CONCLUSIONS

The reactions of nopyl tosylates and 4α -hydroxymethyl- Δ^2 -carene with Et₃Al and (i-Bu)₃Al are accompanied by skeletal rearrangements, leading to bi- and tricyclic hydrocarbons, containing small rings. The previously unknown rearrangement of nopyl tosylate into brendane series of hydrocarbons has been established.

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REDUCTIVE TRANSFORMATION OF ISOPRENOID CYCLOSULFONATES INTO LINEAR HOMOALLYLIC ALCOHOLS AND AMINES

HONORELIDIC RECONCES AND ANIMES

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In continuation of the study of the chemical properties of the isoprene (Ia), myrcene (Ib) and ocimene (Ic) sultones, previously described by us in [1], in the present article we discuss their reductive transformation into the corresponding allylsulfinic acids (II). As known [2], these compounds are unstable and readily undergo desulfonylation, as shown in the scheme, with the formation of the corresponding olefins (III). The use of this retroenic reaction opens the possibility of the synthesis of the difficultly obtainable linear isoprenoid homoallylic alcohols and related amines from the appropriate cyclosulfonates of series (I).

The reductive cleavage of the S-O bond in sultones (Ib, c) as a direct route to the preparation of sulfinic acids (II), as in the case of the previously studied isoprene representative (Ia), was found to be inapplicable in view of the preferential hydrogenolysis of the C-O bond [1]. On the other hand, as we already have shown [3], sultone (Ia) can be readily converted into the sulfonyl chloride (IVa) and be further reduced by the method in [4] by the action of 2 mole equivalents of PhMgBr into a Mg sulfinate of series (V). It was found that its treatment with water gives benzoate (IIIa) in an almost quantitative

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1820-1823, August, 1985. Original article submitted April 6, 1984. yield, which in its properties is identical with the benzoylation product of 3-methylbut-3enol. In a similar way, cyclosulfonates (Ib, c) were transformed into acid chlorides (IVb, c), and then into the corresponding benzoates (IIIb, c) in an overall yield of \sim 50%. A hydride reduction of (IIIb, c) led to myrcenol (VI), whose PMR spectrum was identical with that described in [5] for this monoterpenol, while from (IIIc), by the same method, isogeraniol (VII) was obtained that was identified by a direct comparison (PMR, GLC) with an authentic sample [6].



We also studied the reduction of sulfonyl chlorides (IV) by the method in [7] by means of Zn in AcOH. In the case of the slowly proceeding reaction with (IVa) in the range of 50-70°C, clearly via the stage of Zn sulfinate of series (V) and the corresponding acid



(II), the yield of the benzoate (IIIa) is $\sim 60\%$, while on transition from (Vb, c) to (IIIb, c) it does not exceed 20\%, possibly because of the competitive electrophilic cyclization of the initial and final dienes. Nevertheless, this method was found to be applicable for the reduction of betains (VIIIa, b), which are readily obtainable from sultone (Ia) [8]. Thus, conversion of the latter by the action of POCl₃ into the intermediate acid chlorides and their treatment without addition purification by excess Zn in AcOH medium gave after the alkalization of the reaction mixtures the corresponding tertiary amines (IXa, b) in a yield of up to 50\%. The structure of (IXa, b) follows from the data of PMR spectra, containing broadened signals of the methyl ($\delta \sim 1.70$ ppm) and vinyl ($\delta \sim 4.65$ ppm) protons characteristic of the isopropenyl fragment, and was confirmed by the elemental analysis of their hydrochlorides.

EXPERIMENTAL

The IR spectra (in $CHCl_3$) were obtained on a UR-20 apparatus. The PMR spectra were measured with reference to TMS on Varian DA-60-IL or Tesla BS-497 spectrometers (100 MHz). The GLC was carried out on a LKhM-8M chromatograph with a 2.5 mm × 70 m glass capillary column with OV 17 or SE-20. The Rf values were measured on plates with a fixed Silufol brand SiO₂ layer.

