After pumping of the sample at 373-473 K, the PMR spectra at 293-77 K are analogous to the spectrum of the starting scolecite. The intensity of the narrow component increases and the intensity of the broad component decreases with increasing temperature of the pumping (503 K) (Fig. 1c). Only a narrow line is observed at the 623 K pumping temperature. The increase in the intensity of the narrow component is related to OH group formation.

CONCLUSIONS

The formation of OH groups occurs at pumping temperature 503 K and is complete at 623 K.

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HYDROGENATION AND ISOMERIZATION OF ALLYLBENZENE IN THE PRESENCE

OF THE (Cp₂TiCl)₂-LiAlH₄ CATALYTIC SYSTEM

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The reaction of Cp₂TiCl₂ with LiAlH₄ gives low-valence titanium hydride complexes, which are efficient homogeneous catalysts for hydrogenation, isomerization, and hydrometallation of unsaturated compounds under mild conditions [1-4]. Evdokimova et al. [3, 4] also used the (Cp₂TiCl)₂-LiAlH₄ system. The Al/Ti ratio, which determines the direction of the catalyzed reaction, holds considerable importance. However, such data were obtained for only a narrow range of substrates such as aliphatic $C_6-C_8 \alpha$ -olefins and cyclohexene [2-4].

In order to obtain new data on the catalytic properties of the (Cp₂TiCl)₂-LiAlH₄ system, we studied the transformations of allylbenzene (AB) on systems with A1/Ti from 0.25 to 1.5.

The hydrogenation of AB on $(Cp_2TiCl)_2$ -LiAlH₄ in benzene-ether was found to be accompanied by isomerization with the formation of trans-propenylbenzene (I), independently of the Al/Ti ratio. In contrast to the analogous reactions of 1-hexene, for which maxima in the rates of hydrogenation [3] and isomerization [4] are observed at A1/Ti = 0.5 and 1.0, respectively, the decrease in the initial hydrogenation rate upon change in the Al/Ti ratio is only slight. The initial rate of isomerization of AB is approximately an order of magnitude greater than the rate of hydrogenation of the substrate. When Al/Ti = 1.0, these rates are 5.9 and 0.6 moles/g-atom Ti·min, respectively. Figure 1a, which gives a plot of the mole fraction N vs. τ , shows that the rate of isomerization 10 min after the reaction onset decreases, which leads to the formation of a $\sim 1:1.5$ mixture of propylbenzene (II) and (I). This composition is not altered subsequently.

Upon the repeated introduction of LiAlH4, the activity of the catalytic system is restored such that the β -olefin accumulated is fully hydrogenated to (II) (Fig. 1b). This process begins after the complete transformation of AB. This effect may apparently be attributed to a rapid hydrometallation reaction [1] of the residual AB in the case of excess

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Fig. 1. Transformations of allylbenzene (1) to propylbenzene (2) and trans-propenylbenzene (3) in the presence of $(Cp_2TiCl)_2$ -LiAlH₄ at 20°C: a) H₂, Al/Ti = 1.0; b) H₂, after the introduction of a new portion of LiAlH₄, Al/Ti = 1.5; c) Ar, Al/Ti = 1.5.

 $LiAlH_4$. When a new portion of AB is introduced (immediately after the addition of $LiAlH_4$), this compound is converted at a rate which is 80-85% of the initial rate.

A relatively high reaction rate is observed when the isomerization of AB is carried out in argon (Fig. 1c), and the conversion of AB to (I) is 92% after 60 min. A feature of this process is the finding of a threshold value Al/Ti \approx 1, below which the isomerization does not occur. A total of 5-7% (II) is formed in addition to (I). This finding cannot be explained by a side hydrometallation reaction. Even if we assume that there is limited hydrometallation, leading to a tetraalkylaluminum derivative [1, 4], we would obtain \leq 4 moles (II) per mole excess LiAlH₄ upon their subsequent decomposition by hydrolysis prior to gas-liquid chromatographic analysis. In our experiments, the mole ratio of (II) to excess LiAlH₄ was \geq 6.5. Hence, under these conditions, there is partial reduction of the substrate by hydrogen transfer, probably from the solvent or Cp ligands.

