Cobalt-mediated Radical Reactions in Organic Synthesis. Oxidative Cyclisations of Aryl and Alkyl Halides leading to Functionalised Reduced Heterocycles and Butyrolactones

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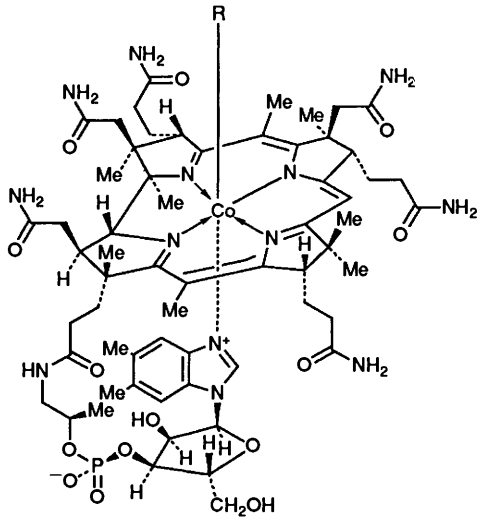
Reactions between the Co' species derived from cobalt(III) salen (**11**) or cobalt(II) salophen (**12**) and (*O*-allyl) or (*O*-but-3-enyl) iodophenols lead to isolatable cobalt complexes, *viz.* (**16**) and (**27**), which can be converted into substituted benzofurans, *i.e.* (**17**) and (**23**), and benzopyrans, *i.e.* (**28**) and (**34**); similarly, interaction between compound (**36**) and Co' salen led in one step to 1,3-dimethylindole (**37**). Radical cyclisation of the acetal (**38a**) in the presence of Co' cobaloxime [from (**10**)] leads to the *cis*-ring-fused alkyl cobalt complex (**42**), which can be converted in a preparative manner into lactone (**44**) following 1,2-elimination [to (**43**)] and hydrolysis/oxidation, and into lactone (**53**) following insertion of molecular oxygen [to (**50**)], reduction [to (**51**)] and hydrolysis/oxidation.

Cobalt is the 'core' transition metal in vitamin B_{12}, or cyanocobalamin (**1a**).[1] Vitamin B_{12} is essential in the nutrition of humans, and it plays a crucial role in the important biochemical reactions whereby fats, proteins, and carbohydrates are used to produce energy in living cells. The biochemically active form of B_{12} is adenosylcobalamin or coenzyme B_{12} (**1b**) which contains an adenosyl moiety bonded covalently through its 5'-carbon to the cobalt atom in the corrinoid. Coenzyme B_{12} orchestrates a range of subtle molecular rearrangements *in vivo*, in which a group X in a substrate migrates to an adjacent carbon centre at the same time as a hydrogen atom migrates from the adjacent carbon to the one where the X-group was originally bonded. The mechanisms of these coezyme B_{12}-dependent reactions have been studied in immense detail. These investigations have demonstrated the enzyme reactions are triggered by homolytic cleavage of the carbon-to-cobalt bond in the coenzyme, leading initially to a methylene radical of deoxyadenosine together with a Co^{II} species. The adenosyl radical then abstracts an H-atom from the substrate producing a new carbon-centred free radical and deoxyadenosine. Rearrangement of radical (**2a**) to radical (**2b**) (Scheme 1), followed by re-abstraction of an H-atom from deoxyadenosine, finally completes the sequence of events resulting in overall 1,2-shift *via* radical intermediates.[2]

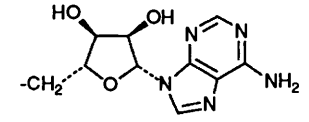
Studies of the mode of action of coenzyme B_{12} have told synthetic chemists two principal things: (i) cobalt forms weak ($\sim$20–30 kcal mol^{-1})† covalent bonds to carbon, leading to relatively stable organocobalt compounds, and (ii) homolysis (heat or *hν*) of these organocobalt molecules provides a rich source of carbon radicals.[3] With this information it was our contention that single-electron transfer from a nucleophilic Co^{I}-reagent to the C–X bond in a substrate (**3**) should lead to the carbon-centred radical (**4**) or to the corresponding organocobalt precursor molecule (**6**). The radical should then undergo addition to an appropriate double bond leading to a new product-radical centre (**5**) and this centre might then be trapped by Co^{II} (generated in the initial redox reaction) leading to the cobalt-functionalised molecule (**7**). Subsequent homolysis of the carbon-to-cobalt bond in intermediate (**7**) in the presence of radical-trapping agents could then be used to introduce a variety of functionality at the product radical centre, *i.e.* leading to products (**8**). In an intramolecular operation this sequence of events could lead to the formation of cyclic molecules with simultaneous incorporation of functionality (Scheme 2). The



(1)

