Phenolic Oxidations with Phenyliodonium Diacetate

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Phenyliodonium diacetate (PIDA) in methanol interacts smoothly with phenols to yield *p*-quinones, *o*-quinones, 4,4-dialkoxycyclohexa-2,5-dienones or 4-alkyl-4-alkoxycyclohexa-2,5-dienones, dependant on the constitution of the phenolic substrate. The reactions proceed in mild conditions and good yields and are synthetically useful.

Phenolic oxidation is an important natural process, which occurs on a massive scale in the production of lignin,[1] a process that is neither chemo- nor stereo-selective. However, from the same precursors, lignans are produced with great specificity.[2] Phenolic coupling plays an important role in the biosynthesis of many natural products[3–9] including tannins,[10,11] plant and insect pigments,[9] some antibiotics[9] and an estimated 10% of all alkaloids.[9]

It is generally agreed that most biosynthetic phenolic oxidations proceed by one electron processes to give aryloxy radicals, ArO• **1**, and that these neutral species undergo further reaction. Processes such as homolytic coupling, heterolytic coupling, radical insertion and quinone methide formation occur, each being available to all of the many forms of the radicals concerned.[8,12] Specificity, when it occurs, is enzyme imposed.

In the laboratory, a very wide variety of oxidants have been utilised[3,9] for phenolic oxidations, including Fe^{III},[3,5,6,9,12–19] Ag^{I},[19] Pb^{IV},[20] Mn^{III},[21] Va^{IV},[22] Va^{V},[23,24] Tl^{III},[25] Cu^{II}[26] and Bi^{V}.[27] Electrochemical methods have been used to induce and study one-electron phenolic oxidations.[28–32] Where there are some constraints, for example in some cases of intramolecular coupling,[20,23] high yields have been recorded, but generally the reactions are non-specific and low yielding.

Two electron phenolic oxidation processes to give aryloxenium ions, ArO^+ **2**, have been less well explored. They have been implicated in biological processes either directly[9,14,33] or through derived quinone-methides.[34] They have been proposed as possible intermediates in phenolic oxidations using Tl^{III},[35] Cu^{II}[36] and HIO_4,[37] and have been implicated in the release of 'metaphosphate' from quinol monophosphates.[38] Some examples of the aryloxenium ions **2** have been generated and studied electrochemically[39–41] and highly delocalised examples of **2** are stable enough to be isolated.[42]

Aryloxenium ions **2** have been less explored as intermediates in syntheses than the corresponding radicals **1**, although they would seem to offer several advantages, as follows. (a) Some attractive methods for the production of the aryloxenium ions **2** are shown in equations (1)–(3).

$$\underset{}{ArOH} \longrightarrow \underset{\mathbf{3}}{ArOX} \longrightarrow \underset{\mathbf{2}}{Ar\overset{+}{O}} + X^- \quad (1)$$

$$\underset{}{ArOH} \longrightarrow \underset{\mathbf{4}}{ArOX^+} \longrightarrow \underset{\mathbf{2}}{Ar\overset{+}{O}} + X \quad (2)$$

$$\underset{}{ArOH} \longrightarrow \underset{\mathbf{5}}{ArOX[N]} \longrightarrow \underset{\mathbf{2}}{Ar\overset{+}{O}} + X[N-2] \quad (3)$$

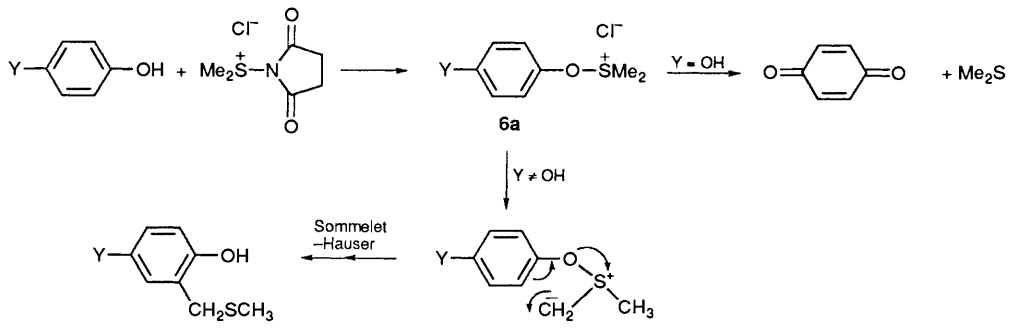
(X is a heteroatom capable of a ready change of valency from N to $N - 2$)

