# *p-Hydroxy-Benzyl Ethers As Lignin Models. II.*

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It is now generally accepted that the sulfonatable groups of lignin are not unique and consist of three different types of groups, namely X, Z, and B[1]. The constitutions of these groups are concluded mainly from the experiments on model compounds and the analyses of lignosulfonic acids. Recently Lindgren and Adler gave very useful reviews concerning the sulfonatable groups of lignin[2].

In the present paper the constitution of X group is discussed from the results of the hydrogen sulfide cookings of *p*-hydroxybenzyl ethers as lignin models. A series of experiments of Lindgren, Enkvist, Erdtman, Adler, Leopold and Migita et al. On the sulfonation (rapid sulfonation of *p*-hydroxybenzyl alcohols and slow sulfonation of *p*-methoxybenzyl alcohols[3]) and sulfidation (former compounds

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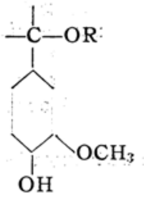
[1] Lindgren, *Acta Chem, Scand.* **5**, 603 (1951). Mikawa, Sato, Takasaki and Okada, *J. Soc. Chem. Ind. Japan*, **54**, 299 (1951); TAPPI in the press. Mikawa, *ibid*, **54**, 651. 741, 762 (1951). **55**, 294, 342 (1952).

[2] Lindgren, *Svensk Papperstidn.* **55**, 78 (1952). Adler and Lindgren, *ibid.* 565.

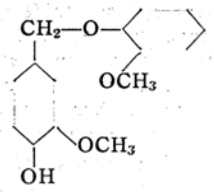
[3] Lindgren, *Acta. Chem. Scand.* **1**, 779 (1947); **3**, 1011 (1949). Erdtman and Leopold, *ibid*, **3**, 1358 (1949). Adler and Yllner, *Svensk Papperstidn.* **55**, 238 (1952). Adler, Lindgren and Saeden, *ibid.* **55**, 245 (1952). Migita, Nakano, Ichino and Mikawa, *Tech. Assoo. Pulp and Paper Ind. Japan*, in the press.

react with $H_2S$[4] but the latter compounds do not[5]) of model compounds have definitely established that X group of lignin must have phenolic OH group in its para position. Though the results of experiments on vanillyl alcohol and *p*-oxybenzyl alcohol suggest that X group is a free benzyl alcoholic group, Lindgren found that pinoresinol is sulfonated comparatively rapidly at higher *p*H[6] and he pointed out the possibility that X group is the benzyl alkyl ether grouping.

As we have demonstrated, one of the most striking characteristics of X group is its reactivity with $H_2S$ at *p*H 7[1]. It will be, therefore, most desirable to test at the same *p*H the reactivity of $H_2S$ with benzyl ethers which have a phenolic OH group in its para position[7].

