NITRATION OF CERTAIN MODEL LIGNIN COMPOUNDS WITH NITRIC ACID SOLUTION IN ETHANOL

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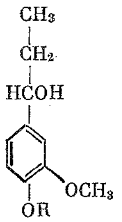
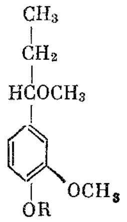
UDC 542.958.1+547.458.84

We previously demonstrated [1] that, when lignin not isolated from wood (spruce sawdust) is treated with an HNO_3 solution in ethanol by Kuerschner's method [2], both nitration and ethylation of the lignin take place. It must be assumed that ethylation can occur by etherification of the arylcarbonyl groups of the lignin or by formation of acetals. It was established that the newly introduced ethoxyl groups are readily hydrolyzed by boiling nitrolignin with 12% HCl.

In order to determine the nature of the ethoxyl groups introduced into lignin during alcoholic nitration and to obtain additional information on the processes that occur during nitration of this material with HNO_3 solution in ethanol, we nitrated certain model lignin compounds under similar conditions: the compounds employed were veratrylethylcarbinol (I), guaiacylethylcarbinol (II), methyl veratrylethylcarbinyl ether (III), and methyl guaiacylethylcarbinyl ether (IV):



(I) R=CH$_3$
(II) R=H



(III) R=CH$_3$
(IV) R=H

The choice of these compounds was dictated by the following factors. First of all, according to current concepts of the structure of lignin, compounds containing an etherified phenol hydroxyl can be regarded as models of the central subunits of the lignin macromolecule, while compounds with a free phenol hydroxyl serve as models of its terminal subunits. Secondly, the aforementioned compounds have reactive functional groups, principally benzylalcoholic and benzyletheric groups, as well as a free or etherified phenol hydroxyl in the para-position with respect to the side chain. The benzylalcoholic and benzyletheric groups are known to be largely responsible for certain characteristic reactions of lignin: its sulfitization during sulfite digestion of wood [3], its reaction with thioglycolic acid [4], its alkylation during treatment with $CH_3OH + HCl$ [5], etc. Finally, these compounds were previously used to study the nitration of lignin in anhydrous media [6-8]. These models should therefore illustrate the course of the electrophilic substitution reaction during nitration in ethanol and the behavior of the benzylalcoholic and benzyletheric groups under these conditions, which is closely related to the destruction of lignin during its nitration by Kuerschner's method.

Diagrams 1 and 2 show the results obtained in alcoholic nitration of the aforementioned model compounds. As can be seen from Diagram 1, the principal reaction product obtained by nitration of compound I with HNO_3 solution in ethanol was ethyl 6-nitroveratrylethylcarbinyl ether (V), whose yield was about 60% of theoretical; on this basis, we can conclude that, in addition to the electrophilic substitution at position 6 of the aromatic ring, the alkylcarbinol group of the molecule is ethylated. It must be noted that, under the conditions in question, equilibrium is apparently established between the etherification of the alkylcarbinol

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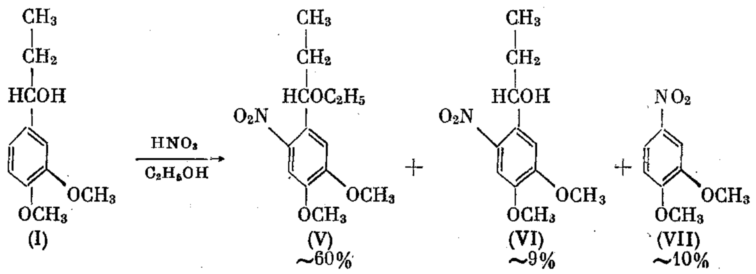
N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 645-649, March, 1970. Original article submitted October 14, 1968.

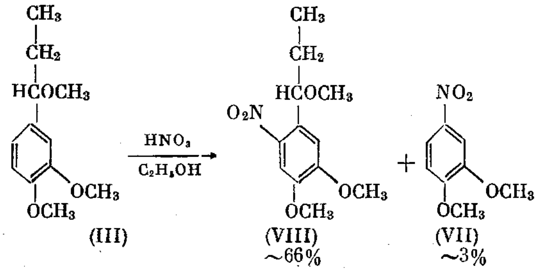
Diagram 1



group and the saponification of the ethyl ether formed, as was indicated by the isolation of 6-nitroveratrylethylcarbinol (VI).