In equations (1) and (2), the actual production of an aryloxenium ion is simply a dissociation rather than a step requiring an oxidation. In equation (3), the dissociation is accompanied by a valency change in the previously attached group X. In all three equations *if X can be attached to a particular hydroxy group, then the following reactions are specific, even if other oxidisable groups are present.* (b) It has been pointed out[43] that, whereas aryloxy radicals **1** would dimerise mainly by C–O–C bond formation, aryloxenium ions would interact with uncharged species predominantly by C–C bond formation. (c) Although it is easy for the neutral radicals, ArO• **1** to dimerise in any of a number of ways, aryloxenium ions **2** *will not readily react with each other.* They will instead react with nucleophiles by controllable inter- and intramolecular reactions. (d) A benzylic proton could be readily lost to give quinone methides ready for substitution,[44] cyclisation[34,44] and rearrangement.[33,45]

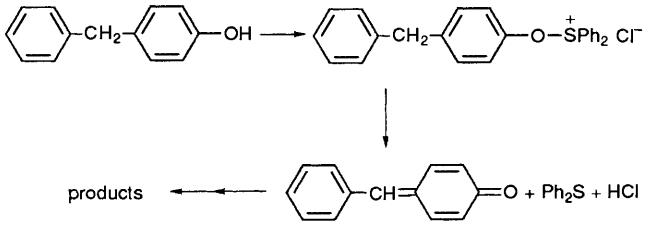
Clearly the group X must be an excellent leaving group, as the natural polarisation of a phenol to a phenoxy anion is being reversed. Moreover, in many cases it is difficult to ascertain whether a particular reaction proceeds *via* aryloxenium ions or whether directly from the intermediates **3**, **4** or **5**. Nevertheless, PhO^+ has been generated from PhONHOTs in strongly acidic conditions and proved to be a powerful electrophile which coupled directly even with a weak nucleophile such as benzene.[46,47] Compounds **3** (X = SAr[48]) have also been shown to provide the aryloxenium ion ArO^+ Compounds **4** [X = $S(Pr^i)NR_2$,[49] $S(Tol)NR_2$,[49] SMe_2[50]] also yield ions **2**. Of particular interest is the thermal decomposition of the intermediate **4** (X = C_5H_5N)[51,52] to generate ion **2**. In that case, when the aryl groups lacked electron-withdrawing groups then only C–C bond products were formed in reactions with nucleophiles. Compounds **5** are involved in oxidations involving metal ions including Tl^{III},[35] Cu^{II},[36] Pb^{IV},[53] Cr^{VI}.[54] In addition, electrochemical oxidation may give the aryloxenium ion **2**.[39–41,55]

Present work.—In any consideration of the generation of ArO^+ using equations (1), (2) or (3), it is clear that the choice of nucleofugal group, X, is critical. For synthetic purposes the following conditions should be fulfilled. (i) ArOX should be readily accessible; (ii) ArOX should decompose in mild conditions to ArO^+; (iii) X should not be a strong nucleophile, in order to avoid attack on ArO^+. As a result, we decided to concentrate on studies of compounds **6**, **7** and **8**.

Compounds **6a** containing *o*- or *p*-hydroxy groups are reported to give quinones in good yields,[50] a finding that we readily verified using the *N*-chlorosuccinimide–dimethyl sulphide (NCS–SMe_2) system (Table 1, experiment 1). However, when no appositely placed hydroxy groups are present, then



Scheme 1



Scheme 2

Sommelet–Hauser rearrangements occur (Scheme 1), and therefore the method cannot be used generally.

To overcome the problem of rearrangement, we tried a new reagent consisting of *N*-chlorosuccinimide–diphenyl sulphide (NCS–SPh_2), which would lead to an intermediate **6b** with no protons α to the sulphur. The diphenyl sulphide system readily gave quinones in excellent yields (Table 1, experiments 2 and 6) after addition of base. No quinones resulted before base addition, showing that **6b** is a fairly stable species. We then treated 4-benzylphenol with the NCS–SPh_2 system. Unfortunately, under a wide variety of conditions the product always consisted of a complex mixture of chlorinated phenols, presumably formed by addition of hydrogen chloride to an intermediate quinone-methide, followed by further chlorination (Scheme 2).

Martin's sulphurane reagent[56] $\{Ph_2S[OC(CF_3)_2Ph]_2\}$ has once been observed to react as an oxidant.[57] However, in our hands, this reagent did not oxidise 1,4-quinols to 1,4-quinones, starting material only being recovered. Therefore, we turned to the hypervalent iodonium compounds, PhI(OH)OTs **9** and $PhI(OAc)_2$ **10** in methanol.

Our expectations with regard to **9** and **10**, using Koser's reagent[58] **9** as an illustration, are shown in Scheme 3.