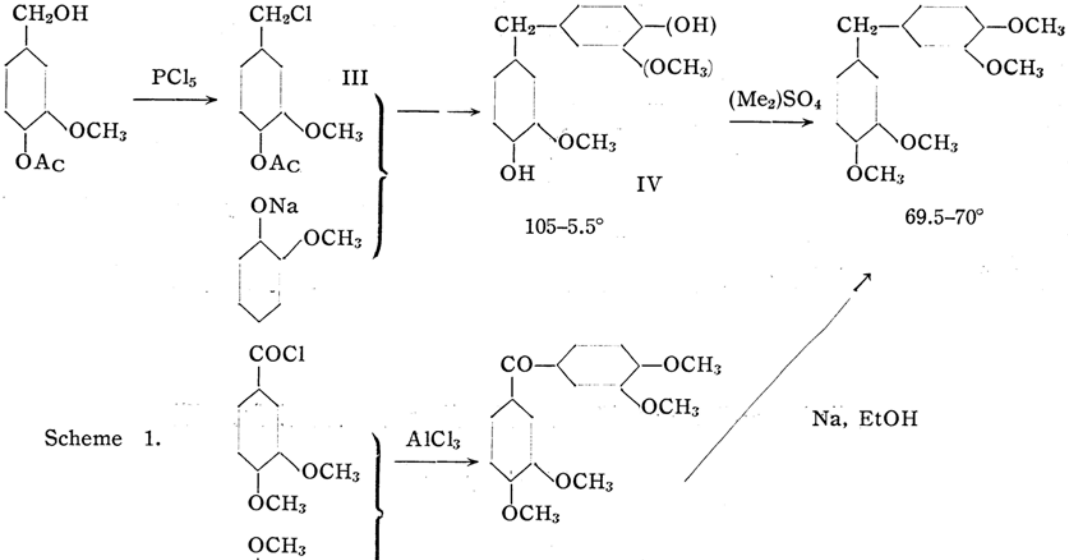


I

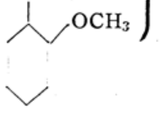


II

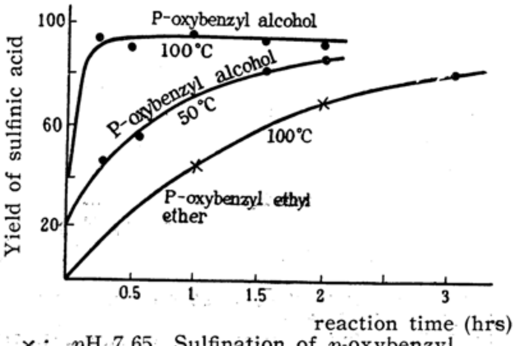
The syntheses of compounds of the type, for example, I is highly desirable for our purposes. Synthesis of II was attempted at first according to scheme 1, but the condensation of sodium guaiacolate and III in toluene (which contains a little alcohol) gave diphenylmethane derivative IV, m.p. 105–5.5°, which on methylation gave 3, 4, 3′, 4′-tetramethoxydiphenylmethane. The melting point, 69.5–70°, of the methylated product of IV was not depressed in admixture with the authentic sample of 3, 4, 3′, 4′-tetramethoxydiphenylmethane (which was synthesized from 3,4,3′,4′-tetramethoxybenzophenone according to the method of Robinson[8]) but showed marked depression with the authentic sample of veratryl guaiacyl ether, m.p. 78–9°. The structure of IV is therefore either 4, 4′-dioxy-3, 3′-dimethoxy- or 4, 3′-dioxy-3, 4′-dimethoxy-diphenyl-methane, although, of course, the former structure is by far the more probable.



Scheme 1.



As, therefore, the syntheses of the compounds of type I seemed to be comparatively



×: *p*H 7.65 Sulfination of *p*-oxybenzyl
●: *p*H 6.22 alcohol (5% $SO_2$, 1% NaOH)
and
*p*-oxybenzyl ethyl ether (*p*H 6.22 & 7.65)

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[4] Enkvist and Mollanen, *Svensk Papperstidn.* **52**, 183 (1949). Mikawa, cf. previous paper.

[5] Enkvist, unpublished (cf. (2)).

[6] Iindgren, *Acta Chem. Scand.* **6**, 91 (1952).

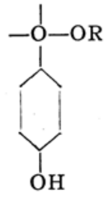
[7] T. Enkvist made recently profound investigations on the sulphidation of model compounds. cf. *Svensk Papperstidn.* **55**, (1952). In this paper he reaches already the conclusion that the compounds with benzyl ether linkage activated by phenolic OH group in its orth and para position combine with sulfur by hydrosulfide cooking at *p*H 7.

[8] Robinson, *J. Chem. Soc.*, **107**, 273 (1915).

TABLE 1. SULFONATIIN OF *p*-OXYBENZYL ETHYL ETHER 100°C

| hr / pH | 1 | 2 | 3 |
|---|---|---|---|
| 6.22 | 45.8 | — | 86.3 |
| 7.65 | 46.4 | 73.2 | — |

difficult[9], it was aimed at reaching the compounds of the type V, as it was made clear from the following results (a) and (b) that the methoxyl group in the meta position does not seem to exert any significant effect on the reactivity of the groups in the side chain, which fact Lindgren has already suggested in his review[2].



V

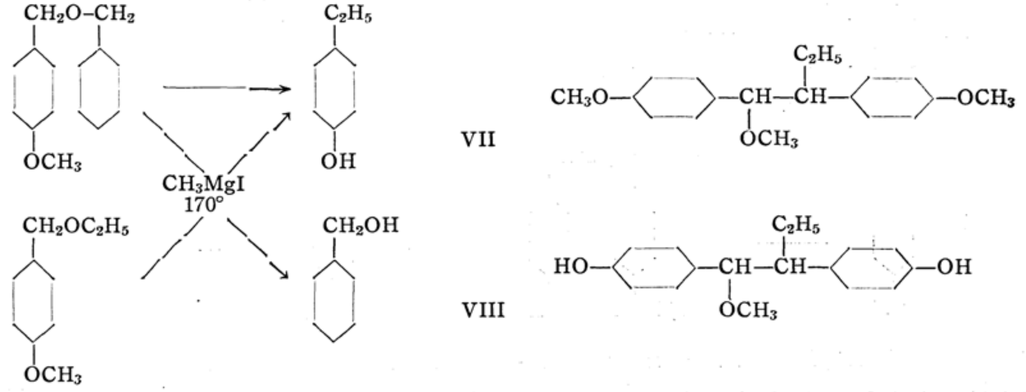
(a) *p*-Oxybenzyl alcohol is sulfonated as vanillyl alcohol quite rapidly and almost quantitatively with sulfite solution to give *p*-oxybenzyl sulfonic acid, as is evident from the figure[3].

