Short Communication

On the Acidolytic Cleavage of Arylglycerol β-Aryl Ethers

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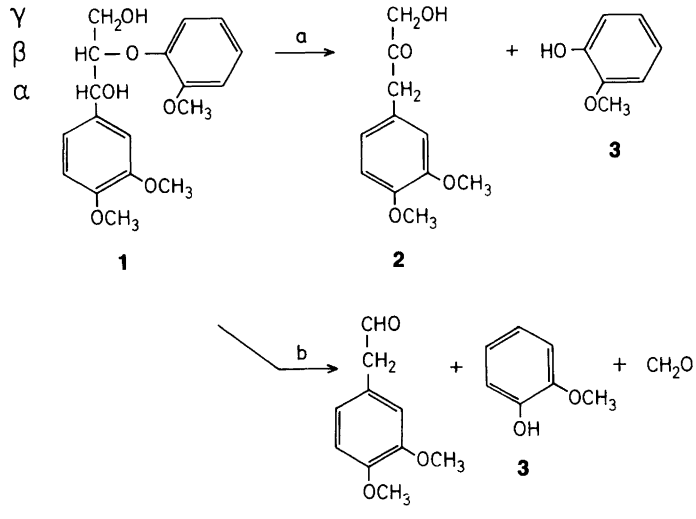
Arylglycerol β-aryl ethers constitute the major type of structural element in lignins. Such ethers undergo acid-catalysed cleavage under relatively mild conditions. Thus, heating a model compound representing lignin structures of the pre sent type (**1**) under reflux with 0.2 M HCl in dioxane/water (9:1) results in the cleavage of the β-ether bond.[1,2] Ketol **2** and guaiacol (**3**) are the primary reaction products (reaction route a, Scheme 1). Continued acid treatment causes the slow conversion of ketol **2** to isomeric ketols, the half-life being in the range 60–80 h (cf. Ref. 2); this is also true when H_2SO_4 or CF_3SO_3H (see below) is used as catalyst. Evidence has been presented[2] which shows that the cleavage reaction is neighbouring-group assisted. It has been proposed that an initially formed benzylium ion undergoes elimination of the β-hydrogen with



1 **2** **3** **3** **4**

Scheme 1.

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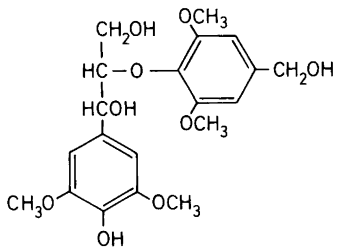

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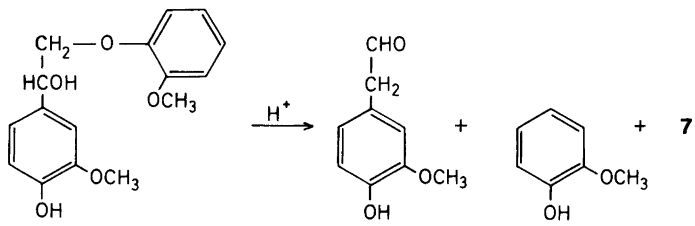
formation of an enol ether, and that this intermediate is then hydrolysed to **2** and **3**.[1,2] Ito *et al.*[3] have recently studied the reactions of model compounds for arylglycerol β-aryl ethers which take place upon heating under reflux with 5 % H_2SO_4 in dioxane/water (5:1). Their results deviate rather markedly from what could be expected on the basis of earlier acidolysis work with HCl as catalyst. Condensation reactions and elimination of formaldehyde (in the case of model compound **1** this is represented by reaction route b, Scheme 1) seem to be favored when H_2SO_4 is used as catalyst. A probable explanation is that the chloride ion catalyses the elimination of the β-hydrogen better than the hydrogen sulfate ion; this has been suggested by Yasuda *et al.*[4] in a discussion of the differences in product composition observed when lignin model compounds of the 1,2-diaryl-1,3-propanediol type are heated under reflux with 0.2 M HCl and 0.1 M H_2SO_4, respectively, in dioxane/water (9:1). Degradations of β-ether models such as **1** with HCl and H_2SO_4 have hitherto not been performed under strictly comparable conditions, and a good basis for conclusions regarding the effects of the two catalysts has been lacking. We have therefore studied the formation of ketol **2** from **1** upon heating under reflux for 4h with 0.2 M HCl, 0.1 M H_2SO_4 and 0.2 M H_2SO_4, respectively, in dioxane/water (9:1). While HCl gave, as expected,[2] substantial amounts of ketol **2**, only trace amounts of this compound were formed in the H_2SO_4 experiments. The reaction products were examined by ^1H NMR spectroscopy and TLC. Both HCl and H_2SO_4 catalysed the isomerization of the *erythro* form of **1** to give a mixture of similar amounts of the *erythro* and *threo* forms.

