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Oxidation of substituted phenols with metal dioxygen carrier, Co(salen) pyridinate: solvent effects†

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Abstract. The course of the oxidation of substituted phenols with Co[*bis*(salicylaldehyde)-ethylenediimine]pyridinate-dioxygen complex is found to be dependent on the nature of the solvents used. The various oxidation products of 2,6-dimethylphenol, 2,6-di-*t*-butylphenol, 2,6-di-*t*-butyl-4-methylphenol and hydroquinone in chloroform and methanol solvents have been isolated and characterized. Plausible intermediates leading to these reaction products are discussed.

Keywords. Oxidation; metal-dioxygen adduct; substituted phenols; cobalt *bis*(salicylaldehyde) ethylenediimine pyridinate.

1. Introduction

In the course of an earlier study on the oxidation of 2,6-di-*t*-butylphenol with various metal chelate-dioxygen complexes, it was observed that Co(salen)Py [salen—*bis*(salicylaldehyde)ethylenediimine] is an efficient oxygen carrier and that variation in the structure of the metal chelate had a pronounced effect on the nature of products formed (Satish *et al* 1985). The present study concerns the effect of solvents viz. chloroform and methanol on the oxidation of 2,6-dimethylphenol, 2,6-di-*t*-butylphenol, 2,6-di-*t*-butyl-4-methylphenol and hydroquinone using Co(salen)Py-O_2 complex under homogeneous conditions.

2. Results and discussion

Oxidation of 2,6-dimethylphenol (Ia) with molecular oxygen in the presence of Co(salen)Py as catalyst in chloroform and (methanol) as solvent (25°C, oxygen pressure 1 kg/cm^{2}g, 6 hr, catalyst to substrate ratio 1:20) gave 2,6-dimethyl-1,4-benzoquinone (IIa) 57·4% (59·1%); 3,3′, 5,5′-tetramethyl-4,4′-diphenoquinone (IIIa) 1% (4·1%) and 4,4′-dihydroxy-3,3′,5,5′-tetramethylbiphenyl (IVa) 4% (3·6%) (scheme 1). The formation of products can be explained on the basis of well known metal-dioxygen adduct mechanism (Zombeck *et al* 1981). Benzoquinone IIa is formed by transfer of an oxygen atom from the metal-dioxygen adduct to the phenoxide radical, whereas IIIa and IVa arise from the coupling of two phenoxide radicals. Product distribution was essentially similar in both chloroform and methanol. However, oxidation of 2,6-di-*t*-butylphenol

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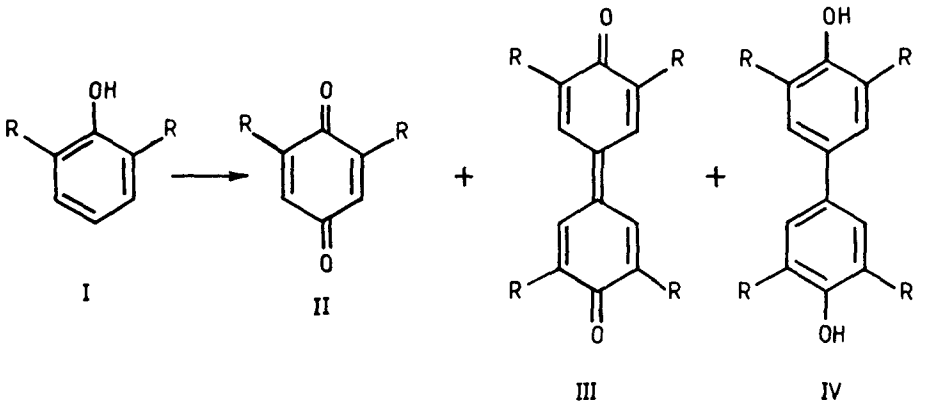
SCHEME 1

