ACTION OF NITRIC ACID ON THE β-GUAIACYL ETHER OF α-VERATRYL-GLYCEROL

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In a previous communication [1] we described the behavior of the lignin models, derivatives of 1-(3,4-dimethoxyphenyl)-propane and 1-(4-hydroxy-3-methoxyphenyl)-propane, under the action of nitric acid. In the present work, we continued the study of the nitration of lignin on a model, namely, a dimer. As the model we chose the β-guaiacyl ether of α-veratrylglycerol. According to the data of Adler [2], the β-guaiacyl ether of α-veratrylglycerol should be regarded as an accurate model of lignin. During ethanolysis [3], sulfite treatment [4], and oxidation with hypochlorite [5], compounds like β-aryl ethers of α-guaiacylglycerol showed properties similar to those of lignin. The coniferyl ether of 4-hydroxy-3-methoxyphenylglycerol was obtained by Freudenberg during the enzymatic synthesis of biochemical lignin from coniferyl alcohol [6].

We synthesized the β-guaiacyl ether of α-veratrylglycerol by the method of Adler, Lindgren, and Sacden [7]. The β-guaiacyl ether of α-veratrylglycerol (1 mole) was nitrated in CCl_4 with nitric acid (6 mole) at 5-6°. The reaction products were separated on silica gel. As a result we obtained a dinitro derivative of the β-guaiacyl ether of α-veratrylglycerol with the composition $C_{18}H_{20}N_2O_{10}$; molecular weight 437 (cryoscopically in benzene); m.p. 67°. Found: OH 8.00; NO_2 21.50%; $C_{18}H_{20}N_2O_{10}$. Calculation: OH 8.02; NO_2 21.7%.

Oxidation of this nitro compound with $KMnO_4$ in a weakly alkaline medium yielded 6-nitroveratric acid. Consequently, one nitro goup apparently entered each nucleus during the nitration of the β-guaiacyl ether of α-veratrylglycerol. Willstatter's nitration products of lignin, which were obtained under analogous conditions, contained ~4% of nonester nitrogen, i.e., somewhat less than one nitro group to each structural unit. The glycerol side chain of the model was unchanged during the action of nitric acid under the given conditions. During the nitration of monomers, it was observed that the alcohol group of 1-(3,4-dimethoxyphenyl)-2-propanol was more vulnerable to the oxidizing action of nitric acid than the OH groups of 1-(3,4-dimethoxyphenyl)-1- and 3-propanols. It may be assumed that etherification of the OH group in the position β to the nucleus protects it from oxidation.

Despite the presence of an alcohol group in the position α to the nucleus in the β-guaiacyl ether of α-veratrylglycerol, treatment of the dimer with nitric acid did not lead to the formation of polymers as was observed in the nitration of monomeric lignin models (guaiacyl and veratryl 1-propanols). It may be considered that during the nitration of lignin, there is no condensation due to the alcohol group in the position α to the aromatic nucleus.

EXPERIMENTAL

The β-guaiacyl ether of α-veratrylglycerol was obtained by the method of Adler, Lindgren, and Sacden according to the following scheme:

Veratrole → acetoveratrone → ω-bromo-3,4-dimethoxyacetophenone → ω-(2-methoxyphenoxy)-acetovera-

trone → α-(2-methoxyphenoxy)- β-hydroxypropio-veratrone → β-guaiacyl ether of α-veratrylglycerol.

Acetoveratrone was obtained by condensation of veratrole with acetyl chloride in the presence of $AlCl_3$ [8]; b. p. 158° (10 mm).

ω-Bromo-3,4-dimethoxyacetophenone was obtained by bromination of acetoveratrone (31 g) in chloroform at room temperature [9]. The yield was 18 g and the m. p. 81° (from chloroform + ether).

ω-(2-Methoxyphenoxy)-acetoveratrone was synthesized by condensation of ω-bromo-3,4-dimethoxyacetophenone (19 g) with guaiacol in dry acetone in the presence of K_2CO_3. The yield was 16 g and m.p. 92° (from methanol).

