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SHORT COMMUNICATIONS

Transformations of α - and β -Ionones in the Presence of Al₂O₃ in a Supercritical Solvent in a Flow Reactor

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Abstract—The reactivity of α - and β -ionones under the supercritical conditions in a flow type reactor in the presence of Al₂O₃ at 200–230°C was studied. α -Ionone was reduced to α -ionol, while β -ionol was unstable already at 200°C and underwent dehydration. The secondary reaction products were the corresponding megastigmatrienes.

Keywords: ionone, triene, Meerwein–Ponndorf–Verley reaction, supercritical solvent, alumina. **DOI:** 10.1134/S0036024413110046

INTRODUCTION

 α - and β -Ionones are widespread in nature [1]. They are used in perfumery industry [2–4] and synthesis of biologically active compounds, including β carotene [5]. One of the important transformations of ionones **1** and **2**



is the reduction of the carbonyl group to the corresponding alcohol [6, 7].

Recently, we developed an effective system that allows the reduction of carbonyl groups to be performed in aldehydes and aromatic ketones in a flow reactor in a complex supercritical solvent isopropanol/CO₂ in the presence of Al_2O_3 [8–10]. The reducing agent in this reaction was isopropanol, which transformed into acetone (Meerwein–Ponndorf–Verley reaction). We showed that the corresponding alcohols or substituted styrenes could be obtained as the main products from acetophenone and its derivatives (depending on the reaction temperature) [10]:



~5 min, $scCO_2/iPrOH$, Al_2O_3 .

The aim of this work was to study the reactivity of α - and β -ionones **1** and **2** in the isopropanol/CO₂ supercritical solvent in the presence of Al₂O₃ in a flow reactor.

EXPERIMENTAL

We used mixtures of α - and β -ionones 1 and 2, in which one of these components was dominant, in ratios of 2.2 : 1 and 1 : 2.2 and Al₂O₃ (Macherey-Nagel, pH 7 \pm 0.5, 50–200 μ m, free surface ~130 m²/g (BET)). The experimental studies of the reactions under the supercritical solvent conditions were performed on a laboratory unit [11, 12] with a tube reactor $(6.0 \times 0.8 \text{ mm}, \text{ length } 3.0 \text{ m})$, which contained 42 cm^3 (39.1 g) of granulated Al₂O₃. The reaction mixture was fed into the reactor in two flows. The first flow, supercritical CO_2 (5 mL/min), was fed, using a syringe pump, into a mixer located at the inlet of the reactor through a heat exchanger, where the flow was heated to the reaction temperature. The second flow, 1%solution of a mixture of ionones in isopropanol (3 mL/min), was fed in the same mixer using a piston pump.

The reaction mixture at the outlet of the reactor was cooled and forwarded for analysis. The composition of the reaction products was analyzed by GC-MS on an Agilent 6890N gas chromatograph with an Agilent 5973N quadrupole mass analyzer as a detector. An HP-5MS quartz column (5% diphenyl–95% dimethylsiloxane copolymer) with a length of 30 m, inner diameter of 0.25 mm, and film thickness of the stationary phase of 0.25 μ m was used for analysis. The scanning was at *m*/*z* from 29 to 500. The components of the reaction mixture were qualitatively analyzed by

Reagents	T, °C	Conversion, %		Content, %				
		1	2	3	4	5	6	UPs
1 : 2 = 2.2 : 1	200	59	61	32	2	3	4	19
	230	96	94	29	20	9	8	29
1 : 2 = 1 : 2.2	230	94	97	10	12	36	22	17

Transformations of α - and β -ionones 1 and 2 (UPs are unidentified products)

comparing the retention times of the components and their complete mass spectra with the data of the NIST and Wiley7 databases. The structure of megastigma-4,7,9-triene (4), megastigma-5,7,9-triene (5), and megastigma-4,6,8-triene (6) was determined by comparing their mass spectra with the corresponding literature data.

<u>Megastigma-4,7,9-triene (4)</u>. Mass spectrum, m/z (relative intensity): 176 (13), 161 (5), 120 (98), 119 (15), 107 (15), 105 (100), 91 (42), 79 (26), 77 (26), 65 (22), and 55 (13). The spectrum coincided with the one given in [13].

