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HETEROGENEOUS NICKEL-COBALT CATALYSTS IN THE ENANTIOSELECTIVE HYDROGENATION OF ETHYL ACETOACETATE

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In previous work [1], we showed that Raney cobalt catalysts modified by optically active hydroxyacids and amino acids perform the asymmetric hydrogenation of ethyl acetoacetate (EAA) with optical yields (p, %) up to 5-8%. On the other hand, the introduction of cobalt into intermetallide hydrides with the formula $\text{LnNi}_{5}\text{H}_{n}$ leads to a significant improvement in the asymmetrizing properties of this type of catalyst (p $\ge 30\%$) [2]. In this regard, it was of interest to study the behavior of bimetallic nickel-cobalt catalysts in this reaction. In other work [3], we showed that the optical yield of this reaction does not exceed 10-15% upon hydrogenation without solvent and without additives. On the other hand, both additives of acetic acid and NaBr and the nature of the solvent affect the dissymmetric properties of the nickel catalysts [4]. In this work, results are given of a study of the asymmetric hydrogenation of EAA in the presence of bimetallic nickel-cobalt powder catalysts differing in composition, modified with RR-(+)-tartaric acid (TA), using ethyl acetate (EA) as the solvent and acetic acid as an additive.

EXPERIMENTAL

Powdered nickel-cobalt catalysts were prepared by the decomposition of a mixture of nickel and cobalt acetates at 450°C over 3.5 h in a nitrogen stream with subsequent hydrogenation of the metal oxides obtained in a hydrogen stream at 350°C over 1.5 h. The catalysts were modified in a thermostatted cell by aqueous TA at 95°C over 1.5 h (pH 4.1). EAA was hydrogenated in a glass ampul within an autoclave at 120°C with p_{H_2} 110 atm over 12 h. The experiments were carried out with 6 ml EAA in 12 ml EA and 0.5 g catalyst. Then 0.1 ml acetic acid was added. After the reaction, the catalyst was separated by centrifugation and the catalysate was distilled in vacuo. The conversion (Y, %) of EAA to (-)-ethyl- β -hydroxy-butyrate (EHB) was determined on an LKhM-8MD chromatograph with a flame ionization detector on a column packed with 10% PEG-15,000 on Chromatone N-AW silanized with DMCS at 100°C. The nitrogen flow rate was 40 ml/min. The optical rotation (α_{obs}) was measured at 589 nm on an AI-EPO polarimeter. The specific rotation of EHB ($[\alpha]_{589}^{20}$ 24°) was used to calculate p.

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Sample no.	Ni content in the Ni-Co catalyst, %	Tartaric acid concentra- tion, %	Convession Y. %	Optical yield, p, %
1 2 3 4 5 * 7 8 9 10 ** 7 8 9 10 ** 7 8 9 10 ** 7 8 9 10 ** 7 8 9 10 ** 7 8 9 10 ** 7 8 9 10 **	0 10 25 50 50 75 75 75 75 100 100 100 Raney Ni	1 1 1 5 1 1 5 1 1 5 1 1 5 1	43 99 90 92 56 74 100 89 78 97 93 100 86	$\begin{array}{c} 1.0\\ 5.7\\ 20.0\\ 46.0\\ 50.0\\ 44.0\\ 52.0\\ 54.0\\ 54.0\\ 60.5\\ 65.0\\ 48.5\\ 47.5\end{array}$

TABLE 1. Hydrogenation of EAA in the Presence of Ni-Co and Ni Catalysts

*Hydrogenation in a solution of 12 ml dimethoxyethane. **pH_{mod} 5.1.

***pHmod 3.1, hydrogenation temperature 110°C.

RESULTS AND DISCUSSION

Table 1 gives the results of the study of the effect of the composition of the bimetallic Ni-Co catalysts and TA concentration of the modifying solution on the optical yield of the hydrogenation of EAA.

