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SYNTHESIS AND OXIDATION OF PHENYLHEXANES

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Abstract. *During the research, by alkylation of benzene with hexanol-1 the mixture consisting of 60-65% 2-phenylhexane and 35-40% 3-phenylhexane was synthesised. The paper explores the promising but understudied process of this mixture aerobic liquid-phase oxidation to corresponding hydroperoxides for further obtaining of higher ketones. As a result, the use of N-hydroxyphthalimide at this stage allows us to achieve technological conditions for mixture industrial implementation. The conversion of the phenylhexane mixture is more than 30% within 60 minutes of reaction with high selectivity of hydroperoxide formation.*

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Introduction

Higher ketones are valuable raw materials for the production of a wide range of materials. Every year demand for ketones in various fields is growing. Currently, ketones are used in the production of oils, medicines, varnishes, cleaning products, cosmetics, as solvents, in polymer processing, etc. The higher ketones are widely used in perfumery [1]. Ketones can be the regulators and the additional source of energy for heart and vascular system in both healthy people and people with heart deseases or after myocardial infarction [2]. Higher ketones are the main antifungal compounds and also used in the food industry in the production of cheese [3, 4].

2-Hexanone is a raw material used in the production of paints and thinners, solvents for oils and waxes. It is used for printing on plasticised fabrics and creating waterproof clothing [5]. 3-Hexanone is mainly used as a reagent in the chemical industry. Compounds based on it show high efficiency in combating cardiomyocyte apoptosis – one of the key factors of ischaemic heart disease [6].

The known methods for obtaining ketones mainly involve the catalytic oxidation of alkanes [7], alkenes, and secondary alcohols [8, 9] with strong oxidants. The catalytic oxidation

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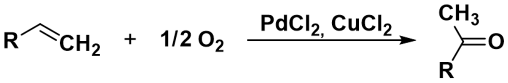
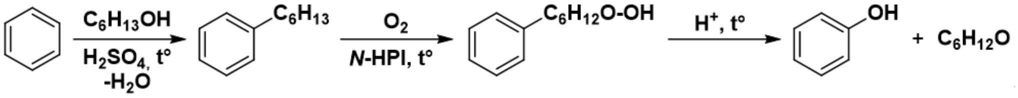
of alkenes is an industrial redox process for the synthesis of ketones using metal complex catalysts, known as the Wacker process [10]:



The use of the traditional homogeneous chloride system $PdCl_2/CuCl_2/O_2$ and its modifications for the oxidation of unbranched alkenes shows decreasing of the reactivity of 1-alkenes with increasing carbon chain length. Thus, the propylene oxidation at 50-120 °C and a pressure of 9.8 MPa leads to the formation of acetone with a yield of 99%. The oxidation of *n*-butenes at 100 °C and a pressure of up to 4.5 MPa yields methyl ethyl ketone with a selectivity of about 80% [11, 12]. In addition, the limitations of the Wacker system, associated with high corrosion activity and the formation of chloroketones, the amount of which increases with increasing copper salt concentration and solution acidity [13], restrict its practical use in the synthesis of phenylhexanes.

The modifications of higher ketones production method involve the use of various additives to address the problems of the traditional system. For example, it has been proposed to perform the process in aqueous-organic media [14] with the addition of interfacial transfer catalysts (cyclodextrins, polyethylene glycols, calixarenes, and quaternary ammonium salts) [15, 16], heteropolysubstances [12, 14] as co-catalysts, and peroxides as oxidants [17]. However, a lot of problems remain; they are mainly related to the use of elevated pressure, high cost, and instability of catalytic systems.

This research is devoted to an alternative method for obtaining higher ketones together with phenol; the method consists of obtaining phenylhexane, oxidising it to hydroperoxide, and decomposing it with acid:



However, along with hexanones and phenol, the intermediate compound phenylhexane is also of practical importance. It is used in the production of surfactants, oil additives, auxiliary substances in polymer chemistry, pesticides and extractants [9], and for research purposes [18].

This study is devoted to the first two stages of the process: the synthesis of phenylhexane and the study of the patterns of its aerobic liquid-phase oxidation.