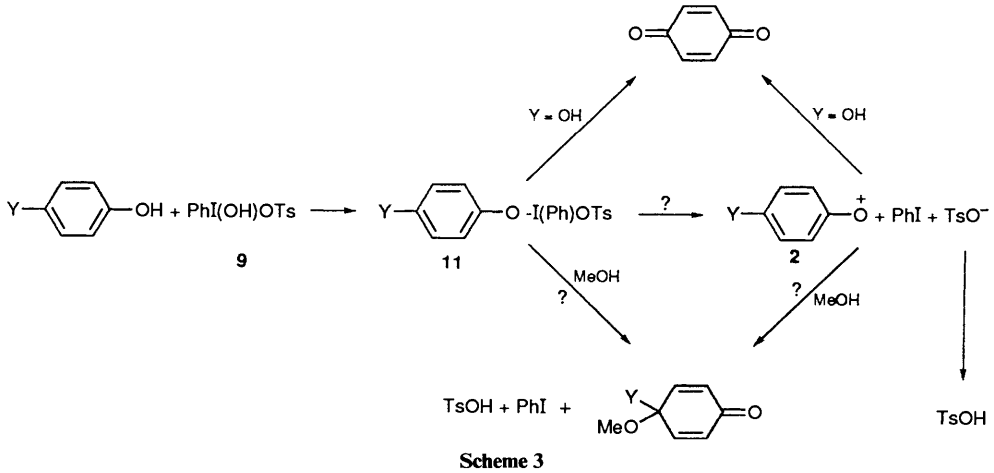
The interactions of phenols with **9** leads to **11** which could react with methanol, directly or through the intermediacy of an aryloxenium ion. It seemed to us that the by-products, iodobenzene and toluene-*p*-sulphonic acid were not sufficiently nucleophilic as to compete with methanol for reaction with **11** or **2**.

In practice **9** oxidised 1,4-quinols to 1,4-quinones in good yields and without the need to add base to induce reaction (Table 1, experiments 3 and 7). However, the reagent totally failed to induce reaction with the extended quinol, 4,4′-biphenol (Table 1, experiment 12) or with 4-benzylphenol (Table 2, experiment 14), and was clearly limited in its applications.

We next examined commercially available phenyliodonium diacetate [$PhI(OAc)_2$, PIDA], which could react with phenols to give ArOI(Ph)OAc, which should then react in an analogous fashion to that envisaged for Koser's reagent (Scheme 3). It was known that oxidations of phenols with PIDA (2 equiv.) gave the corresponding 4-acetoxyphenols in low yields when hydrogen or bromine were at the 4-position.[59] During this work a preliminary note of a study of phenolic oxidations using phenyliodonium bis(trifluoroacetate) appeared.[60] Iodoxybenzene has been shown to oxidise β-naphthol and 2,4-di-*tert*-butylphenol to the corresponding *ortho*-quinones.[61]

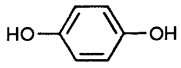
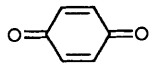
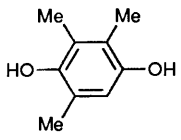
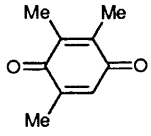
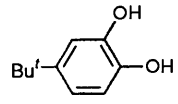
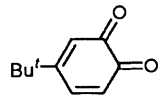
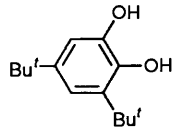
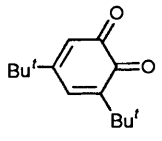
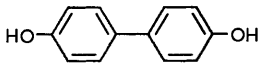
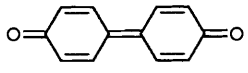
Table 1 shows that PIDA interacts with all the benzene-1,2- and -1,4-diols assayed to give the corresponding 1,4- and 1,2-quinones in excellent isolated yields (Table 1, experiments 4, 8, 9 and 10). In addition, it readily oxidises 4,4′-biphenol to the corresponding extended quinone (Table 1, experiment 11) in contrast to Koser's reagent, which did not oxidise this substrate.

Table 2 (experiments 15, 16 and 17) shows that 4-alkylphenols readily yield 4-alkyl-4-methoxycyclohexa-2,5-dienones in acceptable isolated yields. 4-Benzylphenol gave 4-benzyl-4-methoxycyclohexa-2,5-dienone with PIDA (Table 2, experiment 15), whereas Koser's reagent left the phenol unaffected and the NCS–Me_2S system gave mixtures of chlorinated phenols.



