NIT RATION OF THE LIGNIN MODEL COMPOUNDS

3 - (3,4 - DIMETHOXYPHENYL) - 1 - PROPANOL

AND 3-(4-HYDROXY-3-METHOXYPHENYL)-1-PROPANOL

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We have previously demonstrated the difference in behavior of 3-(3,4-dimethoxyphenyl)-1-propanol (I) and 3-(4-hydroxy-3-methoxyphenyl)-1-propanol (II), which are models of "middle" and "end" units of lignin models respectively, in nitration by concentrated nitric acid in a carbon tetrachloride medium [1].



In the nitration of (I) with 1 M and 3 M nitric acid we obtained the mononitro compound 3-(4,5-dimethoxy-2-nitrophenyl)-1-propanol (III). In the nitration of (II), the model compound with the unsubstituted phenolic group, with2 M and 3 M nitric acid we obtained a light-brown amorphous nitrogen-containing powder, and in the nitration of(II) with 1 M nitric acid a resin separated from the reaction mixture, and after the ether extraction of this we obtaineda powdery residue in a yield of about 50% on the starting substance. For purification the product was given three $successive precipitations from alcohol with ether, dried in a vacuum desiccator over <math>P_2O_5$, and analyzed. Found: C 58.63; H 5.52; N 2.77; OCH₃ 8.73; OH 11.00%. The product of the nitration of (II) with 2 M nitric acid contained: C 55.99; H 5.34; N 4.73; OCH₃ 6.54; OH 9.21%. The analyses show that the methoxyl contents of the nitration products are considerably lower than that of the expected nitro compound (OCH₃ content of starting substance 15.8%). We were unable to separate the mixtures obtained into individual substances by chromatography on alumina because the substances were then very firmly adsorbed. The instability of o-methoxyphenols to nitration has been pointed out by Andersen [2].

When nitration is carried out in carbon tetrachloride, the reaction takes place in a heterogeneous medium, as a result of which a locally high nitric acid concentration is created which can lead to profound oxidation of the starting substance; in our further work we therefore carried out the nitration in dry ether, in which both the model compounds and nitric acid are readily soluble. In this way a homogeneous medium is created and the necessary concentration of nitric acid can be obtained in an anhydrous medium.

In the nitration of (I) with 4 N ethereal nitric acid for 60 min at about 20° we obtained the same mononitro compound as we did in a carbon tetrachloride medium [3-(4,5-dimethoxy-2-nitrophenyl)-1-propanol (III))], but in higher yield (up to 67%). In the nitration of (II) with 4 N ethereal nitric acid there was an almost immediate precipitate of bright-red crystals of (IV), obtained in about 25% yield. When the reaction was carried out with 2 N ethereal nitric acid the yield of red crystals rose to 66%. The nitration of (II) with 1 N ethereal nitric acid did not lead





Fig. 1. Infrared spectrum of 5-(3-hydroxypropyl)-3-nitro-o-benzoquinone.

Fig. 2. Infrared spectrum of 3-(3,4-dihydroxy-5-nitro-phenyl)-1-propanol (V).

to the precipitation of red crystals, and most of the starting substance was recovered unchanged from the reaction mixture. The red substance is unstable in the nitric acid - ether system, and shortly after its separation it turned into a resin. After being separated and washed free from acid, (IV) was found to be fairly stable, but when kept it gradually lost its crystalline structure and turned into a brown amorphous powder. After recrystallization from a mixture of benzene and ether we obtained bright-red needles of m.p. 110-111°. Mol.wt. 211; 216 (determined cryoscopically in acetic acid). The nitro compound (IV) does not contain methoxy groups. An aqueous solution of (IV) liberates iodine from acidified potassium iodide solution. The infrared spectrum of (IV) (Fig. 1) contains intense absorption bands characteristic for o-quinones ($\nu = 1670 \text{ cm}^{-1}$) [3]. It also contains bands characteristic for alcoholic OH ($\nu \sim$ 3350 cm⁻¹), and for a nitro group attached to the nucleus adjacent to the quinone grouping ($\nu = 1352 \text{ cm}^{-1}$) [4]. Its chemical behavior and the analytical and spectroscopic results indicate that (IV) is a nitro derivative of a substituted o-quinone, namely 5-(3-hydroxypropyl)-3-nitro-o-benzoquinone. The nitro compound (IV) is not reduced by SO₂ in



