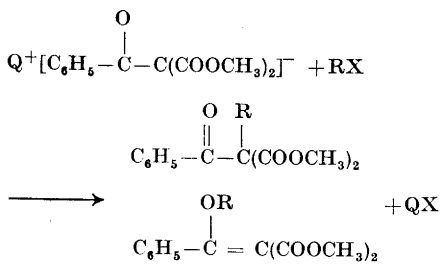

Experimental. Tetrabutylammonium salt of dimethyl malonate. 11.8 g (0.05 mole) of dimethyl benzoylmalonate [5] in 50 ml of chloroform was shaken with a solution containing 17 g (0.05 mole) of tetrabutylammonium hydrogen sulphate (Astra-Meditec) and 4 g (0.1 mole) of sodium hydroxide in 50 ml of water. The chloroform layer was evaporated and the residue recrystallized from ethyl acetate. The yield was 15.5 g (64 %) of a salt melting at 109–110°C.

Alkylation procedure. About 0.05 mole of the tetrabutylammonium salt of dimethyl benzoylmalonate was dissolved in 100 ml of chloroform. An excess of alkyl iodide was added to the stirred solution. The reaction with methyl iodide was exothermic and was complete after a few minutes. With ethyl, isopropyl, and butyl iodides, however, it was necessary to heat to about 55°C for 15–30 min. The chloroform was then evaporated and the tetrabutylammonium iodide was precipitated with ether. The salt was filtered off and the ether evaporated. The residue was analysed by NMR in a chloroform solution.

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Hydrolysis of the Quinol Ether Dimer Obtained on Oxidation of 2,6-Di-*t*-butyl-4-propionylphenol

GÖSTA BRUNOW

Department of Organic Chemistry, Chalmers University of Technology and University of Göteborg, S-402 20 Göteborg 5, Sweden

In connection with studies on the biosynthesis and biological decomposition of lignin we are investigating the mechanism of the oxidative cleavage of side-chains from various lignin model compounds. In a recent investigation [1] it was shown that a side-chain containing an α-carbonyl group can be split off from a phenolic model compound by the action of phenol oxidases. It is known [2] that a phenoxy radical is formed as the first product when a phenol is attacked by a phenol oxidase. In a first approach to the study of the reactions of phenoxy radicals carrying an α-carbonyl (or α-carbinol) substituent in the 4-position, the sterically hindered 2,6-di-*t*-butyl-4-propionylphenol (I) was oxidized to a stable free radical and its reactions studied.

This radical in solution is in equilibrium with a dimer which can be isolated as a colourless crystalline compound. This behaviour of (I) is in analogy with that of the corresponding acetyl compound.[3] The dimer dissolves in organic solvents with a deep blue-green colour; an absorption maximum at 700 nm was observed which was strongly temperature dependent, the colour disappearing at low temperatures. At room temperature a strong ESR signal was obtained. The dimer can be ascribed the 2,5-cyclohexadienone structure (II) mainly on the evidence of the NMR spectrum measured at −60° (Fig. 1). Two *t*-butyl peaks at δ 1.10 and 1.35 ppm and the single quinonoid proton peak at 6.14 ppm indicate that the solution at this temperature contained mainly a 2,5-cyclohexadienone.

The dimer (II) proved to be unstable in the presence of dilute mineral acid. At low temperatures, when the concentration of dimer was sufficiently large, the addition of dilute hydrochloric acid gave propionic acid in a rapid reaction. The yields varied with varying temperatures;

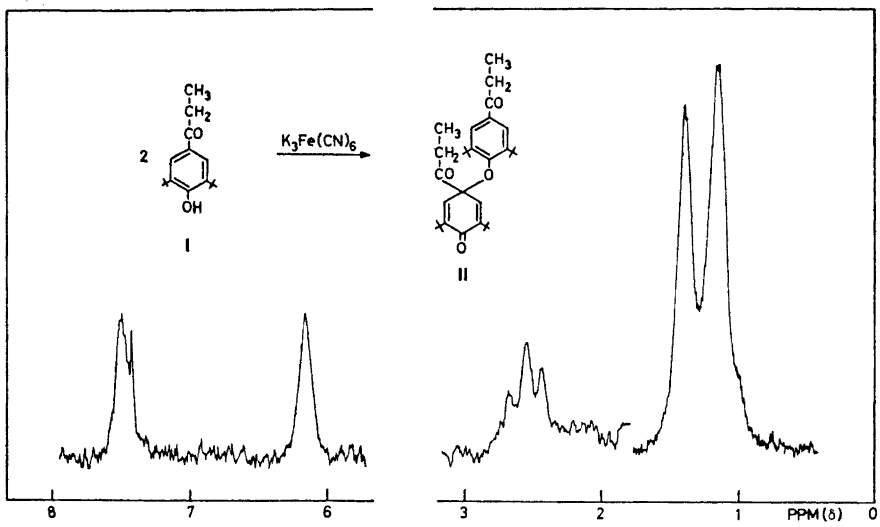


Fig. 1. NMR spectrum of dimer (II) in $CDCl_3$ at −60° with TMS as internal standard.

at the optimal temperature range, −20 to −30°, the yield was 0.35−0.40 moles per mole of dimer. When the temperature was raised to room temperature, slow formation of 2,6-di-*t*-butyl-*p*-benzoquinone (V) was observed. The yield of quinone was equivalent to the yield of propionic acid (Fig. 2). The rest of the material was mainly 2,6-di-*t*-butyl-4-propionylphenol (I).

