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Abstract

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OXIDATION OF MONOMETHYL-SUBSTITUTED PARAFFIN HYDROCARBONS IN THE LIQUID PHASE IN THE PRESENCE OF BORIC ACID

It was previously established ([1],[2]) that, in the oxidation of *n*-paraffin hydrocarbons in the liquid phase (in the presence of boric acid), secondary alcohols are formed predominantly, possessing the same skeleton and the same number of carbon atoms in the molecule as the starting hydrocarbon. The secondary alcohols formed are a mixture of all possible isomers. No appreciable difference was found in the reactivity toward oxygen of the secondary carbon atoms of molecules of higher paraffin hydrocarbons of normal structure.

The aim of the present investigation was to clarify the influence of the tertiary carbon atom in the molecule of monomethyl-substituted paraffins on their oxidative transformations and on the composition of the alcohols formed, which is of considerable interest for elucidating the mechanism of alcohol formation, as well as for selecting raw materials and using them in the production of alcohols ([3]). For this purpose we synthesized, by the Grignard method, 2-methyldodecane and 8-methylpentadecane. The constants of the synthesized hydrocarbons are given in Table 1.

Table 1

Characteristics of the hydrocarbons

Hydrocarbon	b.p., °C/mm found	b.p., °C/mm lit. ([4])	n_D^{20} found	n_D^{20} lit. ([4])	d_4^{20} found	d_4^{20} lit. ([4])	Crystallization temp., °C found	Crystallization temp., °C lit. ([4])
2-Methyldodecane	103–104/10.5	103/10.5	1.4240	1.4235	0.7540	0.7542	−27.2	−27.6
8-Methylpentadecane	149–149.5/15	150/15	1.4348	1.4341	0.7743	0.7744	−29.5	−29.3

The oxidation of the hydrocarbons obtained was carried out in the apparatus described earlier ([1]), at normal pressure, with a nitrogen–oxygen mixture con-

taining 3.0-3.5% O_2, at a flow rate of the oxidizing gas of 800 l/kg·hr, a reaction temperature of 165-170°, and a duration of 3-4 hr. The amount of acid added was 5% of the initial hydrocarbon.

As can be seen from the data given in Table 2, the principal products of the conversion of the individual hydrocarbons are hydroxyl-containing compounds.

The oxidate obtained was saponified with water (95°) to decompose the boric esters. The saponified oxidate was treated with an alcoholic solution of caustic potash in order to decompose esters. To isolate the alcohols, chromatographic separation of the oxidates on ASK-grade silica gel was used. Petroleum ether boiling up to 60° (at 20°), benzene (at 50°), and acetone (at 20°) were used as eluents. The sequence of component isolation was as follows: hydrocarbons, monofunctional compounds, bifunctional compounds ([5]). The monofunctional compounds isolated chromatographically were purified from ketones through boric esters and distilled in vacuum. The analysis of the isolated alcohols is given in Table 3. It was found that, in the oxidation of individual monomethyl-substituted paraffin hydrocarbons, the hydroxyl numbers of the oxidates and of the alcohols isolated from the oxidation products, determined by the acetylation method, are lower than the hydroxyl numbers determined by the Chugaev-Tserevitinov method (Tables 2, 3).

It is generally known that tertiary alcohols are not determined quantitatively by the acetylation method. On this basis one may assume that, in the oxidation of monomethyl-substituted paraffin hydrocarbons, a certain amount of tertiary alcohols is formed. (It was established experimentally that 2-methyldodecanol-2 and 8-methylpentadecanol-8 readily react with boric acid, forming trialkyl borates that are stable under the oxidation conditions adopted.)

Table 2

Characteristics of the oxidates

Starting hydrocarbon	Duration, h	Acid number	Ester number	Carbonyl number	Hydroxyl number, KOH mg/g (acetylation method)	Hydroxyl number, KOH mg/g (Terevitinov method)	Conditional oxidation depth, nmol/g	Distribution of products in oxidate, mol. %: free and bound acids	Distribution of products in oxidate, mol. %: carbonyl compounds	Distribution of products in oxidate, mol. %: free and bound alcohols
2-Methyldodecane	1	0	0	9.3	23.7	33.4	0.76	0	21.8	78.2
2-Methyldodecane	2	1.4	3.7	15.1	45.7	68.8	1.65	5.5	16.3	78.2
2-Methyldodecane	3	3.2	10.2	15.4	56.2	89.3	2.29	10.5	12.0	77.5
2-Methyldodecane	4	5.8	12.3	17.7	67.5	113.8	2.89	11.2	11.0	77.8
8-Methylpentadecane	1	1.2	0	14.2	13.2	21.0	0.65	8.3	39.0	57.7
8-Methylpentadecane	2	3.2	6.7	15.2	30.5	42.6	1.33	13.3	20.4	66.3
8-Methylpentadecane	3	5.3	11.8	16.8	47.4	63.5	1.94	15.6	15.3	69.1
8-Methylpentadecane	4	7.6	14.1	16.9	54.9	82.3	2.41	16.1	12.5	71.4

Table 3

Characteristics of alcohols obtained by oxidation of monomethyl-substituted paraffin hydrocarbons

