I. REDUCTIVE DECOMPOSITION WITH METALLIC SODIUM IN LIQUID AMMONIA OF 1-(4-HYDROXYPHENYL)-2-(2'-METHOXYPHENOXY)PROPANE-1,3-DIOL

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It has been established by a number of authors [1] that the lignin of coniferous and broad-leaved trees and, particularly, of annual plants contains, in addition to the β-guaiacyl ether of α-guaiacylglycerol, the β-guaiacyl ether of α-(p-hydroxyphenyl)glycerol. It is extremely likely that this grouping plays an important role in the lignin of the lower plants. In view of this, we have performed the synthesis of 1-(4-hydroxyphenyl)-2-(2'-methoxyphenoxy)propane-1,3-diol (the β-guaiacyl ether of α-(p-hydroxyphenyl)glycerol) and have performed its decomposition with metallic sodium in liquid ammonia, which was done by the method developed by Semechkina and Shorygina [2].

The completeness of the decomposition of the β-guaiacyl ether of α-p-hydroxyphenylglycerol was determined by paper chromatography from the absence of the light yellow spot with $R_f = 0.57$ that is characteristic for the dimer among the decomposition products. And, furthermore, as follows from the results obtained by GLC (Table 1), 1 mole of dimer taken for decomposition yielded 1 mole each of catechol and guaiacol, which is possible only if the β-ether bond of the dimer cleaved completely.

The qualitative analysis of the composition of the phenols obtained was performed by paper chromatography in parallel on "crab" paper and Leningrad slow paper. As markers we used phenols that we had synthesized. Figure 1 gives the results of the analysis.

In order to confirm the reliability of the identification of the composition of the phenols and to determine their amounts in the decomposition products, we used gas–liquid chromatography, for which purpose the mixture of phenols was treated with dimethyl sulfate in an alkaline medium, and then the methyl ethers obtained were separated on a chromatograph.

Figure 2a gives the chromatogram of a model mixture and Figure 2b a chromatogram of the decomposition products. On the basis of a comparison of the chromatograms the presence of the following substances was established in the methylated decomposition products: 1,2-dimethoxybenzene, 4-methoxyphenyl-propane, 1-(4-methoxyphenyl)propan-1-ol, 3-(4-methoxyphenyl) propan-1-ol, and an unidentified substance (peak 5).

Table 1 gives the results of the quantitative analysis of the products of the decomposition of the β-guaiacyl ether of α-p-hydroxyphenylglycerol. As follows from this table, the relative error of the determination of the combined phenols in moles is approximately 10.0%, which must be regarded as completely satisfactory if one considers that the results of the analysis were extrapolated to the initial dimer taken for decomposition by metallic sodium in liquid ammonia.

EXPERIMENTAL

Synthesis of 1-(4-Hydroxyphenyl)-2-(2'-methoxyphenoxy)propane-1,3-diol (VII). The synthesis of this dimer was based on Kratzl's scheme [4], which he used to obtain 1-(4-hydroxy-3-methoxyphenyl)-2-(2'-methoxyphenoxy)propane-1,3-diol. At the same time, because the reactivity of a p-hydroxyphenyl residue is higher than that of a guaiacyl residue, we found different conditions for performing the individual stages. As applied to the synthesis of

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TABLE 1. Amounts of Phenols* in the Phenolic Fraction of the Products of the Decomposition of 1-(4-Hydroxyphenyl)-2-(2'-methoxyphenoxy)-propane-1,3-diol by Metallic Sodium in Liquid Ammonia

Names of the phenols	Yield cal. on initial dimer	
	%	in moles per mole of dimer
4-Hydroxyphenylpropane	32,8	0,70
Catechol + guaiacol	40,4	1,00
1-(4-Hydroxyphenyl)propan-1-ol	9,0	0,17
3-(4-Hydroxyphenyl)propan-1-ol	15,0	0,29
Unidentified substance	2,8	—

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*In the calculation, the yield of the ethers of the methylation of the corresponding phenols with dimethyl sulfate was taken into account.

