed on 25 g of SiO₂. Gradient elution from hexane to ether gave 0.11 g of (X) and 0.4 g (83%) of (XI) in the form of a colorless oil, R_f 0.40 (ether-hexane, 4:1). IR spectrum (ν , cm⁻¹): 720, 1020, 1080, 1150, 1220, 1310, 1370, 1450, 1640, 2960, 3000, 3060, 3500, 3610. PMR spectrum (δ , ppm, J, Hz): 1.66 br.s (3H, CH₃), 1.8-2.2 m (4H, CH₂), 3.5 m (1H, HCS), 4.0 m (2H, CH₂O), 4.9 m (2H, H₂C=C), 5.32 br.t (1H, HC², J = 6), 5.6 m (1H, HC⁷), 7.4-7.8 m (5H, C₆H₅). Mass spectrum (m/z), 280 (M⁺), 139 (M - PhSO₂)⁺, 121, 95, 81, 69; calculatated for C₁₅H₂₀O₃S: mol. wt. 280.4.

<u>Acetate (XIa)</u> - colorless oil, R_f 0.42 (ether-hexane, 3:1). Found, %: C 63.55, H 7.11, S 9.83. C₁₇H₂₂O₄S. Calculated, %: C 63.33, H 6.88, S 9.94.

<u>3-Methylocta-2E,7-dien-1-ol (XII)</u>. A solution of 0.8 g (2.85 mmoles) of (XI) in 5 ml of THF was added in the course of 10 min to a solution of 0.53 g (23.1 mg-atom) of Na in 50 ml of NH₃ vigorously stirred at -70° C (Ar). The reaction mixture was held for 30 min at -70° C, and then was decomposed by excess NH₄Cl. Ammonia was evaporated, and the residue

was treated with ether and water. The aqueous layer was separated and extracted with ether. By usual treatment of the combined extract, ~0.35 g of a product was obtained, which was chromatographed on 15 g of SiO₂. Gradient elution from hexane to ether (up to 15% of the latter) gave 0.25 g (63%) of (XII) in the form of a colorless liquid, bp 45-46°C (1.5 mm), $n_D^{2^0}$ 1.4690. IR spectrum (v, cm⁻¹): 815, 990, 1230, 1385, 1440, 1640, 1665, 2940, 3000, 3080, 3610. PMR spectrum (δ , ppm, J, Hz): 1.5 m (2H, HC⁵), 1.68 br.s (3H, CH₃), 2.05 m (4H, HC⁴, HC⁶), 4.16 br.d (2H, CH₂O, J = 8), 4.9-5.1 m (2H, H₂C=C), 5.41 br.t (1H, HC², J = 8), 5.8 m (1H, HC⁷). Found, %: C 77.50, H 11.55; 122 (M - 18)⁺. C₉H₁₆O. Calculated, %: C 77.09, H 11.50; mol. wt. 140.2.

<u>7-Oxo-3-methyloct-2E-en-1-ol E-(IX)</u>. A solution of 2.34 g (10.94 mmoles) of NaIO₄ in 50 ml of H₂O was added in the course of 5 min to a solution of 1.37 g (7.28 mmoles) of E-(VIII) in 45 ml of THF, stirred at 20°C. The reaction mixture was allowed to stand for 30 min at 20°C, was concentrated under vacuum to ~1/3 of its volume and then was extracted with ether. By the subsequent usual treatment of the extract, ~1.2 g of a product was obtained, which was chromatographed on 50 g of SiO₂. Gradient elution from hexane to ether gave 0.93 g (82%) of E-(IX) in the form of a colorless liquid, bp 102-104°C (0.08 mm), nD²⁰ 1.4715. IR spectrum (v, cm⁻¹): 990, 1160, 1220, 1360, 1440, 1660, 1710, 2890, 3000, 3450, 3600. PMR spectrum (δ , ppm, J, Hz): 1.67 br.s (3H, CH₃), 1.7 m (2H, HC⁵), 2.02 br.t (2H, HC⁴, J = 7.5), 2.13 s (3H, CH₃CO), 2.41 t (2H, HC⁶, J = 7), 4.11 br.d (2H, CH₂O, J = 7), 5.39 br.t (1H, HC², J = 7). Found, %: C 69.21, H 10.52; 138 (M - 18)⁺. C₉H₁₆O₂. Calculated, %: C 69.19; H 10.32; mol. wt. 156.2.