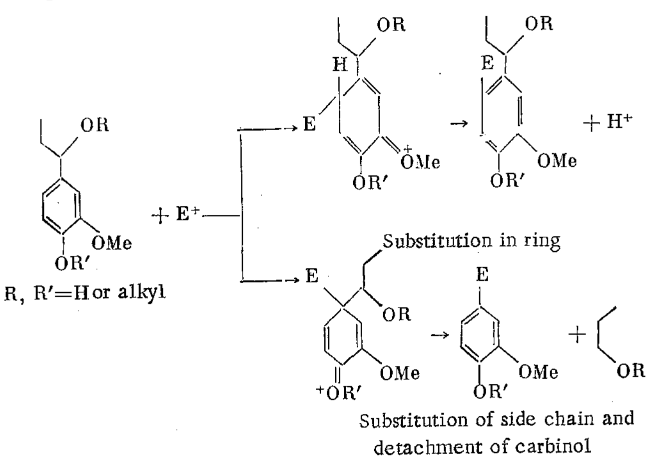
The principal product of the nitration of compound III was methyl 6-nitroveratrylethylcarbinyl ether (VIII), which was obtained with a yield of about 66%. It can therefore be concluded that the etherification of benzylmethyl ethers does not occur during nitration in ethanol. A certain amount of 4-nitroveratrol (VII) was formed during nitration of both veratrylethylcarbinol (I) and its methyl ether (III); the amount of this compound was substantially smaller in the latter case, which indicates that preliminary methylation of the benzyl alcoholic group reduces the possibility of electrophilic replacement of the side chain by a nitro group. It is interesting to note that this process was weaker during nitration in ethanol than during nitration of compounds I and III with HNO_3 in anhydrous media [6-8].

Diagram 2



Finally, the sole product we were able to isolate after nitration of compounds II and IV, which had a free phenolic hydroxyl group, was 4,6-dinitroguaiacol.

The data obtained in our experiments with model compounds enable us to advance a number of hypotheses regarding the processes that occur during alcoholic nitration of lignin in wood by Kuerschner's method, which we studied previously [9]. The reaction of an electrophilic reagent (E^+) with the lignin macromolecule can, depending on the reaction conditions, take one of two pathways or proceed by both pathways simultaneously for electrophilic substitution (nitration, chlorination, etc.) [10]; these can be represented as



On the basis of our data, we can conclude with a high degree of probability that the main reaction pathway for alcoholic nitration of lignin is electrophilic substitution in the aromatic ring; the nitro group enters the 6th (for etherification of the phenol hydroxyl) or 5th (for a free phenol hydroxyl) position of the aromatic ring. The electrophilic replacement of the side chain by the nitro group is slight, especially after preliminary methylation of the benzyl alcoholic groups with $CH_3OH + HCl$. Ethylation of the lignin takes place simultaneously with nitration, resulting from etherification of its arylcarbinol groups and not from acetal formation. This has been confirmed by the results obtained in nitration of unisolated lignin in carbon-tagged ethanol [11]. Moreover, our experiments with model compounds give us grounds for surmising that equilibrium is obviously established between the ethylation of the benzyl alcoholic groups and the saponification of the benzylethyl ethers formed during alcoholic nitration of lignin.

EXPERIMENTAL

Production of Model Compounds. The guaiacylethylcarbinol (II) was produced by exposing valine to C_2H_5MgBr; it had a melting point of 85-86° (from benzene). Found: 65.80% C, 7.75% H, 19.02% OCH_3; $C_{10}H_{14}O_3$. Calculated: 65.93% C, 7.69% H, 19.14% OCH_3. The veratrylethylcarbinol (I) was synthesized under the same conditions, reacting veratryl aldehyde with C_2H_5MgBr; it had a boiling point of 146° (2 mm). Found: 67.34% C, 8.22% H, 31.24% OCH_3; $C_{11}H_{16}O_3$. Calculated: 67.35% C, 8.16% H, 31.63% OCH_3. The methyl veratrylethylcarbinyl ether (III) was produced by treating 6 g of compound I with 41 ml of a 0.15 M solution of gaseous HCl in absolute methanol at room temperature for 24 h. After the reaction had gone to completion, the mixture was neutralized with a 2 N methanol solution of KOH. The precipitate formed was filtered out, most of the methanol was distilled off in a vacuum, and the precipitate was dissolved in ether. The etheric solution was washed with water, dried over $MgSO_4$, and distilled to remove the solvent. The resultant precipitate was vacuum-distilled. We obtained 5.14 g (80%) of compound III with a boiling point of 74° (0.07 mm). Found: 68.78% C, 8.51% H, 44.05% OCH_3; $C_{12}H_{18}O_3$. Calculated: 68.57% C, 8.57% H, 44.29% OCH_3. The methyl guaiacylethylcarbinyl ether (IV) was produced by methylation of 6 g of compound II under the same conditions; the yield was 4.9 g (69%) and the boiling point was 96° (0.5 mm). Found: 67.46% C, 8.15% H, 31.47% OCH_3; $C_{11}H_{16}O_3$. Calculated: 67.34% C, 8.16% H, 31.63% OCH_3.

