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HYDROGENATION OF α - AND β -ACETYLENIC HYDROCARBONS BY CATALYST SYSTEM $\text{NiCl}_2 \cdot 6\text{H}_2\text{O} + \text{NaBH}_4$ IN DIMETHYLFORMAMIDE

Treatment of NiCl_2 or $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ with sodium boron hydride in dimethylformamide (DMF) produces a homogeneous hydrogenation catalyst working under mild conditions. Methylinoleate [1] and acrylic ethyl ester [2] as unsaturated compounds were hydrogenated to give a *cis*-monoenoic product and a saturated ester, respectively.

W. Strohmeier and H. Steigerwald [2] and A. Hinze and D. Frost [3] have found that nickel chloride in a complex with NaBH_4 and DMF as a hydrogenation catalyst exhibits low isomerization activity.

We now report a brief comparative investigation of the use of the catalyst system $\text{NiCl}_2 \cdot 6\text{H}_2\text{O} + \text{NaBH}_4$ in DMF for the hydrogenation of 1-pentyne, 2-pentyne, phenylacetylene and isopropenylacetylene in DMF solution.

Experimental

1-Pentyne, 2-pentyne, isopropenylacetylene and phenylacetylene were purified in a small distillation apparatus by column distillation and stored under nitrogen.

The catalyst was prepared by dissolving 18 mg of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 10 ml of carefully degassed DMF by shaking under argon for 5 min. Then the nickel chloride solution in DMF was treated with 6 mg of powdered sodium boron hydride until the solution became deep brown. After that argon was replaced by hydrogen. When the catalyst solution was saturated with hydrogen, 0.2 ml of unsaturated hydrocarbon were injected via a serum cap into the reaction flask. For each run, the catalyst solution was freshly prepared.

The reaction was performed in a conical flask. The hydrogenated products were analysed during the hydrogenation.

The reaction flask, immersed in a thermostatic water-bath, was connected with a gas burette system. Hydrogen uptake was measured with a gas burette with a levelling bulb. The content of the flask was vigorously agitated by a magnetic stirrer.

The analyses were carried out by gas chromatography. For the products of hydrogenation of 1-pentyne, 2-pentyne and isopropenylacetylene, a 6 m column of β , β' -oxydipropionitrile was used, and the hydrogenation products of phenylacetylene were analysed using a PEG-6 000 column.

Results and discussion

The results of the hydrogenation are shown in Fig. 1. Much trouble was experienced in obtaining reproducible rates of hydrogenation despite many precautions that were taken. The hydrogenation rates of the investigated compounds showed rather great differences. The rate of hydrogenation of 1-pentyne was highest and that of phenylacetylene lowest. The hydrogenation rate considerably slowed down during the reaction.

Figs. 2 to 5 show the dependence of the composition of the hydrogenated products of 1-pentyne, 2-pentyne, phenylacetylene and isopropenylacetylene on hydrogen consumption, respectively. The hydrogenation of 1-pentyne, after absorption of a 1.2 molar equivalent of hydrogen, yielded 89% 1-pentene and 11% *n*-pentane. After the uptake of a 1.93 molar equivalent

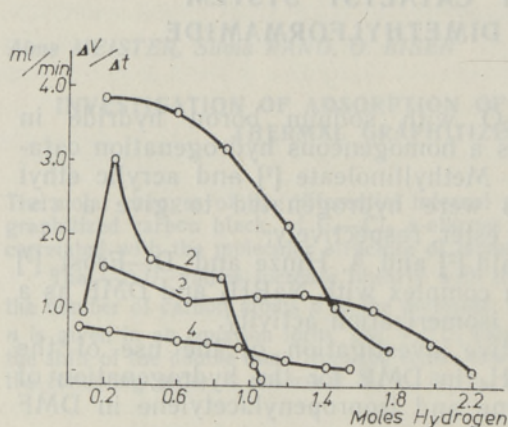


Fig. 1. The rate of hydrogenation of 1-pentyne (1); 2-pentyne (2); isopropenylacetylene (3); phenylacetylene (4).

