

Practical Process for the Air Oxidation of Cresols: Part A. Mechanistic Investigations

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Abstract:

The catalytic air oxidation of *p*-cresol and 2,6-di-*tert*-butyl-4-methylphenol to the corresponding benzaldehydes was investigated to determine the mechanism at work in these oxidation reactions. A number of intermediates and byproducts, mainly in the form of dimers, were observed during the course of the reactions, and their structures were elucidated by spectroscopic and chromatographic methods. The existence of these compounds in the reaction mixtures, and their proposed methods of formation, provided further insight into the mechanism involved in these oxidations.

Introduction

Hydroxy-substituted benzaldehydes are important intermediates for a large variety of chemical products used in consumables such as soaps, fragrances, pharmaceuticals, preservatives, plant protection chemicals, etc.^{1–5} Hydroxy-substituted benzaldehydes can be produced either from phenols^{1,6} (e.g., by Reimer–Tiemann, Vilsmeier, and Saligenin reactions and by means of glyoxilic acid condensation with phenol) or from cresols^{1,6–8} (e.g., by side-chain halogenation/hydrolysis or catalytic and electrochemical oxidations). Despite the disadvantage of the higher cost of cresol feed as opposed to phenol feed, there has been considerable interest in the use of oxidative technologies for the production of hydroxybenzaldehydes in view of the potential advantages in respect of selectivity and decreased effluent problems. Current oxidation routes include an electrochemical *p*-cresol oxidation process⁷ and a phenol/glyoxilic acid condensation,⁸ followed by oxidation of the resultant *p*-hydroxymandelic acid.

Studies on the partial air oxidation of substituted methyl phenols to phenolic aldehydes have been reported in considerable detail in the literature.^{9,10} To avoid the formation of polymers and tars, the phenolic group is conventionally protected as either the acetate (in an acetic anhydride and acetic acid medium¹¹) or phenolate (in an alcohol-based medium¹²).

Recently, it was shown that certain supported platinum group metal (PGM) catalysts could be used to afford benzylic oxidation of a cresol without protection of the phenolic group with reasonable success.¹³ These procedures are supposed to be flexible enough, particularly with hindered cresols, to allow for the selective preparation of various oxidation products, including nucleophilic addition products and a range of coupled compounds.¹⁴ However, most of these reactions are characterized by low yields to the desired aldehyde and the formation of further oxidized and/or oligomerization products. Deactivation of the very expensive PMG catalysts is partially relieved by the use of transition metal promoters. Regeneration of such catalysts is, however, problematic and, therefore, expensive.^{13,14}

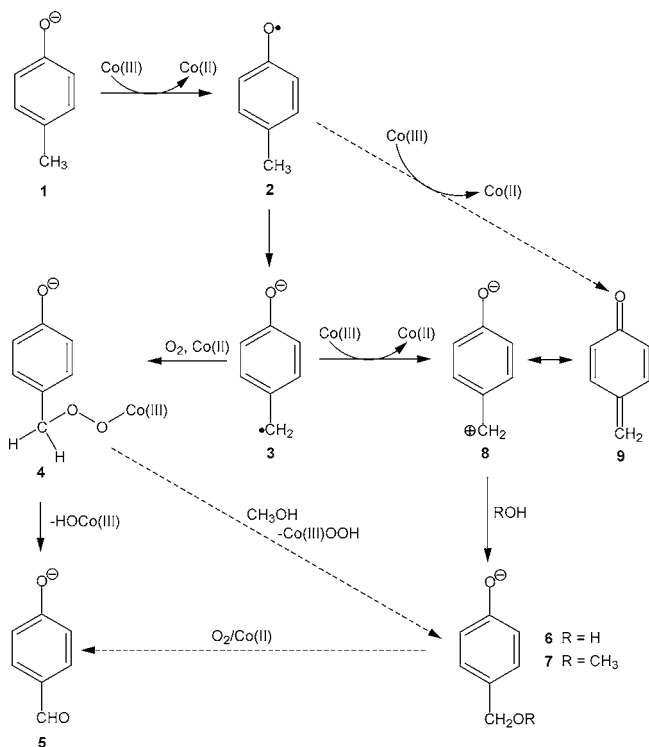
In view of the availability of a wide variety of phenolic compounds from the Fischer–Tropsch process operated by Sasol in South Africa, there has been a considerable interest in the beneficiation of these compounds. The catalytic air oxidation of *p*-cresol to 4-hydroxybenzaldehyde/4-hydroxybenzoic acid is but one example of such interest in downstream processing. In this series of two papers, we wish to report the results of our own efforts to develop a safe, technically feasible process for the oxidation of *p*-cresol and other hydroxy-substituted alkylaromatics. These results are presented in two parts: Part A deals with aspects of the mechanisms at work during catalytic air oxidations, and Part B deals with the evaluation of an approach to effect such oxidations, postulated on the hand of the proposals described in Part A.