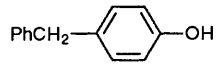
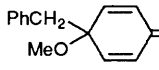
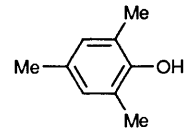
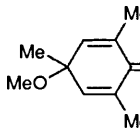
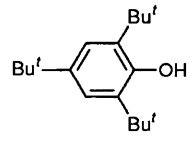
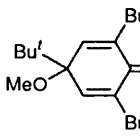
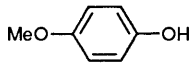
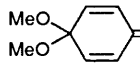
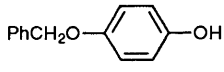
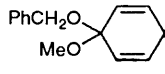
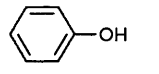
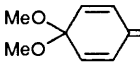
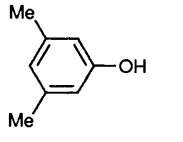
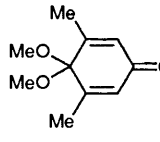
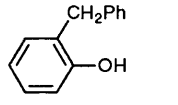
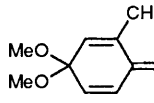
Scheme 3

Table 1 The oxidation of benzene-1,2- and -1,4-diols

Exp.	Substrate	Oxidant[a]	Product	Yield (%)[b]
1		Me_2S–NCS[c]		77
2	"	Ph_2S–NCS[c]	"	84
3	"	PhI(OH)OTs[d]	"	80
4	"	$PhI(OAc)_2$[e]	"	94
5		Me_2S–NCS[b]		98
6	"	Ph_2S–NCS[c]	"	98
7	"	PhI(OH)OTs[d]	"	84
8	"	$PhI(OAc)_2$[e]	"	100
9		$PhI(OAc)_2$[e]		99
10		$PhI(OAc)_2$[e]		91
11		$PhI(OAc)_2$[e]		70 (94[f])
12	"	PhI(OH)OTs[d]	No reaction	–

[a] 1 Equiv. used. [b] All yields are isolated, pure products. [c] Reaction at −40 °C in MeCN–CH_2Cl_2. [d] Reaction at 20 °C in MeCN–CH_2Cl_2. [e] Reaction at 20 °C in MeOH. [f] HPLC yield.

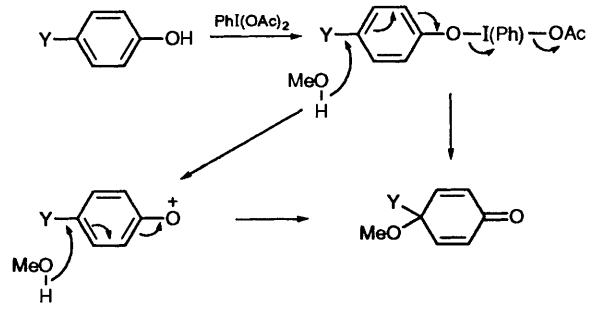
Table 2 Oxidations of monohydric phenols

Exp.	Substrate	Oxidant[a]	Product	Yield (%)[b]
13		Ph_2S–NCS[c]	Chlorinated phenols	–
14	"	PhI(OH)OTs[d]	No reaction	–
15	"	$PhI(OAc)_2$[e]		65
16		$PhI(OAc)_2$[e]		72
17		$PhI(OAc)_2$[e]		94
18		$PhI(OAc)_2$[e]		99
19		$PhI(OAc)_2$[e]		92
20		$PhI(OAc)_2$[e,f]		68
21		$PhI(OAc)_2$[e,f]		80
22		$PhI(OAc)_2$[e,f]		83

[a] 1 Equiv. of oxidant used unless otherwise stated. [b] Yield of isolated, characterised, pure product. [c] Reaction at −40 °C in MeCN–CH_2Cl_2; 1 equiv. NEt_3 added. [d] Reaction at 20 °C in MeCN–CH_2Cl_2. [e] Reaction in MeOH at 20 °C. [f] 2 Equiv. of PIDA used.

When the substituent on the phenol is an alkoxy group then 4,4-dialkoxycyclohexa-2,5-dienones (quinone ketals) result in excellent yields (experiments 18 and 19). Experiment 19 shows one method in which *mixed* quinone ketals can be readily made. Though we have not tried it, presumably the substitution of another alcohol for methanol would also be a flexible method for the production of such mixed quinone ketals.[49]

Very great interest centres on the *direct conversion of* 4-*unsubstituted phenols to quinone ketals* by use of 2 equiv. of PIDA (Table 2, experiments 20,* 21 and 22). Even though a 2-position of our phenols was unsubstituted, the reaction always resulted in 4-substitution, and this was so even when the 4-position was relatively hindered (Table 2, experiment 21) or when a fairly stable *o*-quinone could result (Table 2, experiment 22). A very recent extension[62] of our reaction showed that in certain cases some 2-substitution does, in fact, occur.