A suspension of 0.5 g (3.57 mmoles) of (XII), 75 mg (0.42 mmole) of $PdCl_2$, and 0.21 g (1.06 mmoles) of Cu_2Cl_2 in 1.3 ml of DMF and 0.2 ml of water was stirred at 20°C in an O_2 atmosphere for 3 h. The reaction mixture was then diluted with ether, the precipitate was filtered off, the filtrate was dried over MgSO₄, evaporated in vacuo, and the residue (~0.5 g) was chromatographed on 20 g of SiO₂ under the conditions of the preceding experiment. Yield 0.38 g (68%) of E-(IX), which was identical (PMR) with the above-described sample of this alcohol.

<u>tert-Butyldimethylsilyl Ether E-(IXa)</u>. tert-Butyldimethylsilyl chloride (0.6 g, 3.98 mmoles) was added in portions in the course of 5 min to a solution of 0.5 g (3.2 mmoles) of E-(IX) and 0.41 g (6.02 mmoles) of imidazole in 1 ml of DMF stirred at 20°C. The reaction mixture was allowed to stand for 1 h at 20°C, and then was treated with hexane and ether (1:1) and water. The aqueous solution was separated and extracted with hexane. The combined organic layer was dried over MgSO₄, evaporated under vacuum, and the residue (~1 g) was chromatographed on 25 g of SiO₂. Gradient elution from hexane to ether (up to 15% of the latter) gave 0.84 g (97%) of E-(IXa) in the form of a colorless oil, R_f 0.28 (ether-hexane, 1:4). IR spectrum (v, cm⁻¹): 840, 1060, 1110, 1260, 1365, 1470, 1715, 2860, 2960. PMR spectrum (ô, ppm, J, Hz): 0.08 s (6H, CH₃), 0.91 s [9H, (CH₃)₃C], 1.60 br.s (3H, CH₃-C³), 1.6-2.0 m (4H, CH₂), 2.12 s (3H, CH₃CO), 2.40 br.t (2H, HC⁶, J = 8), 4.18 br.d (2H, CH₂O, J = 7.5), 5.30 br.t (1H, HC², J = 7.5). Mass spectrum (m/z): 270 (M⁺); calculated for C₁₅-H₃₀O₂Si: mol. wt. 270.5.

 $\frac{7-0\text{xo}-3-\text{methyloct}-2Z-\text{en}-1-\text{ol}\ Z-(IX).}{(IX)}$ As described for E-(IX), from 0.42 g (2.23 mmoles) of Z-(VIII) and 0.72 (3.37 mmoles) of NaIO₄ in 15 ml of THF and 15 ml of water, ~0.3 g of a product was obtained which was chromatographed on 10 g of SiO₂. Gradient elution from hexane to ether gave 0.27 g (77%) of Z-(IX) in the form of a colorless liquid, bp 98-99°C (0.08 mm), np²⁰ 1.4714. IR spectrum (v, cm⁻¹): 990, 1160, 1220, 1375, 1405, 1450, 1640, 1710, 2880, 2960, 3000, 3460, 3600. PMR spectrum (δ , ppm, J, Hz): 1.7 m (2H, HC⁵), 1.73 br.s (3H, CH₃), 2.07 br.t (2H, HC⁴, J = 8), 2.14 s (3H, CH₃CO), 2.42 t (2H, HC⁶, J = 7), 4.09 br.d (2H, CH₂O, J = 6.5), 5.46 br.t (1H, HC², J = 6.5). Found, %: C 69.48, H 10.66; 138 (M - 18)⁺. C₉H₁₆O₂. Calculated, %: C 69.19, H 10.32; mol. wt. 156.2.

<u>endo-1,5-Dimethyl-7-tert-butyldimethylsilyloxymethyl-6,8-dioxabicyclo[3.2.1]octane endo-(XIIIa)</u>. A solution of 0.7 g (2.59 mmoles) of E-(IXa) and 0.54 g (3.13 mmoles) of MCPBA in 15 ml of CH_2Cl_2 was stirred at 20°C (Ar) for 30 min, then was diluted with an ether-hexane (1:1) mixture and filtered through a layer (20 cm) of Al_2O_3 . The filtrate was evaporated under vacuum and the residue (~1 g) was chromatographed on 30 g of SiO₂. Gradient elution from hexane to ether (up to 40% of the latter) gave 0.53 g (65%) of endo-(XIIIa) in the form of a colorless oil, R_f 0.53 (ether-hexane, 1:4). IR spectrum (ν , cm⁻¹): 895, 940, 970, 1010, 1040, 1070, 1100, 1120, 1180, 1245, 1380, 1480, 2870-3000. PMR spectrum (δ , ppm, J, Hz): 0.08, 0.91, 130 and 1.43 s (21H, CH₃), 1.4-1.8 m (6H, CH₂), 3.6-4.0 m (3H, CH₂O, HC⁷). Mass spectrum (m/z): 286 (M)⁺; calculated for $C_{15}H_{30}O_3Si$; mol. wt. 286.5.