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Scheme 1. Sheldon and de Heij¹⁷ mechanism for cresol oxidation in alkaline medium

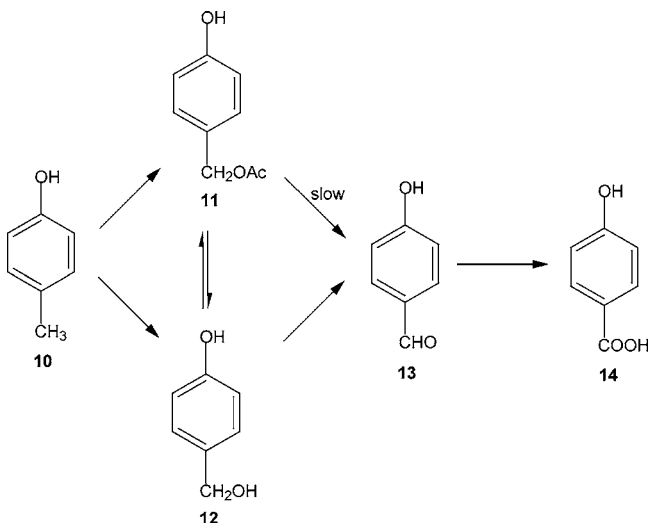


Results and Discussion

There have been a number of studies reported in the open literature^{14–21} that explored the nature of the mechanism of alkylphenol autoxidation, both in alkaline alcoholic media and in carboxylic acid media. These reports formed the basis of our investigations, as our primary interest was to determine the feasibility of manipulating aspects of the mechanism to improve the said oxidations in respect of safety, yields and selectivity, and decreased environmental impact. We therefore need to give a very brief summary of those aspects of mechanisms that have been reported in the literature that are of direct interest to this investigation.

Sheldon and de Heij¹⁷ proposed the reaction pathway that is illustrated in Scheme 1 to explain the observed formation of oxidation products during the cobalt-based catalytic air oxidation of cresols and substituted cresols in alkaline methanolic solutions. They suggested that the phenolate anion **1**, present in this form due to the basic nature of the reaction medium, is oxidized to the phenoxyl radical **2** by means of reaction with the Co(III) species present in the medium. Radical **2** then undergoes further reaction to form the benzylic radical **3**, followed by its conversion to the peroxycobalt(III) complex **4**, and subsequent decomposition

Scheme 2. Fache et al.¹³ reaction pathway for cresol oxidation in acetic acid medium



to the corresponding aldehyde **5**, with concomitant release of a hydroxy-cobalt(III) complex. This Co(III) complex may then participate, as shown in the scheme, in the initiation step.

According to this scheme, neither the benzylic alcohol **6** nor the benzyl methyl ether **7** is considered to be major intermediates in the formation of the aldehyde. Conversion of the benzylic radical **3** to the carbocation **8** (a resonance form of quinomethide **9**), followed by subsequent reaction with ROH to afford **6** or **7**, is merely perceived as being parallel side reactions only.

Other authors^{9,18} have carried out similar oxidations and proposed mechanisms that do not involve their corresponding benzyl alkyl ethers as significant intermediates in the formation of the aldehyde. The schematic reaction pathways for their proposals are omitted here for the sake of brevity.

Oxidations of cresols through acetoxylation of the cresolic methyl group using acetic acid media in the presence of palladium catalysts have also been investigated extensively.^{13,14} Fache et al. have proposed the following reaction pathway to explain their observations under these reaction conditions (Scheme 2):¹³ According to their proposal, *p*-cresol **10** is oxidized primarily to 4-hydroxybenzyl acetate **11** when the solvent is glacial acetic acid. This acetate is then only slowly oxidized to the aldehyde **13**. However, in the additional presence of water, an equilibrium is established between **11** and 4-hydroxybenzyl alcohol **12**, the latter being readily oxidized to **13**. The main disadvantage of their system is the requirement that low substrate loadings (2–5 mass%) be used, since dimers and oligomers result at higher loadings.

In our investigations, observations have been made that have led us to propose a more detailed and, compared to some authors, different mechanism at work in these reactions. The results of oxidation reactions carried out in both aqueous acetic acid and alkaline methanol media using either *p*-cresol or a substituted analogue are now reported.

***p*-Cresol Oxidation in Aqueous Acetic Acid Medium.** *p*-Cresol **10** (20 mmol) was oxidized in aqueous acetic acid

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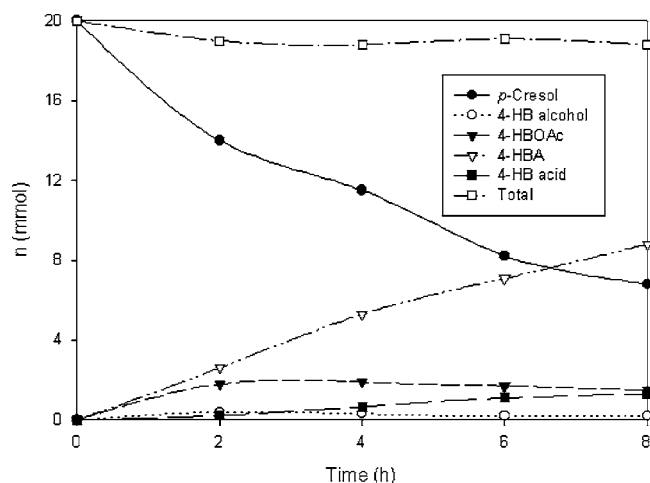
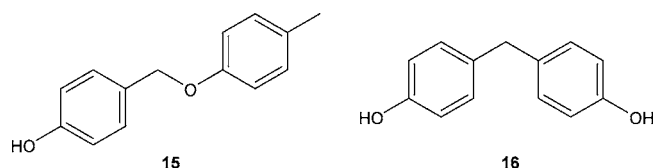


