

CATALYTIC HYDROGENATION OF ALKYNES TO CIS-ALKENES

ON A MODIFIED BORON-NICKEL CATALYST

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UDC 66.094.17:547.314

Hydrogenation of alkynes from decyne and dodecyne (C_{10} - C_{12}) with the triple bond at C^3 , C^4 , C^5 , and C^6 led to the corresponding alkenes on a boron-nickel catalyst modified by 1-phenyl-2,3-dimethyl-4-amino-5-pyrazolone (4-aminoanti-pyrene). The stereospecificity for formation of the cis-alkenes was 95-98%.

Catalysts obtained from Ni(II) salts and $NaBH_4$ in aqueous media are used along with Raney nickel in the catalytic hydrogenation of the triple bond to a double bond in hydrocarbons and their derivatives [1, 2]. Special attention has been given to the hydrogenation of terminal C_4 - C_6 alkynes [3].

In the present work, we studied the stereospecific hydrogenation of alkynes with the triple bond at C^3 , C^4 , C^5 , and C^6 to the corresponding cis-alkenes in the presence of a boron-nickel catalyst modified by 1-phenyl-2,3-dimethyl-4-amino-5-pyrazolone (4-aminoanti-pyrene).

EXPERIMENTAL

The starting alkynes were synthesized according to standard procedures [4] and purified by distillation. The physicochemical properties of these compounds are given in Table 1. Gas-phase chromatography on polyethylene glycol indicated $\geq 99\%$ purity for these samples.

The modified boron-nickel catalyst was prepared by the coprecipitation of nickel(II) acetate and $NaBH_4$ in 1:5 mole ratio in ethanol with added 4-aminoantipyrene [6]. The catalyst proved about 10 times more active than the catalysts obtained with 1:1 and 1:12 mole ratios of these salts.

The mole ratio of the starting alkyne to the catalyst was 1:1 in most of the experiments. A total of 1.4 mass % 4-aminoantipyrene relative to the alkyne was added.

The hydrogenation was carried out at atmospheric hydrogen pressure in a long-necked glass reactor maintained at constant temperature at $10^\circ C$ with rapid stirring.

The reaction mixtures were analyzed by gas-liquid chromatography on capillary columns packed with 1,2,3-tris(2-cyanoethoxy)propane. The division of the helium gas carrier flow stream was 1:200. The column and injector temperatures were 70 and $170^\circ C$ for the C_{10} hydrocarbons, 80 and $180^\circ C$ for the C_{11} hydrocarbons, and 85 and $200^\circ C$ for the C_{12} hydrocarbons respectively.

The steric specificity was given as the ratio of the amount of cis-alkene formed to the sum of the cis- and trans-alkenes (%).

TABLE 1. Physicochemical Properties of Individual Alkynes [5]

Alkyne	Bp, K	n_D^{20}	d_4^{20} , g/cm ³
3-Decyne	451.97	1.43427	0.7709
5-Decyne	450.48	1.43383	0.7691
4-Undecyne	471.6	1.4369	0.7752
3-Dodecyne	492.42	1.44039	0.7836
4-Dodecyne	491.59	—	—
5-Dodecyne	490.82	1.43962	0.7809
6-Dodecyne	490.65	1.43979	0.7813

Institute of Chemistry, Academy of Sciences of Estonia, Tallinn. Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2884-2886, December, 1991. Original article submitted December 30, 1990.

TABLE 2. Results of the Hydrogenation of Alkynes on a Modified Boron-Nickel Catalyst

Starting alkyne	Product composition, mole %				Stereospecificity, %
	alkyne	cis-alkene	trans-alkene	alkane	
3-Decyne	0.6	94.7	1.8	2.9	98.1
5-Decyne	0.3	96.6	1.4	1.6	98.6
4-Undecyne	41.4	57.0	1.0	0.6	98.3
3-Dodecyne	12.3	85.0	1.2	1.5	98.6
4-Dodecyne	0.9	94.2	2.8	2.0	97.1
5-Dodecyne	0.3	97.0	1.7	1.0	98.3
6-Dodecyne	40.0	55.9	2.6	1.5	95.6

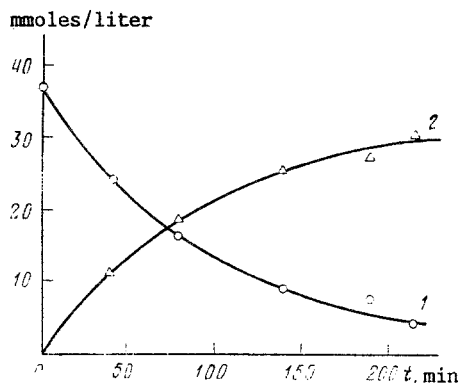
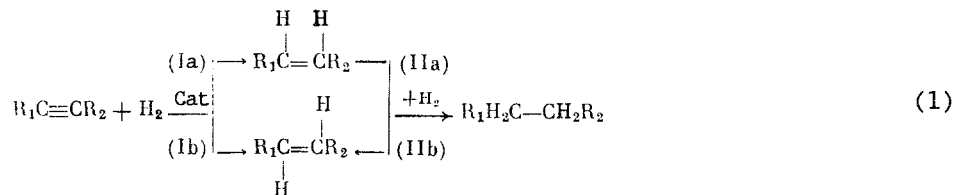


Fig. 1. Kinetic curves for the hydrogenation of 5-dodecyne: 1) 5-dodecyne and 2) cis-5-dodecene.

RESULTS AND DISCUSSION

After addition of the first hydrogen molecule to the alkyne (step Ia), there is only slight subsequent reduction to the alkane. The greatest extent of hydrogenation to the alkane was 2 mass % relative to the total amount of hydrogenation products. Table 2 shows that the steric specificity of this reaction is 95% in the hydrogenation of the symmetrical alkyne (6-dodecyne) and above 98% for the asymmetric alkynes.



Typical kinetic curves for the hydrogenation of alkynes are given in Fig. 1. The reaction is pseudo-first-order relative to the starting alkyne (the hydrogen concentration in the reaction mixture is virtually constant).

LITERATURE CITED

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