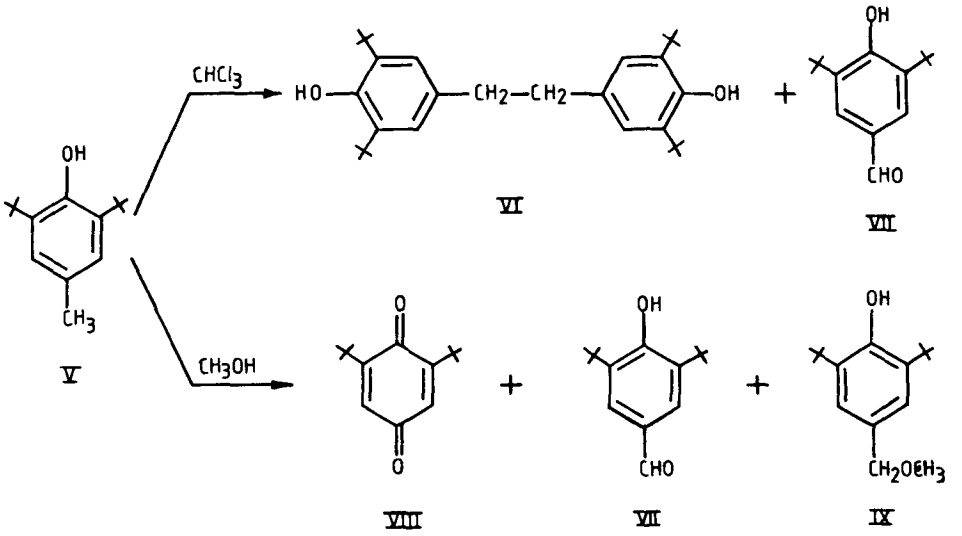


under the same conditions was solvent sensitive. In methanol the product was exclusively 2,6-di-*t*-butyl-1,4-benzoquinone (IIb), (89·1 %), whereas in chloroform relatively smaller amounts of benzoquinone IIb (1·8 %), along with diphenoquinone IIIb (7·8 %), were formed. Overall conversion in case of chloroform was poor (9·6 %). Higher selectivity towards benzoquinone in polar solvent can probably be explained on the basis of stabilization of a Co^{II}-O_2 complex in polar solvents (Stynes and Ibers 1972). However the similar reactivity of 2,6-dimethylphenol in chloroform and methanol in contrast to the marked difference of reactivity of 2,6-di-*t*-butylphenol in these solvents is not very clear at present.

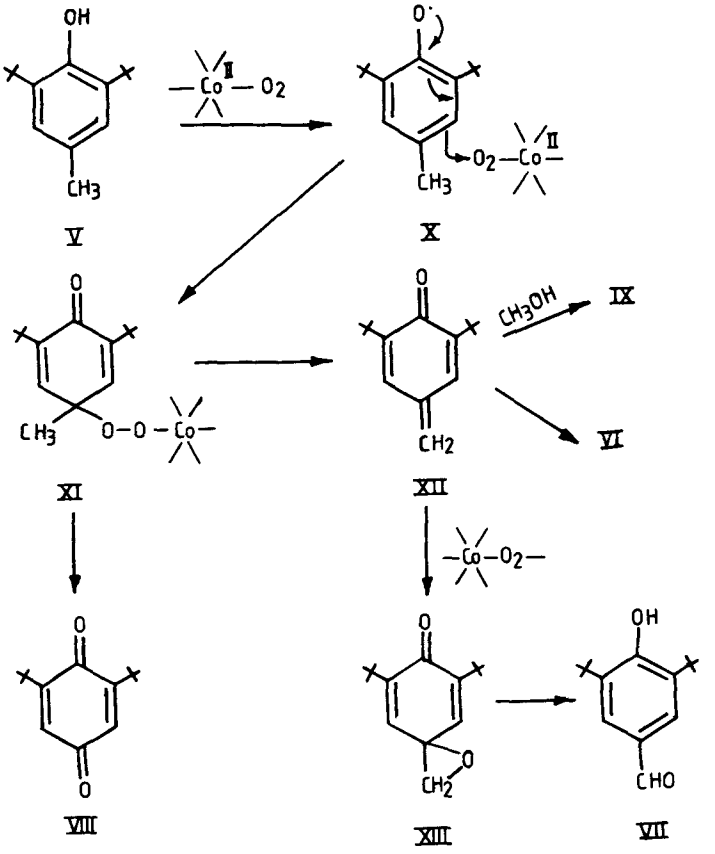
Oxidation of 2,6-di-*t*-butyl-4-methylphenol (V) showed significant differences in product distribution in chloroform and methanol (scheme 2). The products obtained in the oxidation of 2,6-di-*t*-butyl-4-methylphenol can be explained on the basis of a common intermediate phenoxide radical (X) (scheme 3). The radical X reacts with metal-dioxygen species to give peroxy quinolato-Co^{II} complex XI. The peroxy metal complex XI can either lose a methyl radical to form VIII or a hydrogen radical to form a quinone methide intermediate (XII). The intermediacy of quinone methide XII has been implicated in the oxidation of 4-substituted phenols by a variety of oxidizing agents (Gorbunova *et al* 1966; Magnusson 1966; Macomber 1982; Omura 1984). The quinone methide is trapped by methanol to give methyl ether IX in methanol and aldehyde VII presumably via XIII as shown in scheme 3. In a nonnucleophilic medium such as chloroform which is incapable of trapping it, the quinone methide forms a tail-tail dimer VI (Macomber 1982). For reasons not clear to us at present, methanol leads to products from both the intermediates XI and XII, whereas in chloroform only products derived from quinone methide are formed.