ether and chloroform. By its reduction in aqueous suspension with SO_2 we obtained two substances: a red crystalline substance (V), m.p. 137-139°, and a dark-violet crystalline substance, m.p. 149-150°, which was probably the nitro quinhydrone (VII). The infrared spectrum of (V) (Fig. 2) contains absorption bands characteristic for nitro-substituted aromatic rings (810, 850, 1062, 1125, 1538 and 1635 cm⁻¹). The spectrum contains also an absorption band at 1360 cm⁻¹ due to the nitro group. The frequency of this band is characteristic for a nitro group ortho to a phenolic hydroxy (probably in the 5-position with respect to hydroxypropyl). Also, the spectroscopic investigation of (V) showed that OH groups are present.

By the acetylation of (V) with acetic anhydride in presence of pyridine we obtained the acetyl derivative (VI) as white crystals of m.p. 122.5-124°. The infrared spectrum of (VI) (Fig. 3) did not contain hydroxyl absorption bands in the range $3600-3200 \text{ cm}^{-1}$, but contained bands characteristic for the nitro group ($\nu = 1376 \text{ cm}^{-1}$). Such a frequency is characteristic for a nitro group in the ortho position (probably in the 5-position) to an acetoxy group.

By the acetylation of (VII) with acetic anhydride in presence of pyridine we obtained an acetyl derivative as white needles, m.p. 87-88°.

To determine the effect of the OH group in the 3-position of the side chain on the specific features of the nitration we carried out the nitration of 2-methoxy-4-propylphenol (VIII). It is known that in the nitration of 2-methoxy-4-propylphenol with ~ 0.4 N ethereal nitric acid 2-methoxy-3-nitro-4-propylphenol is formed [5]. In the



Fig. 3. Infrared spectrum of the acetyl derivative (VI) of 3-(3,4-dihydroxy-5-nitrophenyl)-1-propanol.

nitration of (VIII) with 2 N ethereal nitric acid under the conditions for the nitration of (II) we were unable to isolate a quinone, but the reaction mixture went deep red as in the case of the nitration of (II). The infrared spectrum of the mixture contained an absorption band at 1672 cm^{-1} , characteristic for an o-quinone. It may be supposed that in the case of 2-methoxy-4-propylphenol, as in the nitration of (II) with ethereal nitric acid, demethylation occurs with formation of an o-quinone derivative.

It has been shown previously that in the nitration of lignin its demethoxylation is observed to occur to a greater or less extent whatever the experimental conditions may be [6]. Freudenberg and Dürr [7] supposed that in the nitration of lignin with nitrogen dioxide the process goes in several stages with elimination of methyl nitrite and formation ultimately of a nitrophenol. Dence and Sarkanen [8], who

studied the chlorination of lignin and its models, showed that in the chlorination of vanillyl and veratryl alcohols an absorption maximum appeared in the spectrum of the reaction mixture which was similar to the absorption maximum of o-benzoquinone.

In the work of Sobolev [9], who studied the action of dilute nitric acid on creosol (IX), it was shown that both in an aqueous medium and in the chloroform - acetic acid system the final product is the nitro p-quinone, 2-hydroxy-5-methyl-3-nitro-p-benzoquinone (X). It is evident that the nitration conditions have a substantial effect on the course of the reaction. This is confirmed by the results of Ley and Müller [10], who in the nitration of 2,4,6-tri-tbutylphenol (XI) with nitric acid in dry petroleum ether obtained 4,6-di-t-butyl-3-nitro-o-benzoquinone (XII). The same compound was obtained by Ley and Müller by the action of HNO_3/CH_3COOH on 4,6-di-t-butylguaiacol.



The formation of a nitro o-quinone in the nitration of 3-(4-hydroxy-3-methoxyphenyl)-1-propanol supports the view that the demethoxylation of lignin in the course of nitration goes in a similar way with the formation of quinones.

It is known that the nitration of lignin is accompanied by its oxidation, which leads to an accumulation of carboxy groups. It is possible that the formation of quinones is an intermediate stage in the oxidation, the final products of which are acids.