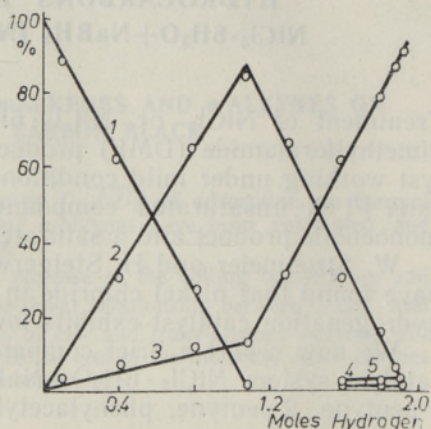


Fig. 2. Product distribution during the hydrogenation of 1-pentyne: 1-pentyne (1); 1-pentene (2); pentane (3); *trans*-2-pentene (4); *cis*-2-pentene (5).

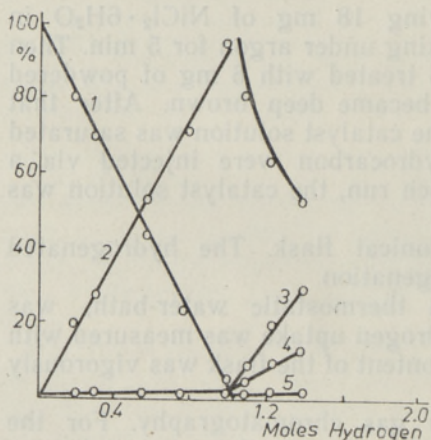


Fig. 3. Product distribution during the hydrogenation of 2-pentyne: 2-pentyne (1); *cis*-2-pentene (2); pentane (3); *trans*-2-pentene (4); 1-pentene (5).

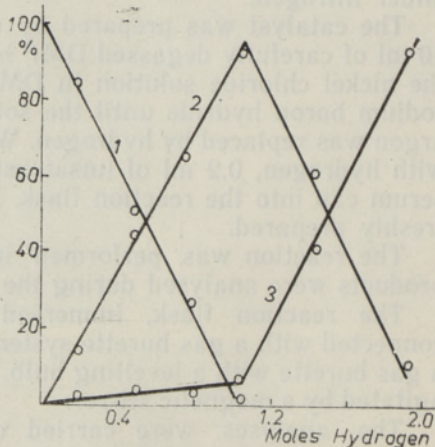


Fig. 4. Product distribution during the hydrogenation of phenylacetylene: phenylacetylene (1); styrene (2); ethylbenzene (3).

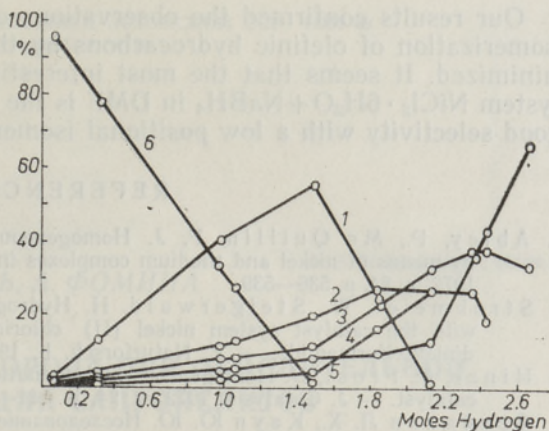


Fig. 5. Product distribution during the hydrogenation of isopropenylacetylene: isoprene (1); 3-methyl-1-butene (2); 2-methyl-1-butene (3); 2-methyl-2-butene (4); methylbutane (5); isopropenylacetylene (6).

of hydrogen, 93.4 pentane, 1.8 *cis*-2-pentene and 4.8 per cent *trans*-2-pentene were obtained. The results of hydrogenation of 1-pentyne showed that the isomerization of olefins was minimized by the nickel complex catalyst system.

