

Synthesis of Unsaturated Spiroacetals, Cyclopentanone Derivatives, in the Presence of Natural Aluminosilicate Modified with Zirconium Cations

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Abstract—Conditions for the condensation of cyclopentanone and *n*-valeric aldehyde to 2-pentylidenecyclopentanone in the presence of an alcoholic solution of piperidine have been developed. The isomerization of the latter in a continuous-flow system over γ -Al₂O₃ yields 2-pentylcyclopent-2-en-1-one. The condensation of the obtained unsaturated ketones with ethane-1,2-diol in the presence of a heterogeneous catalyst, a natural aluminosilicate (perlite) modified with zirconyl sulfate, has been studied. The optimum conditions for the preparation of the corresponding unsaturated spiroacetals have been found. The synthesized compounds can be used as synthetic fragrances for different purposes.

Keywords: cyclopentanone, *n*-valeric aldehyde, 2-pentylidenecyclopentanone, natural aluminosilicate, unsaturated spiroacetals

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INTRODUCTION

Cyclic acetals and ketals (1,3-dioxalanes), which are the products of condensation of carbonyl compounds with vicinal di- and triols, find practical application as monomers, intermediates, and auxiliary substances in the synthesis of general rubber goods and paint-and-lacquer materials [1–3] or perfumery and cosmetics [4–6]. Recently, these compounds have also been attracting special interest in connection with the possibility for their use in the composition of motor fuels for improving octane characteristics, increasing phase stability of alcohol-containing gasolines, and decreasing the toxicity of exhaust gases. Ketals obtained via the interaction of acetone, butanone, or cyclohexanone with ethylene glycol, propylene glycol, and glycerol have been studied as components of fuel blends in most detail [7–10].

Both homogeneous (sulfuric and orthophosphoric acids and toluenesulfonic acid) and heterogeneous (cation-exchange resins, zeolites, and polyoxometalates supported onto a mesoporous or carbon-based material) catalysts are used for the preparation of ketals [10–12].

Earlier, we reported the preparation of spiroacetals via the condensation of alkyl- and cycloalkylcyclopentanones and cyclohexanones with dihydric alcohols in the presence of various homogeneous and heterogeneous catalysts [12–14].

This communication presents the results of studying the condensation of unsaturated ketones, 2-pentylidenecyclopentanone and 2-pentylcyclopent-2-en-1-one, with ethylene glycol in the presence of a heterogeneous catalyst, a zirconyl cation-modified natural aluminosilicate (perlite), as well as the influence of various factors at each stage of preparation of unsaturated ketones and acetals.

EXPERIMENTAL

Cyclopentanone obtained via dry distillation of adipic acid in the presence of barium oxide hydrate [14], *n*-valeric aldehyde, and reagent grade ethylene glycol were used as the reactants after their appropriate purification.

Preparation Procedure for Unsaturated Ketones

2-Pentylidenecyclopentanone was obtained via crotonic condensation of cyclopentanone with *n*-valeric aldehyde. Cyclopentanone in an amount of 42 g (0.5 mol), 50 mL of propan-2-ol (as a solvent), and 21.5 g (0.25 mol) of *n*-valeric aldehyde were simultaneously placed into a 250-mL flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser. A 15% aqueous sodium hydroxide solution or a 5% piperidine solution in alcohol was added to the mixture dropwise in equal portions at 20°C. The reac-

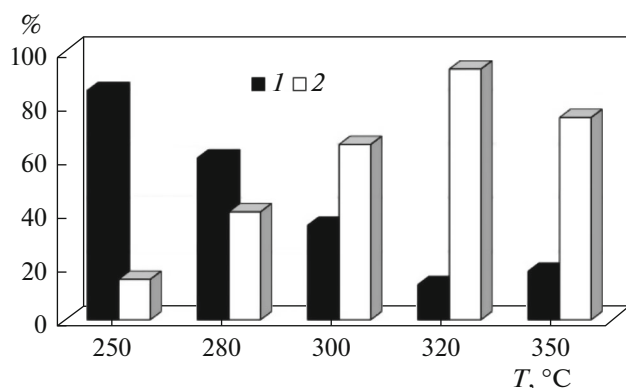


Fig. 1. Results of the isomerization of (1) 2-pentylidenecyclopentanone to (2) 2-pentylcyclopent-2-en-1-one over γ - Al_2O_3 at different temperatures.