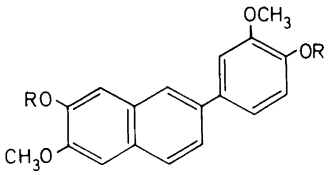
The studies of the acid degradation of **1** were continued in experiments in which HCl and H_2SO_4 were replaced by a variety of other catalysts [CH_3SO_3H (0.2 M), CF_3SO_3H (0.2 M), HBr (0.2 M and 0.05 M), $BF_3 \cdot (C_2H_5)_2O$ (0.2 M) and CF_3COOH (0.2 M)]. Except for CF_3COOH, all the compounds catalysed isomerization of the starting material. HBr led to practically complete decomposition of the starting material and catalysed the formation of ketol **2** much more efficiently than HCl (cf. Ref. 2); 0.05 M HBr gave rise to approximately the same amount of ketol **2** as did 0.2 M HCl. BF_3 gave rise to substantial amounts of ketol **2** but the yield was considerably lower than in the HCl-catalysed reaction. The other catalysts gave rise to small or negligible amounts of ketol **2**. Besides the diastereomers of **1** and some guaiacol (**3**), trace amounts of homoveratraldehyde (**4**) and the (*E*) and (*Z*) forms of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethene (^1H NMR data for these compounds and homoveratraldehyde are given in Ref. 5) were present in the reaction mixtures.

It is notable that an acid as strong as CF_3SO_3H is inefficient as a catalyst for the formation of ketol **2**. We interpret the results as suggesting that not only the acid strength of the catalyst but also catalytic effects of the anion present in the



9 **10** **3**

Scheme 2.



6 R = CH_3
7 R = H
8 R = $COCH_3$

reaction mixture are important for the formation of ketol **2** from **1**. Further studies of the acid-catalysed formation of ketols from arylglycerol β-aryl ethers are underway.

Recent investigations[6] of the HCl-catalysed degradation [heating at 100 °C with 0.2 M HCl in dioxane/water (9:1)] of β-ether model **5** showed that, in addition to the expected ketol, minor amounts of products with a chlorine atom in the side chain were formed [e.g. R−CH(OH)−CH(Cl)−CH_2OH; R=4-hydroxy-3,5-dimethoxyphenyl]; to explain this one has to consider an additional principle for the acid-catalysed decomposition of β-aryl ethers. Formation of products with a chlorine atom in the β-position may be due to replacement of an aryloxy group by a chlorine atom in a straightforward substitution reaction, but a neighbouring-group assisted pathway involving a cyclic oxonium ion also seems possible.