Our observations are in slight variance with the results reported earlier (Nishinaga *et al* 1974) that the oxidation of 2,6-di-*t*-butyl-4-methylphenol with Co(salen) in methanol gave rise to four products of which only two (VII and VIII) were obtained by us. They did not report the formation of methyl ether IX.

SCHEME 2



SCHEME 3



Oxidation of hydroquinone (XIV) with dioxygen in the presence of Co(salen)Py in chloroform gave 1,4-benzoquinone XV (40·7%) and quinhydrone XVI (35·2%) (scheme 4). Whereas oxidation of hydroquinone in methanol under similar conditions gave only polymeric material, van Dort and Geursen (1967) have reported similar results with a tetradentate cobalt complex, Co(salen) in the oxidation of hydroquinone. In contrast to this, oxidation of hydroquinone using Co[acacen-N,N′-ethylene *bis*(acetylacetoimine)]$2H_2O$ as catalyst in ethanol gave 1,4-benzoquinone, 64% (Mckillop and Ray 1977).

3. Experimental

The m.p's are uncorrected; IR and NMR spectra were recorded on Perkin-Elmer 567 and Varian EM-360L, 60 MHz NMR spectrometer respectively. The NMR chemical shifts are in the δ scale. Yields refer to the pure isolated materials. All oxidation reactions were carried out in a tubular glass reactor provided with a gas inlet and outlet facility and a pressure gauge. The gas outlet was connected to a condenser and a solvent trap. Oxygen flow was controlled with the help of a stopcock fixed at the top of the condenser.

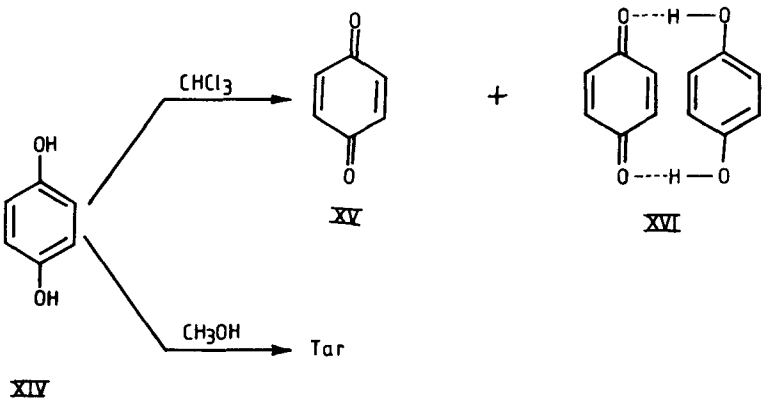
3.1 *Materials*

2,6-Dimethylphenol, 2,6-di-*t*-butylphenol, 2,6-di-*t*-butyl-4-methylphenol and hydroquinone were used as supplied. Chloroform and methanol used were of high purity grade. Co(salen)Py was prepared by known methods (Bailes and Calvin 1947) and satisfactory elemental analysis was obtained. High purity oxygen gas from M/s Indian Oxygen Ltd. was used. Petroleum ether refers to the fraction b.p. 60–80°C.

3.2 *Oxidation of 2,6-dimethylphenol*

3.2a *In chloroform*: 2,6-Dimethylphenol (10 g, 82 m mole) was dissolved in chloroform (500 ml) and placed in the reactor. To it was added Co(salen)Py (1·65 g, 4·1 m mole) and oxygen was bubbled through the solution. Escaping oxygen was throttled in such a way

SCHEME 4



XIV XV XVI

as to give a pressure of 1 kg/cm^2 g inside the reactor. After 6 hr, pressure was released and chloroform distilled off. The resulting mass was extracted with warm petroleum ether (2 × 100 ml). The petroleum ether extracts were evaporated to give an orange solid (7·0 g). The petroleum ether insoluble material was extracted with benzene (50 ml) and this on evaporation and drying gave a dark mass (2·2 g).

