SYNTHESIS AND PROPERTIES OF UNSATURATED THIETANES

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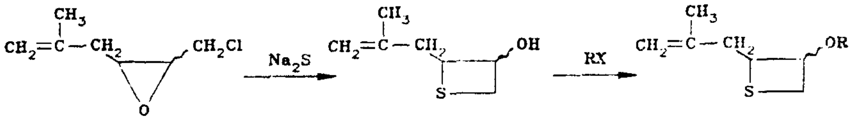
Reaction of unsaturated epichlorohydrins with sodium sulfide in aqueous-alcoholic solution leads to 3-hydroxythietanes. Ethers of the latter can be prepared by phase transfer catalysis using acetic anhydride and alkyl halides.

Thietanes can be obtained from thioepichlorohydrin and potassium hydroxide [1] but also via aliphatic alcohols, containing the thietane ring, from dichloro alcohols and alkali metal sulfides [2]. The synthesis of unsaturated thietanes is of interest both in terms of a search for biologically active materials and for the synthesis of novel heterocyclic systems.

Reaction of a mixture (4:1) of trans- and cis-5-methyl-1-chloro-2,3-epoxyhex-5-enes (Ia, b) with an aqueous-alcoholic solution of sodium sulfide gives a 60% yield of the stereoisomers of 2-(2-methylpropen-2-yl)-thietan-3-ols (IIa, b). The structure and configuration of alcohols IIa, b were confirmed by IR and PMR spectroscopic data and by chemical transformations. The IR spectra of IIa, b show intense bands at 3360-3410 cm^{-1} which are assigned to OH group absorption and also to bands near 1645 cm^{-1} for the C=C bond.

Treatment of the alcohols IIa, b with acetic anhydride in the presence of pyridine gives a 3.3:1 mixture of acetates IIIa and IIIb. Under phase transfer conditions [3] IIa, b and alkyl halides give the ethers IVa, b-VIa, b in around 90% yield. The structures of IIIa, b-VIa, b were also confirmed by IR and PMR spectroscopy. According to the PMR data, ethers VIa, b exist in the ratio 3.7:1. In agreement with the stereochemical composition of ethers III and VI, the alcohols IIa and IIb exist as a 3.5:1 mixture in the starting material.



Ia, b IIa, b IIa, b-VIa, b

III R=CH_3CO; IV R=$H_2C{=}CHCH_2$; V R=$C_6H_5CH_2$; VI R=$HC{\equiv}CCH_2$, a trans;
b cis

EXPERIMENTAL

The GLC analysis was carried out on an LKhM-8MD instrument with thermal conductivity detector, steel column (1000 × 3 mm) with 15% PEGA on Dinakhrome, helium bas carrier, and column temperature of 90-140°C. The PMR spectra were recorded on Bruker 250 MHz and Tesla BS-487 (80 MHz) instruments using CCl_4 or $CDCl_3$ solvent and HMDS internal standard. The IR spectra were taken on Specord-80 or UR-20 instruments as thin films.

Stereoisomers of 2-(2-Methylpropen-2-yl)thietan-3-ol (IIa, b, $C_7H_{12}OS$). A mixture of Ia, b (14.6 g, 110 mmoles) [4], $Na_2S \cdot 9H_2O$ (31 g, 130 mmoles), water (70 ml), and ethanol (75 ml) was stirred for 4 h at 60-70°C, cooled, extracted with ether (3 × 50 ml), and the extracts dried over $MgSO_4$. Removal of ether under reduced pressure gave a residue which was distilled in vacuo to give IIa, b (8.6 g, 60%) with bp 98-99°C (1 hPa), n_D^{20} 1.5228, and d_4^{20} 1.0601. Found MR_D 41.55; calculated 41.65. IR spectrum: 3446-3360 (OH), 1645 cm^{-1} (C=C). PMR spectrum for IIa: 4.70 (1H, s, CH_2=);

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4.68 (1H, s, CH_2=); 4.34 (1H, quint, J = 8 Hz, CHO); 3.44 (1H, d, J = 8 Hz, OH); 3.77 (1H, ddd, J = 9, 8, 5 Hz, SCH); 3.08 (2H, d, J = 8 Hz, SCH_2); 2.56 (1H, dd, J = 15, 5 Hz, CH_2); 2.24 (1H, dd, J = 15, 9 Hz, CH_2); 1.66 ppm (3H, s, CH_3). For IIb: 4.76 (1H, s, CH_2=), 4.63 (1H, s, CH_2=); 4.95 (1H, quint, J = 8 Hz, CHO); 3.77 (1H, ddd, J = 9, 8, 5 Hz, SCH); 3.23 (2H, d, J = 8 Hz, SCH_2); 3.20 (1H, d, J = 8 Hz, OH); 2.61 (1H, dd, J = 15, 5 Hz, CH_2); 2.44 (1H, dd, J = 15, 9 Hz, CH_2); 1.68 ppm (3H, s, CH_3).

