

α -Carbonyl Groups as Sensitizers in the Photo-dehydrogenation of Phenolic Structures in Lignin

GÖSTA BRUNOW and BRITA ERIKSSON

Department of Chemistry, University of Helsinki, Helsinki, Finland

The lignin in wood and high-yield pulps is rapidly discoloured under the influence of daylight and air.¹ From the yellowing patterns of esterified and alkylated wood and newspaper, Leary² concluded that the yellowing of lignin components normally begins with the oxidation of the phenolic structural units of the lignin. He proposed a mechanism for this reaction where the phenolic units are oxidised by hydrogen atom transfer to a neighbouring excited molecule or free radical. A phenol dehydrogenation reaction analogous to lignin biosynthesis would then lead to coloured products, such as *para*- and *ortho*-quinones and substituted diphenoquinones.^{3,4} In a recent article,⁵ Lin and Kringstad stated that lignin building units having saturated side chains are insensitive to light of 300–390 nm and hence that the major components of lignin are presumably not involved in the yellowing process. Lignin model compounds containing α -carbonyl groups, however, absorb light of 300–390 nm and form coloured products and give $\Delta\epsilon$ -curves similar to those of milled wood lignin. The authors therefore concluded that α -carbonyl groups play a major part in the yellowing of lignin. In view of the fact⁶ that α -carbonyl group content of unaltered lignin (*ca.* 0.06/OCH₃, mainly in non-phenolic units) is low, it seemed of interest to investigate whether such groups can transfer their excitation energy to other parts of the lignin molecule and thus function as the photosensitizers postulated by Leary.²

The purpose of the present investigation was to observe with appropriate model compounds whether an addition of a small amount of an α -carbonyl compound does accelerate the photodecomposition of a phenolic benzyl alcohol. ESR-spectroscopic evidence for an energy transfer of this kind has been reported by Kringstad and Lin.⁷

Results. *p*-Hydroxybenzyl alcohol (*1*) was chosen as a simple model of a phenolic lignin structural unit. It was irradiated in

an ethanol solution which was kept saturated with air at room temperature. The light source was a mercury lamp (S 81, Quarzlampengesellschaft Hanau) and the light was filtered through Pyrex glass. The changes in the concentration of *1* in the solution were measured by gas chromatography. As shown in Fig. 1, the concentration of *1* does not change significantly during 24 h irradiation.

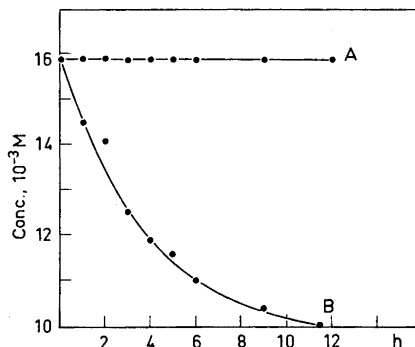


Fig. 1. Irradiation of a solution of *p*-hydroxybenzyl alcohol (*1*) (15.8×10^{-3} M in ethanol) with Pyrex-filtered light. Curve A: concentration of *1* as a function of time when irradiated alone. Curve B: the same when the solution also contained acetoguaiacone (*2*) (1.7×10^{-3} M).

Addition of a small amount of acetoguaiacone (*2*) causes a marked increase in the rate of decomposition. This demonstrates that lignin structural units similar to acetoguaiacone that contain α -carbonyl groups are able to sensitize the photodecomposition of phenolic structural units with a saturated side chain. The UV spectra (Fig. 2) show that the reaction is accompanied by an increase in absorption at wavelengths between 350 and 450 nm. Investigation of the reaction mixture after 66 h irradiation by column chromatography and preparative thin layer chromatography revealed that compound *1* had disappeared, but more than half of the original acetoguaiacone remained. Other compounds identified were the ethyl ether of *1* and propioguaiacone. The remaining material was strongly coloured and had low R_F values. This mixture was reduced with NaBH₄, methylated with dimethyl sulphate, oxidized with KMnO₄ and meth-

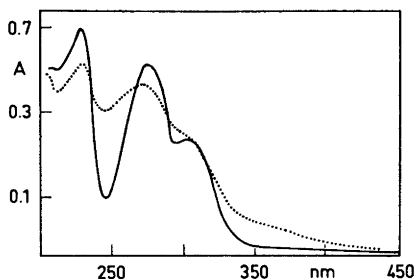
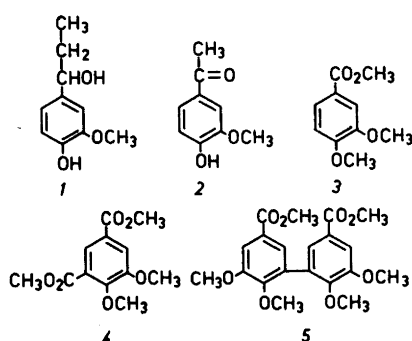


Fig. 2. UV spectra of a solution of *p*-hydroxybenzyl alcohol (1) (15.8×10^{-3} M) and acetoguaiacone (2) (1.7×10^{-3} M) before irradiation (solid line) and after 24 h irradiation (dotted line).