Figure 1. Product distribution diagram for the oxidation of *p*-cresol in aqueous acetic acid medium. [4-HB alcohol = **12**, 4-HBOAc = **11**, 4-HBA = **13**, and 4-HB acid = **14**; Total = the sum of amounts of compounds **10–14**.]

using oxygen in the presence of KOAc and palladium supported on activated carbon. The reaction was carried out at 100 °C and was continued for 8 h. Initially, the substrate loading was kept below 5% (m/m). The main reaction products detected by chromatographic techniques were acetate **11**, alcohol **12**, and aldehyde **13**. Increasing the substrate loading above 5% (m/m) resulted in the formation of 4-hydroxybenzyl 4-methylphenyl ether **15** and trace amounts of bis(4-hydroxyphenyl)methane **16**. Figure 1 illustrates a



typical product distribution diagram for the oxidation of *p*-cresol in aqueous acetic acid solutions.

It is important to note that, under these oxidative conditions, *m*-cresol did not oxidize at all, whilst *o*-cresol did, in fact, oxidize, but to a lesser extent as compared with *p*-cresol.

To obtain further information related to the mechanism at work in this reaction, a few supplementary experiments were conducted in the absence of catalyst and oxygen feed, but otherwise under the same reaction conditions. These experiments and the results thereof are listed below:

(1) *p*-Cresol **10** was heated in aqueous acetic acid; irrespective of the loading, no reaction occurred under these conditions.

(2) *p*-Hydroxybenzyl alcohol **12** was heated in aqueous acetic acid; this substrate reacted rapidly with the acetic acid to afford *p*-hydroxybenzyl acetate **11**. The amounts of **11** and **12** in the final reaction mixture were approximately equivalent; small amounts of the methane **16** were also present.

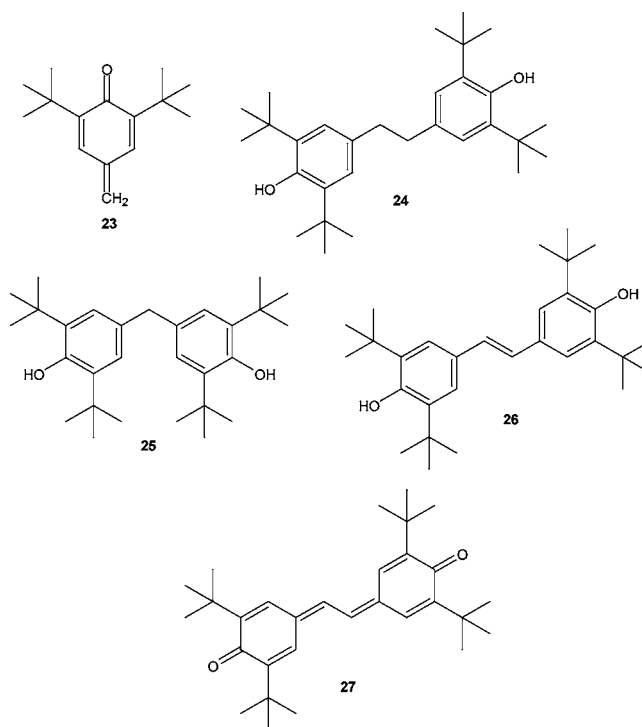
(3) A mixture of alcohol **12** and cresol **10**, at high cresol loadings, was heated in aqueous acetic acid; the diaryl compounds **15** and **16** were observed in the reaction mixture, indicating that these do not require catalysis to form.

2,6-Di-*tert*-butyl-4-methylphenol Oxidation in Aqueous Acetic Acid Medium. The oxidation, in aqueous acetic acid, of the 2,6-disubstituted cresol **17** was studied as an example of a hindered cresolic substrate. The substrate was not very soluble in this medium, and so the substrate loading was kept low. Oxidations were initially performed in glacial acetic acid, and 10% water was added only after the elapse of 20 min. The main product in this 10% water/acetic acid mixture was 3,5-di-*tert*-butyl-4-hydroxybenzyl acetate **18**, with trace amounts of the alcohol **19**, aldehyde **20**, and acid **21** being detected. One prominent secondary product identified was the diphenoquinone **22** (Scheme 3).

Once again, supplementary experiments were carried out using the hindered cresol, the corresponding benzyl alcohol, and mixtures of the two, in 10% aqueous acetic acid at 100 °C. Both the catalyst and oxygen were omitted in these reactions. Below is a summary of the experiments together with the results thus obtained.

(1) The hindered cresol **17** was heated in aqueous acetic acid; no reaction occurred under these conditions.