Thus, these results indicate that the conversion of AB in the presence of $(Cp_2TiCl)_2$ -LiAlH₄ is complex in nature and may be given by the following scheme:



AB undergoes isomerization to (I) with subsequent hydrogenation to (II), direct hydrogenation, reaction with $LiAlH_4$, and reduction by hydrogen transfer from the solvent or Cp ligand.

EXPERIMENTAL

In light of the high sensitivity of the catalysts toward oxygen and water, all the experiments were carried out in vacuum or in argon. Ether, benzene, and ethylbenzene freshly distilled over LiAlH₄ or CaH₂ were used as the solvents. The AB sample was purified on a silica gel L column with subsequent distillation over CaH₂ prior to use. LaCo₅H_x served as the source of pure H₂. (Cp₂TiCl)₂ was synthesized by the reduction of Cp₂TiCl₂ using dichloroalane etherate [5] with subsequent recrystallization from THF. The purity of the compounds obtained was monitored by elemental analysis and was found to be 95-98%.

0.02-0.05 M solutions of the Ti(III) complexes were obtained by the reaction of $LiAlH_4$ in ether with $(Cp_2TiCl)_2$ in benzene. The concentration of $LiAlH_4$ in the ethereal solution was determined iodometrically [6]. The study of the catalytic properties of the Ti(III) complexes with substrate/Ti ratio from 50 to 150 was carried out at 20 ± 2°C and atmospheric pressure in a 15-cm³ glass reactor with a magnetic stirrer. The samples were decomposed upon contact with air. The composition of the reaction products was determined by gas-liquid chromatography on an LKhM-8MD chromatograph using a 3 m \times 3 mm column packed with 15% Triton X-305 on Celite 545 with nitrogen as the gas carrier and PhEt as the internal standard.

CONCLUSIONS

1. The $(Cp_2TiCl)_2$ -LiAlH₄ system with A1/Ti from 0.25 to 1.5 catalyzes both the homogeneous hydrogenation and isomerization of allylbenzene.

2. In an argon atmosphere, allylbenzene is isomerized to trans-propenylbenzene with 90-92% selectivity when Al/Ti = 1-1.5.

3. The possibility was demonstrated for reactivation of this catalytic system by its retreatment with LiAlH_4 .

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POLYCONDENSATION OF KETONES CATALYZED BY 12-PHOSPHOTUNGSTIC ACID

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Kargin et al. [1, 2] have examined the possibility of the polymerization and polycondensation of ketones as a result of an ordered arrangement of the monomer molecules. In the case of polycondensation at 453 K in the presence of $ZnCl_2$ or $TiCl_4$ with the exclusion of air, these authors obtained stable polyvinylenes. The condensation of acetone was observed also upon dissolving anhydrous 12-th series heteropoly acids (HPA) in this ketone [3]. In this case, the reaction proceeded under normal conditions, while distillation of the reaction mixture together with the catalyst at 323-523 K gave liquid alkylbenzenes. However, a detailed study of this reaction was not carried out. We have extended this investigation and isolated products, whose characteristics are given in Table 1, from solutions with $R^1R^2CO:H_3PW_{12}O_{40}$ ratio = 30:1, maintained for several months at 293 K by extraction in DMSO and CCl_4 .

A PMR, IR, and ¹³C NMR study of freshly prepared solvates of phosphotungstic acid with ketones showed that well-known condensation products are formed in the initial stage of the acetone transformations, including diacetone alcohol (DA), mesityl oxide (MO), mesitylene (M), and isophorone (IP). Analogous products are obtained from methyl ethyl ketone (MEK). Furthermore, $CH_3-CH=C(CH_3)-CH_2-C-CH_2$ is also formed. This product is the

result of the presence of the ethyl group in MEK.

Both carbonyl compounds and the products of their condensation acquire reactivity as a result of the formation of complexes with protons involving a heteropoly anion containing $C_{\cdots}C$ and $C_{\cdots}O$ bonds with bond order 1.5. The $C_{\cdots}O$ bonds in the complexes with ketone condensation products are so weakened that their stretching band in the IR spectrum appears at 1540 cm⁻¹.

The spectral data indicate that the final product of the polycondensation of acetone is not polymethylvinylene, which was isolated by Kargin et al. [1]. Comparison of the

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