

## UTILIZATION OF MENTHADIENS THROUGH ISOMERIZATION AND LIQUID PHASE OXIDATION

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### ABSTRACT

Systematic investigations on the isomerization and oxidative transformations of some menthadiens in the presence of different additives have been carried out. In the obtained reaction masses have been identified hydrocarbons, ketones, alcohols and oxides which are prospective raw materials for aromatic production, perfumery and cosmetics.

Keywords: limonene, isomerization product, oxidation product, additive, oxidation, selectivity, odour.

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### INTRODUCTION

Menthadiens with different position of the double bonds and available substitutes have high reaction ability and are interesting objects for obtaining intermediates and even final products for syntheses of important and scarce bioactive substances with interesting odour and other valuable characteristics. In this respect the products of the isomerization and their oxidation products are of particular attention. The isomerization can occur as a parallel process when the main transformation of the menthadiens is the oxidation or Prins reaction.

Usually the isomerization is conducted in the presence of catalysts, suitable for special transformations and based on preliminary available information. The isomeric products thus obtained are suitable for production of oxidized products. These transformations are usually carried out in liquid phase because of the more appropriate technological parameters [1, 2].

### EXPERIMENTAL

To implement the isomerization, oxidation and Prins reaction as accessible and suitable model compounds two limonenes have been chosen: L-limonene

and DL-limonene (dipentene) with purity 97 %<sub>mass</sub>. For the isomerization the following acids were used as additives: monochloroacetic, formic and sulfuric acids, as well as ion exchange resins (OK-80 and KS-10). The oxidation of limonenes and obtained during the isomerization menthadiens was carried out in two modes: kinetic study using pure oxygen as an oxidizing agent and at barbotage using purified dry air. The additives used were esters (tri-n-propylborat), metal salts (acetates, bromides, chlorides), naftenates, carbonates and aldehydes (benzaldehyde) as well as their combinations (benzaldehyde:acetate:anhydrous Na<sub>2</sub>CO<sub>3</sub> = 0.40:0.001:0.040 [2]). In some experiments the acetates are replaced by lithium or palladium chloride, copper bromide or cobalt acetate. In a series of oxidation monochlorobenzene was introduced as medium. Paraformaldehyde, acetic or formic acid as well as ion exchange resins were used as reagents in Prins reaction.

All transformations of initial and obtained menthadiens are conducted in standard glass installation at intensive mechanical or pneumatic stirring.

During the isomerization the temperature varied in the interval of 30-100°C, the duration of process was 6-12 hours and the revolutions of the mechanical stirrer 2000-2650 min<sup>-1</sup>. The obtained isomerides

were characterized by their appearance, refractive index ( $n_D^{20}$ ) and composition.

In the case of kinetic investigations the extent of oxidation and oxidizability of the final menthadiens were studied, and during the barbotage - the variations in the maximal selectivities obtained towards alcohols ( $c_{alc}$ ) and carbonyl compounds ( $c_{CB}$ ) [3,4]. The kinetic investigations were carried out at the following conditions: mass of the initial diene - 10 g, temperature 30 - 80°C, duration 1 - 4 h. The barbotage experiments were carried out at oxidizing agent rate 5 - 20 dm<sup>3</sup> h<sup>-1</sup>, temperature 60 - 100°C and blow period 4 - 6 h. The composition of some of the oxidation products was analyzed by gas chromatograph. The odour of all isomerides and oxidation products was determined organoleptically.

The products of isomerization and oxidation were analysed by a gas chromatograph with flame ionizing detector and a packed column filled with FFAP W/AWASTM on Chromosorb 60-80 mesh using argon as carrier gas and programmed temperature (120- 180°C).

