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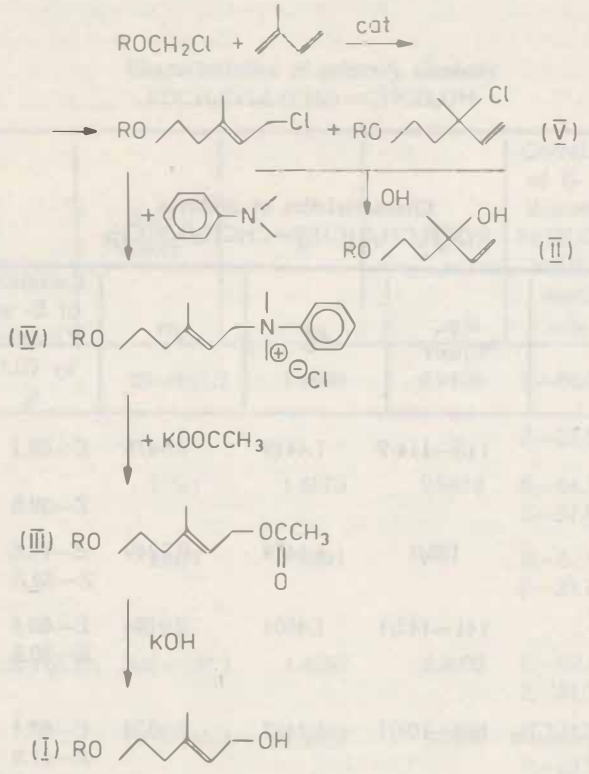
SYNTHESIS AND FRAGRANT CHARACTERISTICS OF METHYLPENTENOL 5-OXA-DERIVATIVES

Many oxa-compounds are known as fragrances, for example ethers (benzyl phenyl ether, isoamyl benzyl ether etc.) and oxa-derivatives with various functional groups (anisaldehyde, eugenol, vanillin, phenoxyacetaldehyde, phenoxyethyl acetate, etc.) [1]. A new interesting fragrance is cyclogalbamat (cyclohexoxyallylacetate) with fragrant characteristics green, galbanum, very tenacious [2].

In this work the synthesis of methylpentenol 5-oxa-derivatives was carried out according to the following scheme:



These compounds have been synthesized from chloromethyl ethers and isoprene [3]. From adducts (V) of chloromethyl ethers and isoprene tertiary alcohols (II) which are fragrances were synthesized by hydroxylation. The primary adducts were separated from total adducts as water-soluble quaternary salts (IV) obtained with dimethylaniline [3]. From the quaternary salts esters (III) which are fragrances were synthesized. From the latter primary alcohols (I) which are also fragrances [4, 5] were synthesized.

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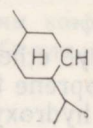
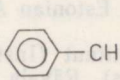
Experimental

1. Synthesis of tertiary alcohols (II)

To 30.0 g (0.13 mole) of cyclohexylchloromethyl ether, 10.5 g (0.16 mole) of isoprene, 30.0 ml of petrol ether and 2.0 ml of a 3% solution of tin tetrachloride in dichloroethane was added and stirred at 20—28 °C for 2 h. Then the mixture was washed with water. The unreacted substances and solvent were distilled off. To the 24.3 g of residue (adduct, V) 20 ml of toluene, 120 ml of water and 12.0 g of sodium hydrocarbonate was added and stirred at 95—100 °C for 24 h. Then the layers were separated. The organic layer was washed with water, toluene was distilled and from the residue alcohols were distilled in vacuum at 120—130 °C/1 torr, n_D^{20} 1.5142. The yield of alcohols was 15.6 g (82% of the chlorine compounds of the adduct): 63% 5-cyclohexoxy-3-methyl-1-pentene-3-ol and 30% 5-cyclohexoxy-3-methyl-2-pentene-1-ol (22% E- and 8% Z-isomer). Fragrant characteristic: fruity.

Table 1

Characteristics of acetates
$ROCH_2CH_2C(CH_3)=CHCH_2OOCCH_3$

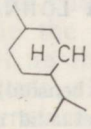
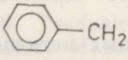
No.	R	B.p., °C/torr	n_D^{20}	d_4^{20}	Correlation of E- and Z-isomers by GLC, %	Fragrant characteristics
1	n-C_4H_9	113—114/2	1.4449	0.9476	E—65.1 Z—32.5	fruity, green
2	n-C_6H_{13}	125/1	1.4479	0.9249	E—64.6 Z—32.3	fruity, sweet
3	n-C_8H_{17}	141—142/1	1.4504	0.9154	E—63.5 Z—30.8	fruity, oily, faint
4	$(CH_3)_2CHCH_2CH_2$	102—104/1	1.4457	0.9276	E—63.1 Z—31.8	fruity, fatty
5		143—149/1	1.4696	0.9527	menthyl E—50.2 Z—10.3 isomenthyl E—28.3 Z— 6.8	fruity, camphoric, warm, faint
6		127—129/1	1.4710	0.9856	E—69.0 Z—29.8	fruity, green
7		157—159/1	1.5060	1.0991	E—67.2 Z—23.9	fruity, green, faint

