# CATALYTIC HYDROGENATION OF ALKYNES TO CIS-ALKENES

## ON A MODIFIED BORON-NICKEL CATALYST

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

Catalysts obtained from Ni(II) salts and NaBH<sub>4</sub> in aqueous media are used along with Raney nickel in the catalytic hydrogenation of the triple bond to a double bond in hydro-carbons and their derivatives [1, 2]. Special attention has been given to the hydrogenation of terminal  $C_4-C_5$  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°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°C for the  $C_{10}$  hydrocarbons, 80 and 180°C for the  $C_{11}$  hydrocarbons, and 85 and 200°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 (%).

| Alkyne   | Bp, K  | n <sup>20</sup> _D  | $d_{4^{26}}$ , g/cm <sup>3</sup>         |  |
|--|--|---|--|--|
| 3-Decyne<br>5-Decyne<br>4-Undecyne<br>3-Dodecyne<br>4-Dodecyne<br>5-Dodecyne<br>6-Dodecyne | $\begin{array}{c c} 451.97 \\ 450.48 \\ 471.6 \\ 492.42 \\ 491.59 \\ 490.62 \\ 490.65 \end{array}$ | $\begin{array}{c} 1.43427\\ 1.43383\\ 1.4369\\ 1.4369\\ 1.44039\\ -\\ -\\ 1.43962\\ 1.43979\end{array}$ | 0.7709<br>0.7691<br>0.7752<br>0.7836<br> |  |

TABLE 1. Physicochemical Properties of Individual Alkynes [5]

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| Starting<br>alkyne   | Product composition, mole % |                |                  | Stereospeci- |              |
|----------------------|-----------------------------|----------------|------------------|--------------|--------------|
|                      | alkyne                      | cis-<br>alkene | trans-<br>alkene | alkane       | ficity, %    |
| 3-Decyne<br>5-Decyne | 0.6                         | 94,7           | 1.8              | 2.9          | 98.1<br>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         |

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



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).

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#### HOMOLYTIC DISSOCIATION OF THE CARBON-ELEMENT

 $\sigma$  BONDS BY GRIGNARD REAGENTS

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The reaction of 2-ethyl-3-tetrahydrofuryl thiocyanate (I) and triphenylacetonitrile (VIII) with methylmagnesium iodide in ether was studied using GC/MS, PMR and <sup>13</sup>C NMR spectroscopy. The reaction of (I) with  $CH_3MgI$  gives the product of the homolysis of the C-S  $\sigma$  bond, namely, bis(2-ethyl-3-tetrahydrofuryl) disulfide (II), in 81% yield. This reaction is assumed to be general in nature since triphenylacetonitrile (VIII) is also homolytically cleaved by the action of  $CH_3MgI$  to give triphenylmethane.

The reaction of thiocyanates with Grignard reagents has not been sufficiently studied. Aliphatic thiocyanates react with organomagnesium compounds to give mixtures of the corresponding sulfide, nitrile, and thiol [1] but a detailed study of the reaction of thiocyanates with Grignard reagents has not been carried out.

We studied the reaction of 2-ethyl-3-tetrahydrofuryl thiocyanate (I) with methylmagnesium iodide in ether using GC/MS, PMR and <sup>13</sup>C NMR spectroscopy.

Bis(2-ethyl-3-tetrahydrofuryl) disulfide (II) is obtained in 81% yield along with small amounts of 2-ethyl-3-tetrahydrofuryl methyl sulfide (III) and 2-ethyl-3-tetra-hydrofurylthiol (IV).

In our opinion, (II) - (IV) are products of the homolysis of starting thiocyanate (I) by the action of the Grignard reagent. One of the possible pathways for the conversion of (I) to disulfide (II) may involve electron transfer. Thiocyanate (I) acts as an oxidizing agent to accept an electron in the lowest unoccupied antibonding orbital of the thiocyanate group from MeMgI and is converted to radical-anion (A). The Grignard reagent is thereby oxidized to radical-cation (B). Radical-anion (A) then decomposes to give the (2-ethyl-3-tetrahydrofuryl)thiyl radical (C) and a cyanide ion. Radical-cation (B) fragments to give a methyl radical and the MgI<sup>+</sup> cation.

Thiyl radical (C) dimerizes to give (II) and reacts with the methyl radical to give sulfide (III). Thiol (IV) is apparently formed upon the reaction of (A) with the solvent. The cyanide ion was isolated from the reaction mixture as ferric ferrocyanide:



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