

Metal-containing catalysts for the hydrogenation process of substituted 5-acyl-1,3-dioxanes

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Abstract: Hydrogenation of substituted 5-acyl-1,3-dioxanes was used to synthesize heterocyclic alcohols in the presence of metal-containing catalysts. It has been established that the best catalyst for the reduction of substituted 5-acyl-1,3-dioxanes is Pd/C, which makes it possible to achieve a high selectivity for the formation of the corresponding heterocyclic alcohols at a conversion of the initial ketones of 60-90%.

Keywords: hydrogenation, 5-acyl-1,3-dioxanes, metal-containing catalysts.

Introduction

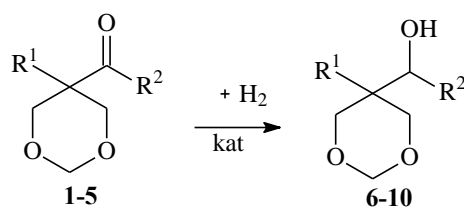
Oxymethyl-1,3-dioxacycloalkanes and their derivatives – ethers and esters, thioethers and other are used as corrosion inhibitors, plant protection chemicals, and also exhibit various biological activities [1-3].

The main method for obtaining alcohols containing a cycloacetal fragment is the condensation of 1,1,1-trioxymethylalkanes with carbonyl compounds [4, 5]. However, in some cases, secondary 1,3-dioxacycloalkane alcohols are necessary, so it was proposed to obtain them by reduction of the keto group in 5-acyl-1,3-dioxanes with metal hydrides [6]. At the same time, this hydrogenation method is of little use for preparative synthesis under industrial conditions.

In this regard, we studied the heterogeneous catalytic reduction of substituted 5-acyl-1,3-dioxanes in the presence of various metal-containing catalysts (Pd/C, Ni on kieselguhr, Pt/Re, Ni/Mo) in this work.

Result and discussion

Previously [7] we showed that in a hydrogen flow in the presence of a Pd/C catalyst, 5-acyl-1,3-dioxanes are reduced to the corresponding heterocyclic alcohols. Continuing this work, we studied the hydrogenation of heterocyclic ketones **1-5** in the presence of a number of industrial metal-containing catalysts: Pd/C, Ni/kieselguhr, Pt/Re, or Ni/Mo.



$R^1 = \text{CH}_3, R^2 = \text{CH}_3$ (**1, 6**), $R^1 = \text{C}_2\text{H}_5, R^2 = \text{CH}_3$ (**2, 7**)

$R^1 = i\text{-C}_3\text{H}_7, R^2 = \text{CH}_3$ (**3, 8**), $R^1 = \text{CH}_3, R^2 = \text{C}_2\text{H}_5$ (**4, 9**)

$R^1 = \text{CH}_3, R^2 = \text{Ph}$ (**5, 10**)

Scheme 1. Hydrogenation of 5-acyl-1,3-dioxanes.

The best result was shown by Pd/C among the studied catalysts (Table 1), which is used in the reduction of unsaturated and carbonyl compounds [8, 9]. The conversion on Pt- and Ni-containing catalysts is 1.5-2.5 times lower, while the selectivity in all cases is more than 70%.

Table 1 Hydrogenation of substituted 5-acyl-1,3-dioxanes **1-5** in the presence of various catalysts

Synthesis conditions: 200°C, reaction time = 1 h, molar ratio ketone : H₂ = 1:6.

Reagents	Products	Catalyst							
		Pd/C		Pt/Re		Ni on kieselguhr		Ni/Mo	
		C*, %	S*, %	C, %	S, %	C, %	S, %	C, %	S, %
1	6	80	98	70	95	50	85	40	95

2	7	90	95	50	95	40	80	40	90
3	8	80	95	40	95	30	80	20	95
4	9	60	95	50	80	30	60	30	80
5	10	65	95	40	70	25	75	20	70

*C – conversion, %; S – selectivity, %.

The conversion of ketones **1-5** is also affected by substituents with different structures at the carbonyl group and in the 5th position of the 1,3-dioxane ring. The ethyl and phenyl radicals at the C=O group reduce the conversion of compounds **4, 5**. The activity of ketones **2, 3**, containing ethyl or isopropyl groups in the 5th position, slightly decreases compared to the methyl ethyl ketone (MEK) derivative **1**. Note that during the hydrogenation of the ketone **5** no products of complete or partial reduction of the aromatic nucleus were found.

Conclusion

The heterogeneous Pd/C catalyst makes it possible to reduce 5-acyl-1,3-dioxanes to the corresponding alcohols with a selectivity of more than 95%. Catalysts containing Ni are substantially less active in this process.

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