(b) As was shown in the previous paper, *p*-oxybenzyl alcohol reacts with $H_2S$ at *p*H 7 very easily and 4, 4′-dioxydibenzyl sulfide was obtained, just as vanillyl alcohol is.

Demethylations of *p*-methoxybenzyl ethers with methyl magnesium iodide were attempted at first[10]. *p*-Methoxydibenzyl ether VI gave a considerable amount of benzyl alcohol and *p*-ethylphenol, when treated with methyl magnesium iodide at 170°. *p*-Methoxybenzyl ethyl ether gave similarly *p*-ethylphenol under the same conditions (see scheme 2). It was therefore made clear that the selective cleavage of arylether linkage of these compounds with the reservation of benzyl ether linkage is fairly difficult under these conditions. T. Takahashi was able, however, recently to demethylate VII to VIII with methyl magnesium iodide[11].

Scheme 2.

VI

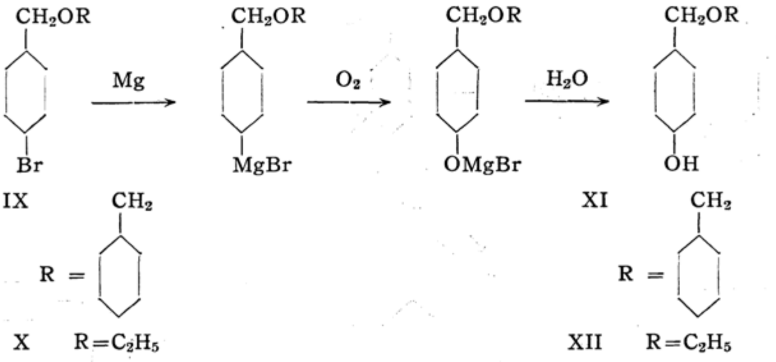


VII

VIII

At last, *p*-oxybenzyl ethers (XI and XII) were synthesized from the corresponding *p*-bromobenzyl ethers (IX and X) via their Grignard compounds as shown in the scheme 3[12]. The actual Yeilds of XI and XII were 20 and 23% of the theoretical respectively.

Scheme 3.



IX

X R=$C_2H_5$

XI

XII R=$C_2H_5$

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[9] However, B. Leopold synthesized recently vanillyl methyl ether in a very simple way. cf. *Svensk Papperstidn*, **55**, 816 (1952).

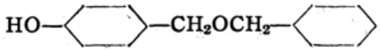
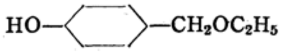
[10] Späth, *Monatsh.* **35**, 319 (1914); **36**, 6 (1915). Luttinghaus and Saar: *Angew. Chem.*, **51**, 915 (1938). Kharasch and Huang, *J. Org. Chem.*, **17**, 669 (1952).

[11] Takahashi: *J. Chem. Soc. Japan*, in the press.

[12] Porter and Steel, *J. Am. Chem. Soc.*, **42**, 2650 (1920). Ivanoff, *Bull. Soc. Chim.*, **1**, 47 (1925). Bert and Dorier, **182**, 63 (1926). Smith, Hoehn and Ungnade, *J. Org. Chem.*, **4**, 351 (1939).

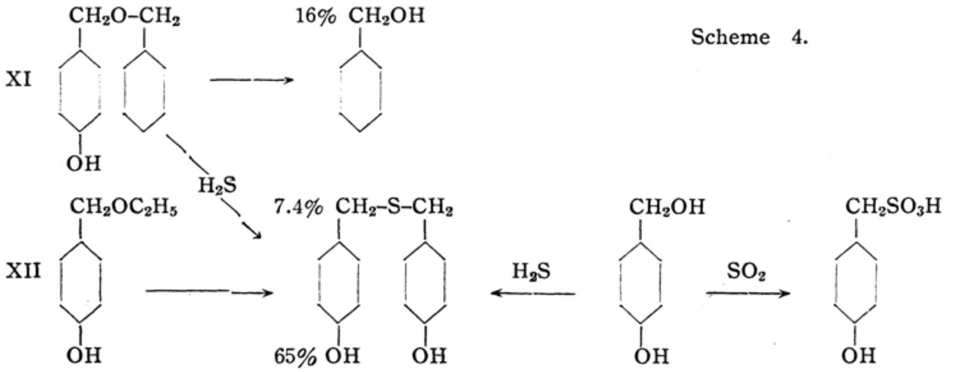
The boiling and melting points of these compounds and the melting points of some of their derivatives were shown in Table II.