tion mixture was stirred for additional 2 h at 30°C; the organic phase was separated from the catalyst, washed to a neutral reaction, and dried over Na_2SO_4 ; and the desired product was isolated by fractional distillation under vacuum.

The isomerization of 2-pentylidenecyclopentanone to 2-pentylcyclopent-2-en-1-one was performed in a continuous-flow system including a fixed-bed glass reactor with grade A alumina at 300–320°C and a feed space velocity of 0.5 h^{-1} .

The catalyst for the condensation of unsaturated ketones with ethane-1,2-diol was prepared by impregnating samples of natural perlite from the Kemerli deposit (Azerbaijan) with a size of 2–3 mm by an aqueous–alcoholic solution of reagent grade $\text{ZrO}(\text{NO}_3)_2$ or ZrOCl_2 followed by their treatment with 70% H_2SO_4 , drying at 100–120°C, and calcining at 400–420°C.

The preparation procedure of spiroacetals is presented in [12].

The purity and isomeric composition of the synthesized compounds were determined by GLC using a Tsvet-500 chromatograph, equipped with a thermal conductivity detector, on a column of a 2 m length and a 2 mm diameter packed with 10 wt % polyethylene glycol succinate-coated Chromosorb N-AW. The column temperature was 100–120°C, the evaporator temperature was 230–250°C, the detector temperature was 200–210°C, the detector bridge current was 100–110 mA, and the carrier gas (helium) flow rate was 30–40 mL/min.

The structure of the synthesized product was confirmed by the data of elemental analysis and IR spectroscopy (Alpha in the range of 400–4000 cm^{-1}), gas chromatography–mass spectrometry (GC–MS), and ^1H NMR spectroscopy (Bruker, 300.18 MHz).

RESULTS AND DISCUSSION

The main products of the catalytic conversion of cyclopentanone with *n*-valeric 2-cyclopentylidenecyclopentanone, 2-pentylidenecyclopentanone, 2-pentylcyclopent-2-en-1-one, and 2-(1-hydroxypentyl)cyclopentanone, as well as the aldehyde and ketone dimerization products 2-propylhept-2-en-1-al and 2-cyclopentylidenecyclopentanone, respectively. The ratio of these products depends on the reaction conditions, namely, the temperature, the reaction time, the molar ratio of the reactants, and amount of the catalyst (Table 1).

The results of the study show that the yield and composition of the desired product strongly depend on both the amount of piperidine (or NaOH) and the reaction temperature. For example, the main product of condensation of cyclopentanone and *n*-valeric aldehyde at 3°C is ketoalcohol C (50.6%). With an increase in the temperature, the yield of ketoalcohol decreases from 54.3 to 32.3 wt %.

By varying other parameters affecting the yield and composition of the desired product (reaction time and ketone to aldehyde molar ratio), the optimum conditions for the condensation of cyclopentanone with *n*-valeric aldehyde in the presence of piperidine were found to be as follows: a ketone : aldehyde molar ratio of 3 : 1, a temperature of 3–5°C, and a reaction time of 3 h. Under these conditions, the yield of ketoalcohol is 54.3% and the yield of unsaturated ketone is 16.6 wt %. Ketoalcohol C undergoes dehydration during vacuum distillation.

According to the GLC data, the obtained product of crotonic condensation of cyclopentanone with *n*-valeric aldehyde consists of two isomers, 2-pentylidenecyclopentanone D (85.0) and 2-pentylcyclopent-2-en-1-one E (15.0%).