<u>endo-1,5-Dimethyl-7-hydroxymethyl-6,8-dioxabicyclo[3.2.1]octane endo-(XIII).</u> A 1-m1 portion of a 2.14 M solution of t-BuO₂H in toluene (2.14 mmoles) was added in the course of 5 min to a suspension of 0.3 g (1.92 mmoles) of E-(IX) and 20 mg (0.075 mmole) of VO(acac)₂ in 3 ml of benzene, stirred at 10°C (Ar). The reaction mixture was heated in the course of 20 min to 20°C, held at this temperature for 1.5 h, and was then treated as described above for E-(VII). Thus, ~0.3 g of a product was obtained which was chromatographed on 15 g of SiO₂. Gradient elution from hexane to ether (up to 75% of the latter) gave 0.25 g (76%) of endo-(XIII) in the form of a colorless liquid, bp 68-70°C (1 mm), nD^{2°} 1.4696. IR spectrum (v, cm⁻¹): 960, 1020, 1070, 1120, 1170, 1230, 1380, 1450, 2880, 2970, 3450, 3600. PMR spectrum (δ , ppm, J, Hz): 1.26 and 1.44 s (6H, CH₃), 1.5-2.0 m (6H, CH₂), 3.6-3.8 m (2H, CH₂O), 3.95 m (1H, HC⁷). Found, %: C 62.77, H 9.36; 172 (M⁺). C₉H₁₆O₃. Calculated, %: C 62.76, H 9.37; mol. wt. 172.2.

A solution of 1.37 g (4.34 mmoles) of $(n-Bu)_4N^+F^-$ in 5 ml of THF was added to a solution of 0.45 g (1.57 mmoles) of endo-(XIIIa) in 1 ml of THF, stirred at 20°C. The reaction mixture was stirred at 20°C for 15 min, and then was diluted with ether and a saturated solution of NaCl. The aqueous layer was separated, extracted with ether, and the organic layer was dried over Na₂SO₄, evaporated under vacuum, and the residue (~0.5 g) was chromatographed on 25 g of SiO₂. Gradient elution from hexane to ether (up to 75% of the latter) gave 0.23 g (85%) of endo-(XIII), which was practically identical (TLC, PMR) to the bicyclic alcohol described above.

 $\frac{\text{exo-1,5-Dimethyl-7-hydroxymethyl-6,8-dioxabicyclo[3.2.1]octane exo-(XIII).}{\text{from 0.27 g (1.73 mmoles) of Z-(IX), 20 mg (0.075 mmole) of VO(acac)_2 in 3 ml of benzene and 1 ml of a 2.14 M solution of t-BuO_2H in toluene (2.14 mmoles), ~0.3 g of a product was obtained, which was chromatographed on 15 g of SiO_2. Gradient elution from hexane to ether (up to 80% of the latter) gave 0.25 g (84%) of exo-(XIII) in the form of a colorless liquid, bp 70-72°C (2 mm), <math>n_D^{2^0}$ 1.4638. IR spectrum (v, cm⁻¹): 1010, 1030, 1060, 1120, 1175, 1240, 1385, 1455, 2880, 2950, 3000, 3580. PMR spectrum (δ , ppm, J, Hz): 1.24 and 1.42 s (6H, CH₃), 1.2-1.9 m (6H, CH₂), 3.5 m (2H, CH₂O), 3.95 m (1H, HC⁷). Found, %: C 62.91, H 9.40; 172 (M)⁺. C₉H₁₆O₃. Calculated, %: C 62.76, H 9.37; mol. wt. 172.2.