Scheme 4

Discussion.—The methodology described in this paper is of obvious preparative value, and this has been highlighted since our preliminary note[63] by its use to make spirodienones,[64–66]

* We thank Ms. Laura Aalberg for this experiment.

lignans[67] and anthraquinones.[62] The products are characteristic of two-electron oxidation processes[68] but the mechanisms of the reactions are unknown. They may proceed *via* transient aryloxenium ions, or methanol may attack the intermediate directly (Scheme 4).

Experimental

Instrumentation.—IR spectra were recorded on a Unicam SP1050 IR spectrometer using polystyrene absorbances at 1602 and 1495 cm^{-1} as references. UV spectra were recorded on a Perkin-Elmer 402 spectrometer using 10 mm cells. ^1H NMR spectra were taken on either a Varian HA-100 (100 MHz) or a Bruker WM-250 (250 MHz) spectrometer, using $CDCl_3$ as solvent and Me_4Si as internal standard. ^{13}C NMR spectra were recorded on a Varian XL-100 spectrometer. Coupling constant (J) values are given in Hz.

Boiling points were determined by Kugelrohr distillation, in which case the temperature given is that of the oven, or by micro-boiling point. Melting points were taken on a Gallenkamp hot-stage apparatus and are uncorrected. TLC Analyses were performed using either silica gel (Merck) or alumina, plastic or aluminium backed plates with a fluorescent indicator (254 nm). Preparative chromatography was carried out on silica or alumina. HPLC Analyses were performed using a LDC/Milton Roy constametric spectromonitor. Microanalyses were determined using a Carlo Erba Strumentazione Elemental Analyser.

Reagents.—All reactions were carried out using purified anhydrous reagents. Chloroform and acetonitrile were distilled from P_2O_5 and triethylamine from CaH_2. Methanol was refluxed over magnesium activated by iodine followed by distillation. Dichloromethane was shaken with H_2SO_4, H_2O, 5% aqueous NaOH and H_2O, pre-dried with $CaCl_2$ and then distilled from P_2O_5. Tetrahydrofuran (THF) was passed through dry neutral alumina under N_2, dried over Na–Ph_2CO and distilled under N_2.

Glassware was dried at 120 °C for at least 4 h, assembled hot and cooled under N_2.

General Preparative Procedures

1. Oxidation of Phenols using N-*Chlorosuccinimide* (*NCS*) *and Dimethyl Sulphide.*—A dry 100 cm^3 round-bottomed flask was charged with NCS (1.335 g, 10 mmol) and a magnetic follower, sealed with a septum cap and flushed with nitrogen. Dry dichloromethane (50 cm^3) was added *via* syringe and the mixture stirred at −40 °C under nitrogen. Dimethyl sulphide (DMS) (0.73 cm^3, 0.62 g, 10 mmol) was added by syringe in a dropwise fashion over 15 min, after which a white suspension formed. A cooled solution of the benzenediol (10 mmol) in dry acetonitrile (15 cm^3) was transferred dropwise over 20 min by double-ended needle under nitrogen pressure, to the stirred reaction mixture at −40 °C.

Dry triethylamine (1.53 cm^3 10 mmol) was added dropwise to the stirred reaction mixture at −40 °C using a syringe and a bright yellow colour appeared. The mixture was maintained at −40 °C for a further 15 min and then allowed to warm to room temp. over 40 min. It was then washed with saturated aqueous $(NH_4)_2SO_4$ (10 cm^3) and water (2 × 20 cm^3). The organic layer was separated, dried ($MgSO_4$), filtered and concentrated. The residue was sublimed to give the pure quinone. The quinones produced in this way were (i) p-*Benzoquinone* (0.833 g, 77%), m.p. 115 °C; Found: M^+, 108.021 37. $C_6H_4O_2$ requires M, 108.021 129, identical in all respects with an authentic sample (Table 1, experiment 1). (ii) 2,3,5-*Trimethyl*-1,4-*benzoquinone* (1.47 g, 98%), m.p. 28–29 °C (lit.,[69] m.p. 29 °C) (Table 1, experiment 5) Found: $M^{\cdot+}$, 150.068 03. $C_6H_{10}O_2$ requires M, 150.068 08; δ_H 2.0 (9 H, s, C-CH_3) and 6.5 (1 H, s, 6-H); δ_C 11.99, 12.3 (C-7, C-8, C-9), 133.67 (C-6), 140.7, 140.86 (C-2, C-3, C-5) and 187.3 and 187.7 (C-1, C-4); λ_{max}/nm 250 (3.1); ν_{max}(KBr)/cm^{-1} 2950, 1650 and 1460; m/z 160 (100), 122 (28), 121 (13) and 107 (36).

