USA

10 OCTOBER

INTERNATIONAL SIMPOSIUM OF YOUNG SCHOLARS

OpenAIRE
Open Access Infrastructure for Research in Europe

Mendeley

Google Scholar

doi

International Simposium of Young Scholars (USA)

Table of Content

Biological Significance of Keto Esters

Karomatov Sardor Aminovich
Xatamov Umedjon Farhod o'g'li

Annotation:

Homogeneous asymmetric catalytic hydrogenation of parochial carbonyl compounds is of great interest, since the resulting optically active secondary alcohols are valuable choral blocks for fine organic synthesis. The substrates well studied in this reaction include a- and/3-ketoesters and their functional derivatives. Being less reactive, u-ketoesters as parochial substrates have not been studied practically.

Keywords: asymmetric hydrogenation, binuclear complexes, catalysis

In this regard, an important aspect is the search for effective catalytic systems for the reaction of asymmetric hydrogenation of u-ketoesters based on the study of the regularities and mechanism of the reaction by kinetic and spectral methods. In addition, there is no general method in the literature for the synthesis of y-alkyl- and y-aryl-substituted lactones in enantiomerically pure form, which can be obtained in one stage by catalytic hydrogenation of y-ketoesters. The possibility of recycling expensive chiral catalysts is also an important problem that has not yet been solved to date. This approach allows, on the one hand, reducing the cost of the process of obtaining u-lactones and, on the other hand, meets the principles of "green" chemistry.

For the first time, a systematic study of homogeneous asymmetric hydrogenation of u-ketoesters using ruthenium complexes with chiral bisphosphine ligands as catalysts was carried out. Highly efficient Ru(II)- and Ru(III)-containing catalytic systems for homogeneous asymmetric hydrogenation of esters of y-ketocarboxylic acids with various substituents at the y-carbonyl carbon atom have been created. It has been established that mineral acid additives lead to a sharp increase in the rate of asymmetric catalytic hydrogenation of y-ketoesters with high enantiomeric purity of the resulting y-lactones. The kinetics and mechanism of asymmetric catalytic hydrogenation of u-ketoesters are investigated using isotopic and spectral methods; it is assumed that the catalytically active intermediates are binuclear Ru(II) hydride complexes formed as a result of H2 heterolysis. A universal preparative method has been developed for obtaining enantiomerically pure y-alkyl- and y-aryl-substituted lactones based on the reaction of asymmetric hydrogenation of y-ketoesters in the presence of catalytic systems [RUCH(BINAP)] - HCI and RuCb-BINAP-HCl. Using the example of asymmetric hydrogenation of methylevulinate, a reaction with repeated recycling of a metal-complex catalyst deposited on a solid organic polyelectrolyte was carried out for the first time.

A number of reviews have been devoted to the asymmetric catalytic hydrogenation of prohiral substrates, including ketoesters. In contrast to asymmetric hydrogenation using heterogeneous catalysts, when the catalysis is carried out surface complexes of metals such as nickel or platinum ' , the achievements of recent years in the field of homogeneous asymmetric hydrogenation are associated with the use of chiral complexes of ruthenium and rhodium. It was for outstanding achievements in this field that in 2001 W. Knowles and R. Noyori were awarded the Nobel Prize in Chemistry. As for the homogeneous asymmetric hydrogenation of ketoesters with catalysts based on other metals, such information is practically absent in the literature. In this review, we have summarized the literature data related to the reactions of homogeneous asymmetric hydrogenation of a-, (3- and 7-ketoesters occurring with high enantioselectivity (at least 80% of it). Its lower values are given only for comparison. The review considers the

formation of effective metal-complex catalysts, the influence of the nature of chiral and achiral ligands, as well as reaction conditions on the conversion of initial ketoesters and enantioselectivity of asymmetric hydrogenation.

Highly efficient Ru(II)- and Nii(W)-containing catalytic systems for homogeneous asymmetric hydrogenation of esters of y-ketocarboxylic acids with various substituents at the y-carbonyl carbon atom have been created. Ru(COD)(MA) systems showed the highest activity and enantioselectivity in situ2 - BINAP - HC1, [RUC12(DMOD)]2 - BINAP - HC1 and RuCl3-BINAP-HC1, the latter system being used for the first time in asymmetric catalytic hydrogenation.

The kinetics of the reaction of asymmetric hydrogenation of methylevulinate - the simplest u-ketoester - with hydrogen and deuterium in the presence of a catalytic Ru(COD)(MA) system has been studied2 - BINAP - HC1. It is found that the kinetic order for H2 and the catalyst is the first, and for the substrate and HC1 it changes from the first to zero with an increase in their initial concentrations. Kinetic isotopic effect is absent or insignificant.

Based on kinetic data and spectral study of metal-containing intermediates, a mechanism of catalytic hydrogenation of u-ketoesters is proposed, including reversible stages of coordination of H2 molecules by binuclear complexes of Ru(II), heterolysis of coordinated H2 with the formation of active hydride intermediates and an irreversible stage of hydride transfer to the acid-activated keto group of the initial substrate.

A universal preparative method for obtaining enantiomerically pure y-alkyl- and y-aryl-substituted lactones based on an asymmetric catalytic hydrogenation reaction in the presence of Ru(COD)(MA) systems has been developed2 - BINAP - HC1 hRUC13-BINAP-HC1.

Solid organic polyelectrolyte – poly (diallyldimethylammonium) was used for the first time in homogeneous metal-complex catalysis in order to recycle the catalyst and its repeated usehexafluorophosphate. It is shown that the activity of the catalyst does not decrease during three cycles, while the enantio selectivity remains high (98-99%) during at least five cycles.

Literatures:

1. Windaus, Klaenhardt Chem. Ber., 1921,54,585.
2. Mandal, Arun K.; Mahajan, S. W. Synthesis, 1991,4,311-312.
3. Mutalipova Diloromkhon Bakhtiyorjon qizi, Bakhranova Dilnoza Akhmedovna and Karomatov Sardor Aminovich. “Chemical analysis of essential oils extracted from medicinal plants growing in Uzbekistan.”WEB OF SCIENTIST: International Scientific Research Journal 2.5(2021): 501-505.
4. Qizi M. D. B., Qizi O. M. K., Axmedovna B. D. Synthesis of essential oils based on local raw materials //ACADEMICIA: An International Multidisciplinary Research Journal. – 2020. – Т. 10. – №. 6. – С. 1090-1094.
5. Mutalipova Diloromkhon Bakhtiyorjon kiziand Tosheva Dilnora Zohid kizi. “Different chemical analysis methods of extracting aromatic essential oils based on local raw materials.” ORIENTAL RENAISSANCE:Innovative, educational, natural and social sciences. Scientific Journal Impact Factor 1.4(2021): 1437-1441.