TABLE II.

| | | b.P., m.p. | | $p$–nitrobenzoate | 3, 5–dinitrobenzoate | acetate |
|---|---|---|---|---|---|---|
|  | XI | b.p. 0.005 | 130–5° | m.p. 74–5° | — | m.p. 45.5–6° |
|  | X | b.p. 0.8 | 105° | m.p. 74–5° | m.p. 107–8° | — |
| | | m.p. | 50–1° | | | |

$p$-Oxydibenzyl ether XI was sealed in an ampoule with $H_2S$ water of $p$H 7, shaken well and heated for 15 hours at 100°C. Because of the low solubility of this compound the reaction was heterogeneous. 4,4'-dioxydibenzyl sulfide and benzyl alcohol were obtained in the yields of 7.4 and 16% (of the theory) respectively. The former was separated as such and the latter as its 3,5-dinitrobenzoate. The yields were calculated from those of the products of correct melting points.

$p$-Oxybenzyl ethyl ether XII was treated similarly for 18 hours. Pure 4,4'-dioxydibenzyl sulfide was obtained in the yield of 65% (of the theory). In this case the reaction was homogeneous. These results were shown in scheme 4.

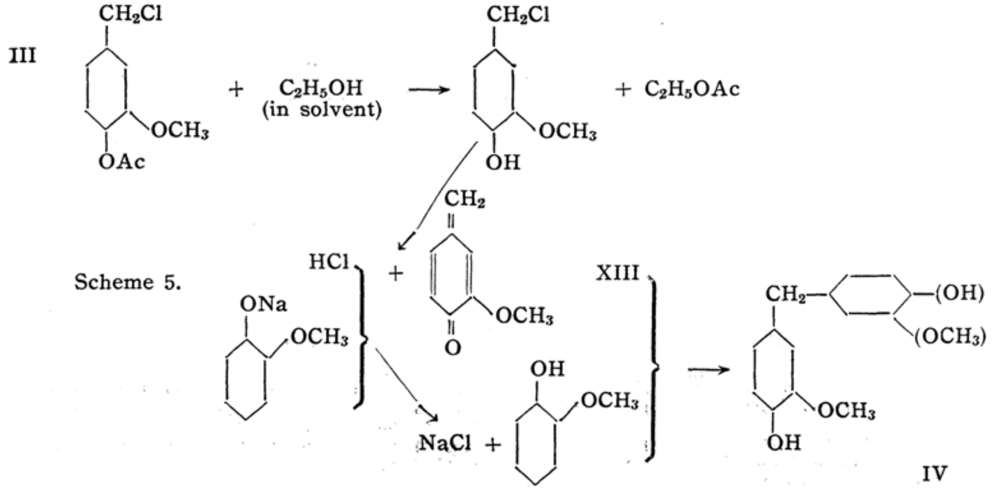


Scheme 4.

$p$-Oxybenzyl ethyl ether XII was sulphonated at pH 6.22 and 7.65. As is shown in the figure and Table 1, the sulfonation was very rapid.

## Discussion

i) The Condensation of sodium guaiacolate and III in toluene containing a small amount of alcohol to give diphenylmethane derivative IV at comparatively low temperature suggests to us that the reaction has proceeded via the methylene quinone structure XIII as is shown in scheme 5. It is a well known fact,



Scheme 5.

that pseudophenol alcohol halides condense with phenols or dimethylanilines to give diphenylmethane derivatives[13].

ii) No attempt have been made to cleave lignin molecule with grignard reagent of its building stones[14]. As at least about 50% of the building stones of native lignin are thought to be linked through aryl ether linkage between the hydroxyl group of the side chain and the phenolic OH group in its para position[2], it will be very interesting to use grignard reagent to cleave these linkages.

iii) The fact that the *p*-oxybenzyl ethers XI and XII are easily hydrolyzed even at pH 7 at 100°C and react with $H_2S$ to give 4,4′-dioxydibenzyl sulfide is completely in line with the properties of X group[1].

