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HYDROGENOLYSIS OF LIGNINS : NICKEL BORIDE CATALYST

B. LOUBINOUX, M. HEITZ, G. COUDERT and G. GUILLAUMET

Chimie Organique, Groupe de Recherches en Chimie du Bois
Université de Nancy I, Faculté des Sciences, C.O. 140, 54037 NANCY Cédex

Nickel boride generated within the wood structure allows the selective hydrogenolysis of wood meals. 4-n-Ethylguaiacol and 4-n-Ethylsyringol are prepared with interesting yields.

The conversion of lignins into phenolic materials has been studied for almost sixty years. Various lignins have been subjected to pyrolysis, alkali fusion, oxydation and hydrogenolysis. However, until now, commercial production has played only a very small role because the products are complex mixtures with many components (1,2). The expected shortage of crude oil or natural gas has recently stimulated the search for other raw materials and lignocellulosic materials are particularly promising (3).

Catalytic hydrogenolysis of lignins has been the subject of numerous investigations (4-8). It has been performed on wood meals, isolated lignins and by-products of pulping processes. Frequently no selectivity is observed in the reaction and the best yields of monomeric phenols ranged from 15 to 40 % according to the kind of wood and the catalyst. Some catalysts are effective in the formation of a limited number of monomeric phenols under low hydrogen pressure. Of the many catalysts studied, active metal catalysts of group VIII have been given particular attention. Rhodium on charcoal, for instance, was shown to convert aspen wood meal into a monomeric fraction with 40 % yield ; four phenols were detected by gas-liquid chromatographic analyses : 4-n-Propylguaiacol (6.3 %), 4-n-Propylsyringol (3.6 %), Dihydroconiferyl alcohol (11 %) and Dihydrosinapyl alcohol (21.9 %) (9). Hydrogenation of acid hydrolysis lignin from beech wood with nickelocene yielded 36 % of monomeric phenols ; 4-n-Ethylguaiacol (15.1 %), 4-n-Propylguaiacol (12.1 %), 4-n-Ethylsyringol (18.6 %), 4-n-Propylsyringol (19 %) were the main products of the mixture (10).

We want to report here our first results on the hydrogenolysis of wood meal in the presence of nickel boride (11-12) generated within the wood structure. After wood impregnation by an aqueous solution of nickel acetate, sodium borohydride was added under nitrogen. When the reduction of the nickel salt was achieved, hydrogenolysis was performed in a basic medium.

Gas-liquid (C.P.V.) and thin-layer (T.L.C.) chromatographic analyses of the ether soluble fraction obtained showed that only one or two main monomeric phenols were formed as well as very small amounts of some other products (4-n-Ethylguaiacol from soft woods, 4-n-Ethylguaiacol and 4-n-Ethylsyringol from hard woods). Envisaging the reaction as a preparative procedure for the phenolic lignin derivatives, we separated these main phenols by liquid-solid chromatography in each run. Our main results are collected in the table.

The results indicate that the nickel boride catalyst is effective for the preparation of phenols from wood meals. Although the reaction conditions have not been optimized, yields and specificity appear to be competitive with those obtained with other catalysts and particularly with other nickel catalysts (13-14). Nickel boride can be used in relatively low amounts. Is is easy to prepare, non pyrophoric and cheaper than noble metal catalysts such as rhodium or palladium. Preparation of the catalyst within the wood structure had been previously done by Snajberk and Zavarin (14) ; as these authors, we obtained a good reproducibility of the results even in microscale preparations provided that impregnation of the wood was made without an excess of solvent. Furthermore, it appeared than grain sizes did not have a significant influence on the results.

Highest yields of monomers were obtained at 8-12 hours reaction times. Longer reaction times influenced yields adversely. Better yields were obtained when the catalyst was prepared in ethanol (method B) instead of water (method A). The difference between the two procedures is particularly marked at short reaction times (compare runs 1 and 8).

Some unreported experiments were made with the criteria considered being the weights of the ether soluble fractions, C.P.V. and T.L.C. analyses. The influence of the catalyst-to-wood ratio was found to be significant and a bad selectivity was obtained for 0.6 matomgrams of nickel per gram of wood. When hydrogenolysis was performed in the absence of NaOH, yields of phenols were poor ; 1.5 g of NaOH was found to be the optimum amount for 4 g of wood and 50 cm^3 of solvent. A decrease of initial hydrogen pressure led to a decrease in yields. At 250°C, higher yields of phenols were obtained but no selectivity was observed.