<u>1-Benzoyloxy-3-methylbut-3-ene (IIIa).</u> A suspension of Mg sulfinate (V, R = R¹ = H) and Mg salts (5 g), obtained as described in [3], from 2.9 g (10 mmoles) of (IVa) in 60 ml of ether and 22 ml (22 mmoles) of a 1 M solution of PhMgBr in ether, in 80 ml of hexane and 50 ml of H₂O was stirred for 1 h at 25°C. The hexane layer was separated, dried over MgSO₄, and evaporated in vacuo. Yield, 1.77 g (93%) of (IIIa) in the form of colorless oil, bp 89°C (1 mm), n_D^{25} 1.5105. PMR spectrum (CCl₄, δ , ppm): 1.80 br. s (3H, CH₃), 2.44 br t (2H, CH₂, J = 7 Hz), 4.36 t (2H, CH₂O, J = 7 Hz), 4.76 br. s (2H, H₂C=C), 7.8-8.6 m (5H, C₆H₅). Found: C 75.46; H 7.56%. C₁₂H₁₄O₂. Calculated: C 75.76; H 7.42%.

A 2 g portion of Zn dust was added to a solution of 0.8 g of (IVa) in 25 ml of AcOH. The suspension was stirred for 1 h at 50°C, and after the addition of 1 g of Zn dust, for another hour. The mixture was filtered, the residue was washed on the filter with AcOH. The filtrate was diluted twofold with H_2O and neutralized with Na_2CO_3 in the presence of ether. The subsequent conventional treatment of the ethereal solution gave 0.34g (65%) of (IIIa) that was identical (GLC, PMR) with the above described sample.

Compound (IIIa) was obtained in a yield of 90% by benzoylation of 3-methylpent-3-enol under standard conditions.

<u>4-Benzoyloxy-2-(4'-methylpent-3'-en)ylbut-2Z-ene-1-sulfonyl Chloride (IVb).</u> A 0.5 M KOH solution was added dropwise to an emulsion of 0.81 g of (Ib) [1] in 30 ml of H_2O , placed in a pH-meter chamber and vigorously stirred at 45°C, at a rate which allowed us to maintain the pH of the medium between 7 and 9, while at the end of the reaction the pH should have been 7.3. After evaporation in vacuo, 0.98 g (98%) of the potassium salt of 4-hydroxy-2-(4'-methylpent-3'-en)ylbut-2z-ene-1 sulfonic acid was obtained in the form of a light-yellow powder. PMR spectrum (CD₃OD, δ , ppm): 1.60 and 1.67 br. s (6H, CH₃), 2.2 m (4H, CH₂), 3.62 br. s (2H, CH₂S), 4.13 d (2H, CH₂O, J = 7 Hz), 5.08 br. t (1H, HC^{3'}, J = 7 Hz), 5.61 br. t (2H, HC³, J = 7 Hz).

The benzoate was obtained according to [3] as a light yellow powder. IR spectrum (v, cm⁻¹): 690, 718, 760, 1040, 1115, 1180, 1276, 1453, 1491, 1714 (KBr). PMR spectrum (CD₃OD, δ , ppm): 1.56 br. s (6H, CH₃), 2.3 m (4H, CH₂), 3.76 br. s (2H, CH₂S), 4.93 d (2H, CH₂O, J = 7 Hz), 5.15 br. t (1H, HC³', J = 7 Hz), 5.66, br. t (1H, HC³, J = 7 Hz), 7.3-8.0 m (5H, C₆H₅).

A suspension of 0.85 g of the above benzoate in 6 ml of $POCl_3$ was stirred for 30 min at 25°C, excess $POCl_3$ was distilled off in vacuo at 50°C, and the residue was treated with ether. The ethereal solution was washed with H_2O , neutralized with NaHCO₃, and dried over MgSO₄. The solution was evaporated in vacuo, and the residue (0.73 g) was chromatographed on 30 g of SiO₂. A gradient elution from hexane to ether (up to 30% of the latter) gave 0.6 g (80%) of (IVb) in the form of a light yellow oil, Rf 0.53 (ether-hexane, 1:9). IR spectrum (v, cm⁻¹): 950, 1030, 1070, 1110, 1170, 1280, 1380, 1455, 1710. PMR spectrum (CCl₄, δ , ppm): 1.59 br. s (6H, CH₃), 2.3 m (4H, CH₂), 4.66 br. s (2H, CH₂S), 4.87 d (2H, CH₂O, J = 7 Hz), 4.98 br. t (1H, HC³⁺, J = 7 Hz), 5.92 br. t (1H, HC³, J = 7 Hz), 7.3-8.1 m (5H, C₆H₅).