Experimental part

Commercially available reagents were used in the study: hexanol-1 (TU 6-09-3499-79), benzene, p.a., (GOST 5955-75), sulphuric acid, c.p., (GOST 4204-77), acetic acid, c.p. (GOST 61-75), potassium iodide, p.a. (GOST 4169-76), sodium hyposulfite (TU-6-09-2540-72), sodium hydroxide, p.a., (GOST 4328-77), anhydrous calcium chloride (TU 6-09-4711-81), *N*-hydroxyphthalimide (Sigma-Aldrich, 97%).

We synthesised phenylhexane using a well-known method by alkylating benzene with hexanol-1 in the presence of concentrated sulfuric acid [19]. The alkylation reaction products (a mixture of liquid substances) were separated by vacuum rectification as a fraction of 85-90 °C at a residual pressure of 0.2 atm. The reaction products were analysed by gas-liquid chromatography, IR and ^1H NMR spectroscopy.

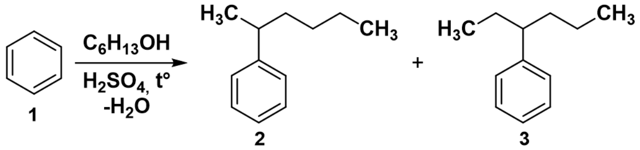
We conducted the oxidation of phenylhexane in a closed-loop flow system using the method described in [20]. During the reaction, we measured the amount of oxygen absorbed. We analysed the reaction products using iodometric titration [21].

We performed chromatographic analysis using the Chromatec-Crystal 5000.2 hardware and software complex. IR spectroscopic analysis was performed on an IR Fourier RX-1 in the 4000-400 cm^{-1} range in the form of a microlayer between potassium bromide glasses or in a potassium bromide cuvette with d = 0.0011 cm. We recorded ^1H NMR spectra on a Bruker DRX 400 spectrometer (400 MHz). DMSO was used as the solvent. Tetramethylsilane was used as the internal standard.

Main body

There is a lot of information on the patterns of aromatic hydrocarbons alkylation with olefins or alcohols. However, there is a few data on the synthesis of phenylhexane in scientific and technical literature. Methods for obtaining 2-phenylhexane by alkylation of benzene with 1-chlorohexane [22] and 1-hexene with various acid catalysts, such as antimony pentafluoride, scandium trifluoromethanesulfonate (III) [23], phosphoric acid [24], heterogenised aluminium chloride [25], and using platinum- and gallium-modified zeolites are described [26]. However, these processes have not found industrial application.

We conducted research aimed at obtaining phenylhexanes by alkylation of benzene with hexanol-1 in the presence of concentrated sulphuric acid according to the following scheme:



The effect of temperature in the range from 60 to 80 °C and the duration of the process up to 5 hours on the parameters of benzene alkylation with hexanol-1 were studied. Two isomers of phenylhexane were found in the reaction products: 2-phenylhexane and 3-phenylhexane; the ratios are shown in Table 1. No linear structures were found. The by-products are mainly disubstituted hexylbenzenes, which appear as seven adjacent peaks in GC-MS. Table 1 shows the data obtained.

Table 1. Regularities of the benzene alkylation process with hexanol-1. The molar ratio of benzene : hexanol-1 : sulphuric acid = 3:1:3.

Temperature, °C	Reaction time, h	2-Phenylhexane / 3-phenylhexane ratio	Yield of phenylhexanes to charged hexanol-1
60	5	1.44	62
70	3	1.40	71
	4	1.39	65
	5	1.44	66
80	1	1.86	53
	2	1.49	76
	3	1.49	76
	4	1.45	72
	5	1.40	68

The experimental data show an ambiguous effect of reaction duration. On the one hand, there is a decrease in the ratio of 2-phenylhexane to 3-phenylhexane in the reaction products from 1.9 in the first hour of the reaction to 1.4 after 5 hours. This is apparently due to the transition from kinetic to thermodynamic control of the reaction. On the other hand, the yield of phenylhexanes peaks in the 2-3 hours interval, after which it begins to decline slightly, mainly due to polyalkylation reactions.

At a temperature of 80 °C and a reaction time of 2 hours there was the maximum yield of phenylhexanes (76%); the material balance of the process under these conditions is shown in table 2.

Table 2. Material balance of the benzene alkylation process with hexanol-1 at 80 °C for 2 hours, molar ratio of benzene : hexanol-1 : sulphuric acid = 3:1:3.