2. Oxidation of Phenols using N-*Chlorosuccinimide and Diphenyl Sulphide.*—A dry nitrogen-flushed round-bottomed flask fitted with a magnetic follower and a septum cap was flushed with nitrogen and charged with NCS (1.335 g, 10 mmol) and dry dichloromethane (50 cm^3). The mixture was stirred and cooled to −10 °C, and diphenyl sulphide (1.66 cm^3, 1.86 g, 10 mmol) was added by syringe over 10 min under nitrogen. The mixture was stirred at −10 °C for 5 min and then a cooled solution of the benzenediol (10 mmol) in dry acetonitrile (15 cm^3) was transferred by double-ended needle to the reaction mixture at −40 °C. The temperature was maintained at −40 °C for 15 min. Dry triethylamine (1.53 cm^3, 10 mmol) was added dropwise by syringe to the stirred reaction mixture, at −40 °C, and the temperature held at this for 15 min; it was then allowed to rise to room temp. over 40 min.

The reaction mixture was worked up as in Section 1, to give (i) p-*benzoquinone* (0.907 g, 84%), m.p. 115 °C (Table 1, experiment 2), and (ii) 2,3,5-*trimethyl*-1,4-*benzoquinone* (1.47 g, 98%), m.p. 28–29 °C (Table 1, experiment 6).

3. Oxidation of Phenols with Koser's Reagent.—Koser's reagent[58] [PhI(OH)OTs] (4.1 g, 10 mmol) was dissolved in dry dichloromethane (50 cm^3) and added to a stirred solution of the phenol (10 mmol) in dry acetonitrile (20 cm^3) at room temp. The reaction mixture was stirred for 30 min after which Na_2CO_3 (5 g) was added and stirring continued for a further 15 min. The mixture was then filtered, washed with water (20 cm^3) and the organic layer separated, dried ($MgSO_4$), filtered and evaporated to give a yellow oil. This was purified by chromatography on silica gel (230–400 mesh) using gradient elution [100% light petroleum (40–60 °C) to 100% chloroform]. The quinones so produced were (i) p-*benzoquinone* (0.86 g, 80%), m.p. 115 °C (Table 1, experiment 3) and (ii) 2,3,5-*trimethyl*-1,4-*benzoquinone* (1.26 g, 84%), m.p. 28–29 °C (Table 1, experiment 7).

4. Oxidation of 4-*Substituted Phenols with Phenyliodonium Diacetate* (*PIDA*).—A dry nitrogen flushed 100 cm^3 round-bottomed flask containing a magnetic follower and sealed with a septum cap was charged with the 4-substituted phenol (5 mmol) and dry methanol (10 cm^3). A solution of PIDA (1.61 g, 5 mmol) in methanol (25 cm^3) was transferred *via* a double-ended needle to the stirred phenol solution at room temp. over 40 min. The solution turned reddish yellow and then yellow.

The reaction was followed by TLC to monitor the disappearence of starting material, which in all cases was complete within 40 min. Removal of the methanol gave a yellow oil which was purified by gradient elution on silica gel (230–400 mesh) [100% light petroleum (40–60 °C) to 100% dichloromethane]. Compounds produced in this way are given below.

(i) 4-*Benzyl*-4-*methoxycyclohexa*-2,5-*dienone.* (0.695 g, 65%) (Table 2, experiment 15) clear oil. Found M^+, 214.0989. $C_{14}H_{14}O_2$ requires M, 214.0993. δ_H 2.95 (2 H, s, CH_2), 3.14 (3 H, s, OCH_3), 6.24 (2 H, d, J 10, 6-H, 2-H), 6.7 (2 H, d, J 10, 3-H, 5-H) and 7.0–7.29 (5 H, m, C_6H_5); δ_C 46.4 (C-7), 53.2 (OCH_3), 75.5 (C-4), 127.0 (C-11), 128.0 (C-2,6), 130.7 (C-10,12), 131.3 (C-9,13), 134.9 (C-8), 150.6 (C-3,5) and 185.9 (C-1); λ_{max}/nm 228 (4.7); ν_{max}(film)/cm^{-1} 2840, 1680, 1640, 860, 730 and 700; m/z 214(7), 149(4), 123(15), 95(6) and 91(100).