The fact suggests to us again a possibility that this group is a benzyl alkyl ether group with phenolic OH group in its para position. As the sulfidation velocity of X group is approximetely known[1], we will be able to compare the velocity with that of the models, if the latter is measured with sufficient accuracy. It is, therefore, very interesting to measure accurately the sulfidation velocity of model compounds with the so-called dilution method[15] using radioactive mono sulfide.

*p*-Oxybenzyl ethyl ether was sulfonated with neutral sulfite solutions and moreover the velocities of sulfonation do not seem to depend on the pH values. These findings are also completely parallel with the properties of X group.

**Added in proof.** According to the private communication of Dr. J. de Jonge, Philips Research Laboratories, Holland, our sample of *p*-hydroxybenzyl ethyl ether was hydrolyzed very quickly. i.e., at pH 6.8 after 3 hours and at pH 5.2 after 6 hours it was completely hydrolyzed into *p*-hydroxybenzyl alcohol at 100° and somewhat less completely at pH 8.1 after 6 hours at 100°. It may, therefore, safely be concluded that in the reaction with $H_2S$ hydrolysis of ether to the corresponding alcohol predeeds the formation of the sulfide.

## Experimental Part

**1. Synthesis of 3-Methoxy-4-acetoxybenzyl Chloride.** Acetylvanillin was reduced to acetylvanillyl alcohol according to the method used by Carothers and Adams[16]. 0.2 g. of $PtO_2 \cdot H_2O$ (according to Adams et al.[17]) was added to a solution of acetylvanillin (14 g.) and $FeCl_2$ (0.5 cc. of 0.2 mol. solution) in 200 cc. of absolute ethanol and was shaken with hydrogen (4 atm.) until no more hydrogen was absorbed. Acetylvanillyl alcohol (11.2 g.) was obtained as a very viscous oil.

2 g. of this acetylvanillyl alcohol was dissolved in 20 cc. of dry chloroform and pulverized $PCl_5$ (2 g.) was added slowly (during which some heat and HCl gas were evolved). The chloroform solution was washed well with water, dried with $Na_2SO_4$, the solvent removed in vacuo and the residue (1.9 g.) crystallized from petroleum ether (1.0 g.). The product obtained melted at 46–7° and the analyses agree with the compound being 3-methoxy-4-acetoxybenzyl chloride. Found: Cl, 15.9; $CH_3O$, 14.0, Calculated for $C_{10}H_{11}O_3Cl$: Cl, 16.6; $CH_3O$, 14.4%.

**2. Condensation of 3-Methoxy-4-acetoxybenzyl Chloride with Sodium Guaiacolate.** Sodium (1.1 g.) was dissolved in 20 cc. of anhydrous ethanol and guaiacol (7 g.) and toluene (40 cc.) were added. 3-Methoxy-4-acetoxybenzyl chloride (8 g.) was dissolved in toluene (70 cc.). The two solutions were mixed at once and the whole was warmed at 40° for 30 minutes, the rest stood over-night and was poured into a dilute solution of NaOH and well shaken. Neutral fraction (4.22 g.) was extracted with ether. The aqueous layer was acidified, extracted with ether, and the solvent removed. The residue (6.1 g.) solidified on standing, which was rubbed on a clay plate, dissolved in ether, passed through active $Al_2O_3$, ether removed and recrystallized from benzene to give white needles (4.06 g.), m.p. 105–5.5° (I).

(I) was methylated with dimethyl sulfate and alkali and recrystallized from aqueous ethanol to give white leaflets, melting at 69.5–70° (II), which was not depressed in admixture with the authentic sample of 3, 4, 3′, 4′-tetramethoxydiphenylmethane. (I) was therefore either 4, 4′-dioxy-3, 3′-dimethoxydiphenylmethane or 4, 3′-dioxy-3, 4′-dimethoxydiphenylmethane. The methoxyl values of (I) and (II) and the mixed melting points of them with several compounds are as follows:

(I), m.p. 105–5.5°, mixed melting point with vanillyl alcohol, 90–2°. Found: $CH_3O$, 23.5, Calculated for $C_{15}H_{16}O_4$: $CH_3O$, 23.8%.

(II), m.p. 69.5–70°, mixed melting points with diveratryl ether and veratryl guaiacyl ether, 54–7° and 58–61° respectively. Found: $CH_3O$, 42.5, 42.6, calculated for $C_{17}H_{20}O_4$: $CH_3O$, 43.0%.