Compound	Molar weight, g/mol	Loaded		Obtained	
		g	weight %	g	weight %
Benzene	78.11	169.2	37.1	71.8	15.7
Hexanol-1	102.17	73.7	16.2	0	–
Sulfuric acid	98.08	212.6	46.7	212.6	46.7
Phenylhexanes	162.28	0	–	89.0	19.5
By-products	–	0	–	14.0	3.0
Losses	–	0	–	68.1	15.1
Total	–	455.5	100	455.5	100

A mixture of phenylhexane isomers was isolated from alkylation products by vacuum rectification. According to the results of chromatographic analysis, the purity of the product was 97.3%. The qualitative composition of the mixture of phenylhexane isomers was confirmed by IR and ^{1}H NMR spectroscopy.

IR-spectrum, ν/cm^{-1}: 3084, 3036, 3028 (=C–H), 2957, 2925, 2872 (CH_3), 1604, 1494 (–C=C–), 1452.5, 1377.8 (CH_2).

NMR spectrum ^{1}H (DMSO-d$_6$, δ, ppm, *J*/Hz): 7.31-7.23 (m, 5H, Ph$^{(3)}$), 7.19-7.10 (m, 5H, Ph$^{(2)}$), 2.63 (sextet, 1H, CH$^{(2)}$, *J* = 7.1), 2.39 (tt, 1H, CH$^{(3)}$, *J* = 9.5, 5.3), 1.67-1.42 (m, 6H, $CH_2^{(2)}$, 2$CH_2^{(3)}$), 1.30-1.01 (m, 9H, $CH_3^{(2)}$, 2$CH_2^{(2)}$, $CH_2^{(3)}$), 0.85-0.75 (m, 6H, $CH_3^{(2)}$, $CH_3^{(3)}$), 0.70 (t, 3H, *J* = 7.4, 3H, $CH_3^{(3)}$).

The refractive index of this substance, obtained experimentally using a refractometer, coincides with the index from the reference data (1.486) [27].

Thus, effective conditions for the synthesis of a mixture of 2-phenylhexane and 3-phenylhexane with a yield of 76% have been found. This is comparable to the alkylation of benzene with *n*-hexene in the presence of heterogenised $AlCl_3$ [25]. However, the ratio of 2-phenylhexane to 3-phenylhexane in this case is 1.8 : 1; it is compared to the ratio of 1.4 : 1 obtained in this study.

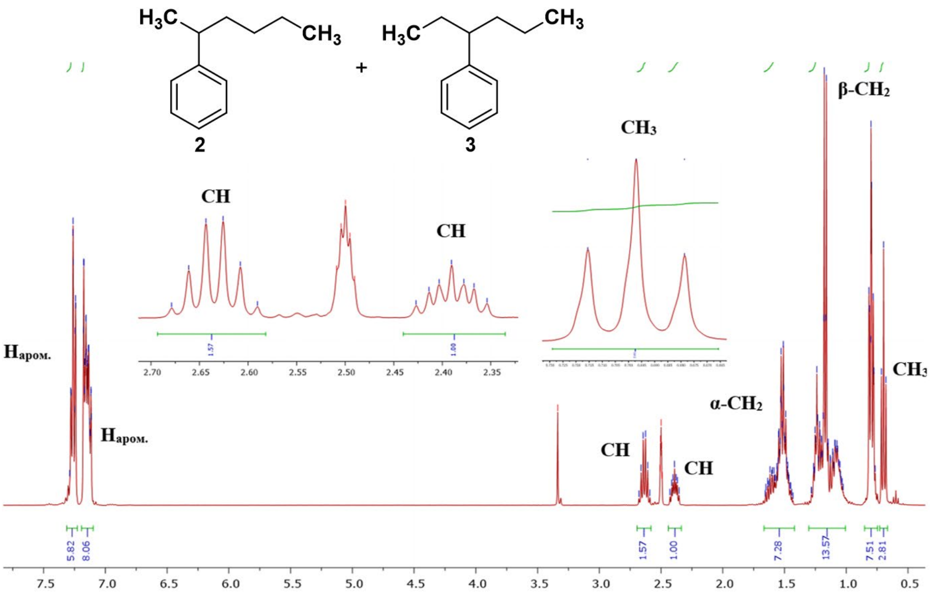
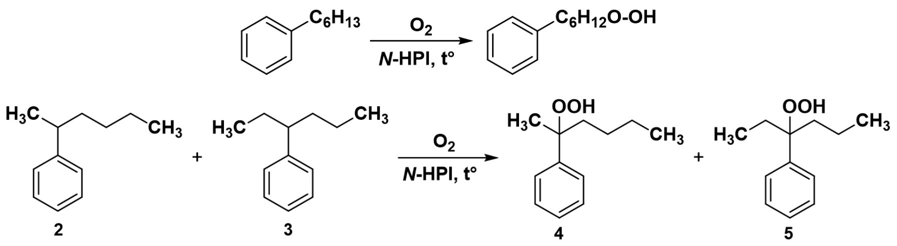


