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Ionic liquid [BMIM]PF_6 as a medium for the selective hydrogenation of 1,4-diacetoxybut-2-yne on the Pd-containing catalysts

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A possibility of using a ionic liquid, 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6), as a reaction medium in the liquid-phase hydrogenation of 1,4-diacetoxybut-2-yne was examined. Two types of catalysts were studied: Pd(10%)/C and the palladium-containing catalytic system based on the biopolymer chitosan supported on silica gel (Pd(1%)/chitosan/SiO_2). The data obtained indicate high selectivity of hydrogenation of 1,4-diacetoxybut-2-yne to *cis*-1,4-diacetoxybut-2-ene under selected conditions.

Key words: ionic liquids, 1,4-diacetoxybut-2-yne, *cis*-1,4-diacetoxybut-2-ene, Pd-containing catalysts, hydrogenation.

cis-1,4-Diacetoxybut-2-ene is widely used as a synthone in organic synthesis.[1,2] One of the main methods for its preparation is the selective hydrogenation of 1,4-diacetoxybut-2-yne or but-2-yne-1,4-diol followed by acylation. The problem of selective catalytic hydrogenation of alkynes to alkenes with a certain configuration of the double bond and, particular, to but-2-yne-1,4-diol and its diacetate attracted attention of researchers attention for many years and still remains urgent.[3—5]

In recent years, ionic liquids have found wide use in many areas of chemistry. Numerous data on the use of ionic liquids in organic synthesis, catalysis, electrochemistry, and gas and liquid chromatography are presently published.[6—12] For instance, the ionic liquids as solvents corresponding to the requirements of "green" chemistry have emerged in organic chemistry as an alternative to low-boiling solvents.[10] As for the application of ionic liquid in catalysis, the available data predominantly concern the homogeneous catalytic reactions.[13—15] Nevertheless, they indicate specific merits of using ionic liquids in heterogeneous catalysis, in particular, in hydrogenation of various polyfunctional compounds.[16,17] For example, the selective hydrogenation of α,β-unsaturated aldehydes (cinnamaldehyde and citral) was carried out on Pd/C in diverse hydrophilic and hydrophobic ionic liquids.[18] In this case, the selectivity of reduction of the C=C double bond was increased compared to the use of standard organic solvents. At the same time, the reaction rate decreased when the hydrogenation was carried out in the ionic liquids.[17,18]

The purpose of this work was to reveal a possibility of selective catalytic hydrogenation of 1,4-diacetoxybut-2-yne by molecular hydrogen using ionic liquids as a reaction medium under the heterogeneous catalytic conditions. 1-*n*-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6) was chosen for the present study. It is known that this ionic liquid is resistant to the action of air and moisture and is characterized by an insignificant vapor pressure, low viscosity, and high thermal and chemical stability.[7] The classical catalyst Pd(10%)/C and the Pd-containing system based on chitosan supported on silica gel (Pd(1%)/chitosan/SiO_2) were used as hydrogenation catalysts. We have previously[19] shown that the hydrogenation of but-2-yne-1,4-diol in EtOH with the use of the Pt/chitosan catalysts proceeds with high selectivity and predominant formation of the *cis*-isomer of but-2-ene-1,4-diol. Therefore, it was of interest to study the influence of the ionic liquid on the selectivity of formation of *cis*-1,4-diacetoxybut-2-ene in the presence of the system Pd(1%)/chitosan/SiO_2 in the ionic liquid medium.

Experimental

The ionic liquid [BMIM]PF_6 (Merck kGAa) was used as a medium for the hydrogenation of 1,4-diacetoxybut-2-yne. Hydrogenation was carried out on Pd(10%)/C (AlfaAesar) and on the catalyst Pd(1%)/chitosan/SiO_2, which was prepared according to the known procedure.[20]

Catalytic experiments were carried out under the following conditions: a catalyst (1 mol.% Pd) and [BMIM]PF_6 (1—2 mL)

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were placed in the Schlenk vessel under argon atmosphere, and the vessel was evacuated and purged with argon with stirring. This procedure was repeated three times. Then the system was again evacuated and filled with hydrogen (3 times). The catalyst was pre-treated with hydrogen for 10 min in the temperature range from 20 to 60 °C. Then 1,4-diacetoxybut-2-yne (0.4—0.8 mmol, 68.0—136.0 mg) was added. Hydrogenation was carried out with magnetic stirring (1400 rpm, 1 atm H_2, 20—60 °C).

The reaction course was pre-monitored by TLC on plates of silica gel 60 F254 (Merck) using $CHCl_3$ as an eluent; two successive runs of the eluent were used for better separation. The composition of the catalytic mixture was analyzed by GLC and NMR. Each control sample was extracted with Et_2O (5×1 mL), and the extracts were evaporated and dissolved in $CDCl_3$ for recording ^1H NMR spectra. The GLC analysis was performed on a Biokhrom-1 chromatograph equipped with a flame-ionization detector on capillary columns SE-30 and FFAP.

