Autoxidation of 4-Alkyl-2,6-di-t-butylphenols with Di-(3-Salicylideneaminopropyl)aminecobalt(II) Catalyst

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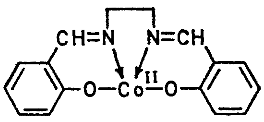
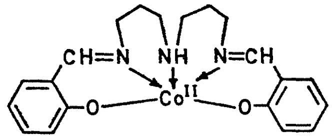
Summary Autoxidation of 4-alkyl-2,6-di-t-butylphenols (III) with di-(3-salicylideneaminopropyl)aminecobalt(II) catalyst in methanol gives the corresponding quinols, 4-alkyl-2,6-di-t-butyl-4-hydroxycyclohexa-2,5-dienones (IV), which are formed *via* the corresponding hydroperoxides (V).

In the catalysed autoxidation of phenols, diphenoquinones, benzoquinones, and polyphenylene ethers can be selectively prepared by an appropriate choice of catalyst, solvent, and starting material.[1–3] The autoxidation of *p*-unsubstituted phenols in the presence of a cobalt(II) complex, Salcomine (I), giving the corresponding *p*-benzoquinones,[2,3] drew our particular attention, because two moles of (I) form a quite stable complex with one mole of oxygen. We now have found that di-(3-salicylideneaminopropyl)aminecobalt(II) (II), an oxygen carrier which forms a complex with one mole of oxygen,[4] also acts as a homogeneous catalyst for the oxidation of phenols with molecular oxygen in organic media, and that the catalytic autoxidation of 4-alkyl-2,6-di-t-butylphenols (III) results in selective introduction of oxygen at the *p*-position to give the corresponding *p*-quinol (IV) in good yield. This provides a convenient method for the preparation of *p*-quinols.

When oxygen was bubbled through a solution of 2,6-di-t-butyl-*p*-cresol (III; R = Me; 8 mmoles) and (II) (3·6 mmoles) in methanol (300 ml) at room temperature until the starting phenol was completely consumed (20 hr.), 2,6-di-t-butyl-4-hydroxy-4-methylcyclohexa-2,5-dienone (IV; R = Me)[5] was obtained in 96% yield. Under similar conditions[6] 2,4,6-tri-t-butylphenol (III; R = Bu^t) gave 2,4,6-tri-t-butyl-4-hydroxycyclohexa-2,5-dienone[7] (IV; R = Bu^t; 60%), an *o*-benzoquinone (V; 6%), and the starting phenol (5·4%).

Although 2,6-di-t-butyl-4-hydroperoxy-4-methylcyclohexa-2,5-dienone (VI; R = Me)[5b] was stable to methanol and to the conditions employed for working-up the reaction mixture from (III; R = Me), it was quantitatively reduced to the corresponding quinol (IV; R = Me) in the presence of cobalt complex (II) in methanol. The catalytic autoxidation of (III; R = Me) with (II) in chloroform or benzene resulted in the formation of a complex mixture of products which showed the same t.l.c. pattern as that of products obtained by treatment of hydroperoxide (VI) with (II) in chloroform or benzene. These results indicate that (III) is first oxidized to (VI) which in turn is reduced in the presence of (II) in methanol to form (IV).


(I)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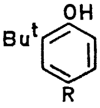
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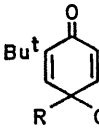
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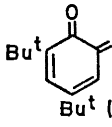
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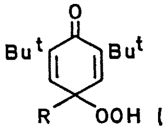
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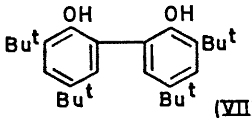
(VII)

The catalysed autoxidation of various phenols with (II) was also carried out in methanol. 2,4-Di-t-butylphenol gave a dimer (VII; 20%), (V; 9·2%), and the starting phenol (70%) after 70 hr 4-Bromo-2,6-di-t-butylphenol (III, R = Br) gave 4 4,4′,4′-tetra-t-butyldiphenoquinone (22%) with the starting phenol recovered (78%) after 140 hr Monoalkylated phenols and 2,6-di-t-butylphenols bearing an electron-withdrawing group (III, R = CN, CHO, or CO_2Et) resisted autoxidation The catalysed autoxidation of (III, R = Me or Bu^t) with Salcomine (I) gave neither quinols (IV) nor hydroperoxides (VI), but unusual products whose structures are currently being investigated

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[1] A S Hay, *U S P* 3 210,384 (1965) (*Chem Abs* 1966 **64** 17494b), A S Hay *Adv Polymer Sci* , 1967 **4** 496, G F Endres and J Kwiatek *J Polymer Sci* , 1962 **58** 593, A Rieche B Elschner and M Landbeck *Angew Chem* , 1960 **72** 385, H Musso, *Angew Chem Internat Edn* 1963 **2** 723, W A Waters Mechanisms of Oxidation of Organic Compounds ' Methuen, London, 1964, W Brackman and E Havinga *Rec Trav chim* 1955 **74**, 937

[2] H M van Dort and H J Geurson *Rec Trav chim* 1967 **86** 520

[3] L H Vogt jun J G Wirth and H L Finkbeiner, *J Org Chem* 1969 **34** 273

[4] R H Bails and M Calvin *J Amer Chem Soc* 1947 **69** 1886, L H Vogt jun *Chem Rev* , 1963 **63** 269

[5] (a) M S Kharasch and B S Joshi *J Org Chem* 1957 **22** 1439, (b) T Matsuura K Omura and R Nakashima *Bull Chem Soc Japan* 1965 **38** 1358

[6] A solution of (III, R = Bu^t, 8 mmoles) and (II, 1 6 mmoles) in methanol (250 ml) was bubbled with oxygen for 25 hr

[7] T Matsuura and K Ogura, *Tetrahedron* 1968 **24** 6167