<u>Megastigma-5,7,9-triene (5)</u>. Mass spectrum, m/z (relative intensity): 176 (27), 161 (36), 147 (34), 133 (42), 119 (46), 105 (100), 91 (90), 79 (31), 77 (32), 67 (23), and 55 (12). The spectrum coincided with the one given in [14].

<u>Megastigma-4,6,8-triene (6)</u>. Mass spectrum, m/z (relative intensity): 176 (37), 161 (45), 133 (28), 119 (100), 105 (72), 91 (46), 77 (32), 65 (12), and 55 (12). The spectrum coincided with the one given in [15].

The percentage composition of the mixtures was calculated from the peak areas in the chromatograms without using adjusting factors. The contact time of the reaction mixture (τ) was calculated as the ratio of the volume of the catalyst in the reactor $V_{\rm C}$ (cm³) to the total flow rate of the mixture at the inlet of the reactor Q (cm³/s) (~5.3 min at a flow rate of 8 mL/min). The transformations were performed at temperatures of 200–230°C and at a pressure p = 180 atm. The temperature and pressure in the reactor that provide the supercritical conditions of the reaction mixture were chosen on the basis of thermodynamic calculations and phase diagrams.

RESULTS AND DISCUSSION

Two mixtures of α - and β -ionones **1** and **2**, in which one of these components was dominant, in ratios of 2.2 : 1 and 1 : 2.2 were used as the starting compounds. Mixtures of α - and β -ionones **1** and **2** in various ratios are commercially available [16]. At the start of the experimental studies we used the mixture of α - and β -ionones **1** and **2** containing mainly α -ionone **1** (2.2 : 1).

The conversion of α - and β -ionones 1 and 2 at 200°C was ~60% (table). The major reaction product was α -ionol 3 formed as a result of the reduction of the

carbonyl group in 1. In addition, the products of secondary transformations, megastigmatrienes 4-6, were identified. Interestingly, β -ionol 7 was not found in the reaction mixture probably because of its low stability under the reaction conditions. Based on the arrangement of double bonds in compounds 4-6, we can assume that megastigma-4,7,9-triene (4) and megastigma-5,7,9-triene (5) formed as a result of the dehydration of α - (3) or β - (7) ionol, respectively, while megastigma-4,6,8-triene (6) might be the product of the transformations of both alcohols 3 and 7.



Compounds 4-6 were identified by comparing their mass spectra with the literature data.

When the reaction temperature was raised to 230° C, the conversion of both ketones increased to nearly quantitative. In addition, the fraction of α -ionol 3 decreased, while the contents of trienes 4-6 and unidentified products increased.

For the mixture of α - and β -ionones 1 and 2 containing mainly β -ionone 2, the contents of 3 and 4 decreased, while the fractions of 5 and, to a lesser extent, 6 increased. The obtained data confirm our assumption that megastigmatriene 6 can form from both ionones 1 and 2. Previously, compound 4 was obtained from α -ionol 3 by dehydration in the presence of (Me₂N)₃PO at 215–230°C for 30 min [13]. The use of the suggested system leads to the formation of triene 4 directly from α -ionone 1 without using expensive reagents during the contact time (6 min).

The formation of compound 5 was observed earlier after β -ionol acetate was treated in the presence of the

Pd[(PPh₃)]₄/PPh₃ complex in DMSO at 100°C for 14 h [17]. Synthesis of triene **6** by the reduction of β -ionone **2** using Na(Me₂N)BH₃ or by dehydration of β -ionol **7** in the presence of (Me₂N)₃PO at 215–230°C for 30 min was described in [18] and [15], respectively. Note that compound **6** is an important component of passion fruit juice that is responsible for its odor [15].

To summarize, we have studied the reactivity of α and β -ionones **1** and **2** under the conditions of a supercritical solvent in a flow reactor in the presence of Al₂O₃. Under these conditions, α -ionone **1** was reduced with the solvent component, giving α -ionol **3**. At the same time, β -ionol **7** was unstable already at 200°C and underwent dehydration. The secondary reaction products were megastigmatrienes **4**–**6**; the fraction of these compounds increased with temperature.

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