α-(2-Methoxyphenoxy)-β-hydroxypropioveratrone was obtained by heating ω-(2-methoxyphenoxy)-acetoveratrone (16 g) with formalin (40%) in ethanol in the presence of K_2CO_3 at 35° for 1 hr. The yield was 10.57 g and the m.p. 116° (from methanol).

The β-guaiacyl ether of α-veratrylglycerol was obtained by reduction of α-(2-methoxyphenoxy)-β-hydroxypropioveratrone (3 g) with sodium boron hydride in alcohol. The yield was 2.6 g. When dried in high vacuum, the thick, colorless sirup was converted into a glassy mass. Found: C 64.70; H 6.61; OH 9.90%. $C_{18}H_{22}O_6$. Calculated: C64.40; H 6.59; OH 10.2%.

Nitration of β-guaiacyl ether of α-veratrylglycerol. A 3-g sample of the substance was mixed with 100 ml of CCl_4. With stirring, 2.23 ml of nitric acid (sp. g. 1.52) in 50 ml of CCl_4 was added over a period of 30 min to the mixture at 6°. A resin separated on the walls of the flask and this was separated from the CCl_4 solution. The resin was dissolved in chloroform and the solution passed through a column of silica gel [10]. The CCl_4 solution of the reaction product was also passed through the same adsorbent. The adsorbents were washed with ether and then with alcohol. After evaporation under vacuum, the ether eluates gave a yellow, powdery substance in a yield of 2 g. The product was dissolved in a large amount of ether and as the latter was removed, the substance was deposited on the walls of the flask in the form of a crust. The precipitate was pressed on a Buchner funnel. This purification operation was carried out twice. The substance was dried in high vacuum. The β-nitroguaiacyl ether of α-6-nitroveratrylglycerol obtained in this way melted at 67°. Found: C 51.80; H 4.90; N 6.5 (by Dumas' method); OH 8.00; NO_2 21.5% (by reduction with subsequent diazotization). $C_{18}H_{20}N_2O_{10}$. Calculated: C 50.94; H 4.72; N 6.60; OH 8.02; NO_2 21.70%.

The hydroxyl group content was determined by Verley's method. A sample of the substance investigated was heated with a solution of acetic anhydride in pyridine for 1 hr 30 min.

SUMMARY

1. The action of nitric acid on a model of lignin, β-guaiacyl ether of α-veratrylglycerol, was studied.

2. Nitration of the β-guaiacyl ether of α-veratrylglycerol with nitric acid in CCl_4 yielded the β-nitroguaiacyl ether of α-6-nitroveratrylglycerol [1-(6-nitro-3,4-dimethoxyphenyl)-1-hydroxy-2-(nitro-2-methoxyphenoxy)-3-propanol].

3. The glycerol side chain of the dimer was unchanged during nitration under the conditions described.

LITERATURE CITED

1. A. A. Chuksanova, L. L. Sergeeva, and N. N. Shorygina, Izvestiya Akad. Nauk SSSR, Otdel, Khim. Nauk, 2219 (1959).
2. E. Adler, Industr. and Engng Chem. 49, 1377 (1957).
3. E. Adler, B. O. Lindgren, U. Sacden, Svensk. papperstidn. 55, 245 (1952); E. Adler, S. Illner, Svensk. papperstidn. 57, 78 (1954); E. Adler, J. M. Papper, E. Eriksoo, Industr. and Engng. Chem. 49, 1391 (1957).
4. B. O. Lindgren, Acta Chem. Scand. 5, 603 (1951); E. Adler, S. Illner, Svensk. papperstidn. 55, 238 (1952); 57, 78 (1954).
5. H. Richtzenhain, B. Alfredsson, Acta chem. scand. 8, 1519 (1954); 10, 719 (1956).
6. K. Freudenberg, Angew. Chem. 68, 508 (1956).
7. E. Adler, B. O. Lindgren, U. Sacden, Svensk papperstidn. 55, 245 (1952).
8. C. Mannich, Archiv der Pharmazie 248, 137 (1910).
9. C. Mannich, F. L. Friedrich, Ber. 44, 1549 (1911).
10. V. L. Kretovich, T. V. Drozdova, and I. S. Petrova, Doklady Akad. Nauk SSSR 80, 409 (1951).