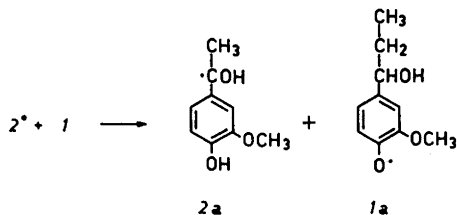
ylated with diazomethane, following a published procedure.⁸ Gas chromatography showed that the main products were the methyl esters of veratric acid (3), isohemipinic acid (4) and dehydrodiveratric acid (5).



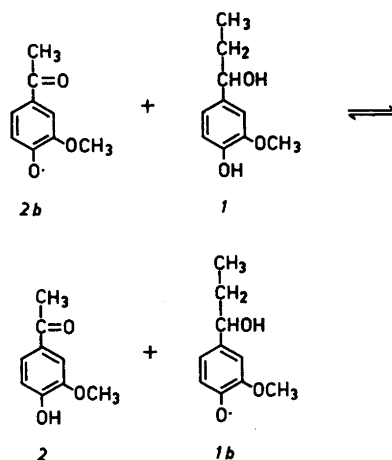
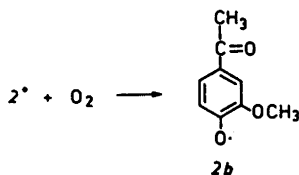
The formation of isohemipinic and dehydrodiveratric acids on permanganate oxidation shows that the irradiated mixture contained coupling products presumably formed by phenol dehydrogenation. Enzymatic oxidation of 1 gives a biphenyl as the first product.⁹ An ESR spectrum indicating the formation of a similar dimer from vanillyl alcohol has been described by Kringstad and Lin.⁷

In what manner acetoguaiacone acts as a sensitizer in this reaction is not known. In one mechanism⁷ proposed for the photochemical decomposition of lignin model compounds in the presence of α -carbonyl compounds, it is assumed that the excited

carbonyl group abstracts a hydrogen atom from the phenol to give a phenoxy radical 1a and a benzyl radical 2a. The latter presum-



ably dimerizes to pinacol derivatives. In the present investigation, it was found that the carbonyl compound is regenerated as it could be recovered at the end of the reaction. It is possible that in this case the benzyl radical 2a reacts with oxygen instead of dimerizing. If, on the other hand, the excited acetoguaiacone reacts directly with oxygen to form a phenoxy radical 2b, this will react with other phenols present and an equilibrium mixture will be formed.



Mahoney and DaRooge¹⁰ have conducted thermodynamic studies on the equilibria between different phenols and phenoxy radicals and found that electron-withdrawing substituents raise the OH-bond energy. In the present case, this means that acetoguaiacone will be favoured at equilibrium and that the main reaction products will be those of radical *Ib*.

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Received August 3, 1971.

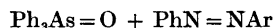
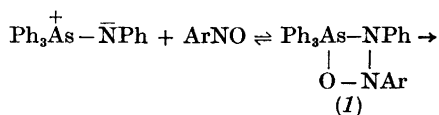
A Synthesis of Azobenzenes from Triphenylarsine Phenylimine and Nitrosobenzenes

PAUL FRØYEN

*Chemical Institute, University of Bergen,
N-5000 Bergen, Norway*

The similarity between the nitroso group and the carbonyl group in the reaction with phosphonium ylides and phosphonate carbanions has been demonstrated by several workers.¹⁻³ Attempts to react phosphine imines with nitrosobenzene

have failed, however.⁴ The present author has found that triphenylarsine phenylimine reacts with nitrosobenzenes under mild conditions to give excellent yield of azobenzenes.



The mechanism of the reaction between triphenylarsine phenylimine and the nitroso compounds is expected to parallel rather closely that of the Wittig reaction between stabilized ylides and carbonyl compounds. Presumably, the reaction is initiated by a nucleophilic attack of the arsine imine on the nitrogen atom of the nitroso compound, synchronized with an attack by the oxygen of the nitroso group on arsenic. The penta-covalent cyclic intermediate (*I*) thus formed undergoes decomposition to arsenic oxide and azobenzene. The reactivity of the nitroso compounds in the reaction with triphenylarsine phenylimine decreases in the order *p*-nitronitrosobenzene > *p*-chloronitrosobenzene > nitrosobenzene > *p*-dimethylaminonitrosobenzene. The same order of reactivity was found in the Wittig reaction between the stabilized ylides fluorenylidene resp. phenacylidene triphenylphosphorane and *para*-substituted benzaldehydes.^{5,6}

In connection with the preparation of *p*-nitroazobenzene an attempt was made to solve the disagreement between the physical data reported for *o*-nitroazobenzene.^{7,8}

o-Nitroazobenzene isolated from the present reaction between *o*-nitronitrosobenzene and triphenylarsine phenylimine had after two recrystallisations from ethanol m.p. 70–71° and is doubtless identical with the compound made by Bamberger and Hübner.⁷ Thin-layer chromatography showed, besides triphenylarsine oxide, a single reaction product. No sign of isomerisation could be detected when the *o*-nitroazobenzene was irradiated with ultraviolet light and afterwards analysed by thin-layer chromatography. In a previous study of the reaction between triphenylarsine phenylimine and carbonyl compounds⁹ it was assumed that triphenylarsine phenylimine was more nucleophilic than its phosphorus analogue. This assumption is confirmed by the