These observations may be explained by the following sequence of reactions:

1. The hydrolysis of the quinol ether (II) gives propionic acid and the diphenyl ether (III). This reaction is analogous to the acid hydrolysis of erdin described by Barton and Scott.[4]

2. The phenolic diphenyl ether (III) is rapidly oxidized by free phenoxy radical which is in equilibrium with starting

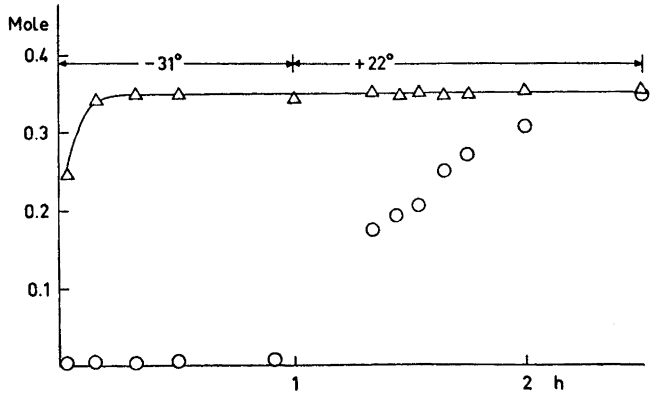
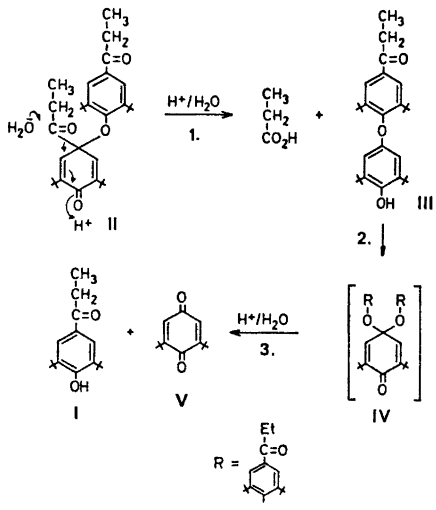


Fig. 2. Formation of propionic acid (△) and 2,6-di-*t*-butyl-*p*-benzoquinone (○) on acid hydrolysis of (II).



material (II). Coupling of the new radical thus formed from (III) with more radical gives a quinone ketal (IV).

3. At room temperature the quinone ketal (IV) is hydrolyzed to (I) and (V).

The stoichiometry of this reaction sequence is: $2(II) \rightarrow 3(I) + CH_3CH_2CO_2H + (V)$. Accordingly, 0.5 mole of propionic acid would be expected per mole of (II). The observed value, 0.35—0.40, is compatible with the proposed mechanism. Furthermore, this reaction sequence accounts for the large difference in rates of formation observed for propionic acid and the benzoquinone.

Experimental. The melting points were determined on a Kofler hot stage and are uncorrected. IR spectra were taken in KBr pellets on a Beckman IR 9, UV spectra on a Beckman DK 2, and NMR spectra on a Varian A-60 (solvent $CDCl_3$ with TMS as internal standard).

2,6-Di-t-butyl-4-propionylphenol (I). This compound was synthesized from 2,6-di-*t*-butylphenol and propionylchloride following a procedure described for the corresponding acetyl compound.[5] M.p. 136—137° (Lit.[6] 137°).

The quinol ether dimer (II). 200 mg of (I) in 20 ml petroleum ether (40—60°) was shaken under nitrogen for 3 min with 1.8 g $K_3Fe(CN)_6$ in 20 ml 2 N KOH. The water layer was separated, the petroleum ether layer washed with water, dried ($CaSO_4$), and evaporated. Recrystallization of the solid residue from ethanol-water at −30° gave colourless crystals, m.p. 101—105° (blue-green melt). IR maxima at 1760 (nonconj. C=O), 1660 and 1638 (sh) cm^{-1} (conj. C=O).

Hydrolysis of (II). *Ca.* 20 mg quinol ether (II) in 0.5 ml 1,2-dimethoxyethane under nitrogen in a serum bottle was cooled to −30° in a dry ice-acetone bath. 50 µl 2 N HCl was added with a syringe and the reaction followed using gas chromatography. Apparatus: Varian Aerograph 1200. Column: 20 % Carbowax 20 M on Chromosorb W, 1/4 stainless steel, length 2 m. Carrier: N_2 30 ml/min. Detector: FID. Temperatures: injector 160°, column 150°, detector 160°. At the end of the reaction TLC (CCl_4-benzene 1:1.7) showed the presence of only (I) and (V) in the reaction mixture.

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