The isomerization of the condensation product in the flow system over γ - Al_2O_3 at 300–320°C results in high yield of 2-pentylcyclopent-2-en-1-one. The isomerization product consists of compounds E (94.0) and D (6.0%). The dynamics of the isomerization of 2-pentylidenecyclopentanone to 2-pentylcyclopent-2-en-1-one is shown in Fig.1.

To determine the optimum conditions for the condensation reaction of 2-pentylidenecyclopentanone and 2-pentylcyclopent-2-en-1-one with ethylene glycol, the influence of temperature, reaction time, reactant molar ratio, catalyst amount, and solvent nature on the yields of the desired products was examined. The dependence of the buildup rate of spiroacetals upon the above factors was monitored using GLC. It was found that the activity of the untreated perlite samples in the condensation reaction of the ketone under study with ethylene glycol was not high (8–15 wt %) (Fig. 2).

However, the successive treatment of perlite with an aqueous alcohol solution of zirconyl

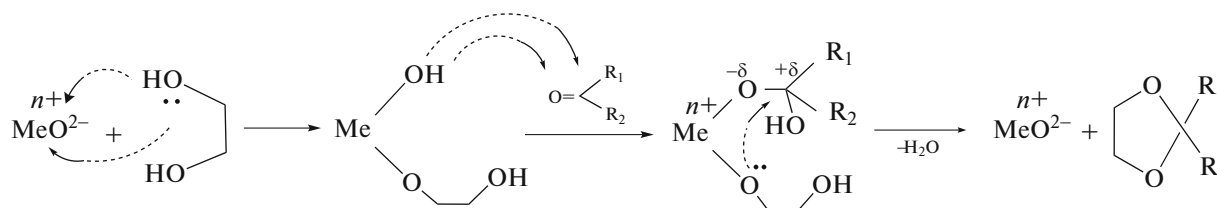
Table 1. Conditions and results of experiments on the condensation of (a) cyclopentanone with (b) *n*-valeric aldehyde

Reaction conditions				Product composition according to GLC data, wt %*				Residue, wt %
temperature, °C	molar ratio a : b	duration, h	amount of catalyst, wt %	A	B	C	D + E	
In the presence of piperidine								
5	1 : 1	2	6	16.8	3.2	26	—	27
5	2 : 1	2	6	13.7	4.3	39	3.2	23
5	3 : 1	2	6	12.6	6.9	48	3.8	22.5
5	4 : 1	2	6	3.8	9.8	50	5.2	20.2
5	5 : 1	2	6	1.9	11.3	50.6	7.3	18.9
10	3 : 1	2	6	6.3	11.4	30.3	10.7	36.3
5	3 : 1	3	6	13.2	7.2	50.3	4.2	23.3
5	3 : 1	1	6	7.5	1.3	19.4	1.4	11.4
5	3 : 1	2	4	11.2	4.4	47.8	2.3	17.6
5	3 : 1	2	8	17.4	14.5	20.1	5.7	21.2
5	3 : 1	4	6	18.2	8.7	43.4	4.8	24.2
In the presence of alkali (NaOH)								
30	2 : 1	2	6	15.6	4.4	4.6	37	25
30	3 : 1	2	6	6.1	8.7	3.0	58.3	22.0
30	4 : 1	2	6	4.6	11.8	3.7	49.7	20.4
30	5 : 1	2	6	2.2	13.5	2.6	47.4	18.6
30	3 : 1	3	6	10.0	9.0	2.0	58.3	20.1
30	3 : 1	4	6	10.3	8.4	1.8	55.5	23.6
30	3 : 1	1	6	3.9	2.3	1.5	49.2	12.7
30	3 : 1	2	4	5.5	6.6	1.9	42.4	11.8
30	3 : 1	2	8	10.8	10.7	0.8	43.3	25.5
25	3 : 1	2	6	10.2	6.3	2.9	49.9	12.1
40	3 : 1	2	6	20.2	14.4	2.7	36.8	26.5

* A is 2-propylhept-2-en-1-al, B is 2-cyclopentylidenecyclopentanone, C is 2-(1-hydroxypentyl)cyclopentanone, D is 2-pentylidenecyclopentanone, and E is 2-pentylcyclopent-2-en-1-one.

nitrate and sulfuric acid results in the formation of zirconyl sulfate, which leads to an increase in the acidity and activity of the system. It is these sites that exhibit high activity in the condensation reaction of unsaturated ketones with ethylene glycol (see Scheme 1).

