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SHORT COMMUNICATIONS

Hydrogenation of Alkenes and Their Derivatives in the Presence of Nano-Sized Metal Iridium

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Noble metals are applied to the practice of organic chemistry as efficient homogenous and heterogeneous catalysts [1–3]. Iridium belongs to the platinum group metals and also possesses some catalytic properties characteristic of these metals. The most part of research using iridium belongs to the field of homogeneous catalysis [4]. These processes are hydrogenation of alkenes and dehydrogenation of alkanes, reduction of carbonyl compounds and compounds containing other multiple bonds.

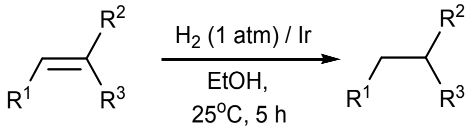
The examples of iridium application in heterogeneous catalysis are extremely rare. A supported catalyst Ir/SiO_2 is used for hydrogenation of *trans*-4-phenyl-3-buten-2-one [5], acetophenones [6], and other aromatic ketones [7]. Certain examples are known of using heterogeneous iridium catalysts in dehydrogenation reactions [8, 9]. A high catalytic activity exhibited a nano-size iridium in a catalyst Ir/TiO_2 [10], where its part consisted in the hydrogen transfer from an aliphatic alcohol with aldehyde formation to nitrobenzene furnishing aniline. The reaction of obtained compounds gave a σ-adduct whose oxidation on the same catalyst resulted in qui-nolone formation. In the majority of mentioned examples the reactions occur at high temperature and/or at high pressure.

We studied the catalytic activity in hydrogenation of alkenes and derivatives of metallic iridium nanopowder (S_{sp} 6.4 cm^2/g according to low-temperature nitrogen adsorption, D 25 nm by the data of electron microscopy) produced in Joint-Stock Co "Ural Metals," (Specification TU 27.41-001-50303674-2011) (Scheme 1).

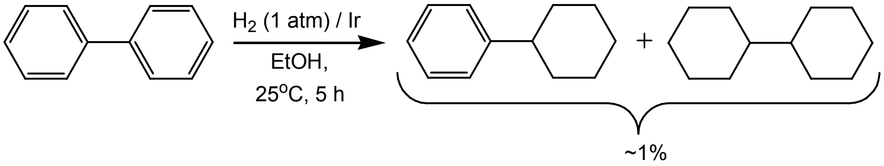
In 6.0 mL of ethanol 0.100 g of alkene was dissolved, 0.050 g of catalyst was added, and hydrogen flow was passed at a rate 50 mL/min at continuous stirring. The reaction was carried out at room temperature for 5 h. The reaction mixture after removing the catalyst was analyzed by GC using the GC-MS instrument Trace GC Ultra DSQ II equipped with a quartz capillary column Thermo TR-ms (phase polydimethylsiloxane containing 5 wt % of phenyl groups) 30 m × 0.25 mm, film 0.25 μm thick. The initial column temperature 40°C (maintaining for 3 min), heating rate 10 deg/min, ramp to 280°C (maintaining for 30 min), vaporizer temperature 250°C, detector temperature 200°C, connecting tube temperature 200°C. Carrier gas helium, split ratio 1 : 50, the flow through the column 1.0 cm^3/min. Input 1.0 μL. The quantity of reaction products was estimated by the internal normalization procedure from the peaks areas. At the use of unsaturated carboxylic acids as substrates the products of hydrogenation were subjected to esterification and analyzed in the form of ethyl esters. The data obtained are compiled in the table.

The hydrogenation of the double carbon-carbon bond in 1-dodecene, maleic, oleic acids, and acrylonitrile occurred quantitatively. Carboxy group is not hydrogenated under the chosen conditions. The nitrile function in these conditions is also stable since

Scheme 1.



Scheme 2.



Results of alkenes hydrogenation

R^1	R^2	R^3	Reaction product	Yield[a], %
$C_{10}H_{21}$	H	H	Dodecane	100
COOH	H	COOH	Succinic acid	100
C_8H_{17}	H	$C_7H_{14}COOH$	Stearic acid	100
CN	H	H	Propionitrile	100
CH_2OH	H	CH_2OH	1,4-butandiol	80
Ph	H	H	Ethylbenzene	98
Me	COOH	H	Butyric acid	98
Ph	COOMe	H	Methyl (3-phenyl)propionate	52

[a] Yield according to the data of GC of reaction mixtures.

adiponitrile does not undergo hydrogenation. The hydrogenation products of *cis*-but-2-ene-1,4-diol along with the main product, 1,4-butanediol, contained a small quantity of 1-butanol (~5%). After styrene hydrogenation in the reaction mixture beside ethylbenzene ethylcyclohexane was detected (~1.5%). The hydrogenation of the benzene ring was also observed in the case of methyl cinnamate with the formation of methyl 3-cyclohexylpropionate (~3.5%). However, the aromatic ring of biphenyl did not suffer hydrogenation, the overall content in the mixture of hydrogenated products of phenylcyclohexane and bicyclohexyl did not exceed 1% (Scheme 2).

The attempts to intensify the process by raising the temperature and prolonging the reaction time did not significantly increase the biphenyl conversion. In contrast to nano-size palladium catalysts [11, 12], the nano-size powder of metal Ir is unfit for biphenyl hydrogenation.

The attempt to reduce 1-dodecene using 2-propanol as hydrogen source was unsuccessful.

Thus the nano-size metallic Ir powder exhibited a high catalytic activity in hydrogenation of alkenes and their derivatives under simple experimental conditions.

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