ENANTIOSELECTIVE HYDROGENATION IN CHOLESTERYL TRIDECANOATE AS A CHIRAL LIQUID-CRYSTALLINE MATRIX

V. A. Pavlov, N. I. Spitsyna,
and E. I. Klabunovskii

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Asymmetric reactions are possible in a medium of cholesteric liquid crystals (CLC) in the temperature range of the mesophase, where a chiral spiral structure is formed. However, the data on the realization of asymmetric synthesis in a medium of CLC as a chiral matrix are contradictory. Thus, together with the communications on realizing a stereospecific Claisen rearrangement in the presence of cholesteryl benzoates [1], the enantioselective decarboxylation of ethylphenylmalonic acid [2], the photochemical synthesis of hexahelicene [3], and photocyclization to give oxaziridine [4], it is mentioned that the asymmetric effect could not be reproduced in some of the above enumerated reactions, and in other reactions it was not detected [4-6]. A negative result in a number of examples is explained [6] by the large spacing of the spirals of the CLC (300-400 nm) and, consequently, by the absence of chirodiastaltic interaction [7] with the comparatively small molecules of the substrate. The appearance of such interaction could be expected in the case of substrate molecules with either a linear of sterically complex structure, which will be manifested in the genesis of induced circular dichroism (ICD) of the reaction product in the absorption band of its chromophore [8]. Starting with this, we studied the possibility of effecting the catalytic enantioselective hydrogenation of N-acetamidocinnamic acid (AACA) to acetylphenylalanine in the presence of Wilkinson catalyst in a medium of the CLC of cholesteryl tridecanoate as the chiral matrix.

The enantioselective hydrogenation of AACA in the presence of chiral rhodium complexes has been studied widely and is used to obtain the optically active unsubstituted amino acid phenylalanine [9]. We used the achiral $RhCl(PPh_3)_3$ catalyst. Since the catalyst and AACA are insoluble in the cholesteryl tridecanoate (CTD) melt we ran the reaction in an n-BuOH–C_6H_6 mixture (2:1 by volume). CTD retains a spiral structure in solution, since in the circular dichroism spectra of solutions of CTD, AACA, and the rhodium complex ICD was observed in the absorption band of these compounds. From Figs. 1 and 2 it can be seen that in the spectra of both the substrate and the catalyst* the maximum on the circular dichroism spectra corresponds to the maximum on the electronic spectra, which testifies to the fact that the observed effect is actually ICD. The appearance of ICD serves as proof that both the spiral structure of CTD in solution and the spiral orderliness of the chromophore molecules are retained [8]. An increase in the maximum of the ICD with time in solutions of both the substrate and the catalyst on reaching stable values in approximately 1 h testifies to the gradual forming of a spiral environment. A comparison of Figs. 1 and 2 shows that the ICD value of the more bulky rhodium complex molecule exceeds by one order of magnitude the value for the substrate and has the same sign.

The catalytic reaction proceeds with the formation of the intermediate catalyst–substrate complex, and consequently we assume that a spiral orderliness of the same sign for both components of the complex will facilitate the genesis of chirodiastaltic interaction and discrimination between the re and si sides of the C=C bond in the substrate that is coordinated in the intermediate complex. Actually, it proved that the prochiral AACA substrate, when treated with the achiral Wilkinson catalyst in CTD as the chiral matrix, is

*The ICD spextrum on the $RhCl(PPh_3)_3$ complex was studied in cholesteryl stearate, and not CTD, as the medium. It may be assumed that the picture would not change essentially in CTD, since both of the CLC in their mesophase form spirals of the same sign and with close spacing [10].

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
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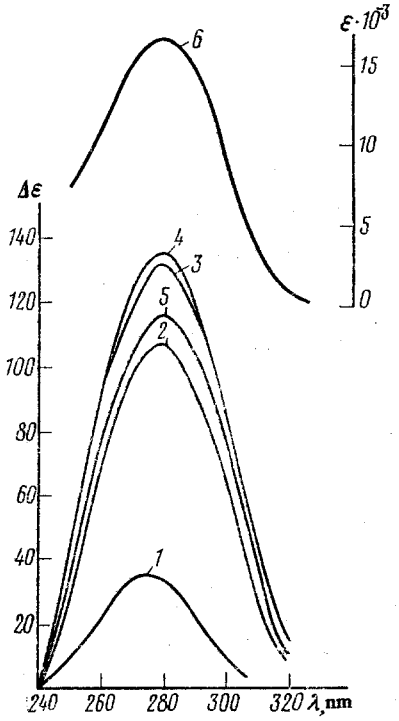