The orange solid obtained from petroleum ether extracts was crystallized from petroleum ether to give 2,6-dimethyl-1,4-benzoquinone (IIa) as orange needles (2·1 g, 18·8%) m.p. 71–72°C (Mckillop and Ray 1977, m.p. 68–70°C). IR (KBr) 1640 cm^{-1} (quinone). The mother liquor on concentration and cooling deposited biphenyl IVa as a grey solid (0·2 g, 2%) m.p. 218–220°C (Tsuruya and Yonezawa 1974, m.p. 220–223°C). IR (KBr) 3350 cm^{-1} (phenolic hydroxyl group); NMR (DMSO-D_6) 2·10 (12H, *s*, four methyls), 6·83 (4H, *s*, aromatic protons) and 7·87 (2H, *s*, hydroxyl protons); Mass M^+ 242, 212, 165 and 121. The filtrate was concentrated and chromatographed over silica gel. Elution with petroleum ether gave more benzoquinone IIa (4·3 g, 38·6%) and starting material (0·21 g, 2%).

The benzene extracted material (2·2 g) was chromatographed over silica gel. Elution with benzene gave biphenyl IVa (0·2 g, 2%) and diphenoquinone IIIa (0·1 g, 1%) as red prisms from methylene chloride, m.p. 218–220°C (Mckillop and Ray 1977, m.p. 212–214°C). IR (KBr) 1625 cm^{-1} (ketone) and 1580 cm^{-1} (C=C).

3.2b *In methanol*: Oxidation of 2,6-dimethylphenol was carried out as above by using methanol as solvent in place of chloroform. Work up of the reaction mixture as mentioned earlier gave benzoquinone IIa (6·59 g, 59·1%); diphenoquinone IIIa (0·4 g, 4·1%); biphenyl IVa (0·37 g, 3·6%); unreacted phenol Ia (0.75 g, 7·5%) and tarry substance (1·1 g).

3.3 *Oxidation of* 2,6-*di-t-butylphenol*

3.3a *In chloroform*: To a solution of 2,6-di-*t*-butylphenol (10·3 g, 50 m mole) in chloroform (500 ml) was added Co(salen)Py (1·01 g, 2·5 m mole) and oxygen was bubbled through it at 1 kg/cm^2 g pressure for 6 hr. The reaction mixture was evaporated and the resultant brown mass extracted with warm petroleum ether (4 × 50 ml). Evaporation of the petroleum ether extracts gave brown oil which on crystallization from methanol gave dark brown needles of diphenoquinone IIIb (0·8 g, 7·8%) m.p. 244° (Mckillop and Ray 1977, m.p. 243°C). IR (KBr) 1625 cm^{-1} (ketone). The mother liquor was evaporated and the resultant brown oil was chromatographed over silica gel. Elution with petroleum ether gave benzoquinone IIb (0·2 g, 1.8%) crystallized as orange needles from methanol, m.p. 63–65°C (Mckillop and Ray 1977, m.p. 60–62°C); IR (KBr) 1640 cm^{-1} (quinone). Continued elution with petroleum ether gave starting phenol Ib.

3.3b *In methanol*: 2,6-Di-*t*-butylphenol (10·3 g, 50 m mole) was dissolved in methanol (500 ml) and to it added Co(salen)Py (1·01 g, 2·5 m mole). Oxygen was bubbled through the solution at 1 kg/cm^2 g pressure for 6 hr, after which pressure was released and the methanol evaporated. Residual mass was extracted with warm petroleum ether (4 × 50 ml). Evaporation of petroleum ether extracts gave an orange mass which crystallized from methanol to afford orange needles of 2,6-di-*t*-butyl-1,4-benzoquinone IIb (9·8 g, 89·1%) m.p. 64–65°C.