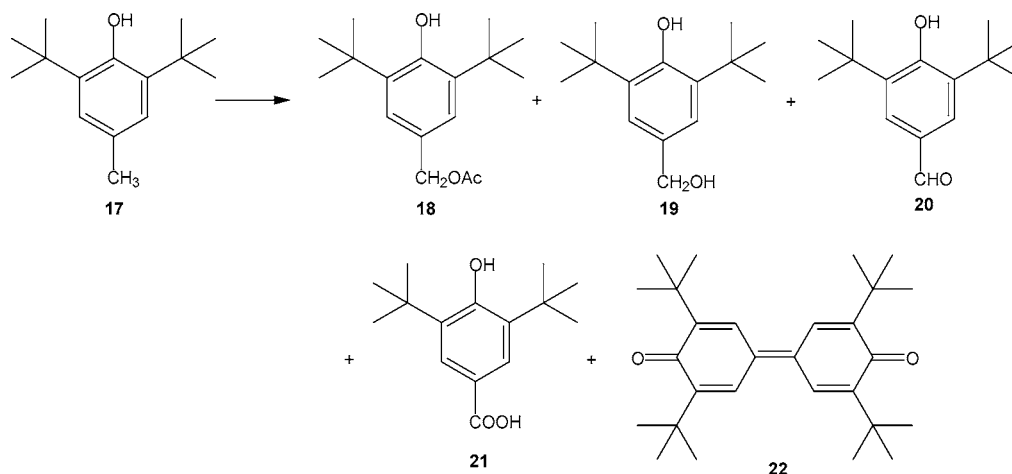
(2) A high concentration (20% m/m) of alcohol **19** was heated in 10% aqueous acetic acid; the benzyl acetate **18** and quinomethane **23** were formed as the main products. Dimer **24** was found to be a major secondary product, with small amounts of the other dimeric compounds **25**, **26**, and **27** also being detected.



(3) A 1:1 mixture of a high (20% m/m) concentration of **17** and **19** was heated in the aqueous solvent; this afforded the same compounds as was observed with alcohol **19** alone (see above), but obviously with some of the cresol **17** also being detected, as expected.

***p*-Cresol Oxidation in Alkaline Methanolic Medium.** *p*-Cresol **10** (200 mmol) was oxidized in an alkaline (NaOH) methanolic medium in the presence of a $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ catalyst. The reaction was carried out at 60 °C and was continued

Scheme 3. Compounds formed in the oxidation of a hindered cresol in acetic acid medium



for 8 h. A typical product distribution diagram for this system is illustrated in Figure 2. (Note that samples were worked up prior to analysis to hydrolyze the sodium phenolates back to the neutral phenolic compounds.)

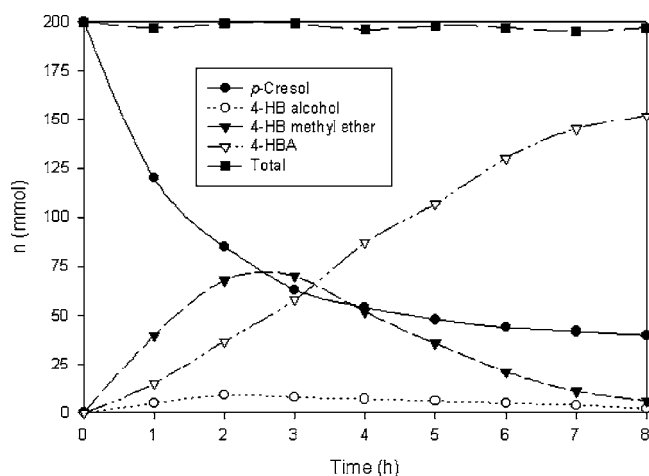
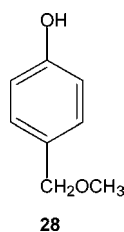


Figure 2. Product distribution diagram for the oxidation of *p*-cresol in alkaline methanolic medium. [4-HB alcohol = 12, 4-HB methyl ether = 28, and 4-HBA = 13; Total = the sum of amounts of compounds 10, 12, 13, and 17.]

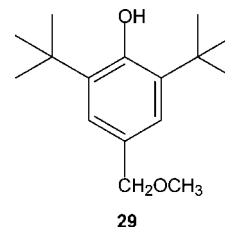
The rate of oxidation of *p*-cresol is fast initially but tails off rapidly as the concentration of substrate decreases. Apart from 4-hydroxybenzaldehyde 13, other detected compounds were 4-hydroxybenzyl alcohol 12 and 4-hydroxybenzyl methyl ether 28.



It is of interest to note that the sum of the substrate 10, alcohol 12, ether 28, and aldehyde 13 remains virtually constant throughout the reaction, suggesting the absence of other intermediates/products in significant amounts. Dimers 15 and 16 were not detected in this oxidation. By considering

the relative amounts of the alcohol 12 and ether 28 during this process, it may be suggested that the ether is the major oxidation intermediate leading from the cresol to the benzaldehyde. These observations are in contrast to those reported by other authors. Sheldon,¹⁷ for example, reported that the amount of alcohol dominated over that of the ether and that neither of these compounds underwent further oxidation to the aldehyde.