<u>1-Benzoyloxy-3,7-dimethylocta-2Z,6-diene-4-sulfonyl Chloride (IVc).</u> As described for (Ib), from 0.9 g of (Ic) [1], 1.03 g (92%) of the potassium salt of 1-hydroxy-3,7-dimethyl-octa-2Z,6-diene-4-sulfonic acid was obtained in the form of a light yellow powder. PMR spectrum (CD₃OD, δ , ppm): 1.61, 166 and 1.84 br. s (9H, CH₃), 2.68 m (2H, HC⁵), 3.71 m (1H, HC⁴), 4.05 d (2H, CH₂O, J = 7 Hz), 4.96 br. t (1H, HC⁶, J = 7 Hz), 5.39 br. t (1H, HC², J = 7 Hz).

A suspension of 0.9 g of the above salt and 0.3 g of Py in 10 ml of PhCOCl was stirred at 25°C for 2 h, washed with ether, and evacuated. The residue (1.8 g) was suspended in 10 ml of POCl₃, the suspension was stirred at 25°C for 30 min, and treated as described for (IVb). Yield: 0.62 g of a product which was chromatographed on 30 g of SiO₂. By a gradient elution from hexane to ether (up to 30% of the latter), 0.37 g (30%) of (IV)c) were isolated in the form of a light yellow oil. PMR spectrum (CCl₄, δ , ppm): 1.56, 1.64 and 1.90 br. s (9H, CH₃), 2.43 m (2H, HC⁵), 4.26 (1H, HC⁴), 4.54 d (2H, CH₂O, J = 7 Hz), 4.94 br. t (1H, HC⁶, J = 7 Hz), 5.58 br. t (1H, HC², J = 7 Hz), 7.3-7.9 m (5H, C₆H₅).

<u>1-Benzoyloxy-3-methylene-7-methyloct-6-ene (IIIb).</u> A 4.2 ml portion (3.7 mmoles) of 0.88 M solution of PhMgBr in ether was added in the course of 2 min to a solution of 0.66 g (1.85 mmoles) of (IVb) in 30 ml of ether, stirred at -50° C. The mixture was heated in the course of 15 min to 25°C, the precipitate that separated was filtered, washed with ether and evacuated. Yield: 0.7 g of Mg sulfinate (V, R = H, R¹ = CH₂CH=CMe₂) in a mixture with Mg salts, which was suspended in 30 ml of ether and 15 ml of H₂O, and acidified by 5% H₂SO₄ to pH 3. The ethereal layer was separated, the aqueous layer was extracted with ether, and the combined extract was neutralized with NaHCO₃, washed with water, and dried over MgSO₄. The solution was evaporated in vacuo, and the residue (0.64 g) was chromatographed on 30 g of SiO₂. Gradient elution from hexane to ether (up to 50% of the latter) gave 0.26 g (52%) of (IIIb) in the form of colorless oil, Rf 0.65 (benzene-hexane, 3:2). IR spectrum (v, cm⁻¹): 710, 900, 1120, 1280, 1380, 1455, 1720. PMR spectrum (CCl₄, δ , ppm): 1.63

and 1.70 br. s (6H, CH₃), 2.1 m (4H, CH₂), 2.45 br. t (2H, HC², J = 7 Hz), 4.36 t (2H, CH₂O, J = 7 Hz), 4.82 br. s (2H, H₂C=C), 5.04 br. t (1H, HC⁶, J = 7 Hz), 7.4-8.0 m (5H, C₆H₅). Mass spectrum, m/z (relative intensity, %): M⁺ 258 (10), 153 (100), 105 (75). $C_{1,7}H_{2,2}O_2$. Calculated: mol. wt. 258.4.

<u>Myrcenol (VI).</u> A 1.6 ml portion (1.1 mmoles) of a 0.7 M solution of LiAlH₄ in THF was added to a stirred solution (-20°C) of 0.14 g (0.54 mmole) of (IIIb) in 5 ml of THF. The mixture was allowed to stand at -20°C for 40 min, and was then diluted with ether and decomposed by 5% H₂SO₄. The subsequent conventional treatment gave 0.14 g of a substance, which was chromatographed on a plate (13 × 20 cm) with a nonstationary layer (2 mm) of SiO₂ (100-160 mesh) in an ether-hexane system (1:1). From the zone with Rf 0.5-0.7, 50 mg (60%) of (VI) were isolated in the form of a colorless oil. PMR spectrum (CDCl₄, δ , ppm): 1.60 and 1.67 br. s (6H, CH₃), 2.0 m (4H, CH₂), 2.23 br. t. (2H, HC², J = 7 Hz), 3.58 br. t (2H, CH₂O, J = 7 Hz), 4.72 br. s (2H, H₂C=C), 5.10 br. t (1H, HC⁶, J = 7 Hz) (cf [5]).

