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Corresponding Member of the Academy of Sciences of the USSR A. N. BASHKIROV, V. V. KAMZOLKIN,

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Abstract

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Corresponding Member of the Academy of Sciences of the USSR A. N. BASHKIROV, V. V. KAMZOLKIN,
M. M. POTARIN, and G. D. KOLOVERTNOV

PREPARATION OF HIGHER ALIPHATIC KETONES BY THE METHOD OF DEHYDROGENATION OF SECONDARY ALCOHOLS

Previously we (^{1}) showed the possibility of synthesizing higher aliphatic ketones by the oxidation of higher secondary alcohols, which in turn were obtained by the direct oxidation of paraffin hydrocarbons in the presence of boric acid (^{2}). The possibility of obtaining ketones by dehydrogenation of the above-mentioned alcohols was also noted (^{1}).

There are reports in the literature on the preparation of lower aldehydes and ketones by this route. The reaction is usually carried out in the vapor phase over catalysts containing iron, zinc, copper, nickel, platinum, etc. (^{3}). It has also been shown that, with increasing molecular weight of the alcohols, the dehydrogenation reaction does not proceed altogether smoothly and is complicated by a side dehydration reaction (^{4}). Dehydrogenation of higher alcohols can also be carried out in the liquid phase over Raney catalyst (^{5}).

The present work presents the results of a study of the dehydrogenation reaction of higher secondary alcohols, with the aim of obtaining the corresponding ketones, on an industrial skeletal nickel catalyst.

The dehydrogenation of higher secondary alcohols in the liquid phase was carried out in a flask equipped with a stirrer and condenser. Heating was performed with a gas burner; the reaction temperature was monitored with a thermometer. When the reaction was carried out under vacuum, the system was connected to a vacuum pump. The reaction product (“dehydrogenate”) was analyzed by the generally accepted procedure. The acid, ester, hydroxyl, carbonyl, and iodine numbers were determined. The amount of catalyst charged in all experiments was 10% of the weight of the alcohols. The alcohols subjected to dehydrogenation were those produced industrially and having d_4^{20} 0.8486; n_D^{20} 1.4496; b.p. 125-170° (1 mm Hg) (C_{16}–C_{19}); pour point +8.0°; acid number 1.1; ester number 3.4; hydroxyl number 220.0; carbonyl number 20.0; iodine number 10.0; hydrocarbon content 6 wt. %. Examination of the kinetic curves obtained when the reaction was carried out on the indicated catalyst (temperature 185°, residual pressure 33 mm Hg) shows that the dehydrogenation reaction of alcohols in the liquid phase proceeds at a high rate and is practically complete in 2

Fig. 1. Kinetics of the dehydrogenation reaction of secondary alcohols on a skeletal nickel catalyst (temperature 185°, residual pressure 33 mm Hg). 1 —ketones; 2 —alcohols; 3 —unsaturated compounds

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Fig. 2. Effect of temperature and pressure on ketone formation during dehydrogenation of secondary alcohols on a skeletal nickel catalyst (reaction time 2 hours). 1 —residual pressure 30 mm Hg; 2 —atmospheric pressure

Figure 2: Fig. 2. Effect of temperature and pressure on ketone formation during dehydrogenation of secondary alcohols on a skeletal nickel catalyst (reaction time 2 hours). 1 —residual pressure 30 mm Hg; 2 —atmospheric pressure

hours, providing a degree of conversion of the alcohols of up to 95 mol. % (see Fig. 1).

In the initial period, vigorous evolution of hydrogen is observed. Simultaneously, the iodine number of the product decreases, which can apparently be explained by the occurrence of a hydrogenation reaction of unsaturated compounds present in the initial alcohols. Subsequently, some increase in the iodine number is observed as a result of the side reaction of dehydration of the alcohols. Chromatographic analysis of the dehydrogenate on silica gel showed that the hydrocarbon content in this case increases from 6 wt. % to 10 wt. %.

The content of acids and complex esters in the reaction products practically does not differ from the content of these compounds in the initial alcohols.

Next, experiments were carried out to determine the effect of temperature and pressure on the alcohol dehydrogenation reaction.

The curves shown in Fig. 2 indicate that, as the temperature is raised, the rate of alcohol dehydrogenation increases. Carrying out the reaction under reduced pressure (residual pressure 33 mm Hg) favors the course of the reaction under study.

The product obtained by dehydrogenation of higher secondary alcohols was freed from small amounts of unreacted alcohols by esterifying the latter with boric acid. The compounds not reacting with boric acid were distilled off from the boric acid esters formed; the distillation was carried out in vacuum at a residual pressure of 7 mm Hg from a Claisen flask. As a result of the distillation, a distillate was obtained boiling

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in the range 115-200° and characterized by d_4^{20} 0.8350; n_D^{20} 1.4440; freezing point +14.5°; carbonyl number 190.0; iodine number 4.6. After it had been freed from hydrocarbons by chromatography on silica gel, a fraction of higher aliphatic ketones was obtained having d_4^{20} 0.8362; n_D^{20} 1.4446; carbonyl number 202.0. The yield of ketones was 85 wt.% of the starting alcohols.

Thus, as a result of the study carried out, the possibility has been shown of obtaining higher aliphatic ketones in high yield by the dehydrogenation of higher secondary alcohols in the liquid phase on skeletal nickel catalysts.

Institute of Petrochemical Synthesis
Academy of Sciences of the USSR

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