Fig. 1

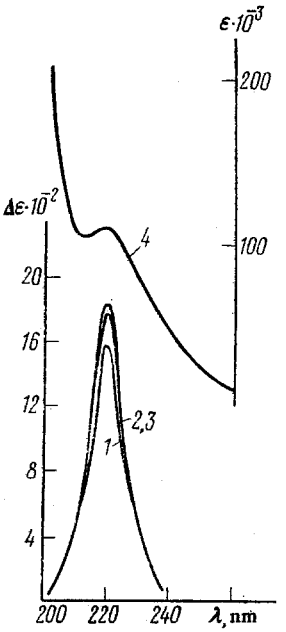

Fig. 2

Fig. 1. Induced circular dichroism spectra (1-5) and UV spectrum (6) of N-acetamidocinnamic acid (0.01 g) in n-BuOH solution (1 ml), containing cholesteryl tridecanoate (0.332 g), at 54°C, layer 20 μm: 1) 15 min; 2) 30; 3) 60; 4) 90; 5) 120 min.

Fig. 2. Induced circular dichroism spectra (1-3) and UV spectrum (4) of $RhCl(PPh_3)_3$ (0.004g) in n-BuOH solution (1 ml), containing cholesteryl stearate (0.332 g), at 67°.

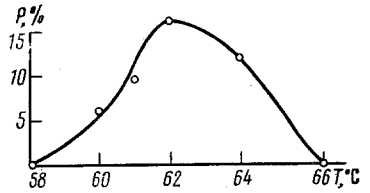

Fig. 3. Optical yield of N-acetylphenylalanine as a function of temperature (1.66 g of CTD, 0.013 g of $RhCl(PPh_3)_3$, 0.107 g of AACA, 4 ml of n-BuOH, and 2 ml of C_6H_6).

hydrogenated enantioselectively. The optical yield of acetylphenylalanine as a function of temperature (Fig. 3) has a maximum, which is found in the middle of the temperature range of the mesophase of CTD [10]. It may be assumed that this range of the mesophase essentially does not change in the CTD—n-BuOH—C_6H_6 system (25, 49, 26%) when compared with the pure CTD.

EXPERIMENTAL

The ICD spectra of the catalyst and AACA in a medium of CLC and the optical rotation of acetylphenylalanine were measured on a Spectropol-1 spectropolarimeter, and the UV spectra were measured on a Specord UV-VIS spectrophotometer. The ICD spectra of the samples in GLC were taken as a 20-μm layer in a thermostatted (±0.5°) cell.

The AACA was recrystallized from alcohol, mp 191°, the CTD was analytical grade, the $PhCl(PPh_3)_3$ was obtained as described in [11], the solvents were made absolute, and the H_2 was freed of O_2.

The hydrogenation was run in a thermostatted glass reactor equipped with a magnetic stirrer. Into the reactor were charged 1.66 g of CTD and a solution of 0.107 g of AACA in 4 ml of n-BuOH, the system was blown with argon, the reaction temperature was set, and a solution of 0.013 g of $RhCl(PPh_3)_3$ in 2 ml of benzene was added from a syringe. A clear orange solution was formed. The stirring was stopped, the system was filled with H_2, and a buret was attached to measure the H_2 absorption. At the end of reaction (8 h) 50 ml of ethanol was added to the reaction mixture, the CTD was filtered, and the filtrate was evaporated to dryness on a rotary evaporator. The dry residue was dissolved by heating in water, made alkaline with 0.1 N NaOH solution, and filtered. The solution was passed through a bed of the cationite Dowex 50W × 8, acidified to pH 4, and evaporated. The obtained product, a mixture of N-acetylphenylalanine and unreacted AACA, was analyzed by spectrophotometry, using the difference in the molar extinction coefficient at 280 nm. The conversion was 98-100%. The optical yield was determined from the $[\alpha]_{400}^{23}$ + 240° (c 2.35, alcohol).

CONCLUSIONS

1. In a liquid crystal medium N-acetamidocinnamic acid and $RhCl(PPh_3)_3$ in solution (n-BuOH–benzene) exhibit induced circular dichroism.

2. The hydrogenation of N-acetamidocinnamic acid in the presence of the achiral $RhCl(PPh_3)_3$ catalyst in solutions, containing cholesteryl tridecanoate, proceeds enantioselectively with an optical yield of up to 16%.

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