<u>1-Benzoyloxy-3,7-dimethoxyocta-3R,6-diene (IIIc)</u> was obtained as described above for (IIIb), from 0.37 g (1.04 mmole) of (IVc) and 2.4 ml (2.11 mmoles) of a 0.88 M ethereal solution of PhMgBr in 20 ml of ether. Yield: 150 mg (55%) of (IIIc) in the form of a colorless oil, Rf 0.60 (benzene-hexane, 3:2). IR spectrum (ν , cm⁻¹): 1120, 1275, 1455, 1720. PMR spectrum (CCl₄, δ , ppm): 1.59, 163 and 1.76, br. s (9H, CH₃), 2.15 m (2H, HC²), 2.5 m (2H, HC⁵), 4.74 t (2H, CH₂O, J = 7 Hz), 5.5 m (2H, HC=C), 7.4-7.9 m (5H, C₆H₅). Found: M⁺ 258. C₁₇H₂₂O₂. Calculated: mol. wt. 258.4.

Isogeraniol (VII) was obtained as described above for (IIIb), from 0.11 g (0.43 mmole) of (IIIc) in 5 ml of THF and 1.5 ml (1 mmole) of a 0.7 M solution of LiAlH₄ in THF. Yield: 35 mg (53%) of (VII) that was identical (PMR, GLC) with an authentic [6] sample of isogeraniol.

<u>1-Dimethylamino-3-methylbut-3-ene (IXa)</u>. A suspension of 5.75 g of (VIIIa) [8] in 45 ml of POCl₃ was stirred for 1 h at 50°C to complete dissolution of the precipitate, the POCl₃ was evaporated in vacuo, and the residue was dissolved in 50 ml of AcOH containing 4 g of Zn dust. The mixture was stirred for 40 min at 50°C, the unreacted Zn was filtered, washed with water, and the filtrate was evaporated in vacuo. The residue (8 g) was dissolved in water, 5% NaOH was added to pH 10, and the base that separated was extracted with ether. The conventional treatment of the extract gave 0.9 (30%) of (IXa) in the form of a colorless liquid, bp 118-120°C. PMR spectrum (CCl₄, δ , ppm): 1.74 br. s (3H, CH₃), 2.2 m (8H, CH₃N, HC²), 2.82 br. t (2H, HC¹, J = 7 Hz), 4.64 br. s (2H, H₂C=C).

Hydrochloride - colorless prisms, mp 300°C (decomp.) (MeOH-ether). Found: Cl 22.89%. $C_{7}H_{16}NCl$. Calculated: Cl 23.17%.

<u>l-Piperidino-3-methylbut-3-ene (IXb)</u>. Similarly, from 2.83 g of (VIIIb) (15 ml of POCl₃, 30 min, 50°C), 2.5 g of proudct was obtained, treatment of which with 7.5 g of Zn dust in 40 ml of AcOH (2 h, 40°C) gave 1.g (50%) of (IXb) in the form of colorless liquid, bp 38°C (6 mm), n_D^{25} 1.4627. PMR spectrum (CCl₄, δ , ppm): 1.5 m (6H, CH₂), 1.72 br. s (3H, CH₃), 2.1-2.4 m (8H, CH₂N, HC²), 4.64 br. s (2H, H₂C=C).

Hydrochloride -- colorless prisms, mp 300°C (decomp.) (MeOH-ether). Found: C 63.23; H 10.54; N 7.72; Cl 18.55%. C₁₀H₂₀NCl. Calculated: C 63.31; H 10.63; N 7.38; Cl 18.67%.

CONCLUSIONS

Isoprene, myrcene, and ocimene sultones were converted into the corresponding linear homoallylic alcohols and amines via the stage of desulfonylation of the in situ generated allylsulfinic acids. A new synthesis of myrcenol and isogeraniol has been carried out.

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