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# THE MECHANISM OF OXIDATION OF ARYLPROPENES TO ARYLPROPENALS BY 2,3-DICHLORO-5,6-DICYANOQUINONE: STRUCTURE OF THE INTERMEDIATE

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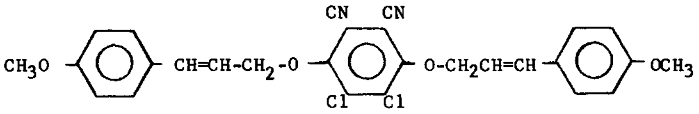
In 1968, we reported that 1- and 3-arylpropenes were readily oxidized by DDQ to give reactive intermediates which could be directly converted to a variety of products.[1] Shortly thereafter, Sadler and Stewart[2] described the conversion of several arylpropenes to aldehydes by excess DDQ. In this report, we wish to define the structure of the unstable intermediate formed from arylpropenes and DDQ, and the mechanism by which they are converted to aldehydes.

Addition of 0.025 mole of 1-p-methoxyphenylpropene (anethole) to 0.025 mole of DDQ in 250 ml of benzene produces an intensely colored molecular complex which fades to a yellow solution within one minute, with concomitant precipitation of 0.0125 mole (50%) of 2,3-dichloro-5,6-dicyanohydroquinone (DDHQ), identified by ir, uv, nmr, and mass spectra and by conversion to the diacetate, m.p. 182-183°.[3] Removal of even part of the solvent at this point gives only polymer; however the product can be stabilized by addition of dioxane (50 ml) and washing with water (5 x 50 ml), after which the solvent may be safely removed _in vacuo_. Brief trituration of the solid residue with ice-cold methanol[4] gives a 55% yield of crude material which on repeated recrystallization from dioxane-hexane (1:3) gives material of constant melting point (124°), identified as 2,3-dichloro-5,6-dicyanohydroquinone _bis_-(3-_p_-methoxyphenyl-_trans_-2-propenyl) ether (I) from the following evidence:



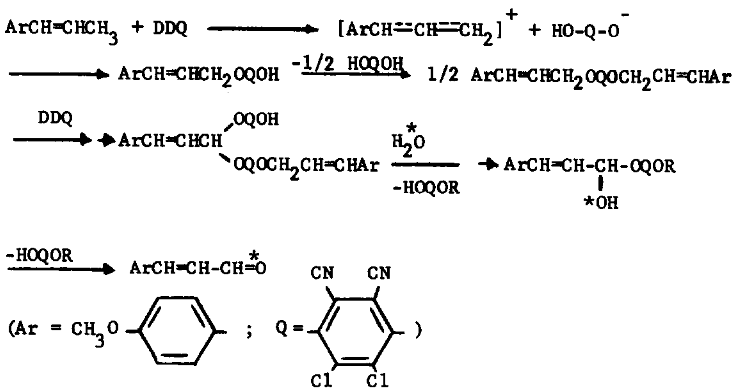
I

The nmr spectrum of pure I in $CDCl_3$ establishes the 3-(p-methoxyphenyl-trans-2-propenyl) moiety [$\delta$6.59 (d, J = 16.0 Hz, 2H) $\delta$6.29 (d of t, J = 16.0, 6.5 Hz; 2H), and $\delta$4.87 (d, J = 6.5 Hz; 4H) in addition to the methoxyl and p-substituted aromatic absorptions]. The same spectrum, except for small solvent shifts, was observed for the initial yellow solution when the reaction of anethole and DDQ was carried out on a small scale in benzene-$d_6$. The position and configuration of the olefinic bonds was supported by uv and ir spectra, respectively. The bis-ether structure was established by microanalysis,[5] ir (strong aromatic ether band at 1244 $cm^{-1}$; no hydroxyl absorption), and uv spectra (the maximum at 268 nm in dioxane had $\epsilon$ = 44,200 showing the presence of two p-methoxycinnamyl moieties per mole),[6] and by independent synthesis of I from p-methoxycinnamyl chloride and the disodium salt of DDHQ.

When anethole is allowed to react with two equivalents of DDQ in benzene, p-methoxycinnamaldehyde is obtained in approximately 50% yield after chromatographic workup.[2] However, when added water is present (1 ml, stirred with 250 ml of benzene) the yield of aldehyde is increased to 75-80%. The fact that water is the source of the aldehyde oxygen was demonstrated by the use of water containing 20% $^{18}O$ (Bio-Rad Laboratories); the resulting p-methoxycinnamaldehyde contained 18.8% $^{18}O$ by mass spectral analysis, or a minimum incorporation of 94%.[7] Reaction of I with excess DDQ in benzene also gave p-methoxycinnamaldehyde, in 73% yield.

