

REACTION OF 2,6-DI-t-BUTYL-4-PROPIONYLPHENOXY
RADICAL WITH ETHYL FERULATE.

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The oxidation of 4-vinyl substituted phenols by one-electron transfer primarily results in coupling at the β -position of the side chain¹. We now wish to report an oxidation of ethyl ferulate which involves coupling through the ortho position to the phenolic hydroxyl.

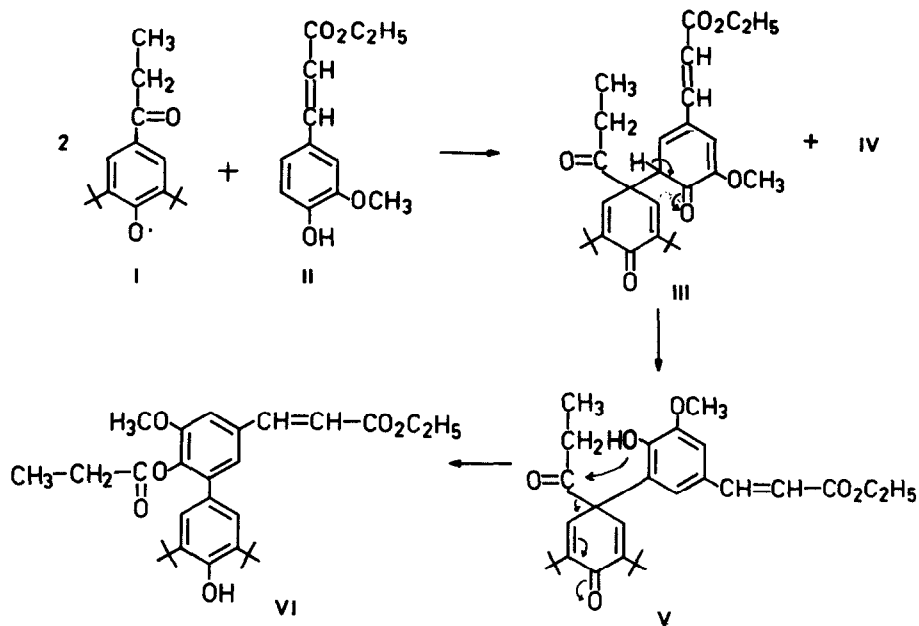
When a solution of ethyl trans-ferulate (II) in dimethoxyethane is added to a solution in the same solvent of 2,6-di-t-butyl-4-propionylphenoxy radical (I) (prepared from 2,6-di-t-butyl-4-propionylphenol (IV) by oxidation with potassium ferricyanide²) until the blue colour of the radical disappears, it is found that one mole of ethyl ferulate consumes two moles of free radical. Chromatographic separation of the reaction mixture yields IV, some polymeric material and, in ca 30% yield, a crystalline substance with m.p. 167°. The new compound was assigned structure VI on the basis of the following analytical and spectroscopic evidence.

The compound analysed for C₂₉H₃₈O₆ (Found: C, 72.4; H, 8.00; mol.wt. by mass spectrometry, 482. Calcd.: C, 72.2; H, 7.90; mol.wt. 482.62).

Spectroscopic data: uv λ_{\max} (EtOH) 271 nm ($\epsilon = 1.5 \times 10^4$); ir (KBr) 1702 cm⁻¹ (conj. ester), 1745 cm⁻¹ (nonconj. ester); nmr (CDCl₃) δ 1.12 (t, 3, CH₂CH₃), 1.34 (t, 3, CH₂CH₃), 1.47 (s, 18, t-Butyl), 2.46 (q, 2, CH₂CH₃), 3.89 (s, 3, OCH₃), 4.29 (q, 2, CH₂CH₃), 5.23 (s, 1, OH), 6.43 (d, 1, J = 16.0 cps, vinyl H), 7.09 (d, 1, J = 2.0 cps, ArH), 7.19 (d, 1, J = 2.0 cps, ArH), 7.23 (s, 2, ArH), 7.73 (d, 1, J = 16.0 cps, vinyl H).

The original trans configuration of ethyl ferulate is retained in the dimer VI. No formation of a cis isomer was observed. Alkaline hydrolysis of VI was found to liberate propionic acid (detected by glc).

The formation of VI may be accounted for by the following reaction sequence.



The primary coupling product III is transformed to V through keto-enol tautomerism. The phenolic group formed in V then undergoes nucleophilic reaction with the side chain carbonyl group of the neighbouring unit which thereby is aromatized to the biphenyl VI. The propionyl side chain of I is retained in the dimer VI as an ester group. A similar ester formation has previously been observed by Pew and Connors³.

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3. J.C. Pew and W.J. Connors, *J. Org. Chem.* 34, 585 (1969); *Nature* 215, 623 (1967).