**3. Synthesis of Veratryl Guaiacyl Ether.** Veratryl chloride was synthesized according to the method of Freudenberg[18]. Metallic sodium (0.31 g.) was dissolved in 100 cc. of absolute ethanol, guaiacol (2 g.) added, a solution of veratryl chloride (2.2 g.) in 10 cc. of benzene added and the whole was refluxed for 1 hour. The neutral fraction of the product was recrystallized from alcohol (1.5 g.), m.p. 78–9°. The analysis shows that the compound is veratryl guaiacyl ether. Found:

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[13] Richter-Anshütz: "Chemie der Kohlenstoffverbindungen" Leipzig 1935, Bd. $II_2$ Seite 371.

[14] Brauns, "Chemistry of Lignin" New York 1952, page 574.

[15] Wahl and Bonner: "Radioactivity Applied to Chemistry" New York 1951, page 94.

[16] Carothers and Adams, *J. Am. Chem. Soc.*, **46**, 1680 (1924).

[17] Adams, Voorhees and Shriner, *Org. Synth.* **8**, 92 (1928).

[18] February, Carrara and Cohn, *Ann.* **446**, 87 (1925).

$CH_3O$, 33.7; Calculated for $C_9H_{11}O_4$: $CH_3O$, 33.9%.

**4. Synthesis of *p*-Oxybenzyl Sulfonic Acid.** *p*-Oxybenzyl alcohol (3.02 g.) was dissolved in a sulfite solution containing 5 and 1% of $SO_2$ and NaOH respectively and heated in an autoclave at 100° for 1 hour. The solution was boiled in vacuo, filtered, passed through ion exchange resin IR 120, boiled again in a vacum, neutralized with excess $BaCO_3$, filtered and the solution of the barium salt was evaporated to dryness. The residue was leached with a little water, filtered and again evaporated to dryness. The residue was extracted with ethanol, which contains a little water, ether was added and the precipitated barium salt was filtered (4.0 g.). The analysis shows that the compound is a salt of *p*-oxybenzyl sulfonic acid. Found: Ba, 26.8; Calculated for $C_7H_7O_4SBa_{1/2}$: Ba, 26.8%.

1.0 g. of the barium salt was dissolved in water, passed through ion exchange resin IR 120, the same pyridine added and the whole was evaporated to dryness in vacuo. The residue was recrystallized from a mixture of dioxane acetone and alcohol to give pyridinium salt of *p*-Oxybenzyl sulfonic acid (0.8 g.) m.p. 129–30°. Found: S, 13.0, Calculated for $C_{12}H_{13}O_4NS$: S, 12.0%.

**5. Synthesis of *p*-Methoxydibenzyl Ether.** 4.2 g. of sodium was dissolved in a solution of anis alcohol (50 g.) in toluene (50 cc.) and when almost all of the metal disappeared, 20 g. of anis alcohol was added in order to complete the reaction. A solution of benzyl chloride (22.7 g.) in 30 cc. of toluene was then added and the mixture refluxed for 1 hour. The toluene solution was washed with water, dried with $Na_2SO_4$, the solvent removed, and the residue was distilled repeatedly in a vacuum in order to remove anis alcohol as far as possible. The yield of *p*-methoxydibenzyl ether of $bp_{0.8}$ 155–60° was 22 g. Found: $CH_3O$, 13.1, Calculated for $C_{15}H_{16}O_2$: $CH_3O$, 13.6%.

**6. Attempted Demethylation of *p*-Methoxybenzyl Ethyl Ether to *p*-Oxybenzyl Ethyl Ether.** *p*-Methoxybenzyl ethyl ether (1.7 g.) was added to a solution of methyl magnesium iodide, which was prepared from 8.5 g. of methyl iodide, 1.45 g. of magnesium and 50 cc. of ether. The ether was distilled off and the residue was heated in an oil bath for 2 hours (the temperature was raised during 1 hour to 170° and kept at that temperature for 1 hour). On cooling, the residue solidified. This was decomposed with a concentrated aqueous solution of $NH_4Cl$, acidified and extracted with ether. The ether extract was shaken with dilute alkali, acidified, extracted with ether, dried with $Na_2SO_4$, the solvent removed and the phenolic residue was converted to its *p*-nitrobenzoate. Repeated recrystallizations from ethanol yielded a product of m.p. 80–1°, not depressed in admixture with *p*-nitrobenzoate of *p*-ethylphenol (m.p. 80–1°) obtained from *p*-methoxydibenzyl ether, when it was decomposed with methyl magnesium iodide (see experiment 7).