An increase in the nickel content up to 50 mass % gives an almost linear increase in p from 1 to 46%. The subsequent increase in p is slower; p is 54% for 90% nickel and 60-65% for the nickel catalyst. The conversion in all these cases was 90-100% but was only 43% for the cobalt catalyst. Nickel is apparently largely responsible for the enantioselective hydrogenation of EAA and, thus, even in the case of a low nickel content in the catalyst, a sharp increase is observed in the optical yield. At rather high nickel contents, this increase is slower.

A change in the TA concentration has a nonuniform effect on Y and p. In the case of nickel catalysts, the conversion is independent of the TA concentration but a decrease is observed in the optical yield from 60 to 48%. In the case of nickel-cobalt catalysts, an increase in the TA concentration from 1 to 5% leads to a slight increase in the optical yield (to 2-4%) but the conversion is considerably reduced: from 92 to 56% for the sample with 50% nickel and from 100 to 78% for the sample with 75% nickel. The replacement of EA by dimethoxyethane does not have a significant effect on the asymmetrizing properties of nickel-cobalt catalysts (sample 6). For comparison, Table 1 gives data for Raney nickel obtained under analogous conditions for the modification and hydrogenation of EAA (sample 13). The values of p were 47-49%, which is somewhat greater than the optical yields in the presence of Raney nickel observed in our previous work [5]. We should note that the optical yields achieved for the hydrogenation of EAA (60-65%) on powdered nickel catalysts are rather high and are 20-25% greater than the p values obtained in the presence of Raney nickel catalysts. These values are comparable with the optical yields on powdered nickel catalysts (63-71%), which were obtained by a more complicated procedure from nickel nitrates using a H_2 -He mixture in the reduction of NiO [6].

CONCLUSIONS

1. Bimetallic powdered nickel-cobalt catalysts differing in composition and modified by RR-(+)-tartaric acid were studied in the asymmetric hydrogenation of ethyl acetoacetate.

2. The optical yield of this reaction is increased to 54% with an increase in the nickel content in the Ni-Co catalyst to 90% and is 60-65% for the nickel catalyst.

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FLUORINATION OF SOME PHOSPHORIC ACID DERIVATIVES

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Anhydrous hydrogen fluoride is commonly used for the preparation of phosphoric and phosphonic acid fluorides [1]. The disadvantages of this reagent include its low boiling point, high toxicity, and the required use of special plastic or metal equipment. In recent years, various workers have shown that solutions of hydrogen fluoride in amines, especially in pyridine [2] and triethylamine [3], are completely stable, may be heated to relatively high temperatures without the loss of HF, do not etch glass, and retain virtually all the properties of hydrogen fluoride. The liquid complex, $Et_3N \cdot 3HF$ (I), is especially stable and may be distilled in vacuum in quartz or even glass vessels. This complex has been used for the synthesis of carboxylic acid fluorides [3], phosphorus trifluoride from PCl₃, and various products $R-PF_5^-$ (R = OAlk and NHAr) and $PF_5 \cdot HNR_2$ [4].

We studied the reaction of complex (I) with a series of phosphoric acid derivatives and found that it fluorinates not only compounds with P-Cl bonds but also compounds with other leaving groups.

Dichlorovinyl phosphates (II) and phosphorylated oximes (III) rapidly and quantitatively react with complex (I) at ~ 20° C in acetonitrile with the formation of diethyl fluorophosphate (IV).



The signal of the starting phosphate (II) or (III) disappears immediately in the ³¹P NMR spectrum after mixing the reagent and the signal of diethyl fluorophosphate appears ($\delta P - 8.47$ ppm, doublet of quintets, $J_{P-F} = 980$ and $J_{P-H} = 9$ Hz). The reaction rate and product yield are virtually unaltered upon varying the (II):(I) or (III):(I) ratio from 1:1 to 3:1 and diethyl fluorophosphate (IV) is formed quantitatively in all cases. When preparative separation of the product is required, the reaction is conveniently carried out not in acetonitrile, in which complex (I) and the triethylamine hydrofluorides obtained are very soluble, but rather in carbon tetrachloride as an emulsion with subsequent separation of the solution of diethyl fluorophosphate in CCl₄ from the insoluble side-products (see Experimental).

The facility of this reaction is undoubtedly a consequence of the advantageousness of formation of the P-F bond and the enolic structure of the leaving group.

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