We are continuing our research using several metal borides, solvents, reaction conditions and wood meals so as to improve the yields in phenols preparations.

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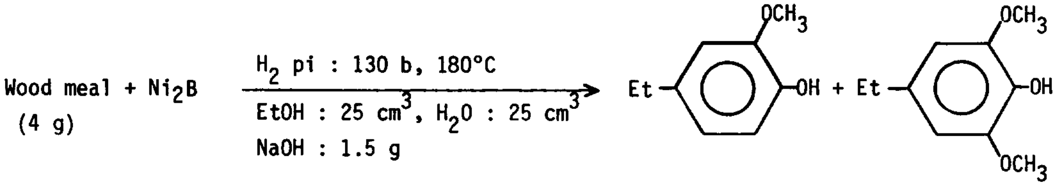
TABLE



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Runs	Wood	Ni_2B (mM)	Ni_2B method of preparation	Time (h)	Phenolic fraction (%) (1)	Main monomers (%) (1)	I (%) (2)	II (%) (3)
1	Beech	5	A	3	42	19	24	76
2	"	5	A	8	45	29	27	73
3	"	5	A	16	55	24	28	72
4	Maple	5	A	8	55	20	28	72
5	Wild Cherry	5	A	8	55	25	21	79
6	Eucalyptus	5	A	8	31	15	17	83
7	Douglas Fir	5	A	8	22	8	100	-
8	Beech	5	B	3	45	25	25	75
9	"	5	B	8	63	30	27	73
10	"	10	B	8	60	33	24	76
11	Maple	10	B	8	45	28	28	72
12	Wild Cherry	10	B	8	69	30	18	82
13	Eucalyptus	10	B	8	42	21	12	88
14	Douglas Fir	10	B	8	39	12	100	-

(1) Isolated yields (based on Klason lignin)

(2) ^{1}H NMR (CCl_4), δ : 1.15, t, 3 H ; 2.50, quad., 2 H ; 3.70, s, 3 H ; 5.60, s, 1 H ; 6.3-6.8, m, 3 H
Mass spectra : 152, 137
4-Nitrobenzoate : F = 94-95°, litt. F = 98-99° (13)

(3) ^{1}H NMR (CCl_4), δ : 1.20, t, 3 H ; 2.50, quad., 2 H ; 3.76, s, 6 H ; 5.20, s, 1 H ; 6.30, s, 2 H
Mass spectra : 182, 167
4-Nitrobenzoate : F = 153°, litt. F = 151-152° (13)

Procedure (for 4 g of preextracted wood and 5 mM of nickel acetate)

Nickel acetate was diluted by the amount of water small enough to insure that the salt was completely absorbed by the wood with no supernatant liquid visible (about 15 cm^3). Impregnation was performed for a minimum of 5 h. The reduction of the nickel salt was achieved under nitrogen. The medium was left from 2 to 20 h at 25°C without modifications in the results.

Method A : 15 cm^3 of an aqueous natrium borohydride solution were added (600 mg of $NaBH_4$ in 0.1 N NaOH). After reduction, decantation allowed elimination of the supernatant water and 25 cm^3 of EtOH were added.

Method B : The water was eliminated under vacuum and the wood suspended in 20 cm^3 of EtOH. 6 cm^3 of a natrium borohydride solution were added (200 mg of $NaBH_4$ in 1 cm^3 of 0.2 N NaOH and 5 cm^3 of EtOH).

The mixture was introduced into a 125 cm^3 capacity bomb of a Prolabo hydrogenator with 25 cm^3 of aqueous NaOH. The reactor was flushed with hydrogen and then filled to an initial pressure of 130 bars. The temperature was raised to 180°C in about half an hour. The reactor was rocked continuously. After cooling, the reaction mixture was suction filtered and the residue washed with water and ethanol. The filtrates were concentrated and ether extraction of the phenolic fraction was carried out in a separatory funnel. The monomer separations were performed on a silica gel column.

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