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Corresponding Member of the Academy of Sciences of the USSR A. N. BASHKIROV, A. I. KISHTANOVA

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Abstract

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ON THE COMPOSITION OF ALCOHOLS OBTAINED IN THE LIQUID-PHASE OXIDATION OF NAPHTHENIC HYDROCARBONS

We oxidized *n*-amyl-, *n*-heptyl-, and *n*-nonylcyclohexanes in the liquid phase in the presence of boric acid. It was established that, under the adopted conditions, hydroxyl-containing compounds constitute about 75 mole %. The alcohols formed are predominantly secondary, having the same skeleton and the same number of carbon atoms in the molecule as the starting hydrocarbon ([1]). We did not detect tertiary alcohol in the oxidation products of *n*-alkylcyclohexanes.*

From the standpoint of the mechanism of alcohol formation, it was of great interest to establish the position of the hydroxyl group in the alcohols formed during the oxidation of alkyl-substituted naphthenic hydrocarbons. For this purpose we used the method of oxidizing alcohols with potassium dichromate in dilute sulfuric acid, followed by isolation and identification of the acids formed. This method had been successfully applied by us in studying the composition of alcohols obtained in the oxidation of normal paraffinic hydrocarbons ([2,3]).

The alcohols obtained by us, as noted above, consist mainly of secondary alcohols, while the molecule of *n*-alkylcyclohexane has secondary carbon atoms both in the side chain and in the ring. It could be expected that the hydroxyl groups would be distributed among these carbon atoms. Therefore oxidation of an alcohol having the hydroxyl group in the side chain of *n*-alkylcyclohexane will lead to a naphthenic acid and to the corresponding acid of the fatty series. Oxidation of an alcohol with the hydroxyl group in the ring should proceed with cleavage of the ring.

The conditions for oxidizing alcohols with chromic mixture and the procedure for isolating and identifying the acids have been described previously ([2,3]). The acids obtained in the oxidation of the alcohols were converted into methyl esters, which were fractionated with a carrier substance. The acids were identified by boiling point and by the silver content in the silver salts of the acids. The possibility of using this method for separating naphthenic acids was first established by us using several acids specially synthesized for this purpose. Alcohols obtained respectively from *n*-amyl-, *n*-heptyl-, and *n*-nonylcyclohexanes were subjected to oxidation with chromic mixture.

In the oxidation of the alcohols $C_{11}H_{21}OH$, the acids $C_7H_{12}O_2$, $C_8H_{14}O_2$, and $C_9H_{16}O_2$ were identified. The acids $C_{10}H_{18}O_2$ and $C_{11}H_{20}O_2$, as we had expected, were not found. This situation also remains valid for the other alcohols obtained by us.

In the oxidation of the alcohols $C_{13}H_{25}OH$, the acids $C_6H_{12}O_2$, $C_6H_{12}O_2$, $C_7H_{12}O_2$, $C_8H_{14}O_2$, $C_9H_{16}O_2$, $C_{10}H_{18}O_2$, and $C_{11}H_{20}O_2$ were identified.

In the oxidation of the alcohols $C_{15}H_{29}OH$, the acids $C_6H_{12}O_2$, $C_7H_{12}O_2$, $C_8H_{14}O_2$, $C_9H_{16}O_2$, $C_{10}H_{18}O_2$, $C_{11}H_{20}O_2$, $C_{12}H_{22}O_2$, and $C_{12}H_{24}O_2$ were identified.

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* We have experimentally established that 1-amylcyclohexanol readily reacts with boric acid, forming a trialkyl borate that is stable under the adopted oxidation conditions.

During distillation of the methyl esters, along with the esters of the acids identified by us, in all cases the formation, in significant amounts, of esters with a sharply elevated boiling point was observed; these remained in the flask. To establish the composition of these substances, the residue obtained in the distillation of the methyl esters of the acids isolated during oxidation of the alcohols $C_{11}H_{21}OH$ (the oxidation product of *n*-amylcyclohexane) was subjected to saponification with an alcoholic solution of caustic potassium. After extraction with ethyl ether, the salts of the acids were decomposed with sulfuric acid. The acid isolated by distillation in vacuo, with a boiling point of 151–156° (residual pressure 1 mm), had an acid number of 260 and a carbonyl number of 135.5; the silver content in the silver salt was 35.4%. The residue after isolation of this acid had an acid number of 434, and the silver content in the silver salt was 46.3%.