It is supposed that the reaction proceeds through the protonation of the basic site of the catalyst (O^{2-}) by glycol and stabilization of the hydroxyethoxo anion on the Lewis acid site to form a glycolate complex followed by the protonation of the carbonyl group in the reactant ketone:

**Scheme 1.**

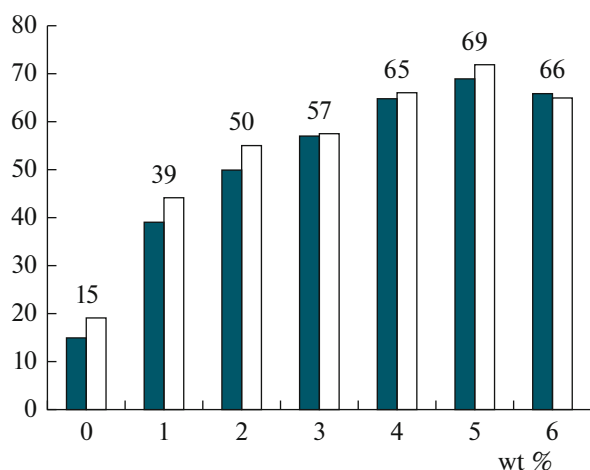


Fig. 2. Dependence of the yield of spiroacetals on the concentration of $ZrOSO_4$ in the natural aluminosilicate ($T=110^\circ C$, $\tau = 5$ h). The dark and light columns refer to 5-pentylidene-1,4-dioxaspiro[4.4]nonane and 5-pentyl-1,4-dioxaspiro[4.4]non-5-ene, respectively.

It is known that reactions of this type require the presence of medium-strength acid–base sites on the catalyst surface [15]. This ketalization mechanism is supported by the fact of formation of a certain amount

of hemiacetal and 1,4-dioxane as a side product of the reaction.

As the $ZrOSO_4$ loading in perlite is increased (from 1 to 5%), the activity of the catalyst in the condensation reaction of 2-pentylidencyclopentanone or 2-pentylcyclopent-2-en-1-one with ethylene glycol increases, and the yields of spiroacetals reach 69.8 and 71.5 wt %, respectively. A further increase in the salt loading leads to an increase in the rate of the side reactions and a decrease in the yield of the desired product.

It was experimentally found that of azeotrope-forming solvents, such as benzene, toluene, and isooctane, toluene is the most appropriate in terms of selectivity for the condensation of alkylidencyclopentanone with ethylene glycol.

One of the important factors affecting the condensation reaction is the molar ratio of 2-pentylidencyclopentanone and ethylene glycol. It was found that increasing the 2-pentylidencyclopentanone : ethylene glycol ratio from 1 : 1 to 1 : 3 promoted an increase in the yield of unsaturated spiroacetal from 40 to 69.8%.

With varying temperature in the range of 80–110°C (depending on the dehydrating solvent), the yield of acetal passes through a maximum. The highest yield of the desired products in the presence of toluene is 71.6%. A further increase in temperature leads to a

Table 2. Conditions and results of experiments on the condensation of (a) 2-pentylidencyclopentanone with (b) ethylene glycol in the presence of natural perlite modified with 5 wt % zirconyl sulfate

