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Catalytic Hydrogen Transfer over Magnesia. XVI.* Liquid Phase Reduction of Cycloalkanones by 2-Octanol

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The methods of selective reduction of the carbonyl group in aldehydes and ketones are still an attractive object for many research groups working in organic chemistry [1–3]. The Meervein-Ponndorf-Verley (MPV) reduction of carbonyl compounds by alcohols in the presence of metal alkoxides, mainly $Al(OR)_3$, is one of these classical methods [4]. In heterogeneous catalysis the hydrogen transfer phenomenon over metal oxides is postulated to resemble the MPV reduction mechanistically [5]. Among various metal oxides used as catalysts magnesium oxide seems to be the most active. In its presence the process can be realized either in vapor or in liquid phase, depending on the reactants volatility and the choice of reaction conditions. Activity of $ZrO_2 \cdot nH_2O$ [6] and Al_2O_3 [7] in the hydrogen transfer to carbonyl compounds has been recently studied.

In our former work the limitations of the method studied as well as the estimation of the influence of the steric hindrance around carbonyl group on the hydrogen acceptor properties of ketone during the liquid phase reduction of various substituted 1-phenyl-1-alkanones by 2-octanol in the presence of MgO have been determined [8]. The present work is concerned with the activity of MgO in the liquid phase reduction of a series of cycloalkanones by 2-octanol. The aim is to determine the differences in the hydrogen acceptor activity of studied cycloalkanones, arising from the ring size of the ketone.

MgO was prepared by thermal decomposition of $Mg(OH)_2$ at 873 K for 1 h in a stream of air and for 5 h in a stream of dry nitrogen. Specific surface area of MgO: 52 m^2/g, pore volume 1.6 cm^3/g. The details of MgO preparation were given in [9]. A cylindrical glass reactor equipped with a magnetic bar and inlet and outlet valves was immersed in a thermostated silicon oil bath, placed on the plate of a magnetic stirrer. The reactor was filled with dry nitrogen and 0.500 g of catalyst was introduced followed by 2-octanol and ketone. The reaction products were analyzed by gc, using 3.5 m long glass column filled with 20% OV-101 on Gas Chrom Q, FID detector.

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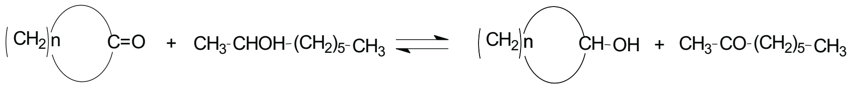
[*] – Part XV – Gliński M., *React. Kinet. Catal. Lett.* (accepted for publication).

Reduction of cycloalkanones by 2-octanol in liquid phase in the presence of magnesia as a catalyst proceeds according to:



A series of cycloalkanones of general formula $(CH_2)_nCO$, where n = 4, 5, 6, 7, 11 and 14, was used as hydrogen acceptors from 2-octanol over pure magnesia catalyst. The results are listed in Table 1.

Table 1. Catalytic transfer reduction of various cycloalkanones by 2-octanol in the presence of magnesium oxide. Donor/acceptor molar ratio = 1.5, acceptor/catalyst molar ratio = 1.0. Reaction temperature 423 K.

Number of CH_2 groups in ketone ring	Reaction time [h]	Conversion [%]	Yield of cycloalkanol [%]	Selectivity [%]
4	1	68.0	2.3	3
	2	73.2	2.5	3
	4	77.5	3.1	4
	6	83.3	3.9	5
5	1	22.9	19.0	83
	2	26.0	22.7	87
	4	33.7	30.4	90
	6	37.5	34.2	91
6	1	0.2	0.2	–[a]
	2	0.5	0.5	–[a]
	4	2.4	2.4	–[a]
	6	3.1	3.1	–[a]
7	1	0.3	0.3	–[a]
	2	0.4	0.4	–[a]
	4	0.5	0.5	–[a]
	6	0.8	0.8	–[a]
11	1	1.9	1.9	–[a]
	2	2.8	2.8	–[a]
	4	3.9	3.9	–[a]
	6	4.3	4.3	–[a]
14	1	–	–	–
	2	–	–	–
	4	0.2	0.2	–[a]
	6	0.3	0.3	–[a]

[a] – Selectivity to cycloalkanol ≥ 98% was observed.

The highest conversions of ketone were obtained during reduction of cyclopentanone. The conversion reached 83% in 6 h of reaction, but the yield of cyclopentanol did not exceed 5%. Similar behaviour of cyclopentanone was observed during classical Meervein-Ponndorf-Verley reduction by 2-propanol in the presence of $Al(OiC_3H_7)_3$; a quantitative conversion of ketone was observed, but the yield of alcohol was only 33%, due to aldol condensation of ketone [10]. Cyclohexanone possessed much higher hydrogen acceptor activity than the former ketone; 34% yield of cyclohexanol was found with selectivity higher than 90% after 6 h of reduction.

The selectivities of reduction of the remaining ketones were in the range 98–100%, but their activities in hydrogen transfer were very low. The highest yield of cycloheptanol was 3.1% and cyclooctanol only 0.8%. Slightly higher yield of product was observed during cyclododecanone reduction, the appropriate carbinol was obtained with the yield of 4.2%. The heaviest ketone used was the least active hydrogen acceptor, its reduction led to 0.3% yield of carbinol. The low reactivity of cyclopentadecanone in vapor phase hydrogen transfer reduction by 2-propanol over zeolites has been reported [11].

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