In two additional experiments, benzyl alcohols 12 and 19 were separately stirred with heating in methanol containing solid sodium hydroxide for 4 h without the addition of a catalyst or oxygen. After the workup, a significant amount of 10 had been converted to ether 28, whilst most of 17 had also reacted to form ether 29.



Proposed Mechanism. The progress of the oxidation of *p*-cresol in our investigations was found to be remarkably similar in both aqueous acetic acid and alkaline alcoholic solutions despite the use of different catalysts and differences in reaction conditions. The primary products of the oxidation of *p*-cresol 10 are the acetate 11 (in 50% aqueous acetic acid media) or the benzyl methyl ether 28 (in alkaline alcoholic solutions), with the alcohol 12 also being formed in both solvent media. These are then converted to either the benzaldehyde 13, or dimeric byproducts (for example 15 and 16, when the reaction is carried out in acidic medium). As discussed earlier, these dimers do not necessarily require oxidative conditions or catalysis for their formation. Interestingly, their formation is suppressed in alkaline methanolic solutions, and possible reasons for this are discussed later.

The Pd-catalyzed benzylic acetoxylation of alkyl aromatics such as toluene in acetic acid solutions is well-known.^{16,22–24} These reactions are normally carried out in the presence of potassium acetate using a cocatalyst (nor-

mally $\text{Sn}(\text{OAc})_2$) and are optionally carried out in the presence of a carrier material such as activated charcoal. In earlier studies, it was suggested that $\text{Pd}(\text{II})$ catalyzed the nucleophilic substitution of the substrate while dioxygen reoxidized $\text{Pd}(\text{I})$ to $\text{Pd}(\text{II})$. In later studies, a free radical process was proposed which generates a tolyl radical cation which reacts with $\text{Pd}(\text{OAc})_2$ to give $\text{Pd}(\text{I})\text{OAc}$ and the benzylic acetate. Still later studies showed that the existence of a free radical mechanism is unlikely, since it was shown that these reactions are catalyzed by heterogeneous palladium–tin species and that the addition of radical scavengers to such reactions has no influence on the reaction progress. Thus, in the case of the oxidation of toluene catalyzed by palladium–tin in acetic acid and in the presence of KOAc , the mechanism appears to be a nonradical nucleophilic attack of an acetate ion on an initially formed palladium–toluene intermediate to give benzyl acetate and palladium(I) hydride, the latter being oxidized by molecular oxygen.

In the case of the oxidation of hydroxy-substituted toluenes, as in our investigations, two important observations indicate that the mechanism differs significantly from that observed for toluenes not containing a hydroxy-substituent: first, *m*-cresol is not oxidized under the present reaction conditions, but both *p*-cresol and, to a lesser extent, *o*-cresol are smoothly oxidized; and, second, the detection of significant quantities of the coupled dimer **22** suggests that the reaction proceeds initially through the formation of a phenoxyl radical, since **22** is most likely the result of the *para*–*para* (C–C) coupling of two such phenoxyl radicals. We therefore propose that the oxidation of hydroxy-substituted toluenes, in both aqueous acetic acid and alkaline methanolic media, rather proceeds through the initial formation of a phenoxyl radical followed by the subsequent formation of the corresponding quinomethide (**9** and **23**), and it is this quinomethide that serves as the main intermediate to all the products that were observed in these reactions, including many of the dimeric species (Scheme 4). This would serve to explain why *m*-cresol does not oxidize under these conditions: it is not possible to construct *m*-quinonoid systems using the normal requirements for bonding.²⁵ Furthermore, *o*-cresol does not behave as efficiently as does *p*-cresol due to the fact that the *o*-quinomethide is much less stable (and is thus higher in energy) than its *para* analogue. This difference in stability is known for the quinones in general.²⁶

For unsubstituted quinomethides (such as **9**), rapid nucleophilic addition by acetic acid leads to the formation of the benzylic acetate **11**; if the nucleophile is water, the benzyl alcohol **12** is formed, or if the nucleophile is methanol, the benzyl methyl ether **28**. Due to the rate of these conversions, the unhindered quinomethide **9** could not be detected.

Experiments suggested too that the benzyl alcohol may, however, also be formed as a result of an equilibrium reaction between the acetate and alcohol. In all cases, the driving force for the rapid formation of the benzylic-substituted products is the rearomatization of the quinomethide. In the case of the hindered quinomethide **23**, the large, bulky *tertiary*-butyl groups are responsible for reducing the rate of rearomatization significantly enough so that it may be detected in solution, as was the case in this investigation; this increased stability of the hindered quinomethide relative to the unhindered methide is due to the stabilizing effect of the positive inductive bulky alkyl groups on the electron poor ring. Experiments further suggested that an equilibrium existed between the hindered alcohol **19** and quinomethide **23**.

Whilst, in acidic media, the benzylic alcohols are readily oxidized to the corresponding benzaldehydes, the corresponding acetates are oxidized only very slowly, and the quinomethides, hindered or not, are not oxidized at all. Since the alcohol and acetate appear to be in equilibrium, oxidation of the acetate to the aldehyde will always be slow, and this provides an explanation for the observation that the major products from the oxidation of **10** and **17** in acidic medium are the acetates **11** and **18**.