Starting hydrocarbon	B.p., °C at 2 mm Hg	n_D^{20}	Hydroxyl number, KOH mg/g (acetylation method)	Hydroxyl number, KOH mg/g (Terevitinov method)	Hydroxyl number, KOH mg/g (calculated)	Alcohol content, mol. %, by dehydration method by water, secondary	Alcohol content, mol. %, by dehydration method by water, tertiary	Alcohol content, mol. %, by dehydration method by olefin, secondary	Alcohol content, mol. %, by dehydration method by olefin, tertiary	Alcohol content, mol. %, spectrophotometrically, secondary	Alcohol content, mol. %, spectrophotometrically, tertiary
2-Methyldodecane	102.0–109.5	1.4418	208.1	277.2	280.5	70	30	71	29	72	28
8-Methylpentadecane	129.5–137.7	1.4481	163.4	229.5	231.8	71	29	72	28	74	26

To determine the content of tertiary alcohols, several methods were used; these showed good agreement of the results (Table 3). The content of tertiary alcohols was determined on the basis of the dehydration reaction of tertiary alcohols in the presence of a catalyst—toluenesulfonic acid—and titration of the water evolved with K. Fischer reagent ([6]), by the method developed by L. N. Petrova ([7]), by a spectrophotometric method based on the absorption spectra of alkylnitrites,* and also by a modification of L. N. Petrova' s method with determination of the olefins formed during dehydration by chromatography on ASK-grade silica gel. Petroleum ether was used as the eluting liquid for olefins, and acetone for oxygen-containing compounds. The isolated olefinic hydrocarbons had iodine numbers of 139.0 and 113.2 (for $C_{13}H_{26}$ the corresponding value is 139.5, and for $C_{16}H_{32}$, 113.0).

The 2-methyldodecene obtained was hydrogenated in an *n*-heptane medium over Raney catalyst at 120 atm and 160°. After distillation, the hydrogenated product had a boiling point of 101/10 mm, n_D^{20} 1.4237, d_4^{20} 0.7539, and a crystallization temperature of −27.1°.

Found, %: C 84.96; H 15.12
$C_{13}H_{28}$. Calculated, %: C 84.78; H 15.22

* This method, as applied to higher tertiary aliphatic alcohols, will be published by us in the near future.

A mixed-melting test of the product obtained with 2-methyldodecane gave no

depression. As can be seen from the data presented, the hydrocarbon obtained is identical with the starting hydrocarbon.

These data make it possible to establish that, in the oxidation of monomethyl-substituted paraffin hydrocarbons by molecular oxygen in the liquid phase under the conditions we adopted, tertiary alcohols containing the same number of carbon atoms as the starting hydrocarbon are formed along with other alcohols. The alcohols that did not undergo dehydration were examined for the content of primary and secondary alcohols by the method described by us earlier [8], and also by the spectrophotometric method from the absorption spectra of alkyl nitrites on an SFD-1 spectrophotometer.

The results of these analyses showed that they are represented by secondary alcohols. Primary alcohols were practically not found. The secondary alcohols were subjected to dehydration over an aluminosilicate catalyst in xylene at 140–142° [2]. The olefin obtained (iodine number 140.0; for $C_{13}H_{26}$, 139.5 is required) was hydrogenated in *n*-heptane in the presence of Raney catalyst at 120 atm and 160°. The hydrocarbon obtained, by its constants, fully corresponded to 2-methyldodecane. To determine the position of the hydroxyl group in the secondary alcohols obtained by oxidation of 2-methyldodecane, we used the method we have described for oxidation of alcohols with potassium dichromate in dilute sulfuric acid, followed by isolation and identification of the acids formed [9]. This method was preliminarily checked on the individual alcohol 2-methyldodecanol-3, synthesized by the Grignard reaction.

Distribution of the acids obtained from 2-methyldodecanols (oxidation product of 2-methyldodecane) (in mole percent): $C_5H_{10}O_2$ 12.4; $C_6H_{12}O_2$ 15.6; $C_7H_{14}O_2$ 18.1; $C_8H_{16}O_2$ 15.4; $C_9H_{18}O_2$ 15.2; $C_{10}H_{20}O_2$ 19.4; $C_{11}H_{22}O_2$ 3.9.

The data obtained make it possible to conclude that the alcohols we investigated are a mixture of possible isomers of secondary 2-methyldodecyl alcohols. Thus, it has been established that, in the oxidation of monomethyl-substituted paraffin hydrocarbons in the liquid phase (in the presence of boric acid), hydroxyl-containing compounds are formed in a yield of about 75 mole %. The alcohols formed have the same carbon skeleton and the same number of carbon atoms in the molecule as the starting hydrocarbon. Investigation of the alcohols showed that they are a mixture of secondary and tertiary alcohols. The amount of tertiary alcohol is about 25–30 mole %. The secondary alcohols represent a mixture of all possible isomers. This gives grounds to believe that, under the oxidation conditions adopted by us, the reactivity toward oxygen of the tertiary carbon atom is higher than that of the secondary carbon atoms of the molecule of higher monomethyl-substituted paraffin hydrocarbons.

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