

route 2 for Ib. The different fragmentation preference for Ia and Ib must lie in the relative stabilities of the entities carrying the substituent R_2 . Again the radical stabilities seems to be more important, *i.e.* a methyl group (compared to a hydrogen atom at a double bond) must be more effective in stabilizing radicals than carbonium ions.

Similar to the aliphatic analogues, fragmentations involving consecutive losses of carbon monoxide are observed. The metastable defocusing technique once again revealed that two molecules of carbon monoxide (or C_2O_2) are ejected simultaneously. These fragmentations leading to fluorenyl cations are dealt with in Scheme 2. The rearrangement of $[M - R_1CH_2]^+$ and the intermediate formation of α -diketones before ejection of C_2O_2 are processes discussed earlier.²

As seen from Table 1 the path through $m/e = 221$ (Ia) or $m/e = 193$ (Ia) and 207 (Ib and Ic) is preferred only to some extent. In fact, the fragmentation route in Scheme 1 is very prominent only for Ia. When $R_2 = Me$ (Ib and Ic) another route seems to be of more importance. Here fragmentation of $M - R_1CH_2$ directly to $m/e = 143$ is preferred, demonstrated by the observation of the proper metastable peak (Scheme 3).

As for the aliphatic analogues,² metastable peaks indicating the elimination of ketenes from I are observed. In these aromatic dilactones such processes must involve rearrangements destroying the aromatic structure in one of the aromatic rings.

However, compared with other processes, only for Ia this represents a major fragmentation path.

Experimental. Mass spectra (70 eV, ion source temperature 230 °C) were obtained on an AEI MS 902 mass spectrometer connected to an AEI DS 30/64/H data system. Peak compositions were within 4 ppm of calculated values. Metastable peaks were observed in the spectra and confirmed by the metastable defocusing technique.

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The Dimerization of Coniferyl Alcohol in Aqueous Sodium Hydroxide*

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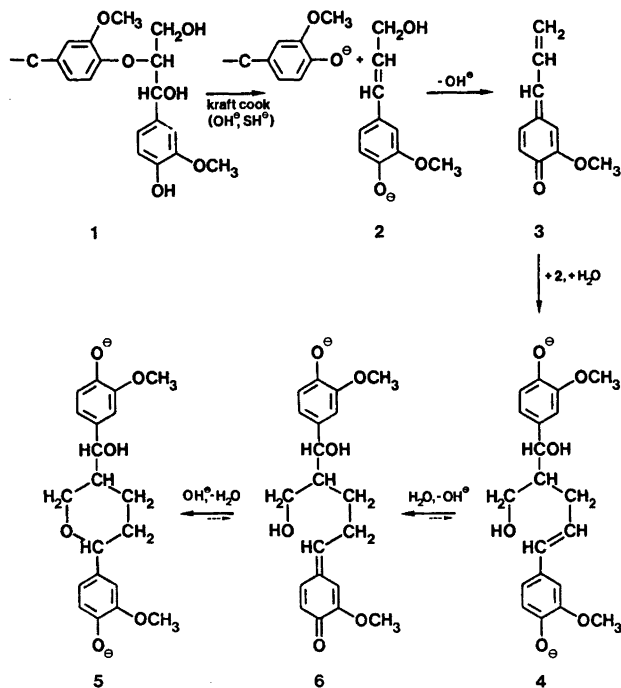
p-Hydroxyaryl glycerol β -aryl ether structures (1), present originally as such or formed during degradation, have been shown to be the major site of lignin fragmentation in kraft pulping.¹ Structures of type 1 fragment to give predominantly *trans*-coniferyl alcohol (2).² This undergoes further transformation, in part via its extended quinone methide 3. By this process the side chains of units derived from 2 and 3 condense to the final product, kraft lignin. The present paper is concerned with the elucidation of some of the reactions by which 2 reacts with the kraft lignin being formed.

Heating of 2 in dilute aqueous sodium hydroxide for 2 h at 170 °C gives a polymer.^{2a,3} Little monomeric or dimeric material remains. The most characteristic feature of this polymer (in a strict sense it should be termed a telomer) is the absence of the γ -hydroxymethyl group present in its precursor 2. This was demonstrated by recording the NMR-spectrum of the acetylated polymer. A similar polymer can be made by alkaline treatment of γ -coniferyl benzoate, which is believed to give primarily the quinone methide 3.⁴

Suitable choice of the conditions of heating coniferyl alcohol in dilute sodium hydroxide (120 °C 1 h) afforded considerable amounts of dimeric material. Gas chromatography of the trimethylsilylated reaction mixture [bis(trimethylsilyl)trifluoroacetamide in pyridine] showed that the dimer fraction has two major components (A and B). Small amounts of these were collected and analyzed by high resolution mass spectroscopy. The fragmentation pattern and determinations of exact masses of the molecular ion (B) and of a prominent fragment (A) suggested structures 4 and 5 for A and B, respectively. Compound 4 is the 1,8-addition product of the carbanion of 2 to the quinone methide 3. Proton abstraction from solvent by the anion of 4 gives a quinone methide (6) which undergoes cyclization with preferential reaction by the less hindered primary hydroxyl group, yielding 5.

p-Coumaryl alcohol reacted in the same way as 2, giving major amounts of the non-meth-

* Part IV of the series "Degradation of Lignin by Kraft Cooking", Part III, Ref. 2a.



Compounds 2, 4, 5, and 6 are shown as anions.

oxylated dimers corresponding to 4 and 5 (at a slightly higher reaction temperature, 135 °C).

The structural assignment for 4 was confirmed by the reaction of γ -coniferyl benzoate with an excess of 2 in aqueous NaOH at room temperature. Apart from some polymeric material the major product of this reaction was 4. The absence of 5 (GLC) is due to the low rate at room temperature of the protonation of the carbanion of 4 leading to formation of 6.

These experiments indicate that the dominant reactions in the base-catalyzed transformation of 2 to dimeric and polymeric products are Michael-type additions, in which 3 provides the unsaturated carbonyl substrate (1,8-addition being preferred to 1,6-addition), and 2 reacts as a carbanion with attack via C_{β} . The condensation products can react in much the same way as do 2 and 3. It should be noted, however, that in contrast to the experiments described here, under the conditions of a kraft cook of lignin, 2 is present in a low, approximately steady-state concentration. Thus dimerization of 2 should be suppressed in favour of Michael-type addition to 3 of other carbanions present.

Precise mass measurement. Tetrakis(trimethylsilyl)ether of 1,5-bis(4-hydroxy-3-methoxyphenyl)-2-hydroxymethyl-4-penten-1-ol [tetrakis(trimethylsilyl)ether of 4]. Peak at $m/e = 558$ [molec-

ular ion at $m/e = 648 - (\text{CH}_3)_3\text{SiOH}\pm$ 3 mmu. Calc. for $\text{C}_{28}\text{H}_{46}\text{O}_6\text{Si}_3$: 558.2653.

Tris(trimethylsilyl)ether of 2-(4-hydroxy-3-methoxyphenyl)-5-[(4-hydroxy-3-methoxyphenyl)-hydroxymethyl]-tetrahydropyran [tris(trimethylsilyl)ether of 5]. Molecular ion. Found: 576.2749 \pm 3 mmu. Calc. for $\text{C}_{29}\text{H}_{48}\text{O}_6\text{Si}_3$: 576.2759.

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