As mentioned previously, some dimers (**15** and **16**) are formed in aqueous acidic media in the absence of catalyst and oxygen feed, from the benzyl alcohol or cresol/benzyl alcohol mixtures. Since experiments suggest that the alcohol is in equilibrium with the quinomethide (since it too was detected in the absence of oxygen and catalyst), it is very likely that these dimers are formed either by S_N reactions involving these substrates or by means of substrate or intermediate acetate/alcohol addition to the reactive quinomethides, with rearomatization once again being a driving force. This explains why the selectivity to dimer **15** increases so significantly in the presence of higher *p*-cresol **10** concentrations.

During the oxidation of the hindered cresol **17**, the steric bulk around the hydroxyl moiety ensures a decrease in the rate of formation of the initial phenoxyl radical but, once formed, results in a radical that is reasonably stable (due to the steric bulk of the *tertiary*-butyl groups and also to their electron-donating inductive ability and thus stabilization of the radical). This results in a low instantaneous concentration of the benzyl acetate **18** and alcohol **19**, and so the only dimer detected during the oxidation reaction is **22** (formed by *para*–*para* coupling of two phenoxyl radicals). The formation of dimers **24** to **27** requires a high concentration of either the benzyl acetate or alcohol, as confirmed by the supplementary experiments discussed previously. Furthermore, due to steric hindrance and, therefore, unlike the unhindered species, the presence of additional cresolic substrate does not influence the formation of the last-mentioned dimers.

The observation that, in alkaline methanolic medium without the addition of a catalyst or oxygen, benzyl alcohols **12** and **19** are readily converted to their corresponding methyl ethers strongly suggests that this conversion occurs *via* the

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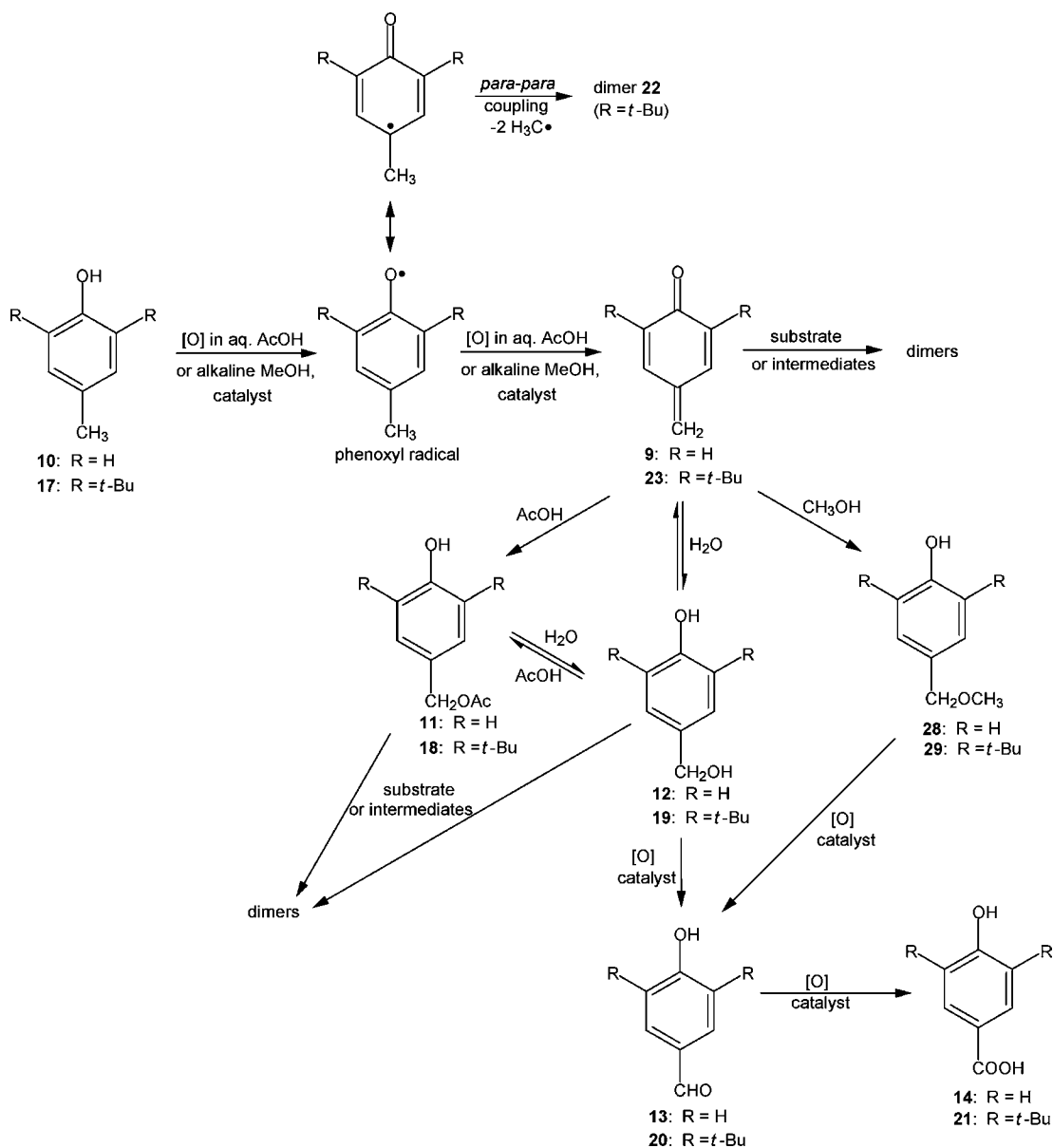
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Scheme 4. Proposed mechanism for the oxidation of *p*-cresols^a



