Chemistry

Corresponding Member of the Academy of Sciences of the USSR A. N. Bashkirov and A. I. Kistanova

1960

SovietRxiv

Abstract

Full Text

Chemistry

Corresponding Member of the Academy of Sciences of the USSR A. N. Bashkirov and A. I. Kistanova

OXIDATION OF NAPHTHENIC HYDROCARBONS IN THE LIQUID PHASE IN THE PRESENCE OF BORIC ACID

In our laboratory, the oxidation of paraffinic and olefinic hydrocarbons in the liquid phase in the presence of boric acid has been studied ([1,2]). It was established that the structure of the hydrocarbon molecule affects the nature of its oxidative transformations. In this connection, it was of considerable interest to study the oxidation of naphthenic hydrocarbons under the same conditions, which ensure a high directionality of the process toward the formation of alcohols.

For this purpose we synthesized, by the Grignard method, a series of naphthenic hydrocarbons with side chains of different length in the molecule (*n*-amylcyclohexane, *n*-heptylcyclohexane, *n*-nonylcyclohexane). The constants of the synthesized hydrocarbons are given in Table 1.

Table 1

Hydrocarbon	Found	Found	Found	Literature data ([8])	Literature data ([8])	Literature data ([8])
	b.p., °C/mm	n_D^{20}	d_4^{20}	b.p., °C/mm	n_D^{20}	d_4^{20}
n-Amylcyclohexane	77–78°/10	1.4449	0.8045	77/10	1.4445	0.8040
n-Heptylcyclohexane	109–110°/10	1.4492	0.8101	109/10	1.4486	0.8100
n-Nonylcyclohexane	138–139°/10	1.4530	0.8172	138/10	1.4522	0.8170

The oxidation of naphthenic hydrocarbons was carried out at normal pressure with a nitrogen-oxygen mixture containing 3.5% O_2, at a specific flow rate of oxidizing gas of 1000 l/kg $\cdot$ h, a reaction temperature of 165°, and an experiment duration of 4 h. The amount of boric acid added was 5%.

The oxidation was carried out in apparatus described by us earlier ([1]). After completion of the experiment, the oxidate was washed with hot water and analyzed. The characteristics of the oxidates are given in Table 2.

Table 2

Hydrocarbon	Hydroxyl number	Acid number	Ester number	Carbonyl number
n-Amylcyclohexane	87.0	5.6	9.0	18.2
n-Heptylcyclohexane	62.0	3.1	4.2	12.5
n-Nonylcyclohexane	89.6	5.8	6.2	15.6

The data presented show that, under the conditions adopted, the principal products of the oxidation reaction of naphthenic hydrocarbons are alcohols.

For the purpose of isolating the alcohols, the oxidate was saponified with water to decompose the boric acid esters. The unreacted hydrocarbons were separated from the oxygen-containing compounds by chromatography on ASK-grade silica gel. Petroleum ether boiling up to 60° and methanol were used as displacing liquids. The complex esters were saponified with caustic potash. The isolated alcohols were purified from ketones via boric acid esters. For separation of bifunctional compounds formed during oxidation in small amounts, a chromatographic method was used.* As displacing liquids in this case benzene (at 60°) and methanol (at 20°) were used. The pure alcohols were distilled in vacuo. The characteristics of the alcohols obtained are given in Table 3.

Table 3

Alcohols	Found: b.p., °C/mm	Found: n_D^{20}	Found: hydroxyl number	Calculated: hydroxyl number
$C_{11}H_{22}O$	81–82°/1	1.4668	321	329
$C_{13}H_{26}O$	99–101°/1	1.4680	280	283
$C_{15}H_{30}O$	119–121°/1	1.4683	240	248

In the alcohols obtained, the contents of primary and secondary alcohols were determined (4). The results of the analysis are given in Table 4.

In order to establish whether the oxidation of the above-mentioned hydrocarbons is connected with destruction of the molecule, the alcohols isolated from the oxidation products of *n*-nonylcyclohexane were dehydrated over anhydrous aluminum oxide at 270° in vacuo. The resulting unsaturated hydrocarbons had iodine number 120 (for $C_{15}H_{30}$, 122 is required). These hydrocarbons were hydrogenated in an *n*-heptane medium over Raney nickel catalyst at a hydrogen pressure of 30 atm and a temperature of 180°, and were purified from *n*-heptane by vacuum stripping of the latter. A comparative characterization of the hydrocarbon obtained from the alcohols and of the initial *n*-nonylcyclohexane is given in Table 5.

Table 4

Alcohols	Content of alcohols, mol.%: primary	Content of alcohols, mol.%: secondary
$C_{11}H_{22}O$	2.7	97.3
$C_{13}H_{26}O$	2.2	97.8
$C_{15}H_{30}O$	1.5	98.5

Table 5

Hydrocarbon	B.p., °C/mm	n_D^{20}	Found, %: C	Found, %: H
Hydrocarbon obtained from the alcohols	99–100°/1	1.4532	85.62	14.38
n-Nonylcyclohexane	99°/1	1.4530	85.59	14.33

The data in Table 5 show that the indicated hydrocarbons are identical. Thus, in the oxidation of naphthenes with a side chain of normal structure in the presence of boric acid, under the conditions adopted by us, there is formed—

* The method developed by us for the isolation of bifunctional compounds will be published in the near future.

alcohols are formed. Oxidation proceeds without destruction of the molecule of the substance being oxidized. The alcohols formed are mainly secondary ones, with the same number of carbon atoms in the molecule as in the starting hydrocarbon.

Institute of Petrochemical Synthesis
Academy of Sciences of the USSR

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

Received
20 X 1959

REFERENCES

1. A. N. Bashkirov, *Khim. nauka i prom.*, **1**, No. 3, 273 (1956).
2. A. N. Bashkirov, Shimon Pal, *DAN*, **128**, No. 6 (1959).
3. W. Schlenk, *Ann.*, **573**, 142 (1951).
4. A. N. Bashkirov, V. V. Kamzolkin et al., *Khim. i tekhnol. topliva i masel*, **4**, 7 (1957).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.