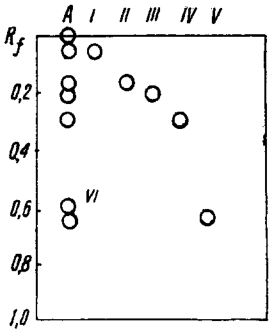

Fig. 1. Chromatogram of the mixture of phenols obtained from the product of the decomposition of 1-(4-hydroxyphenyl)-2-(2'-methoxyphenoxy)-propane-1,3-diol: A) chromatogram of the phenols obtained from the dimer. I-V) Markers: 1-(4-hydroxyphenyl)propan-3-ol; catechol; 1-(4-hydroxyphenyl)propan-1-ol; guaiacol; 4-hydroxyphenylpropane.

(VII) it included the following seven stages: phenyl acetate (I) — p-hydroxyacetophenone (II) — p-benzyloxyacetophenone (III) — p-benzyloxy-ω-bromoacetophenone (IV) — p-benzyloxy-ω-(2-methoxyphenoxy)acetophenone (V) — p-benzyloxy-3-hydroxy-2-(2'-methoxyphenoxy)propiophenone (VI) — 1-(4-hydroxyphenyl)-2-(2'-methoxyphenoxy) propane-1,3-diol (VII). Phenyl acetate (I) and p-hydroxypropiophenone (II) were synthesized by known methods [5, 6].

p-Benzyloxyacetophenone (III). A mixture of 34 g of (II), 62 ml of benzyl chloride, and 15.4 g of NaOH in 625 ml of ethanol was heated in the boiling-water bath for 1.5 h. Then 800 ml of water was added and the mixture was shaken with ether. The extract, after being washed with water and with 5% Na_2CO_3 solution, was dried over Na_2SO_4 and the solvent was distilled off. The residue consisted of (III) with the composition $C_{15}H_{14}O_2$, mp 91-92°C (from a mixture of water, ethanol, and methanol, 1:2:3). Yield 42.6 g (76% of theory). Here and below, the analytical results corresponded to the calculated figures.

p-Benzyloxy-ω-bromoacetophenone (IV). A quartz flask was charged with 40.5 g of (III) dissolved in dry ether and 0.01 g of anhydrous $AlCl_3$. In the light and with stirring, 9.0 ml of a solution of bromine in the same solvent was added to the mixture. Then the contents of the flask were stirred for another one and a half hours and the ether and the HBr were distilled off in vacuum. The crystals of (IV) obtained were filtered off and were washed with a mixture of water and low-boiling petroleum ether (1:1). Compound (IV) had the composition $C_{15}H_{13}O_2Br$, mp 73.5-74°C (from aqueous ethanol). Yield 10.9 g (20% of theory).

p-Benzyloxy-ω-(2-methoxyphenoxy)acetophenone (V). With stirring, 8.13 g of K_2CO_3 was added to a solution of 8.13 g of (IV) and 6.5 g of guaiacol in 30 ml of absolute acetone, and the mixture was heated for 1.5 h. Then it was diluted with 190 ml of water and extracted with chloroform. The extract, after being washed with 5% NaOH and water, and dried over Na_2SO_4, and the solvent was driven off.