^a Note that, for the sake of brevity and where relevant, compounds present in basic methanolic media are shown as neutral phenolics rather than the sodium phenolates.

quinomethide (see Scheme 4): in general, alcohols are usually converted to ethers by specific methods such as, amongst others, the Williamson synthesis in which an alkoxide anion is reacted with an alkyl halide in an S_N1 reaction.²⁷ However, it is obvious that when the alcohols are substrates such as **12** and **19**, the reactive quinomethide intermediate facilitates their conversion without, for example, the Williamson requirements.

The suppression of dimer formation in basic medium is probably a result of the nature of the leaving group (CH_3O^-) present in the benzyl methyl ether, which is not as stable as, for example, the AcO^- leaving group in acidic medium. (It is common knowledge that alkoxy groups are not good leaving groups.) The methyl ethers are therefore less inclined to undergo S_{N} reactions with other substrate/

intermediate species (the result of which would have led to dimer formation). Furthermore, it is envisaged that the formation of the benzyl methyl ether from the quinomethide, in this basic methanolic medium, is a rapid reaction, and so side reactions involving the quinomethide and other substrate/intermediate species to form dimers are also suppressed.

Conclusion

The results described above for the oxidation of *p*-cresol in alkaline methanolic and aqueous acetic acid solutions strongly suggest that the reaction pathways are similar despite the differences in catalyst and reaction medium (Scheme 4). The mechanism proposed envisages the formation of quinomethide as the primary oxidation intermediate, via the phenoxyl radical. The manner in which this intermediate is stabilized determines the efficiency of the oxidation process

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in terms of selectivity to the corresponding aldehyde. Stabilization of the quinomethide as the methyl ether, as in alkaline methanolic solutions, prevents the formation of dimeric byproducts in view of the poor leaving-group properties of alkoxy anions. The ether is, however, smoothly oxidized further to the desired aldehyde which is thus obtained in reasonable yields. Stabilizing the quinomethane as the acetate, as in aqueous acetic acid solutions, however, presents two major problems. First, the acetate, since it is only slowly oxidized to the aldehyde, needs first to be hydrolyzed to the corresponding alcohol before further oxidation can occur to a significant extent. Since the acetate and the alcohol are always in equilibrium, the rate of oxidation (of the alcohol) will always be slow. Second, the acetate anion is a good leaving group, and so undesired dimeric products are able to form readily.

In Part B, following this paper, and using the knowledge gained from the work the results of which have been discussed here, we present a novel practical method for carrying out the oxidation of *p*-cresol and other hydroxy-substituted alkylbenzenes under either alkaline or acidic conditions. It will be shown that these oxidations may be carried out safely and efficiently, without the formation of dimers, in either medium, thus adding credence to proposals made in this current paper.

Experimental Section

General. All standards, reagents, authentic samples, and solvents were obtained from local suppliers and used without further purification.

General Oxidation Setup and Procedure. A 250 cm³ jacketed glass reactor, fully baffled, mechanically agitated, and equipped with a water-cooled condenser, was used for oxidation reactions. A 4.50 cm diameter, four-bladed stainless steel impeller was used for agitation at approximately 800 rpm. The reaction temperature was kept constant (± 0.50 °C) by circulating glycerine through the external heating/cooling jacket of the reactor. Oxygen was supplied to the reactor from the top using a single glass tube inlet. The end of the tube was positioned about 1 cm above the impeller blades.

A. Oxidations in Aqueous Acetic Acid Media: The reactor setup described above was allowed to equilibrate at 100 °C for 1 h, after which the substrate (20 mmol), KOAc (1.97 g; 20 mmol), AcOH/H₂O (1:1, 100 cm³), and 5% Pd/C (0.53 g) were introduced. The mixture was allowed to stand at 100 °C for 20 min after which the reaction was initiated by means of the introduction of oxygen (40 cm³ min⁻¹). The reaction was monitored at intervals of 2 h, for a total reaction time of 8 h, by analyzing aliquots (1.00 cm³) of the reaction mixture by HPLC (using a C₁₈ column and CH₃CN/H₂O at pH 3 (H₃PO₄) as mobile phase).

B. Oxidations in Alkaline Methanolic Media: The same reactor setup described above was allowed to equilibrate at 60 °C for 1 h after which *p*-cresol (21.6 g; 200 mmol), solid NaOH (24.0 g; 600 mmol), CH₃OH (100 cm³), and CoCl₂·6H₂O (0.42 g) were introduced. The mixture was left to stabilize at this temperature for a further 20 min, and then the oxygen was introduced (40 cm³ min⁻¹) to initiate the

reaction. The reaction was continued for 8 h, and aliquots (1.00 g) were withdrawn every hour and analyzed (HPLC, as for the reaction in acidic medium).