**7. Attempted Demethylation of *p*-Methoxydibenzyl Ether to *p*-Oxydibenzyl Ether.** *p*-Methoxydibenzyl ether (2.19 g.) was added to a solution of methyl magnesium iodide, which was prepared from 8.5 g. of methyl iodide, 1.45 g. of magnesium and 50 cc. of ether. The ether was distilled off and the residue was heated as in the experiment 8. The residue was decomposed with a concentrated aqueous solution of $NH_4Cl$, acidified and extracted with ether, the solvent removed and the residue (2.01 g.) was separated into neutral (I) and phenolic (II) fractions.

(I) was distilled in a vacuum and the distilled oil (0.84 g.) converted to its *p*-nitrobenzoate, which melted after recrystallization from ethanol at 82–3° (1.4 g.), not depressed in admixture with the authentic *p*-nitrobenzoate of benzyl alcohol (82–3°).

(II) was also distilled in a vacuum and the distilled oil (0.65 g.) converted again to its *p*-nitrobenzoate, which melted after recrystallization from ethanol at 80–1° (0.9 g.), not depressed in admixture with the *p*-nitrobenzoate obtained in the experiment 8. A part of this *p*-nitrobenzoate was hydrolysed with ethanolic NaOH and converted as usual to the carboxymethyl ether, which melted after recrystallization from water at 96–6.5°. These melting points agree well with those of *p*-ethylphenol[19].

**8. Synthesis of *p*-Bromodibenzyl Ether.** 3g. of potassium was dissolved at the boiling point of toluene in 20 g. of benzyl alcohol, which was diluted with 20 g. of toluene. When almost all of the metal disappeared, 2 g. of K, 5 g. of benzyl alcohol and 5 g. of toluene were added and the reaction was completed. 27 g. of *p*-bromobenzyl bromide in 40 cc. of toluene, which was boiled in a vacuum in order to expel a trace of HBr, was added at once to the suspension of the alcoholate. During ca. 1/2 hours the mixture was maintained at its boiling temperature. Water was added and the reaction product was taken up in ether. The solvent was driven off and the residue was fractionary distilled in a vacuum. The yield of *p*-bromodibenzyl ether of $bp_{0.8}$ 142–45°C was 28 g. (92.5%). Found: Br, 28.9, Calculated for $C_{14}H_{13}OBr$: Br, 28.9%.

**9. Synthesis of *p*-Oxydibenzyl Ether.** A solution of *p*-bromodibenzyl ether (27.6 g.) and ethyl bromide (10.9 g.) in 90 cc. of ether was gradually added during 5 hours to magnesium in a three necked flask, which was equipped with a dropping funnel, stirrer and a reflux condenser. After the reaction was completed, dry oxygen was bubbled through the reaction mixture for 2.5 hours (during which process some heat was evolved and the solution was separated gradually into two layers). All of the reaction products were decomposed with concentrated aqueous solution of $NH_4Cl$ and then with dilute HCl. The products were extracted exhaustively with ether and separated into neutral (16.0 g.) and phenolic (5.5 g.) fractions. The latter was distilled in a high vacuum. Almost all of the oil (yield 4.3 g., 20 % of the theoretical) was distilled at a very constant tmperature of 130–5° 0.005 mmHg.

*p*-Nitrobenzoate: This was synthesized as usual with *p*-nitrobenzoyl chloride and pyridine

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[19] McElvain: "The Characterisation of Organic Compounds" New York 1949, page 251.

and recrystallized from methanol. It melted at 74–5°.

Acetate: This was synthesized as usual with acetic anhydride and pyridine and recrystallized from methanol containing a little water. It melted at 45.5–46°. Found: $CH_3CO$, 16.9, Calculated for $C_{14}H_{14}O_2$: $CH_3CO$, 16.8%.