## RESULTS AND DISCUSSION

Liquid phase isomerization of the utilized limonene in the presence of monochloroacetic acid (limonene: acidic reagent = 1.2 : 1.0) leads to 90.1 - 92.1 %<sub>mass</sub> isomerization products. The refractive indexes ( $n_D^{20}$ ) varied from 1.4796 to 1.4962. Their odour after saponification of chloroacetates and neutralization is freshly terpenic with interesting fruit and wood touch. Their colour varies from light yellow to different shades of brown. The composition of the isomerization products is:  $\beta$ -felandrene (25.1-37.7 %<sub>mass</sub>), sylvestrene (9.3-11.2 %<sub>mass</sub>), terpinolene (6.4-11.2 %<sub>mass</sub>),  $\alpha$ -terpinene

(5.1-9.5 %<sub>mass</sub>), 3,8-menthadien (3.9-5.3 %<sub>mass</sub>), terpinol (1.5-3.9 %<sub>mass</sub>), terpinhydrate (1.5-3.9 %<sub>mass</sub>). The content of terpinolene in the isomerization products is higher (17.3-24.2 %<sub>mass</sub>).

When the isomerization of limonenes was carried out with triple combination monochloroacetic acid:formic acid:sulfuric acid = 1.00:0.43:0.07, similar results were obtained at lower temperatures (30-45°C) and shorter contact time (6 - 8 h). The presence of high boiling products and resins was also decreased. The introduction of ion exchange resins (2 %<sub>mass</sub>) requires increasing of temperature up to 110-120°C and is completed for 20 - 24 h. The light brown isomerization products are characterized by resin shade of the odour. The content of felandrene and terpinolene is 9-10 %<sub>mass</sub> lower.

The oxidation of limonenes at 110 - 120°C in the presence of ion exchange resins (OK - 80) within 10 - 20 h results in yield of 84-92 %<sub>mass</sub> enriched with bergamyl acetate. Its concentration is over 78 %<sub>mass</sub>. The odour of the product is strong, fresh and fruit. Besides acetic acid this transformation can be made with formic acid too. The products obtained have interesting odour characteristics as well. Tender floral odour is clearly expressed. Prospective for application is the product obtained with the participation of paraformaldehyde containing over 67 %<sub>mass</sub> bergamilate.

The kinetics of dipentene oxidation has been studied more intensively, because compared to limonene it is more easily available product. At temperature 60°C and duration of the process about 1 h the oxidation extent varies ( $N \times 10^4$ ) from 29.3 to 292.2 mol O<sub>2</sub>/mol RH. Metal acetates and especially cobalt and manganese acetate tetrahydrates are the most efficient cata-

Table1. Summary of the kinetic studies of oxidation of menthadiens at 60°C and utilization of combined additive benzaldehyde:cobaltacetate-tetrahydrate:anhydrous sodium carbonate = 0,040:0,001:0,040.

Hydrocarbon	Duration, h	Oxidation extent	Induction period, s
dipentene	3.5	292.2	300
L- limonene	3.0	197.3	20
d-limonene	3.3	79.3	30
$\alpha$ -terpinene	3.5	141.2	385
sylvestrene	3.3	123.3	420
terpinolene	3.5	189.6	210
$\beta$ -felandrene	3.0	154.1	360

Table 2. Data about the general conditional selectivity of barbotage oxidation process of menthadiens with triple combination of additives, air rate 10 dm<sup>3</sup> h<sup>-1</sup>, temperature 100°C.

Hydrocarbon	General conditional selectivity	Relative yield of ketones
dipentene	0.35 – 0.48	0.2 – 0.54
I-limonene	0.38 – 0.52	0.25 – 0.61
$\Delta^3$ -p-menthene	0.16 – 0.30	0.20 – 0.28
terpinolene	0.25 – 0.38	0.25 – 0.31
sylvestrene	0.29 – 0.40	0.12 – 0.37
$\beta$ -felandrene	0.32 – 0.41	0.18 – 0.25

Table 3. Oxygen containing compounds and values of the maximum accomplished conditional selectivity towards alcohols ( $s_{alc}$ ) and carbonyl compounds ( $s_{cb}$ ) at introduction of combined additives (esters, aldehydes and salts).