Stability of Substrates and Intermediates in Aqueous Acetic Acid Media. The stabilities of **10** or **17** (20 mmol) and/or **12** or **19** (20 mmol), in the absence of catalyst and oxygen feed, were determined by stirring these substrates, and mixtures thereof, in separate aqueous acetic acid media (H₂O/AcOH = 1:1, 100 cm³) containing KOAc (1.96 g; 20 mmol), for 30 min at 100 °C, followed by sampling and analyses (HPLC). Intermediates, products, and byproducts were identified by means of GC/MS (performed on a Hewlett-Packard 5890 Series II Plus Gas Chromatograph coupled to a 5972 Series Mass Selective Detector; data were manipulated by means of the HP ChemStation software version B.02.05). In addition, dimer **22** was isolated and characterized by means of ¹H NMR, ¹³C NMR, and DEPT-135 techniques.

A. 4-Hydroxybenzyl 4-Methylphenyl Ether (15): *m/z* 214 (M⁺), 199 (M⁺ - 15), 181 (M⁺ - 33), 165 (M⁺ - 49), 152 (M⁺ - 62), 141 (M⁺ - 73), 121 (100%, M⁺ - 93), 107 (M⁺ - 107), 94, and 77.

B. Bis(4-hydroxyphenyl)methane (16): *m/z* 200 (M⁺), 183 (M⁺ - 17), 165 (M⁺ - 35), 152 (M⁺ - 48), 128 (M⁺ - 72), 107 (100%, M⁺ - 93), 94, 77, and 51. This was confirmed by comparison with an authentic sample (Aldrich chemical).

C. 3,3',5,5'-Tetra-*tert*-butyldiphenyl-4,4'-quinone (22): δ_H (CDCl₃)/ppm 1.35 (36H, s, CH₃) and 7.70 (4H, s, Ar); δ_C (CDCl₃)/ppm 29.57 (CH₃), 36.01 (C(CH₃)₃), 126.00 (Ar), 136.12 (Ar), 150.42 (Ar), and 186.46 (C=O); DEPT-135 indicated the total absence of CH₂ carbons; *m/z* 408 (M⁺), 393 (M⁺ - 15), 368 (M⁺ - 40), 351 (M⁺ - 57), 338 (M⁺ - 70), 323 (M⁺ - 85), 309 (M⁺ - 99), 296 (M⁺ - 112), 281 (M⁺ - 127), 239 (M⁺ - 169), 225 (M⁺ - 183), 203 (M⁺ - 205), 165, 146, 128, 91, 57 (100%), and 41.

D. 3,5-Di-*tert*-butyl-4-quinomethide (23): *m/z* 218 (M⁺), 203 (M⁺ - 15), 189 (M⁺ - 29), 175 (M⁺ - 43), 161 (100%, M⁺ - 57), 147 (M⁺ - 71), 128 (M⁺ - 90), 115 (M⁺ - 103), 105, 91, 77, 57, and 41.

E. 1,2-Di(3',5'-di-*tert*-butyl-4'-hydroxyphenyl)ethane (24): 438 (M⁺), 423 (M⁺ - 15), 355 (M⁺ - 83), 341 (M⁺ - 97), 281 (M⁺ - 157), 267 (M⁺ - 171), 219 (100%, M⁺ - 219), 204, 189, 178, 161, 145, 133, 119, 105, 91, 79, and 57.

F. Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)methane (25): *m/z* 424 (M⁺), 409 (100%, M⁺ - 15), 393 (M⁺ - 31), 381 (M⁺ - 43), 367 (M⁺ - 57), 351 (M⁺ - 73), 337 (M⁺ - 87), 281 (M⁺ - 143), 267 (M⁺ - 157), 251 (M⁺ - 173), 233 (M⁺ - 191), 219 (M⁺ - 205), 207, 197, 183, 169, 147, 129, 115, 103, 91, 77, and 57.

G. 1,2-Di(3',5'-di-*tert*-butyl-4'-hydroxyphenyl)ethene (26): *m/z* 436 (100%, M⁺), 421 (M⁺ - 15), 281 (M⁺ - 155), 267 (M⁺ - 169), 253 (M⁺ - 183), 231 (M⁺ - 205), 219

($M^+ - 217$), 207, 191, 175, 159, 147, 133, 115, 96, 73, and 57.

H. 2,2',6,6'-Di-*tert*-butylstilbenequinone (27): m/z 434 (100%, M^+), 419 ($M^+ - 15$), 404 ($M^+ - 30$), 378 ($M^+ - 56$), 364 ($M^+ - 70$), 349 ($M^+ - 85$), 333 ($M^+ - 101$), 321 ($M^+ - 113$), 307 ($M^+ - 127$), 293 ($M^+ - 141$), 281 ($M^+ - 153$), 267 ($M^+ - 167$), 247 ($M^+ - 187$), 231 ($M^+ - 203$), 219 ($M^+ - 215$), 207, 191, 173, 159, 145, 133, 115, 103, 91, 77, and 57.

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