**10. Synthesis of *p*-Oxybenzyl Ethyl Ether.** A solution of *p*-Bromobenzyl ethyl ether (21.5 g.) and ethyl bromide (10.9 g.) in 85 cc. of ether was added dropwise during 2 hours to magnesium (5 g.) in a three necked flask in an atmosphere of hydrogen (during which the content separated into two layers, but the oily heavier layer did not disturb the reaction, because this was not so viscous). After the reaction was completed, the content was evaporated in order to expel hydrogen. Dry oxygen was then passed through the mixture (during which time a very viscous grayish colored mass was deposited, which was stirred frequently during the oxidation). After about 2 hours, the entire content was decomposed with concentrated aqueous solution of $NH_4Cl$ and then acidified with dilute HCl, and extracted with ether. The ether extract was shaken with dilute NaOH solution, which was acidified and extracted again with ether, the solvent removed, and the residual oil (4.63 g.) distilled in a high vacuum. Almost all the oil distilled at 105°/0.8 mmHg (3.9 g., 23% of the theoretical), which solidified the next day, m.p. 50–1°. The analysis shows that the compound is *p*-oxybenzyl ethyl ether. Found: $C_2H_5O$, 28.8, calculated for $C_9H_{12}O_2$: $C_2H_5O$, 28.6%. *p*-Nitrobenzoate: m.p. 74–5°. Found: $C_2H_5O$, 14.5, Calculated for $C_{16}H_{15}O_5N$ : $C_2H_5O$, 15.0%. 3, 5-Dinitrobenzoate: m.p. 107–8°. Found: $C_2H_5O$, 13.5, Calculated for $C_{16}H_{14}O_7N$ : $C_2H_5O$, 13.0%.

**11. Hydrogen Sulfide Cooking of *p*-Oxydibenzyl Ether.** *p*-Oxydibenzyl ether (1.05 g) was added to a solution of $Na_2S \cdot 9HO$ (1.2 g.) in 100 cc. of Clark-Lubs buffer solution (final pH was adjusted to just 7). The mixture was heated in a glass ampoule at 100° for 15 hours (during which the ampoule was shaken vigorously). Because of the low solubility of the phenol the reaction was heterogeneous. After the reaction the organic materials were extracted with ether. The ether extract was dried, the solvent removed, and the faintly pink coloured residual oil (1.10 g.) was let to stand for crystallization. After several days a small amount of crystals separated. Ca. 1 cc. of petroleum ether was added, which did not mix with the oil, and the mixture was kept in a refrigerator further 2–3 days (during which time the amount of the crystalls increased). They were filtered and weighed (50 mg.) (I). The filtrate was diluted with benzene and kept again in a refrigerator to give further 0.13 g. of crystalline material (II), which was filtered and the mother liquor so obtained was separated into phenolic (III) and neutral fractions (IV) which weighed 0.53 and 0.38 g. respectively.

(I) was recrystallized from aqueous ethanol to give leafy plates (40 mg.), m.p. 170.5–71°, which was soluble in dil. NaOH. This was not investigated further.

(II) was also recrystallized from aqueous ethanol, to give 5 mg. or (I) and 50 mg. of 4, 4′-dioxydibenzyl sulfide, having m.p. and mixed m.p. 139–40°.

(III) was acetylated with pyridine and acetic anhydride. 70 mg. of *p*-acetoxydibenzyl ether of correct m.p. was recovered.

(IV) was converted to its 3, 5-dinitrobenzoate, which was recrystallized from ethanol to give 300 mg. of 3, 5-dinitrobenzoate, of benzyl alcohol, having m.p. and mixed m.p. 113–13.5°.

**12. Hydrogen Sulfide Cooking of *p*-Oxybenzyl Ethyl Ether.** *p*-Oxybenzyl ethyl ether (0.76 g.) was added to a solution of $Na_2S \cdot 9H_2O$ (1.2 g.) in 100 cc. of Clark-Lubs buffer solution (pH was adjusted to just 7). The mixture was heated in a glass ampoule at 100° for 18 hours (during which time the phenol went into solution and the reaction proceeded in a homogeneous phase). On cooling, beautiful crystalls of 4, 4′-dioxydibenzyl sulfide separated (final pH of the solution was 7.2), which was filtered (0.61 g.) and recrystallized three times from aqueous ethanol (450 mg.), m.p. and mixed m.p. 139–40°. The yield was 65% of the theory.

**13. Sulfonation of *p*-Oxybenzyl Ethyl Ether at Various pH (cf. figure).** *p*-Oxybenzyl ethyl ether was dissolved (concentration 0.056 mol/l) in a sulfite solution (total $SO_2$ 5%, pH 6.22 or 7.65, 35 cc.), heated at 100° for 1–3 hours in a glass ampoule. The whole content was passed through ion exchange resin IR 120, to remove cations. 7 cc. of 1N $H_2SO_4$ was added, boiled in vacuo to expel $SO_4$, 40 cc. of saturated solution of $Ba(OH)_2$ was added, filtered and passed again through IR 120. The solution so obtained was titrated with 1/10 N NaOH with methyl red as an indicator. Results were shown in the figure and Table 1.

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