3-Acetoxy-2-(2-methylpropen-2-yl)thietane (IIIa, b, $C_9H_{14}O_2S$). A mixture of IIa, b (2 g, 14 mmoles), acetic anhydride (3 g, 29 mmoles), and pyridine (2 g) was heated for 2 h on a steam bath, poured into ice, acidified with HCl, and extracted with chloroform. Removal of solvent gave IIIa, b (2 g, 80%) with bp 102-103°C (7 hPa), n_D^{20} 1.4916, and d_4^{20} 1.0582. Found: MR_D 51.02; calculated 51.17. PMR spectrum for IIIa: 5.19 (1H, q, J = 8 Hz, CHO); 4.66 (1H, s, H_2C=); 4.60 (1H, s, H_2C=); 3.90 (1H, ddd, J = 10, 8, 5 Hz, SCH); 3.13 (2H, d, J = 8 Hz, SCH_2); 2.54 (1H, dd, J = 15, 5 Hz, CH_2); 2.26 (1H, dd, J = 15, 10 Hz, CH_2); 1.93 (3H, s, CH_3CO); 1.62 (3H, s, CH_3). For IIIb, 5.69 (1H, q, J = 8 Hz, CHO); 4.72 (1H, s, H_2C=); 4.58 (1H, s, H_2C=); 3.80 (1H, q, J = 8 Hz, SCH); 3.46 (1H, t, J = 8 Hz, SCH_2); 3.20 (1H, t, J = 8 Hz, SCH_2); 2.45 (2H, d, J = 8 Hz, CH_2); 1.94 (3H, s, CH_3CO): 1.62 ppm (3H, s, CH_3).

3-Allyloxy-2-(2-methylpropen-2-yl)thietane (IVa, b, $C_{10}H_{16}OS$). A mixture of IIa, b (2 g, 14 mmoles), allyl bromide (8.2 g, 68 mmoles), benzyltriethylammonium chloride (0.3 g), sodium hydroxide (50%, 7 ml), and benzene (50 ml) is stirred for 5 h at 40-45°C. Appropriate workup gives IVa, b (2.3 g, 90%) with bp 66-67°C (1 hPa), n_D^{20} 1.4976, d_4^{20} 0.9873. Found: MR_D 54.68, calculated 55.38. IR spectrum: 1645 (C=C), 1024-1292 cm^{-1} (COC). PMR spectrum: 5.85 (1H, ddt, J = 17, 10, 6 Hz, HC=); 5.25 (1H, dq, J = 17, 2 Hz, H_2C=); 5.16 (1H, dq, J = 10, 2 Hz, H_2C=); 3.90 (2H, m, CH_2O); for IVa: 4.72 (1H, s, H_2C=); 4.69 (1H, s, H_2C=); 4.14 (1H, q, J = 7 Hz, CHO); 3.90 (1H, m, SCH); 3.13 (1H, t, J = 7 Hz, SCH_2); 3.07 (1H, t, J = 7 Hz, SCH_2); 2.61 (1H, dd, J = 15, 5 Hz, CH_2); 2.29 (1H, dd, J = 15, 10 Hz, CH_2); 1.69 (3H, s, CH_3); for IVb: 4.78 (1H, s, H_2C=); 4.64 (1H, s, H_2C=); 3.90 (1H, m, SCH); 3.76 (1H, q, J = 8 Hz, CHO); 3.38 (2H, t, J = 8 Hz, SCH_2); 2.61 (1H, dd, J = 15, 5 Hz, CH_2); 2.29 (1H, dd, J = 15, 10 Hz, CH_2); 1.71 ppm (3H, s, CH_3).

3-Benzyloxy-2-(2-methylpropen-2-yl)thietane (Va, b, $C_{14}H_{18}OS$). Reaction of alcohol II (9 g, 63 mmoles), benzyl chloride (32 g, 250 mmoles), triethylbenzylammonium chloride (1.3 g), NaOH (50%, 6 g), and benzene (60 ml) similarly to IIIa, b gave Va, b (13.3 g, 91%) with bp 145-146°C (1 hPa), n_D^{20} 1.5476, d_4^{20} 1.0484. Found: MR_D 70.95, calculated 70.96. According to PMR the Va:Vb isomer ratio was 4:1. PMR spectrum: 7.35 (5H, m, C_6H_5); Va: 4.80 (1H, s, H_2C=); 4.76 (1H, s, H_2C=); 4.50 (1H, d, J = 12 Hz, OCH_2); 4.48 (1H, d, J = 12 Hz, OCH_2); 4.25 (1H, q, J = 8 Hz, CHO); 4.03 (1H, ddd, J = 10, 8, 5 Hz, SCH); 3.22 (1H, t, J = 8 Hz, SCH_2); 3.07 (1H, t, J = 8 Hz, SCH_2); 2.62 (1H, dd, J = 14, 5 Hz, CH_2); 2.33 (1H, dd, J = 14, 10 Hz, CH_2); 1.74 (3H, s, CH_3); Vb: 4.87 (1H, s, H_2C=); 4.76 (1H, s, H_2C=); 4.47 (2H, s, OCH_2); 3.83; (1H, q, J = 8 Hz, CHO); 3.50 (2H, t, J = 8 Hz, SCH_2); 2.68 (2H, d, J = 7 Hz, CH_2); 1.77 ppm (3H, s, CH_3).

2-(2-Methylpropen-2-yl)-3-propargyloxythietane (VIa, b, $C_{10}H_{14}OS$). Reaction of II (5 g, 35 mmoles), propargyl bromide (8 g, 67 mmoles), NaOH (50%, 7 g), triethylbenzylammonium chloride (1.3 g), and benzene (60 ml) gave VIa, b (5.6 g, 89%) with bp 105-106°C (8 hPa), n_D^{20} 1.5104, d_4^{20} 1.0153. Found: MR_D 53.73, calculated 53.67. IR spectrum: 3300 and 2100 ($C\equiv CH$), 1645 (C=C), 1275, 1150-1100 cm^{-1} (COC). PMR spectrum: 4.95 (2H, m, H_2C=); 4.70 (1H, m, CHO); 4.37 (2H, m, CH_2O); 4.12 (1H, m, SCH); 3.04 (2H, m, SCH_2); 2.95-2.12 (3H, m, CH_2, $\equiv CH$); 1.85 ppm (3H, s, CH_3).

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