Fig. 1. ^{1}H NMR spectrum of phenylhexanes

On the second stage of the process for obtaining 2-hexanone and 3-hexanone, the synthesised mixture of isomeric hydrocarbons is oxidised to the corresponding hydroperoxides:



This study investigated the patterns of this process in the presence of *N*-hydroxyphthalimide (*N*-HPI). It has proven to be an effective catalyst in the hydroperoxide oxidation of other hydrocarbons [28]. The influence of temperature, catalyst concentration, and reaction duration on the parameters of the liquid-phase aerobic oxidation of an isomeric mixture of phenylhexanes were studied. Table 2 and Figure 3 present the results.

Table 3. The impact of technological parameters on the content of hydroperoxides in the oxidation products of a mixture of phenylhexane isomers.

Temperature, °C	Reaction time, h	Content of *N*-HPI, % weight of alkylbenzene loaded	Hydroperoxide content in phenylhexane oxidation products, % weight
130	60	2	7
140			18
150	30		13
	60	1	14
		2	31
		4	24
	90	2	18
	120		10
160	60		12

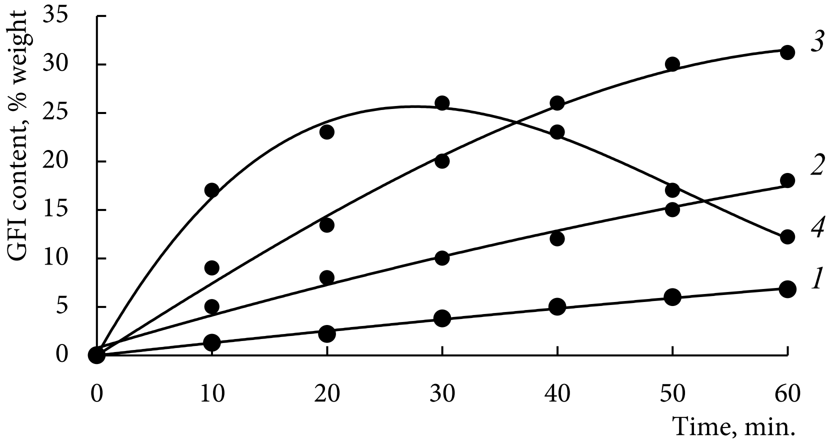


Fig. 2. Kinetic curves of octylbenzene oxidation. *N*-HPI content, 2 weight % of hydrocarbon feed; temperature, °C: 1 – 130, 2 – 140, 3 – 150, 4 – 160.

Therefore, the maximum content of hydroperoxides (31%) in oxidation products is achieved at a temperature of 150 °C after 60 minutes of reaction in the presence of 2 % weight *N*-HPI

Conclusions

The regularities of benzene alkylation processes with hexanol-1 in the presence of concentrated sulphuric acid were studied. A mixture of phenylhexane isomers was synthesised with a yield of 76% and isolated with a purity of over 97%. The purity and structure of the compounds were confirmed by GLC, IR, and ^{1}H NMR spectroscopy.

The regularities of liquid-phase aerobic oxidation of phenylhexane isomers in the presence of *N*-hydroxyphthalimide were studied. The reaction conditions to achieve concentrations of 2-phenylhexane and 3-phenylhexane hydroperoxides of more than 30% were determined.

The resulted parameters of synthesis and liquid-phase oxidation of the obtained phenylhexanes are prospective in terms of industrial application of this process.

Conflict of interest

The authors declare no conflict of interest in financial or any other sphere.

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