Tetrahedron Letters,Vol.27,No.20,pp 2303-2306,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

SYNTHESIS OF BENZOFURANS, INDOLES AND BENZOPYRANS VIA OXIDATIVE FREE RADICAL CYCLISATIONS USING COBALT SALEN COMPLEXES.

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Summary: Reactions between the Co(I) species derived from cobalt(III) 'salen'(1), and (*O*-allyl) or (*O*-but-3-enyl) iodophenol, leads to isolatable cobalt complexes, *viz* (2), (13), which can be converted into substituted benzofurans, *i.e.* (5), (6) and benzopyrans, *i.e.* (14), (15); similarly interaction between (18) and Co(I) 'salen' led, in one step, to the 3-methylindole(19).

Interest in synthetic applications of free radical mediated carbon-to-carbon bond forming reactions has intensified enormously in recent years. Perhaps nowhere has the use of free radical intermediates been better exploited than in the synthesis of ring compounds[1]. The versatility of radical cyclisations would be enhanced still further if practical procedures could be made available to introduce functionality during the cyclisations by use of appropriate radical trapping reagents. This general problem has been addressed by ourselves[2] and by others[3], and in the previous *Letter* we illustrated the use of cobalt(I) reagents [from cobaloximes and Vitamin B_{12}] in the synthesis of functionalised butyrolactones by oxidative free radical cyclisations.[2] In this *Letter*, we show further scope for oxidative free radical cyclisations *via* Co(I) complexes in synthesis, with the preparation of a range of ring-fused benzoheterocycles by intramolecular cyclisation from the corresponding aryl halides in the presence of the cobalt 'salen' complex(1).

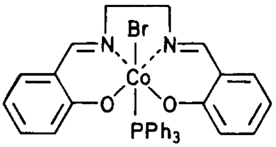
Addition of the black crystalline cobalt(III) salen reagent(1)[4] to a suspension of 1% sodium amalgam in tetrahydrofuran under argon[5], followed by catheter transfer, produced an emerald green solution of the corresponding Co(I) reagent. Introduction of (*O*-allyl)iodophenol(0.5 equivs), at 25°C in the dark under argon, resulted in immediate discharge of the emerald green colour and the production of the new cobalt complex (2; 65%). This cobalt complex(2), which can be obtained as brown crystals m.p.77-9°($CHCl_3$-petrol)[6], results from Co(I)-mediated aryl radical cyclisation followed by trapping of the product radical centre(3), *in situ*, with Co(II). Irradiation of a solution of (2) in dichloromethane, using light from a 100W Hg lamp and in the presence of oxygen(2h) then produced the corresponding peroxy cobalt complex(4), (unstable brown solid)[7] which was immediately reduced ($NaBH_4$, aq.NaOH,MeOH) to provide the carbinol(5) in 25% overall yield[8].

Irradiation of a solution of (2) in benzene under an atmosphere of nitrogen, followed by chromatography, led to the benzofuran(7). The benzofuran results from β-elimination in (2)(to 6) followed by isomerisation, either *in situ* or on chromatography. Interestingly, the heterocycle(6) alone was produced when (*O*-allyl)iodophenol was treated with Co(I) salen under normal laboratory light conditions. In addition, a mixture of (6) and (7), together with a small amount of an unstable complex tentatively assigned as (9), was obtained when (*O*-propargyl)iodophenol interacted with the Co(1) species derived from (1). Attempts to effect radical cyclisations from (*O*-allyl)iodophenol using alternative Co(1) reagents, *i.e.* from cobaloximes and cobalamins, were unsuccessful. This observation is consistent with the known reduced nucleophilicity of these reagents over the corresponding species derived from cobalt 'salen' complexes[9].

When a suspension of a catalytic amount (5%) of the cobalt 'salen' reagent(1) and (*O*-allyl)iodophenol in tetrahydrofuran was treated with sodium amalgam, only the product(10) resulting from reduction was isolated (~30%). The same compound(10) was also produced (~45%) when (*O*-allyl) iodophenol was electrolysed in methanol at -2.2V. In addition, electrolysis of (*O*-allyl)iodophenol in the presence of cobalt salen(1; 10%) led to the benzohydrofuran(11)(32%). 3-Methylbenzodihydrofuran(11) and its analogues can be obtained more conveniently and in higher yields by treatment of (*O*-allyl)iodophenols with tributyltin hydride[10].

By similar methods to those described above, reaction between the (*O*-butenyl)iodophenol(12*a*) and cobalt 'salen' led to the brown cobalt complex(13)(42%), m.p. 79-82°(decomp.) which could be converted into the 4-methylchromene(14) and the carbinol(15). A small amount of the product(12*b*) of reduction of (12*a*) by Co(1) salen was also separated by chromatography, and interestingly only the products of reduction *viz* (16*b*) and (17*b*) were isolated when the corresponding iodo ethers (16*a*) and (17*a*) were treated with Co(1) salen. Finally, further scope for the aforementioned oxidative free-radical cyclisations using cobalt 'salen' was demonstrated when it was found that the (N-allyl)N-methyliodoaniline(18) gave 3-methylindole(19) in one step (32%) on treatment with (1) and sodium amalgam[11].

We thank the S.E.R.C. for a studentship (to V.P.), and May and Baker Ltd. for financial support (CASE award to V.P.).



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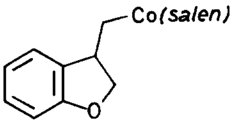

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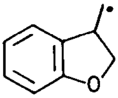

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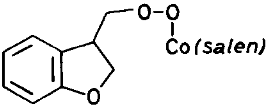

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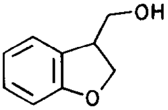

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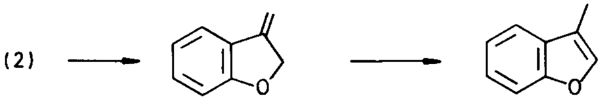

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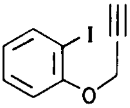

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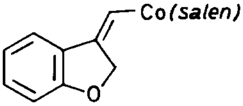

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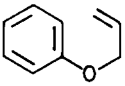

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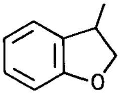

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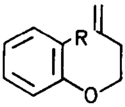

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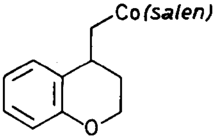

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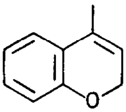

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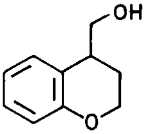

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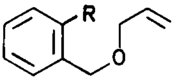

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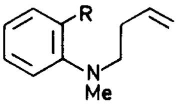

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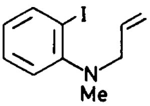

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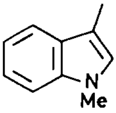

(19)

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(Received in UK 21 February 1986)