Nitration of Model Compounds and Isolation of Reaction Products. A portion of 3 g of each model compound was treated with 37.5 ml of a mixture of 96% ethanol (four parts by volume) and HNO_3 with a specific gravity of 1.4 (one part). The reaction was carried out in a three-necked flask fitted with a reflux condenser and a mixer. The reaction time was 2 h, heating the mixture in a water bath at 72°. In all four cases, the reaction took place in a homogeneous medium. The solution immediately turned dark red during nitration of compounds II and IV; a gradual change in color from greenish to brownish-red was observed during nitration of compounds I and III. After the reaction had gone to completion, the mixture was diluted with about 100 ml of water, which caused a viscous reddish-brown liquid to settle out; after separation from the solution, the liquid was transferred to a column of Al_2O_3. The remaining solution was neutralized to a pH of about 6 with KOH, the ethanol was distilled off in a vacuum, and the solution was acidified to a pH of about 9 with dilute HNO_3 and extracted with ether. The etheric extract was dried over Na_2SO_4, the solvent was distilled off in a vacuum, and the residue, which consisted of a viscous reddish-brown liquid, was transferred to a column. Chromatographic separation was carried out with Al_2O_3 (activity grade II); the column was 2.0 cm in diameter and 65 cm tall, containing 75 g of Al_2O_3.

The reaction products were isolated from the column with the following eluotropic solvent system: low-boiling petroleum ether, CCl_4, benzene, $CHCl_3$, $(C_2H_5)_2O$, acetone, ethanol, water, and acidified HCl.

Nitration of Veratrylethylcarbinol (I). Petroleum ether eluted the syrupy compound, which was then purified by steam distillation. The distillate was extracted with CCl_4. After removal of the solvent, we obtained 2.45 g (60%) of compound V in the form of a reddish-yellow syrup. Found: 57.96% C, 7.17% H, 5.12% N, 34.97% $OCH_3 + OC_2H_5$ (regarded as OCH_3). $C_{13}H_{19}NO_5$. Calculated: 57.99% C, 7.06% H, 5.20% N, 23.05% OCH_3, 16.73% OC_2H_5, 34.57% $OCH_3 + OC_2H_5$ (regarded as OCH_3).

The crystalline compound was eluted with CCl_4 and, after recrystallization from ethanol, yielded light-yellow acicular crystals of compound VII; the yield was 0.27 g (10%) and the melting point was 96°. Found: 53.11% C, 5.04% H, 7.60% N, 33.70% OCH_3. $C_8H_9NO_4$. Calculated: 52.46% C, 4.92% H, 7.65% N, 33.88% OCH_3. A mixed sample containing synthetic 4-nitroveratrol exhibited no melting-point depression.

The benzene eluate yielded 0.32 g (9%) of compound VI with a melting point of 87-88° (from CCl_4). Found: 54.80% C, 6.39% H, 5.78% N, 25.16% OCH_3. $C_{11}H_{15}NO_5$. Calculated: 54.78% C, 6.22% H, 5.81% N, 25.73% OCH_3. This product was identical to a preparation previously obtained by nitration of compound I in ether and CCl_4 [6, 7].