<u>endo-1,5,7-Trimethyl-6,8-dioxabicyclo[3.2.1]octane endo-(XIV).</u> Tosyl chloride (0.4 g, 2.1 mmoles) was added in portions to a suspension of 0.24 g (1.39 mmoles) of endo-(XIII) in 0.46 ml (5.6 mmoles) of pyridine, stirred at 20°C (Ar). The reaction mixture was stirred at 20°C for 1 h, and was then diluted with ether, washed with a saturated solution of NaHCO₃, the aqueous layer was separated and extracted with ether. After the usual treatment of the combined extract, ~0.8 g of a product was obtained, which was chromatographed on 30 g of SiO₂. Gradient elution from hexane to ether (up to 30% of the latter) gave 0.44 g (97%) of a tosylate of the endo-(XIII) alcohol in the form of colorless crystals, mp 90-93°C (etherhexane). IR spectrum (v, cm⁻¹): 830, 980, 1120, 1180, 1190, 1370, 1450, 1600, 2890, 2950, 2980, 3020. PMR spectrum (δ , ppm, J, Hz): 1.26 and 1.40 s (6H, CH₃), 1.5-1.8 m (6H, CH₂), 2.46 br.s (3H, CH₃), 3.78 part X of the ABX spectrum (1H, HC⁷, J_{AX} \approx J_{BX} \approx 6), 4.23 part AB of the ABX spectrum (2H, CH₂O, J_{AX} \approx J_{BX} \approx 6, J_{AB} = 11, δ = 0.12), 7.36 and 7.81 br.d (4H, C₆H₄, J = 9). Mass spectrum (m/z): 326 (M⁺). Calculated for C₁₆H₂₂O₅S: mol. wt. 326.4.

A vigorously stirred suspension of 0.73 g (2.24 mmoles) of the above tosylate and 0.23 g (6.06 mmoles) of LiAlH₄ in 10 ml of THF was boiled for 6 h, and then decomposed according to [12] by a Na₂SO₄·10H₂O-celite mixture (1:1 by volume). The precipitate was filtered, washed on the filter with ether, and the combined filtrate was evaporated at 60°C. Yield ~0.4 g of a product, which was chromatographed on 15 g of SiO₂. Gradient elution from pentane to ether (up to 15% of the latter) gave 0.13 g (37%) of endo-(XIV) in the form of a colorless liquid, bp 83-84° (78 mm), $n_D^{2^0}$ 1.4416. IR spectrum (v, cm⁻¹): 840, 940, 1090, 1120, 1180, 1250, 1270, 1380, 1450, 2860, 2940, 2990. PMR spectrum (δ , ppm, J, Hz): 1.17 and 1.42 s (6H, CH₃), 1.26 d (3H, CH₃, J = 6.5), 1.5-2.1 m (6H, CH₂), 3.76 d.q (1H, HC⁷, J = 6.5 and J = 1.5). Mass spectrum (m/z): 156 (M⁺), 128, 112, 96, 85, 71, 69; calculated for C₉H₁₆O₂: mol. wt. 156.2.

 $\frac{\text{exo-1,5,7-Trimethyl-6,8-dioxabicyclo[3.2.1]octane exo-(XIV).}{\text{g (3.08 mmoles) of exo-(XIII) in 1.2 ml (14.8 mmoles) of pyridine and 0.68 g (3.57 mmoles) of TsCl, ~1 g of a product was obtained, which was chromatographed on 30 g of SiO₂. Gradient elution from hexane to ether (up to 30% of the latter) gave 0.92 g (92%) of a tosylate of the exo-(XIII) alcohol in the form of colorless crystals, mp 100-102°C (ether-hexane). IR spectrum (v, cm⁻¹): 830, 980, 1000, 1120, 1180, 1190, 1370, 1450, 1600, 2928, 2950, 2990, 3020. PMR spectrum (<math>\delta$, ppm, J, Hz): 1.21 and 1.29 s (6H, CH₃), 1.5-1.9 m (6H, CH₂), 2.46

br.s (3H, CH₃), 3.7-4.1 m (3H, HC⁷, CH₂O), 7.36 and 7.81 br.d (4H, C₆H₄, J = 9). Mass spectrum (m/z): 326 (M⁺) calculated for $C_{16}H_{22}O_5S$: mol. wt. 326.4.

As described in the preceding experiment, from 1.04 g (3.19 mmoles) of the above tosylate and 0.3 g (7.91 mmoles) of LiAlH₄ in 12 ml of THF ~0.6 g of a product was obtained, which was chromatographed on 20 g of SiO₂. Gradient elution from pentane to ether (up to 15% of the latter) gave 0.29 g (58%) of exo-(XIV) in the form of a colorless liquid, bp 89-90°C (70 mm), n_D^{20} 1.4392. IR spectrum (v, cm⁻¹): 940, 1030, 1080, 1120, 1180, 1250, 1380, 1440, 1460, 2840, 2880, 2980. PMR spectrum (δ , ppm, J, Hz): 1.06 d (3H, CH₃, J = 6), 1.18 and 1.39 s (6H, CH₃), 1.4-1.9 m (6H, CH₂), 4.04 q (1H, HC⁷, J = 6). Found, %: C 69.38, H 10.41; 156 (M⁺). C₉H₁₆O₂. Calculated, %: C 69.19, H 10.32; mol. wt. 156.2.

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