Reaction conditions			Conversion, %		Acetal yield, wt %	
molar ratio a : b	duration, h	amount of catalyst, wt %	a	b	%	residue, wt %
			%	%		
In benzene, reaction temperature 80°C						
1 : 2	6	1	66.5	73.6	35.9	1.1
1 : 2	6	2	74.0	76.4	47.5	1.3
1 : 2	6	2	79.4	80.8	58.6	1.5
1 : 2	6	4	80.4	84.1	63.4	1.7
1 : 2	6	5	84.1	86.2	69.8	1.9
1 : 2	6	6	85.7	87	68.7	2.2
1 : 3	6	5	84.4	87.3	69.9	1.4
1 : 2	5	5	82.0	85.7	66.3	1.3
1 : 2	7	5	84.6	86.5	69.4	1.5
In toluene, reaction temperature 110°C						
1 : 2	6	5	85.5	88.4	71.4	1.8
1 : 3	6	5	85.2	88.8	71.6	1.5
1 : 4	6	5	85.5	89.5	71.8	1.7
1 : 2	6	4	81.5	84.8	64.2	1.8
1 : 2	6	6	84.8	87.7	68.9	2.4
1 : 2	5	5	82.2	85.5	65.6	1.9
1 : 2	7	5	84.4	87.0	67.9	1.8

decrease in the acetal yield by 12%, a change that is due to an increase in the rate of further transformations of the forming acetals to polyoxy compounds and dehydration of glycol to dioxane.

The results of the experiments on the condensation of 2-pentylidenecyclopentanone with ethylene glycol are presented in Table 2.

Under these conditions, the condensation of 2-pentylcyclopent-2-en-1-one with ethylene glycol also proceeds with high selectivity and the yield of the desired product reaches 71.5%.

The structure of the spiroacetals obtained was confirmed by IR, ^1H and ^{13}C NMR, and GC–MS data.

5-Pentylidene-1,4-dioxaspiro[4.4]nonane. Yield 69.8%. T_b 102–104°C/0.26 kPa. d_4^{20} 0.9685. n_D^{20} 1.4654. IR, ν_1 , cm^{-1} : 3040 ($\nu_1 = \text{CH}$), 2865 ($\nu_1 \text{CH}_2$), 1630 ($\nu_1 \text{C}=\text{C}$), 1265, 1215, 1170, 850 ($\nu_1 \text{C}-\text{O}-\text{C}$) [16, 17]. ^1H NMR, δ , ppm: 0.92 (t, 3H, CH_3 , $J = 8.1$ Hz), 1.27–1.30 (m, 4H, 2CH_2 alkyl), 1.35–1.94 (m, 6H, 3CH_2 cycle), 4.0–4.05 (d, 4H, 2CH_2 , $J = 7.2$ Hz), 5.5 (d, $1\text{H}_1 = \text{CH}_1$, $J = 6.3$ Hz) [18].

5-Pentyl-1,4-dioxaspiro[4.4]non-5-ene. Yield 71.5%. T_b 97–99/0.26 kPa. d_4^{20} 0.9998. n_D^{20} 1.4863. IR, ν_1 , cm^{-1} : 3045, 3020 ($\nu_1 = \text{CH}$), 2860 ($\nu_1 = \text{CH}_2$), 1630 ($\nu_1 \text{C}=\text{C}$), 1470 (δ , CH_3), 1260, 1210, 1170, 850 ($\nu_1 \text{C}-\text{O}-\text{C}$). ^1H NMR, δ , ppm: 0.91 (t, 3H, CH_3 , $J = 8.1$ Hz), 1.29–2.26 (m, 12H, 6CH_2), 3.90 (d, 4H, 2OCH_2 , $J = 7.1$ Hz), 5.35 (d, $1\text{H}_1 = \text{CH}$, $J = 6.3$ Hz).

The synthesized spiroacetals have a jasmine scent and can be used as fragrances.

In summary, it has been shown that zirconyl sulfate-modified samples of the natural aluminosilicate perlite exhibit high activity in the condensation of the unsaturated ketones 2-pentylidenecyclopentanone and 2-pentylcyclopent-2-en-1-one with ethylene glycol to corresponding spiroacetals.

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