Nitration of Guaiacylethylcarbinol (II). The ethanol eluate yielded 0.26 g (8%) of a crystalline substance that produced yellow crystals of 4,6-dinitroguaiacol on recrystallization from ethanol; its melting point was 121-122°. Found: 39.56% C, 3.26% H, 13.49% N. $C_7H_6N_2O_6$. Calculated: 39.25% C, 2.80% H, 13.08% N. The resultant compound did not depress the melting point of synthetic 4,6-dinitroguaiacol.

Nitration of Methyl Veratrylethylcarbinyl Ether (III). Petroleum ether eluted compound VII, which was purified by recrystallization from ethanol; the yield was 0.08 g (3%) and the melting point was 95-96°. Found: 53.14% C, 5.22% H, 7.87% N, 33.20% OCH_3. $C_8H_9NO_4$. Calculated: 52.46% C, 4.92% H, 7.65% N, 33.88% OCH_3.

A syrupy substance was eluted by the CCl_4 and purified by steam distillation. The distillate was extracted with CCl_4. After removal of the solvent, we obtained 2.4 g (66%) of compound VIII in the form of a yellow syrup. Found: 56.94% C, 6.63% H, 5.67% N, 37.00% OCH_3. $C_{12}H_{17}NO_5$. Calculated: 56.47% C, 6.66% H, 5.49% N, 37.20% OCH_3. This product was identical to the preparation previously obtained by Sergeeva and Shorygina [8] on nitration of compound III in ether and CCl_4.

Nitration of Methyl Guaiacylethylcarbinyl Ether (IV). A crystalline substance was eluted by the ethanol and, after recrystallization from ethanol, yielded 0.40 g (13%) of yellow 4,6-dinitroguaiacol crystals with a melting point of 121-122°. Found: 39.48% C, 3.09% H, 13.45% N, 14.30% OCH_3. $C_7H_6N_2O_6$. Calculated: 39.25% C, 2.80% H, 13.08% N, 14.49% OCH_3.

CONCLUSIONS

1. The principal reaction pathways for nitration of guaiacylethylcarbinol and veratrylethylcarbinol by HNO_3 solution in ethanol are incorporation of a nitro group into the aromatic ring and partial ethylation of the arylcarbinol groups.

2. Electrophilic replacement of the side chains by nitro groups occurs when the compounds investigated are treated with nitric acid dissolved in ethanol or with nitric acid in anhydrous media; this process was especially pronounced during nitration of model compounds with a free phenol hydroxyl. The substitution was largely suppressed by preliminary methylation of the arylcarbinol groups with $CH_3OH + HCl$.

3. This reaction is one lignin-destruction pathway during nitration in anhydrous media and, to a lesser extent, during alcoholic nitration by Kuerschner's method.

LITERATURE CITED

1. O. P. Grushnikov, N. N. Porygina, and N. P. Mikhailov, Izv. Akad. Nauk SSSR, Ser. Khim., 2099 (1968).
2. K. Kuerschner and A. Hoffer, Techn. Chem. Papier Zellstoff-Fabr., 26, 125 (1929); Chemiker-Ztg., 55, 161 (1931).
3. B. O. Lindgren, Acta Chem. Scand., 3, 1011 (1949); 4, 1365 (1950); E. Adler and B. O. Lindgren, Svensk Papperstidn., 55, 563 (1952).
4. B. Holmberg, Svensk Kem. Tidskr., 48, 207 (1936); Svensk Papperstidn., 39, 117 (1936).
5. E. Adler and J. Gierer, Acta Chem. Scand., 9, 84 (1955); J. Marton and E. Adler, Tappi, 46, 92 (1963); E. Adler, H. D. Becker, T. Ishihara, and A. Stamvik, Holzforschung, 20, 3 (1966).
6. A. A. Chuksanova, L. L. Sergeeva, and N. N. Shorygina, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 2219 (1959).
7. L. L. Sergeeva, N. N. Shorygina, and B. V. Lopatin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1295 (1962).
8. L. L. Sergeeva and N. N. Shorygina, Izv. Akad. Nauk SSSR, Ser. Khim., 1630 (1965).
9. O. P. Grushnikov and N. N. Shorygina, Izv. Akad. Nauk SSSR, Ser. Khim., 1774 (1967).
10. K. V. Sarkanen, B. Ericsson, and J. Suzuki, Lignin Structure and Reactions, Washington (1966), p. 38.
11. O. P. Grushnikov, N. N. Shorygina, G. V. Isagulyants, and N. N. Rozhdestvenskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 1366 (1969).