(ii) 4-*Methoxy*-2,4,6-*trimethylcyclohexa*-2,5-*dienone.* (0.598 g, 72%) (Table 2, experiment 16) colourless prisms, m.p. 42–44 °C (lit.,[70] m.p. 43–44 °C) Found: M^+, 166.0982. Calc. for

$C_{10}H_{14}O_2$, *M*, 166.0990; δ_H 1.34 (3 H, s, 4-Me), 1.88 (6 H, s, 2-Me, 6-Me), 3.1 (3 H, s, OCH_3) and 6.48 (2 H, s, 3-H, 5-H); δ_C 15.9 (4-Me), 26.6 (2,6-Me), 52.7 (OCH_3), 72.5 (C-4), 136.7 (C-2,6), 146.8 (C-3,5) and 186.5 (C-1); λ_{max}/nm 237 (3.69); ν_{max}(KBr)/cm^{-1} 2980, 1685, 1110 and 656; *m*/*z* 166 (100), 151 (75), 135 (64), 123 (66), 95 (42), 91 (69) and 79 (39).

(iii) 2,4,6-*Tri*-tert-*butyl*-4-*methoxycyclohexa*-2,5-*dienone*. (1.372 g, 94%) (Table 2, experiment 17), m.p. 58–60 °C (lit.,[39] m.p. 58–59 °C) Found: C, 78.2; H, 12.0%; M^+, 292.2404. Calc. for $C_{19}H_{32}O_2$: C, 78.03; H, 11.95%; *M*, 292.2402; δ_H 0.92 [9 H, s, $C(CH_3)_3$], 1.21 [18 H, s, 2 × $C(CH_3)_3$], 3.12 (3 H, s, OCH_3) and 6.5 (2 H, s, 3,5-H); δ_C 25.8 [$C(CH_3)_3$], 29.7 [2 × $C(CH_3)_3$], 30.3 [2 × $C(CH_3)_3$], 35.2 [$C(CH_3)_3$], 52.4 (OCH_3), 79.3 (C-4), 141.1 (C-3,5), 150.5 (C-2,6) and 186.4 (C-1); λ_{max}/nm 242 (4.34); ν_{max}(KBr)/cm^{-1} 2980, 1670, 1650, 1490, 1470, 1365 and 1075; *m*/*z* 293 (100), 247 (11), 237 (27), 235 (90) and 221 (45).

(iv) 4,4-*Dimethoxycyclohexa*-2,5-*dienone*.[71] (0.762 g, 99%) (Table 2, experiment 18) oil (Found: M^+, 154.0621. Calc. for $C_8H_{10}O_3$, *M*, 154.0629); δ_H 3.32 (6 H, s, 2 × OCH_3), 6.24 (2 H, d, *J* 10, 2-H) and 6.84 (2 H, d, *J* 10, 3-H); δ_C 50.4 (OCH_3), 92.6 (C-4), 129.9 (C-2), 143.6 (C-3) and 185.2 (C-1); λ_{max}/nm 221 (3.85); ν_{max}(film)/cm^{-1} 2960, 1700, 1650, 1315 and 1110; *m*/*z* 154 (11), 139 (16), 124 (13), 123 (100) and 95 (32).

(v) 4-*Benzyloxy*-4-*methoxycyclohexa*-2,5-*dienone*. (1.058 g, 92%) (Table 2, experiment 19) Found: M^+, 230.0942. $C_{14}H_{14}O_3$ requires *M*, 230.0942; δ_H 3.32 (3 H, s, OCH_3), 4.58 (2 H, s, CH_2Ph), 7.19 (2 H, d, *J* 10, 2,6-H), 7.83 (2 H, d, *J* 10, 3,5-H) and 8.26 (5 H, m, C_6H_5); λ_{max}/nm 217 (3.61); ν_{max}(film)/cm^{-1} 2960, 1690, 1645, 1180, 1105, 1025, 970, 730 and 692; *m*/*z* 139(16), 124(12), 123(100), 95(10) and 91(58).

5. Oxidation of 4-*Unsubstituted Phenols*.—The oxidation method was the same as that in Section 4, except that 2 equiv. of PIDA in methanol (40 cm^3) were added to the phenol dissolved in methanol. The work-up was also the same. In this way the following compounds were obtained.

(i) 4,4-*Dimethoxycyclohexa*-2,5-*dienone*. (0.53 g, 68%) (Table 2, experiment 20) was obtained as an oil, identical in all respects with the product of experiment 18.