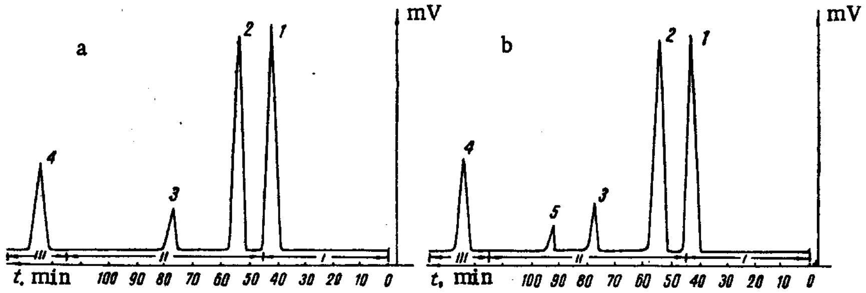

Fig. 2. Chromatogram of a mixture of methylated phenols at the following temperatures: 130°C — I; 130-200°C (1 deg/min) — II; 200°C — III; a) model mixture; b) obtained from the products of the decomposition of 1-(4-hydroxyphenyl)-2-(2'-methoxyphenoxy)propane-1,3-diol: 1) 4-methoxyphenylpropane; 2) 1,2-dimethoxybenzene; 3) 1-(4-methoxyphenyl)propan-1-ol; 4) 3-(methoxyphenyl)propan-1-ol; 5) unidentified substance.

The residue consisted of (V), mp 74-76°C (from ethanol). Yield 5.9 g (64% of theory).

p-Benzyloxy-3-hydroxy-2-(2'-methoxyphenoxy)propiophenone (VI). At 38°C, with stirring, 2.5 ml of 32% formalin and 0.16 g of K_2CO_3 were added to a suspension of 4 g of (V) in 330 ml of 95% ethanol. After 1 h, the mixture was neutralized in vacuum, and the residue was dissolved in chloroform. The extract was washed with a solution of potassium carbonate and with water, and the solvent was distilled off. The residue consisted of (VI), $C_{23}H_{22}O_5$, mp 81-83°C (from a mixture of methanol and water, 6:1). Yield 2.7 g (65% of theory).

1-(4-Hydroxyphenyl)-2-(2'-methoxyphenoxy)propane-1,3-diol (β-Guaiacyl Ether of α-(p-Hydroxyphenyl)glycerol) (VII). In the form of a suspension in 30 ml of 93% CH_3COOH, 2.0 g of freshly prepared $PdCl_2/BaSO_4$ was reduced with hydrogen with stirring for 1.5 h. Then 2.0 g of (VI) in 30 ml of the same solvent was added, and the reaction mixture was left to stand under hydrogen with periodic shaking. In 8 h, 322 ml of hydrogen was absorbed, which corresponds to the amount calculated for the reduction of the benzyl ether and of the >CO group to >CHOH. After the end of the reaction, the catalyst was filtered off and washed with the initial solvent. After neutralization with $NaHCO_3$, the reaction mixture was extracted with chloroform. The extract was washed with water, passed through a column of Al_2O_3, and dried over Na_2SO_4. After the elimination of the solvent, a viscous syrupy residue with a certain amount of crystals interspersed through it was obtained. Yield 1.28 g [83% of theory, calculated on the initial (VI)].

An attempt to crystallize the product obtained was unsuccessful, and this shows that we had obtained a mixture of the isomeric erythro and threo forms of the substance; its composition was $C_{16}H_{18}O_5$ (from the results of elementary analysis and of a determination of OCH_3 groups).

Figure 3 shows the IR spectra of (VI) and (VII). The spectrum of (VII) (Fig. 3a) lacks the absorption band of carbonyl groups at 1690 cm^{-1}, but it shows a diffuse band of hydrogen bonds at 3350 cm^{-1} that is absent from the spectrum of (VI) (Fig. 3b), which shows the completeness of the hydrogenation and the absence of residues of (VI) in (VII).

Thus, the analytical figures, the IR spectra, and the results of the decomposition of (VII) by metallic sodium in liquid ammonia permit its identification as 1-(4-hydroxyphenyl)-2-(2'-methoxyphenoxy)propane-1,3-diol.

Decomposition of the B-Guaiacyl Ether of α-(p-Hydroxyphenyl)glycerol by Metallic Sodium in Liquid Ammonia. A 1.18-g sample of the dimer was dissolved in 400 ml of liquid ammonia. Then 1.0 g of metallic sodium was added in portions to the reaction vessel.