2. Synthesis of esters (III)

24.0 g of adduct [3] of cyclohexylchloromethyl ether and isoprene, 19.5 g of dimethylaniline and 60 ml of methanol were left to stand for 24 h. Then 50 ml of water and 50 ml of petrol ether was added and the mixture was stirred. The water-methanol solution was separated and washed with petrol ether. From the water-methanol solution methanol was evaporated at 35 °C/250 torr. From the water solution the quaternary salt (IV), N-(5-cyclohexoxy-3-methyl-2-pentene-1-yl)-N,N-dimethyl-N-phenylammonium chloride was salted with potash. The quaternary salt was separated and 100 ml toluene was added. Part of toluene was distilled. Then 4.5 g of potassium acetate was added and stirred at 100—110 °C for 4 h. The mixture was washed with 5% hydrochloric acid, 5% sodium carbonate and water. Then toluene was distilled and from the residue the acetate of 5-cyclohexoxy-3-methyl-2-pentene-1-ol was distilled in vacuum. The yield was 8.7 g (57.2% of the chlorine compounds of the adduct). The product is characterized in Table 1, No. 6.

Table 2

Characteristics of primary alcohols
$ROCH_2CH_2C(CH_3)=CHCH_2OH$

No.	R	B.p., °C/torr	n_D^{20}	d_4^{20}	Correlation of E- and Z-isomers by GLC and NMR ^{13}C spectra, %	Fragrant characteristics
1	n-C_4H_9	99—101/1	1.4560	0.9138	E—66.5 Z—32.9	fruity
2	n-C_6H_{13}	115/1	1.4573	0.9018	E—64.1 Z—31.9	fruity
3	n-C_8H_{17}	131/1	1.4591		E—61.0 Z—29.1	fruity, fatty, faint
4	$(CH_3)_2CHCH_2CH_2$	100—102/1	1.4552	0.9032	E—62.4 Z—31.7	fruity, fatty
5		140—145/1	1.4807	0.9396	menthyl E—51.5 Z—10.0 isomenthyl E—28.2 Z— 7.1	fruity, camphoric, warm, faint, green
6		122—124/1	1.4843	0.9721	E—69.1 Z—29.2	fruity, cinnamonic, jasmin, green
7		150—152/1	1.5262	1.0288	E—68.0 Z—23.1	fruity, woody, faint

3. Synthesis of primary alcohols

4.8 g of acetate of 5-cyclohexoxy-3-methyl-2-pentene-1-ol, 1.1 g of potassium hydroxyde and 15 ml of ethanol were refluxed for 3 h. Ethanol was evaporated. The residue was dissolved in toluene and filtered. Toluene was evaporated and from the residue 5-cyclohexoxy-3-methyl-2-pentene-1-ol was distilled in vacuum. The yield was 3.4 g (86%). The product is characterized in Table 2, No. 6.

GLC. Alcohols and acetates were analysed using a Chrom 5 chromatograph with a glass capillary column (47 m×0.3 mm) coated with phenyl diethanolamine succinate at 150 °C, sampler 260 °C, carrier gas Ar (1.5 cm^3/min).

NMR spectra were measured from $CDCl_3$ solutions on a Bruker AM-500 spectrometer.

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METÜÜLPENTENOOLI 5-OKSADERIVAATIDE SÜNTEES JA LÕHNA KARAKTERISTIKA

On sünteesitud metüülpentenooli 5-oksa-(alküül-, tsükloheksüül- ja bensüül)-derivaadid. Nii saadud tertsiaarsed kui ka primaarsed alkoholid ja nende atsetaadid on lõhnaained. Kõigil neil ühendeil on erinevate varjunditega puuviljalõhn.

Хейно РАНГ, Тынис ПЕХК, Сирье ВИЙТМАА, Койт ЛЭЭТС

СИНТЕЗ И ХАРАКТЕРИСТИКА ЗАПАХА 5-ОКСА-ПРОИЗВОДНЫХ МЕТИЛПЕНТЕНОЛА

Получен ряд 5-окса-(алкил-, циклогексил- и бензил)-производных метилпентенола, или третичных и первичных спиртов и их ацетатов, которые являются душистыми веществами, обладающими характерным фруктовым запахом разных оттенков.