The values of the acid number and the silver content in the silver salt for the isolated acid are close to their values for the keto acid $C_{11}H_{22}O_3$, while the carbonyl number is considerably lower. For purification, the acid under study was converted into the methyl ester; the latter, in benzene solution, was applied to ASK-grade silica gel. The column with silica gel was washed successively at room temperature with benzene and then with diethyl ether ([4]). After saponification, the isolated acid had an acid number of 266, a silver content in the silver salt of 35.0%, and a carbonyl number of 205. We were unable to purify this acid completely; however, on the basis of the data obtained, it may be assumed that the indicated keto acid is present, its formation being possible through oxidation of an alcohol in which the hydroxyl group is located in the ring in position 2 relative to the alkyl substituent:

$$[\text{cyclohexane ring bearing } (CH_2)_4CH_3 \text{ and } OH \text{ in the 1,2-positions}] \longrightarrow [\text{ring-opened keto acid: } C(=O)(C$$

The presence of an elevated acid number, as well as the high silver content in the silver salt obtained from the residue after isolation of the keto acid, indicates the presence of a dibasic acid, which could have formed from an alcohol with the hydroxyl group located in the ring in positions 3 and 4 relative to the alkyl substituent:

$$\text{[cyclohexane ring bearing } (CH_2)_4CH_3 \text{ and } OH] \longrightarrow \text{[dicarboxylic acid bearing } (CH_2)_4CH_3,\ COOH,\ COC$$

The investigation carried out on the composition of the acids made it possible to establish that the hydroxyl group in the alcohols obtained in the oxidation of alkyl-substituted cyclohexane is located both in the side chain and in the ring. To confirm the presence of the hydroxyl group in the ring of the alcohol molecule, an additional spectral study was made of the olefins obtained by dehydration of the alcohols $C_{11}H_{21}OH$, the oxidation product of *n*-amylcyclohexane.

Dehydration of the alcohols was carried out over aluminum oxide containing a small amount of alkali, in vacuo, at a temperature of 270°.

In preliminary experiments with allylcyclohexane passed over this catalyst, we established that under the adopted conditions migration of the double bond from the side chain into the ring of the molecule is not observed. The spectrum of the olefins under investigation was compared with the spectrum of cyclohexene and its monosubstituted derivatives, and also with the spectra of normal olefins. The investigation was carried out on an IKS-14 infrared spectrometer.

The spectrum obtained did not contain absorption bands corresponding to terminal double bonds (910, 990, 3097 cm^{-1}), which confirms the absence-

···the presence in the oxidation products of primary alcohols of *n*-alkylcyclohexane. The spectrum contained absorption bands characteristic of ortho-substituted cyclohexene (678, 894, 1103, 1140, 1305, 1381, 1450, 1650 cm^{-1}), which indicates the presence of a hydroxyl group in the ring in positions 2 and 3 relative to the alkyl substituent. On the basis of data obtained in the distillation of the methyl esters, the approximate distribution of the acids formed in the oxidation of the alcohols was compiled (Table 1). It was thereby established that the acids indicated above are formed in approximately equal molar ratios. The proportion of acids with a high boiling point (residue) decreases with increasing length of the side chain of the alkylcyclohexane.

Table 1

Distribution of acids obtained in the oxidation of alcohols with chromic mixture

Acids	Distribution of acids by b.p. of methyl esters, mol.	Distribution of acids by b.p. of methyl esters, %	Acids	Distribution of acids by b.p. of methyl esters, mol.	Distribution of acids by b.p. of methyl esters, %
Alcohols			**Alcohols**		
$C_{15}H_{30}O$			$C_{13}H_{26}O$		
$C_6H_{12}O_2$	1.268	6.24	$C_5H_{10}O_2$	0.247	2.15
$C_7H_{14}O_2$	1.396	6.86	$C_6H_{12}O_2$	0.613	5.35
$C_7H_{12}O_2$	1.396	6.86	$C_7H_{14}O_2$	0.586	5.08
$C_8H_{16}O_2$	1.396	6.86	$C_7H_{12}O_2$	0.586	5.08
$C_8H_{14}O_2$	1.396	6.86	$C_8H_{14}O_2$	0.586	5.08
$C_9H_{18}O_2$	1.345	6.61	$C_9H_{16}O_2$	0.817	7.08
$C_9H_{16}O_2$	1.345	6.61	$C_{10}H_{18}O_2$	1.034	8.95
$C_{10}H_{18}O_2$	1.153	5.68	$C_{11}H_{20}O_2$	0.965	8.35
$C_{11}H_{20}O_2$	1.153	5.68	Residue	6.118	52.8
$C_{12}H_{22}O_2$	1.453	7.14	**Alcohols**		
			$C_{11}H_{22}O$		
$C_{13}H_{24}O_2$	1.793	8.8	$C_7H_{12}O_2$	0.741	7.52
Residue	4.938	24.3	$C_8H_{14}O_2$	1.216	12.3
			$C_9H_{16}O_2$	0.959	9.75
			Residue	6.923	70.2

Thus it has been established that, in the oxidation of *n*-alkylcyclohexane hydrocarbons in the liquid phase (in the presence of boric acid), predominantly secondary alcohols are formed, representing a mixture of isomers with the hydroxyl group located both in the side chain and in the ring of the alcohol molecule. With lengthening of the side chain of the *n*-alkylcyclohexane molecule in the hydroxyl-containing oxidation products, the proportion of naphthenic alcohols with the hydroxyl group at secondary carbon atoms of the side chain increases. The secondary carbon atoms of the side chain possess approximately equal reactivity toward oxygen.

Institute of Petrochemical Synthesis
Academy of Sciences of the USSR

Moscow Institute of Fine Chemical Technology
named after M. V. Lomonosov

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Note: Figure translations are in progress. See original paper for figures.