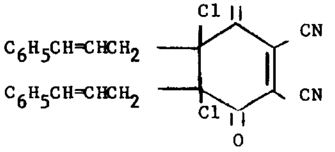
In view of Becker's proposed hydrogen atom abstraction mechanism for the reaction of DDQ with diphenylmethane,[8] the DDQ oxidation of anethole was investigated carefully by electron spin resonance spectroscopy, using a flow system and rapid scanning capable of detecting very short-lived free radical species.[9] Other than the DDQ semiquinone radical (DDSQ) which was present in low concentration throughout (and after) the reaction, there was no evidence for the formation of any free radical species.

The mechanism of aldehyde formation thus appears to be essentially that suggested by Sadler and Stewart,[2] except for the detailed structure of the intermediate I and the role of water in the reaction (see below).



The reaction of DDQ with 3-p-methoxyphenylpropene (estragole) also gave p-methoxycinnamaldehyde, though at least 50 times more slowly and in somewhat lower yields. The lower rate may be due to the much lower affinity of DDQ for the non-conjugated alkene in pi complex formation which precedes hydride transfer. Unlike the reaction with anethole, some aldehyde was produced even when DDQ was not present in excess, presumably because of the lower reactivity of estragole toward DDQ. Also, in the oxidation of estragole, the major reactive intermediate isolated was not the bis-ether I but the monoether, 2,3,-dichloro-5,6-dicyano-4-(3-p-methoxyphenyl-trans-2-propenyloxy)phenol (II), identified by ir (3195 $cm^{-1}$), and uv spectra ($\lambda_{max}$ 267 nm, $\epsilon$ = 24,800) and microanalysis.[10] If II is indeed a precursor of I as shown above, its failure to disproportionate quickly in this case is puzzling, but can be rationalized by postulating that the II→I transformation is (a) catalyzed by some reactive byproduct (acid?)--perhaps the same species which catalyzes polymerization--which is removed by the aqueous wash, and (b) inhibited by unreacted DDQ, which always remains in the oxidation of estragole, but not of anethole.

The oxidation of 1-phenylpropene with DDQ was approximately 100 times slower than that of anethole, but otherwise similar, giving cinnamaldehyde[2] and both mono- and bis-ether derivatives of DDHQ, plus a small amount of an orange compound isomeric with the bis-ether, tentatively assigned the enedione structure III (below) on the basis of nmr, ir, uv, and mass spectral data.



III

The details of all experiments described herein will be included in a later paper.

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## REFERENCES

1. A. E. Asato and E. F. Kiefer, Chem. Commun., 1684 (1968).
2. I. H. Sadler and J. A. G. Stewart, ibid., 773 (1969).
3. J. Thiele and F. Günther, Ann. Chem. **349**, 55 (1906).
4. To remove DDHQ and other polar impurities. This step must be carried out rapidly to prevent methanolysis.
5. Anal. Calcd for $C_{28}H_{22}Cl_2N_2O_4$: C, 64.60; H, 4.27; Cl, 13.64; N, 5.38. Found: C, 64.52; H, 4.00; Cl, 13.71; N, 5.40.
6. T. W. Campbell, S. Linden, S. Godshalk, and W. G. Young, J. Amer. Chem. Soc. **69**, 880 (1947).
7. $H_2{}^{18}O$ was present in 8-fold molar excess. The appropriate exchange experiments with DDQ and aldehyde were considered unnecessary, since the extent of $^{18}O$ incorporation exceeded the theoretical maximum obtainable by simple exchange. The 50% yield of aldehyde obtained in the absence of added water can be accounted for by the presence of as little as 0.02% water in commercial Reagent grade benzene.
8. H.-D. Becker, J. Org. Chem. **34**, 1203 (1969).
9. cf. Isao Yamazaki and L. H. Piette, J. Amer. Chem. Soc. **87**, 986 (1965) and earlier papers. We wish to thank Professor Piette for his assistance in performing the esr experiments.
10. Anal. Calcd for $C_{18}H_{12}Cl_2N_2O_3$: C, 57.80; H, 3.23; N, 7.50; Cl, 18.95. Found: C, 57.58; H, 3.18; N, 7.42; Cl, 18.91. The nmr spectrum of II is almost identical to that of I.