After the blue solution had become decolorized, for which three days was necessary, the ammonia was eliminated from the reaction mixture, and then moist ether, water, and dilute sulfuric acid were added successively to give an acid reaction to Congo Red. The decompo-

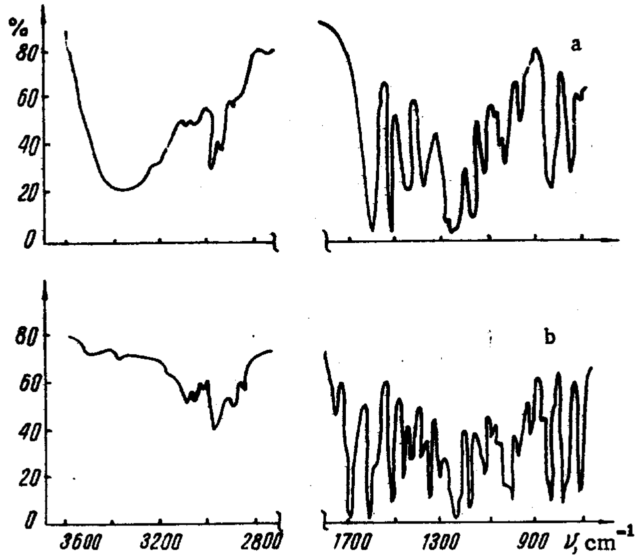

Fig. 3. IR spectra: a) (VII) — 1-(4-hydroxyphenyl)-2-(2'-methoxyphenoxy)propane-1,3-diol; b) (VI) — p-benzyloxy-3-hydroxy-2-(2'-methoxyphenoxy)propiophenone.

sition products were extracted with ether and the ethereal extract was dried over anhydrous Na_2SO_4, after which the ether was distilled off. The yield of decomposition products was 1.03 g (87% of the weight taken).

Paper Chromatography. On a strip of paper 15 × 30 cm, at a distance of 4 cm from the edge, an ethanolic solution of the phenols under investigation was deposited. Chromatography was performed for 4-5 h on "crab" paper and for 6-9 h on Leningrad slow paper using as the mobile phase the organic layer of a mixture of chloroform, n-hexane, methanol, and water (7:5:2:1) by the descending method. Identification was performed from the R_f values and the colors of the spots obtained after treatment of the chromatogram with a solution of diazotized sulfanilamide.

Gas—liquid chromatography (GLC) was performed on a LKhM-7A instrument with a flame-ionization detector (rate of flow of nitrogen 70 ml/min). Two stainless-steel columns (200 × 0.4 cm) were used, one containing 8% of PEGA on Chromosorb G (60-80 mesh) and one containing 15% of Apiezon L on Chromosorb W (60-80 mesh). The columns were thermostatted at temperatures from 130 to 200°C (with a rate of heating of 1 deg/min).

The identification of the substances detected on the chromatogram was performed on the basis of the results of paper chromatography, from the retention times, and from the introduction of standards obtained by methylating the corresponding phenols. For the quantitative analysis of the mixture of decomposition products we used the method of area normalization with the correction coefficients found previously by the chromatographic separation of a model mixture [3].

SUMMARY

1. 1-(4-Hydroxyphenyl)-2-(2'-methoxyphenoxy)propane-1,3-diol has been synthesized for the first time.

2. The reductive decomposition of 1-(4-hydroxyphenyl)-2-(2'-methoxyphenoxy)propane-1,3-diol with metallic sodium in liquid ammonia has been performed, and the presence in the decomposition products of guaiacol, catechol, 4-hydroxyphenylpropane, 1-(4-hydroxyphenyl)propan-1-ol, and 3-(4-hydroxyphenyl)propane-1-ol has been established.

3. A quantitative analysis of the decomposition products has been performed by the GLC method and it has been established that the β-ether bond of the dimer is cleaved completely under the conditions used.

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