EXPERIMENTAL

Nitration of 3-(3,4-Dimethoxyphenyl)-1-propanol (I) with 4 N Ethereal Nitric Acid*. A solution of 8.4 ml of nitric acid in 25 ml of dry ether was added to a cooled solution of 5 g of (I) in 16.6 ml of dry ether. The reaction mixture was left for 60 min with periodic shaking and was then poured into 500 ml of ice water. The ether layer was separated, and the aqueous layer was extracted several times with ether. The combined extracts were dried with an-hydrous magnesium sulfate. Ether was driven off, and the residue was transferred to a column of alumina. Elution was with carbon tetrachloride and with ether. From the carbon tetrachloride solution, after the removal of solvent, we isolate 4.1 g of light-yellow powdery 3-(4,5-dimethoxy-2-nitrophenyl)-1-propanol (III). After being recrystal-lized from hexane this had m.p. 99-100° (softening point about 94°). Found: C 54.70; H 6.19; N 5.96%. C₁₁H₁₅O₅N. Calculated: C 54.77; H 6.22; N 5.80%.

* In all the nitration experiments nitric acid of sp.gr. 1.50 was used.

Nitration of 3-(4-Hydroxy-3-methoxyphenyl)-1-propanol (II) with 2 N Ethereal Nitric Acid. A cooled solution of 8.4 ml of nitric acid in 50 ml of dry ether was added to a cooled suspension of 5.0 g of (II) in 41.6 ml of dry ether. The reaction mixture turned red and became warm, and a red crystalline precipitate of (IV) rapidly formed. After 10-15 min the precipitate was filtered off and washed with ether. We obtained 3.3 g of a substance m.p. 108-110°. After recrystallization from a mixture of benzene and ether we obtained red needles of m.p. 110-111°. Found: C 51.50; H 3.70; N 6.78%. C₃H₃O₅N. Calculated: C 51.18; H 4.26; N 6.63%.

Reduction of (IV). Sulfur dioxide was passed through a suspension of 4.0 g of water. With the passage of sulfur dioxide (IV) dissolved, and the solution gradually darkened. Toward the end of the reduction a precipitate formed. The reaction mixture was extracted with ether, and the extracts were dried with anhydrous magnesium sulfate. Solvent was driven off to give a dry residue, which was washed several times with benzene. Part, (V), dissolved in the benzene, and the rest, (VII), remained as a residue. As benzene was removed, large red needles came down of 3-(3, 4-dihydroxy-5-nitrophenyl)-1-propanol (V), m.p. 137-139° (from benzene). Found: C 50.98; H 4.42; N 6.45 η_0 . C₉H₁₁O₅N. Calculated: C 50.70; H 5.16; N 6.57 η_0 .

The substance (VII), which did not dissolve in cold benzene, was recrystallized from hot benzene. We obtained dark-violet long flat needles, which after being dried in a vacuum desiccator at 60° had m.p. 149-150°. (VII) appears to crystallize with one molecule of water. Found: C 48.75; H 5.18; N 6.20%. $C_{18}H_{20}O_{10}N_2 \cdot 1H_2O$. Calculated: C 48.86; H 4.97; N 6.31%.

Acetylation of (V). 12 ml of acetic anhydride was added to a solution of 0.4 g of (V) in 40 ml of pyridine. After $\overline{24}$ h most of the pyridine was distilled off, and the residue was poured onto ice. The precipitated oil was extracted with ether. The residue remaining after the removal of ether was recrystallized from alcohol, and we obtained white needles of (VI), m.p. 122.5-124°. Found: C 53.10; H 4.75%. C₁₅H₁₇O₈N. Calculated: C 53.09; H 5.01%.

SUMMARY

1. In the nitration of 3-(3,4-dimethoxyphenyl)-1-propanol (I) with 4 N ethereal nitric acid one nitro group enters the aromatic nucleus.

2. In the nitration of 3-(4-hydroxy-3-methoxyphenyl)-1-propanol (II) under the same conditions, as well as nitration in the nucleus demethylation occurs with the formation of an o-quinone. It may be supposed that this is the way in which demethoxylation occurs in the nitration of lignin.

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