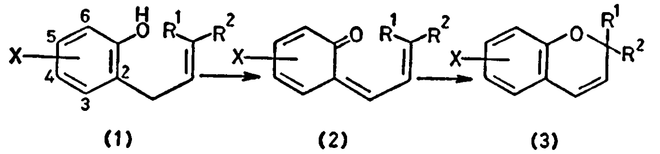
Simple Methods for Oxidation of *o*-Allylphenols to Chrom-3-enes

By Giuliana Cardillo,* Mario Orena, Gianni Porzi, and Sergio Sandri
(Istituto Chimico 'G. Ciamician,' Università di Bologna, Via Selmi 2, 40126 Bologna, Italy)

Summary The reaction of *o*-allylphenols (**1**) with potassium dichromate dissolved in benzene using Adogen 464, a commercial mixture of methyl-trialkyl-(C_8—C_{10})-ammonium chloride, or with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in ether affords the corresponding chrom-3-enes (**3**) in good yields.

SYNTHESIS of chrom-3-enes (**3**) through cyclodehydrogenation of 2-(3,3-dialkylallyl)phenols (**1**) with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) or chloranil has been extensively studied and has wide application.[1] Hitherto the more usual oxidizing reagents, for instance Cr^{VI} salts, have not been used in the preparation of chrom-3-enes. We now report that some Cr^{VI} derivatives are effective in oxidizing *o*-allylphenols to chrom-3-enes. Chromic acid supported on an anionic exchange resin, a reagent prepared in our laboratory to oxidize alcohols and allylic halides to carbonyl compounds,[2] reacts with *o*-allylphenols in refluxing benzene to give chrom-3-enes in 50% yield, the residual starting material being partially adsorbed on the polymeric support.



(**1**) (**2**) (**3**)

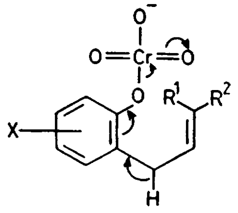
Recently a new method of dissolving the dichromate anion ($Cr_2O_7^{2-}$) in many organic solvents, utilizing Adogen 464, a commercial mixture of methyl-trialkyl-(C_8–C_{10})-ammonium chlorides has been reported.[3] Potassium dichromate readily dissolves in benzene using Adogen 464 (with a 2:1 ammonium salt to dichromate ratio). By adding a benzene solution of methyl-trialkyl-ammonium dichromate (1 equiv.) to a solution of allylphenol (1 equiv.) in refluxing benzene, the oxidation is complete after 1 h. The mixture is then diluted with hexane and the organic layer is washed with 20% aqueous $Na_2S_2O_5$. After removal of the solvent and silica gel chromatography, the chrom-3-ene is obtained in good yield, as reported in Table 1. Good yields are also observed for the oxidation of 2-(3-methylbut-2-enyl)-5-methoxyphenol, which gives, in 83% yield, the corresponding 2,2-dimethyl-7-methoxychrom-3-ene, the well known precocene I, an inhibitor of juvenile hormone (JH) biosynthesis in cockroach corpora allata.[4]

TABLE 1. Oxidation of *o*-allylphenols (**1**) with $Cr_2O_7^{2-}$ to chrom-3-enes (**3**)

	Phenol (**1**)		
X	R^1	R^2	% Yield of (**3**)[a]
5-MeO	Me	Me	83
4-Me	Me	Me	78
3-Pr^i, 6-Me	Me	Me	76
4-Me	Me	$[CH_2]_2CH{=}CMe_2$	77
4-Me	H	Ph	45

[a] Yields refer to pure isolated products.

The oxidation of alcohols by chromic acid is believed to take place by an initial formation of a chromate ester, followed by breakdown of the ester.[5] Oxidation of *o*-allylphenols to chrom-3-enes is assumed to proceed through a similar intermediate (**4**), where Cr^{VI} is capable of effecting a nucleofuge departure yielding an *o*-quinoneallide (**2**). The quinoneallides (**2**) are recognized as intermediates[6] also in DDQ oxidation. Because electrocyclic ring closure readily occurs, any synthesis of *o*-quinoneallides is effectively a synthesis of chrom-3-enes. As reported in the literature,[1] however, the yields from DDQ oxidation of allylphenols to chrom-3-enes in refluxing benzene rarely exceed 50%. We have obtained improved yields after modifying the experimental conditions. Thus, if DDQ (1·1 equiv.) in ethyl ether is added dropwise to a stirred solution of the *o*-allylphenol (1 equiv.) in ether at room temperature, a rapid change of colour is observed. After stirring the solution for 2 h, the organic layer is evaporated and the residue purified by chromatography on silica gel to give chrom-3-enes in good yields. For example, with the more sensitive cinnamylphenols, flav-3-enes are obtained in yields ranging from 80 to 90%, as shown in Table 2.



(**4**)

TABLE 2. Oxidation of *o*-allylphenols (**1**) with DDQ to chrom-3-enes (**3**)

	Phenol (**1**)		
X	R^1	R^2	% Yield of (**3**)[a]
4-MeO	Me	Me	85
4-Me	Me	Me	90
4-Et	H	Ph	90
4-MeO	H	Ph	82

[a] Yields refer to pure isolated products.

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[6] W. D. Ollis and I. O. Sutherland, 'Recent Developments in the Chemistry of Natural Phenolic Substances,' Pergamon, Oxford, 1961, p. 84; L. Jurd, *Tetrahedron*, 1977, **33**, 163; G. Cardillo, R. Cricchio, and L. Merlini, *ibid.*, 1968, **24**, 4825; *Tetrahedron Letters*, 1969, 907.