Results and Discussion

The results obtained are presented in Table 1. The major product of 1,4-diacetoxybut-2-yne hydrogenation is the *cis*-isomer of 1,4-diacetoxybut-2-ene. The following reactions run in parallel: hydrogenation of *cis*-1,4-diacetoxybut-2-ene and isomerization (*cis—trans*-transformation). The selectivity of the process on the studied palladium-containing systems was determined as the ratio of the contents of hydrogenation products in the reaction mixture: $S_1 = cis/cis + trans + ane$, $S_2 = cis + trans/cis + trans + ane$, where *ane* is the content of the completely hydrogenated product (1,4-diacetoxybutane) at ~50% conversion. It is seen that, when Pd(10%)/C is used as the catalyst in $[BMIM]PF_6$ at 20 °C (entry *1*), hydrogenation proceeds with moderate selectivity for the *cis*-isomer of 1,4-diacetoxybut-2-ene (S_1) and for the total amount of the *cis*- and *trans*-isomers of 1,4-diacetoxybut-2-ene (S_2). As the temperature of the reaction rises to 60 °C (entry *2*), 50% conversion is achieved already in 1.5 h (not in 2.5 h as in the previous case). The selectivity of the process also increases for both the total amount of the partial hydrogenation products (S_2) and the ratio to the *cis*-isomer of unsaturated diacetate (S_1).

It is known[21] that the introduction of the nitrogen-containing modifying additives into the heterogeneous catalytic system enhances the selectivity of partial hydrogenation of the triple bond of a series of compounds with respect to the products with the double bond. Indeed, when using the chitosan-based three-component system, Pd(1%)/chitosan/SiO_2 (60 °C), selectivity higher than 97.6% with respect to partial hydrogenation products is achieved, and the selectivity for the *cis*-isomer of unsaturated diacetate increases simultaneously (entry *3*). This is probably associated with the influence of the amino groups of chitosan. In the absence of a ionic liquid, when ethanol is used as the solvent (entry *4*), the hydrogenation reaction occurs somewhat more slowly. A conversion of ~50% is achieved in 3 h; however, selectivity of the process with respect to *cis*-1,4-diacetoxybut-2-ene remains still high, the same as that in $[BMIM]PF_6$.

There are published data on the reduction in $[BMIM]PF_6$ of a series of substituted alkenes and alkynes under the conditions of hydrogen transfer and microwave frequency activation of the reaction mixture (catalyst Pd(10%)/C).[22] In the case of alkynes, the reaction occurs with low selectivity with respect to the partial reduction products (*cis* : *trans* : *ane* = 6 : 1 : 1, conversion 50%) or the exhaustive hydrogenation of the triple bond occurs to form the C—C bond. Thus, the reaction studied is the first example of selective hydrogenation of alkynes to alkenes with molecular hydrogen in ionic liquids.

It follows from the data obtained that the use of the ionic liquid $[BMIM]PF_6$ as a solvent in heterogeneous catalysis is a promising approach to the search for the optimal conditions of selective hydrogenation of alkynes to alkenes. The Pd-containing chitosan-based catalyst immobilized on the mineral support (Pd(1%)/chitosan/

Table 1. Hydrogenation of 1,4-diacetoxybut-2-yne in the presence of the supported palladium catalysts in a ionic liquid medium[a]

Entry	Catalytic system	t^b/h	Composition of reaction mixture (%)				$S_1/S_2{}^c$
			Substrate	*cis*-1,4-*ene*	*trans*-1,4-*ene*	1,4-*ane*	
1[d]	Pd(10%)/C	2.5	49.0	42.0	2.5	6.5	82.4/87.3
2	Pd(10%)/C	1.5	50.6	43.9	2.5	2.9	89.0/94.1
3	Pd(1%)/chitosane/SiO_2	2.0	48.6	47.3	1.9	2.2	93.8/97.6
4[e]	Pd(1%)/chitosane/SiO_2	3.0	51.0	46.3	1.3	1.4	94.5/97.1

[a] Conditions: 68.0—136.0 mg of 1,4-diacetoxybut-2-yne (0.4—0.8 mmol), 1 mol.% Pd, 1—2 mL of $[BMIM]PF_6$, 1 atm H_2, 60 °C.

[b] Reaction time.

[c] $S_1 = cis/cis + trans + ane$, %; $S_2 = cis + trans/cis + trans + ane$, %.

[d] Reaction temperature 20 °C.

[e] Solvent EtOH.

SiO_2) is the most efficient catalyst for hydrogenation of 1,4-diacetoxybut-2-yne in the [BMIM]PF_6 medium.

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