3.4 *Oxidation of* 2,6-*di-t-butyl-4-methylphenol*

3.4a *In chloroform*: To a solution of 2,6-di-*t*-butyl-4-methylphenol V (10 g, 45·4 m mole) in chloroform (500 ml) was added Co(salen)Py (0·917 g, 2·27 m mole) and oxygen was bubbled at 1 kg/cm^2 g. After 6 hr, the pressure was released and chloroform distilled off. The residue was extracted with warm petroleum ether to remove the catalyst. Evaporation of the petroleum ether extracts gave a brown mass (10·7 g) which was chromatographed over silica gel. Elution with petroleum ether gave an oil which crystallized to give light yellow needles (from chloroform-methanol) of bibenzyl VI (2·82 g, 28·3 %), m.p. 173–175°C (Paquette and Farley 1967, m.p. 169–170°C). IR (KBr) 3615 cm^{-1} (hydroxyl group); NMR ($CDCl_3$) 1·45 (18H, *s*, *t*-butyl groups), 2·80 (4H, *s*, CH_2–CH_2–), 4·50 (2H, broad singlet, –OH) and 6·95 (4H, *s*, aromatic protons). Further elution with petroleum ether-benzene (95:5) gave 3,5-di-*t*-butyl-4-hydroxybenzaldehyde (VII) (0·15 g, 1·4 %) as colourless flakes (from methanol) m.p. 180–182°C (Paquette and Farley 1967, m.p. 186–188°C). IR (KBr) 1655 cm^{-1} (aldehyde) and 3420 cm^{-1} (phenolic OH); NMR ($CDCl_3$) 1·43 (18H, *s*, *t*-butyl groups), 2·67 (1H, *s*, –OH, exchangeable with D_2O), 6·47 (2H, *s*, aromatic protons) and 9·50 (1H, *s*, aldehyde proton). Continued elution with petroleum ether-benzene (95:5) gave starting material V (5·54 g, 55·4 %)

3.4b *In methanol*: Oxidation of 2,6-di-*t*-butyl-4-methylphenol was similarly carried out using methanol in place of chloroform. Work up of the reaction mixture as above gave 2,6-di-*t*-butyl-1,4-benzoquinone VIII (2·73 g, 27·3 %), m.p. 62–65°C, (Mckillop and Ray 1977, m.p. 60–62°C); 2,5-di-*t*-butyl-4-hydroxybenzaldehyde (VII) (0·39 g, 3·7 %), m.p. 180–182°C and 2,6-*t*-butyl-4-methoxymethylphenol (IX) (3·1 g, 27·3 %), m.p. 98°C, (Ronlan and Parker 1971, m.p. 98–99°C). NMR ($CDCl_3$) 1·45 (18H, *s*, *t*-butyl groups), 3·35 (3H, *s*, OCH_3), 4·30 (2H, *s*, $-CH_2-O-$), 5·23 (1H, *s*, –OH) and 7·03 (2H, *s*, aromatic protons); Mass M^+ 250, 235, 219, 193 and 57.

3.5 *Oxidation of hydroquinone*

3.5a *In chloroform*: Hydroquinone (10 g, 91 m mole) dissolved in chloroform (500 ml) was placed in the reactor, Co(salen)Py (1·86 g, 4·6 m mole) was added and oxygen bubbled at 1 kg/cm^2 g for 6 hr. At the end of the reaction a dark brown mass precipitated out. It was collected, triturated with acetone (50 ml), and filtered. The acetone solution was concentrated and cooled, when it deposited greenish needles of quinhydrone (2·88 g, 29·1 %), m.p. 170–171°C (Vogel 1978, m.p. 172°C). IR (KBr) 3220 cm^{-1} (OH) and 1620 cm^{-1} (quinone).

Chloroform filtrate of the reaction mixture was evaporated to give a black mass. It was extracted with boiling petroleum ether. The petroleum ether extracts on concentration deposited a black solid which was crystallised from acetone to give more quinhydrone (0·6 g, 6·1 %). The mother liquor was further concentrated and cooled to give long yellow needles of 1,4-benzoquinone (4·0 g, 40·7 %), m.p. 112–114°C (Mckillop and Ray 1977, m.p. 115°C). IR (KBr) 1650 cm^{-1} (quinone).

3.5b *In methanol*: To a solution of hydroquinone (10 g, 91 m mole) in methanol (500 ml) was added Co(salen)Py (1·86 g, 4·6 m mole) and oxygen was bubbled through it at 1 kg/cm^2 g. After 6 hr, the pressure was released and the contents were evaporated to give a polymeric mass which could not be characterized.

4. Conclusion

The solvent has a marked effect on the nature and distribution of reaction products in the oxidation of substituted phenols using a Co(salen)Py-dioxygen compelx under homogeneous conditions. Increase in the polarity of solvent enhances the stability of the Co(salen)Py-O_2 complex, resulting in higher yields of oxidised products (benzoquinones). Variation in product distribution in different phenols can also be ascribed to their structures.

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