Hydrocarbon	Oxygen containing compounds	$s_{alc}$	$s_{cb}$
dipentene	Epoxide, carveol, carvenon, isopiperitone, trans-r-menthene-8-diol-1, 2	0.35- 0.48	0.28-0.51
L-limonene	carvon, carveol, glycol, carvenon, epoxide	0.41-0.58	0.33-0.49
terpinolene	piperitenol, monoxide, piperitenone, glycol	0.36-0.82	0.25-0.61
$\Delta^3$ -p-menthene	carveol, epoxide, glycol, carvenon	0.40-0.70	0.31-0.38
$\beta$ -felandrene	alcohols, ketones, oxides	0.18-0.38	0.24-0.41
sylvestrene	oxides, glycols, ketones, alcohols	0.22-0.38	0.31-0.33

lyzing additives taking part in the triple combination. The corresponding induction periods are 20 - 420 s, at guaranteed high oxidizability of dipentene - above 1.5.

During the kinetic study of dipentene oxidation the influence of the media introduced to the hydrocarbon (monochlorobenzene) on the absorption of oxygen is traced out. The corresponding values increase in the interval 10 – 50 %<sub>vol</sub> C<sub>6</sub>H<sub>5</sub>Cl and then decrease. At 60°C, 10 %<sub>vol</sub> medium and spreading the combined additive with the participation of cobalt acetate tetrahydrate for 1 h, an oxidation degree of 311.7 is reached, and an oxidation extent - 3.5. The data obtained from the kinetic study of dipentene and limonene oxidation at 60°C, are compared to those obtained in the isomerization menthadiens – sylvestrene,  $\beta$ -felandrene,  $\alpha$ -terpinene (Table 1). With these dienes the oxidation

extent is from 123.3 to 189.6 with 3.0 - 3.5 h duration. The higher oxidizability of terpinolene should be marked.

The created and tested combinations of additives with 3 - 4 components (esters, aldehydes and salts) accelerate the oxidation process nearly twice compared to autooxidation. To check the possibilities for regulating to some limits the components of the oxidation products, barbotage oxidations of the menthadiens have been carried out (Tables 2, 3). Tests on the oxidation of dipentene and variation in the air rate and temperature, showed that at air rate 10 dmh<sup>-1</sup> and temperature 100°C there is low resin formation and low yield of volatile products. At similar conditions comparative oxidations of isomerization dienes were carried out.

The general conditional selectivity of transformations to oxygen containing compounds is 0.16 - 0.48 and

depends on the composition of the combined additive. If tri-n-propylborat ( $5\%_{\text{mass}}$ ) and the mixture benzaldehyde:cobalt acetate tetrahydrate:anhydrous sodium carbonate ( $1.5\%_{\text{mass}}$ ) is used, higher values are accomplished. The boron ester acts simultaneously as acid catalyst and alcohols and glycols esterifying agent. Higher values of partial conditional selectivity towards alcohols are reached (0.58 – 0.82). The relative yield of ketones is higher with dipentene and L-limonene (0.54 – 0.61).

Using gas chromatography analyses of oxidation products, some valuable and oxygen containing compounds are established: carvon (13.5 – 22.9 %), carveol (6.7 – 19.9 %), oxides and monoxides (8.5 - 18.7 %), carvenone (5.7 - 15.1 %), trans-p-menthene-8-diol-1,2 (12.8 - 20.2 %). Most of them are used as important precursors in the synthesis of scarce aromatic substances and even of some bioactive substances applied in cosmetics [4, 5].

Neutral oxygen containing compounds, isolated from oxidation products in the form of a mixture, have very interesting odour characteristics of terpenylacetate, woody resinous, fruit, floral and smoky shades. Some of these products were successfully applied in compositions meant for particular articles of everyday life and deodorants for sanitary and other applications.

Liquid phase isomerization of limonenes (L-limonene and dipentene), in the presence of acid agents at comparatively moderate temperatures, is suitable for

obtaining of reaction masses enriched with precious and scarce as initial raw materials menthadiens.

Appropriate catalytic additives in the oxidation processes of the menthadiens are a number of metal acetates, which besides independent application, can be essential components in effective combinations with the participation of esters, aldehydes and other salts. Through skillful combination of the processes isomerization, oxidation and acetoxymethylation, hydrolysis, etc. menthadiens can be successfully utilized in interesting mixtures of hydrocarbons and their oxygen containing derivatives used as raw materials in the aromatic industry.

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