Reaction route b (Scheme 1) is of only limited importance in the HCl-catalysed degradation of **1**.[7] In recent work[5] it was found that the degradation product **4** is converted to a naphthalene derivative (**6**) upon heating under reflux with 0.2 M HCl in dioxane/water (9:1). We have found that homovanillin (**10**), which has been identified in acidolysis mixtures derived from lignin as well as from a model compound of the β-ether type (Ref. 8; see also Ref. 9), analogously gave a naphthalene derivative (**7**) on acidolysis. Heating model compound **9** under reflux with 0.2 M HCl in dioxane/water (9:1) for 4h gave homovanillin (**10**) [TLC, and ^{1}H NMR signals: δ 3.60 (2 H, d, J=2.4 Hz; CH_2), 9.71 (1 H, t, J=2.4 Hz; CHO)], guaiacol (**3**) and small amounts of **7** (Scheme 2); in the reaction mixtures obtained from 6 h treatment, **7** was a major product. Proof of the structure of **7** was obtained from spectral data [MS, ^{1}H NMR of the diacetate (**8**)] and by conversion to the previously known[10] dimethyl ether (**6**).

Experimental

Thin layer chromatography (TLC) was performed on silica gel plates using toluene/dioxane/acetic acid (90:25:4) as eluent. Spots were visualized by spraying with H_2SO_4/formalin (9:1) and subsequent heating. Homovanillin (**10**) appeared as a yellow spot on spraying with 2,4-dinitrophenylhydrazine in 1 M HCl. R_F values: **1** (*erythro*) 0.22, **1** (*threo*) 0.23, ketol **2** 0.26, **7** 0.35, **10** 0.40, **3** 0.53.

^{1}H NMR spectra were recorded with a Bruker WH270 instrument. Chloroform-*d* was used as solvent (internal reference, TMS).

Acid degradation of compound **1**. The reagents were prepared by diluting aqueous solutions of the catalysts with dioxane (reagent grade, distilled over Na) in volumetric flasks. About 25 mg of the *erythro* form of **1**[11] was refluxed for 4h with 10 ml of the reagent. Work-up was performed according to method C described in Ref. 2. The reaction mixtures were examined by ^{1}H NMR and TLC.

^{1}H NMR data for side-chain protons in some of the compounds detected in the reaction mixtures are given below. The *threo* form of **1**: δ 3.48 (1H, dd, J = 3.9 and 12.4 Hz; H_γ), 3.64 (1H, dd, J = 3.3 and 12.4 Hz; $H_{\gamma'}$), 4.03 (1H, m; H_β), 4.99 (1H, d, J = 7.8 Hz; H_α). The *erythro* form of **1**: δ 3.66 (1H, dd, J = 3.4 and 12.2 Hz), 3.91 (1H, dd, J = 6.0 and 12.2 Hz), 4.17 (1H, m; H_β), 4.98 (1H, d, J = 5.0 Hz; H_α). Ketol **2**: δ 3.66 (2H, s; Ar−CH_2−), 4.28 (2H, s; CO−CH_2−O).

Acidolysis of 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-ethanol (**9**). Compound **9**[12] (200 mg) was heated under reflux with 15 ml of 0.2 M HCl in dioxane/water (9:1) for 6 h. Work-up was performed according to method C in Ref. 2. The reaction product was dissolved in 30 ml of ether and the solution extracted with 3×10 ml of a 15 % aqueous solution of $NaHSO_3$ to remove homovanillin (**10**). The residue obtained on removal of the ether was subjected to chromatography on silica gel with dichloromethanethyl acetate (25:1) as eluent. A main fraction (44 mg) consisting of essentially pure **7** was obtained. A second fraction (13 mg) contained, in addition to **7**, small amounts of an unknown compound (R_F 0.31). The product in the main frac-

tion melted at 142–144 °C. Recrystallization from ethanol raised the m.p. to 145 °C. The molecular ion (*m/z* 296) was the base peak in the MS. ^{1}H NMR of the diacetate (**8**): δ 2.35 (3H, s; CH_3CO), 2.38 (3H, s; CH_3CO), 3.92 (3H, s; OCH_3), 3.96 (3H, s; OCH_3), 7.1–7.9 (8H, m; aromatic protons). Methylation of **7** (treatment with CH_3I/K_2CO_3/DMF according to Ref. 13, in argon atmosphere[14]) gave a product which was identified as **6**[5,10] by m.p. and ^{1}H NMR.

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