The degree of selectivity of hydrogenation was calculated with the help of the equation

$$S = \frac{A}{A+B} [4],$$

A — the yield of olefin, B — the yield of paraffin,

$$S_{1\text{-pentyne}} = 0.89.$$

In Fig. 3 the analyses of samples of hydrogenation of 2-pentyne are presented. The hydrogenation of 2-pentyne resulted mainly in *cis*-2-pentene, viz. 96 per cent. The hydrogen absorption stopped after the uptake of a 1.4 molar equivalent.

The degrees of selectivity and stereoselectivity calculated for 2-pentyne were 0.97 and 0.99, respectively.

The hydrogenation of phenylacetylene yielded 95 per cent styrene (Fig. 4)

$$S = 0.95.$$

Isopropenylacetylene (Fig. 5) formed all the possible reaction products already at the beginning of hydrogenation. After consumption of a 1.63 molar equivalent of hydrogen, the reaction product was of the following composition: isopropenylacetylene 0.5, isoprene 52, 3-methyl-1-butene 20, 2-methyl-1-butene 12, 2-methyl-2-butene 6 and methylbutane 9.5 per cent.

The reaction of the hydrogenation of isopropenylacetylene was stopped after the absorption of a 1.8 molar equivalent of hydrogen.

We have observed that the hydrogenation rates of α - and β -acetylene hydrocarbons by the catalyst system $\text{NiCl}_2 \cdot 6\text{H}_2\text{O} + \text{NaBH}_4$ in DMF were comparatively low, decreasing during the hydrogen consumption.

A decrease in the rate of hydrogenation is probably due to the fact that the catalyst system is inactivated by the substrates and reaction products.

The comparison of the results of the hydrogenation of α - and β -acetylene hydrocarbons on a skeletal nickel catalyst [4, 5] with that by the nickel complex catalyst system showed the selectivity by the latter catalyst to be higher.

Our results confirmed the observations of investigators [1-3] that the isomerization of olefinic hydrocarbons by the nickel catalyst system was minimized. It seems that the most interesting property of the catalyst system $\text{NiCl}_2 \cdot 6\text{H}_2\text{O} + \text{NaBH}_4$ in DMF is the ability to combine sufficiently good selectivity with a low positional isomerization tendency.

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**MÖNINGATE α - JA β -ETÜÜNIREA SÜSIVESINIKE HÜDROGEENIMINE
DIMETÜÜLFORMAMIIDIS KOMPLEKSSE NIKKELKATALÜSAATORI MANULUSEL**

Artiklis on kirjeldatud pentüün-1, pentüün-2, 2-metüülbuteen-1-üün-3 ja etüünbenseeni hüdrogeenimist kompleksse nikkeltatalüsaatori $\text{NiCl}_2 \cdot 6\text{H}_2\text{O} + \text{NaBH}_4$ manulusel dimetüülfornamiidis. Uuritud katalüsaator on suhteliselt ebapüsiv ja inaktiveerub hüdrogeenimise kestel. Pentüün-2 hüdrogeenub selle katalüsaatori manulusel selektiivselt ja stereoselektiivselt, pentüün-1, 2-metüülbuteen-1-üün-3 ja etüünbenseen mitteselektiivselt.

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**ГИДРИРОВАНИЕ α - И β -АЦЕТИЛЕНОВЫХ УГЛЕВОДОРОДОВ В ПРИСУТСТВИИ
КОМПЛЕКСНОГО КАТАЛИЗАТОРА В ДИМЕТИЛФОРМАМИДЕ**

Изучено гидрирование пентина-1, пентина-2, изопропенилацетилена и фенилацетилена в присутствии каталитической системы $\text{NiCl}_2 \cdot 6\text{H}_2\text{O} + \text{NaBH}_4$ в диметилформамиде (ДМФ). Пентин-2 гидрируется с высокой степенью селективности и стереоселективно, фенилацетилен, пентин-1 и, в частности, изопропенилацетилен гидрируются неселективно. Комплексный никелевый катализатор малостабилен.