(ii) 4,4-*Dimethoxy*-3,5-*dimethylcyclohexa*-2,5-*dienone*. (0.728 g, 80%) (Table 2, experiment 21) colourless prisms, m.p. 59–61 °C. Found M^+, 182.0933. $C_{10}H_{14}O_3$ requires *M*, 182.0930; δ_H 1.9 (6 H, s, CH_3), 3.02 (6 H, s, OCH_3) and 6.28 (2 H, s, 2-H); δ_C 16.3 (C-CH_3), 50.8 (OCH_3), 98.1 (C-4), 131.8 (C-2), 155.0 (C-3) and 184.7 (C-1); λ_{max}/nm 232 (3.7); ν_{max}(KBr)/cm^{-1} 2960, 2840, 1685, 1650, 1450, 1305, 900 and 700; *m*/*z* 182 (0.5), 167 (100), 151 (67), 135 (33), 127 (41) and 123 (53).

(iii) 2-*Benzyl*-4,4-*dimethoxycyclohexa*-2,5-*dienone*. (1.013 g, 83%) (Table 2, experiment 22) oil. Found: M^+ 244.1103. $C_{15}H_{16}O_3$ requires *M*, 244.1099; δ_H 3.2 (6 H, s, OCH_3), 3.6 (2 H, s, CH_2Ph), 5.12–5.38 (2 H, m, 3-H, 6-H), 6.71 (1 H, dd, J_1 10, J_2 3, 5-H) and 7.0–7.36 (5 H, m, C_6H_5); δ_C 35.1 (C-7), 50.3 (OCH_3), 93.1 (C-4), 126.5 (C-11), 128.6, 129.2 (C-9, C-10), 138.1 (C-8), 130.0 (C-6), 138.1 (C-8), 139.4, 142.9 (C-3, C-5) and 185.0 (C-1); λ_{max}/nm 218 (3.7); ν_{max}(film)/cm^{-1} 1685, 1655, 1120, 1065, 965 and 700; *m*/*z* 244 (15), 214 (22), 213 (100), 153 (31), 152 (19), 141 (18), 115 (20) and 91 (41).

6. Oxidation of Dihydric Phenols.—The method used was exactly the same as in Section 4. The quinones produced by this process were as follows.

(i) p-*Benzoquinone*. (0.507 g, 94%), m.p. 115 °C (Table 1, experiment 4). (ii) 2,3,5-*Trimethyl*-1,4-*benzoquinone* (0.75 g, 100%), m.p. 28–29 °C (Table 1, experiment 8). (iii) *Diphenoquinone* (0.644 g, 70%), m.p. (decomp.) 165 °C (lit.,[72] 165 °C) (Table 1, experiment 11), identical in all respects with an authentic sample. (iv) 4-tert-*Butyl*-1,2-*benzoquinone* (0.812 g, 99%) was isolated as yellow prisms, m.p. 65 °C (lit.,[70] 65 °C) (Table 1, experiment 9) Found: C, 73.1; H, 7.3; M^+, 164.0829. Calc. for $C_{10}H_{12}O_2$ C, 73.20; H, 7.32%; *M*, 164.0937; δ_H 2.2 [9 H, s, $C(CH_3)_3$], 6.21–6.44 (2 H, m, 3-H, 6-H) and 7.16-7.21 (1 H, m, 5-H); δ_C 27.7 [$C(CH_3)_3$], 35.6 [$C(CH_3)_3$], 123.7 (C-6), 129.36 (C-3), 140.18 (C-5), 162.24 (C-4) and 180.35 and 180.4 (C-1, C-2); λ_{max}/nm 241 (4.32); ν_{max}(KBr)/cm^{-1} 2900, 1670, 1410, 1398, 1285, 1250, 1140 and 820; *m*/*z* 164 (11), 121 (32), 108 (28) and 93 (100).

(v) 3,5-*Di*-tert-*butyl*-1,2-*benzoquinone* (1.0 g, 99%) yellow prisms, m.p. 114–115 °C (lit.,[73] m.p. 112–114 °C) (Table 1, experiment 10) (Found: C, 76.2; H, 8.89%; M^+, 220.1464. Calc. for $C_{14}H_{20}O_2$ C, 76.36; H, 9.09%; *M*, 220.1463); δ_H 1.25, 1.21 [18 H, 2 × $C(CH_3)_3$], 6.18 (1 H, d, *J* 3, 6-H) and 6.94 (1 H, d, *J* 3, 4-H). δ_C 28.6, 29.19 (C-8, C-10), 35.42, 35.98 (C-7, C-9), 122.02 (C-6), 133.49 (C-3), 163.24 (C-5) and 180.06, 181.04 (C-1, C-2); λ_{max}/nm 243 (4.27); ν_{max}(KBr)/cm^{-1} 2990, 1670, 1395, 1380, 1250, 890 and 810; *m*/*z* 238 (100%, M + NH_4^+), 224 (12), 223 (80), 222 (32), 221 (26), 207 (33) and 149 (10).

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