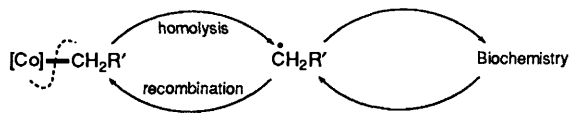
a; R = CN

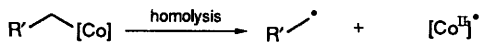
b; R =

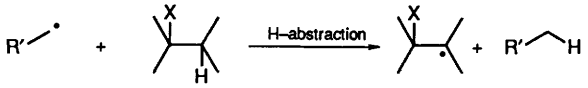


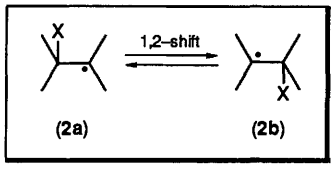
feasibility of these simple propositions forms the basis of this paper and the accompanying papers.[4] In this paper we describe methods for achieving oxidative free radical cyclisations of alkyl and aryl halides by means of cobalt(I) reagents, leading to cobalt-functionalised reduced heterocycles and 5-membered-ring lactones.[5] In the accompanying papers we show how the intermediate organocobalt complexes can be used to synthesize oxygen-, nitrogen-, halogen-, sulphur-, and selenium-substituted adducts,[6] and also to elaborate new alkene

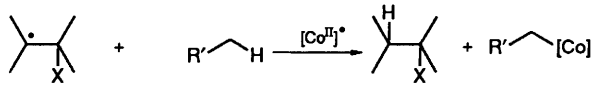
† 1 cal = 4.184 J.



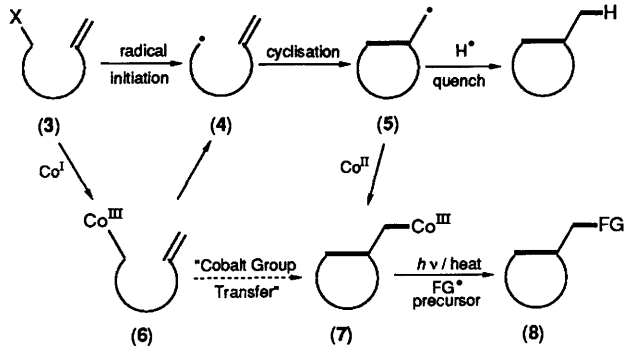








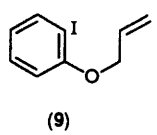
Scheme 1.



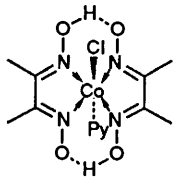
Scheme 2.

products *via* novel intermolecular radical addition–elimination reactions to deactivated carbon-to-carbon double bonds.[7]

The feasibility of using cobalt-mediated radical cyclisation reactions accompanied by quenching of the product radical centre leading to cobalt-substituted cyclic molecules was first investigated using the simple substrate allyl 2-iodophenyl ether (**9**). Some precedent for carrying out similar cyclisation reactions from alkyl halides in the presence of reduced vitamin B_{12} and its analogue dimethylglyoxime (**10**) was available from the earlier investigations by Scheffold[8] and by Tada[9] respectively. Accordingly the iodide (**9**) was treated separately with reduced vitamin B_{12} and cobaloxime(I), but in both instances only starting material was recovered unchanged. We concluded that neither of these cobalt(I) species was a sufficiently powerful electron-transfer (*i.e.*, reducing) agent for the aryl system, and therefore turned to the more nucleophilic cobalt(I) species derived from bromotriphenylcobalt(III) salen (**11**)[10] and cobalt(II) salophen (**12**).[11]

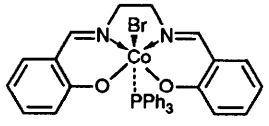


(9)



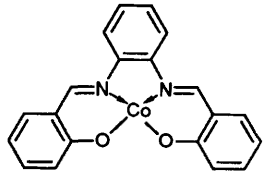
Cobaloxime

(10)



$BrCo^{III}(salen)PPh_3$

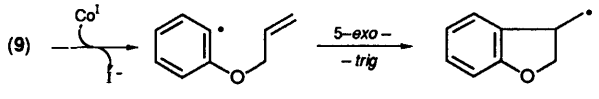
(11)



Co^{II}(salophen)

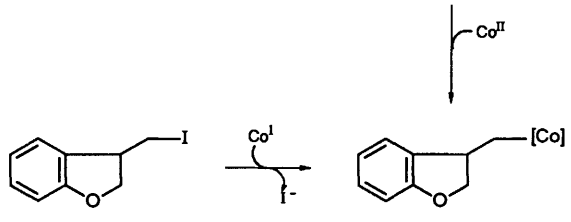
(12)

Thus, addition of the black, crystalline cobalt 'salen' reagent (**11**) to a suspension of 1% sodium amalgam in tetrahydrofuran (THF) under argon, followed by catheter transfer, produced an emerald green solution of the corresponding Co^{I} reagent. Introduction of allyl 2-iodophenyl ether (**9**) at 25 °C in the dark under argon, resulted in immediate discharge of the emerald green colour and the production of a new cobalt salen complex as brown crystals in 65% yield. The new stable complex produced a deep green colour in either chloroform or dichloromethane, which is a characteristic feature of five-coordinate alkylcobalt(III) salen complexes, and showed spectroscopic data consistent with the structure (**16a**). In a similar manner, treatment of the aryl iodide (**9**) with sodium cobalt(I) salophen, prepared by reduction of compound (**12**) with 1% sodium amalgam, produced the corresponding dihydrobenzofuran* cobalt(III) salphen complex (**16b**) as a stable, black, crystalline solid. The salophen complex (**16b**) was identical with an authentic sample prepared by reaction between sodium cobalt(I) salophen and the known 2,3-dihydro-3-(iodomethyl)-benzofuran (**15**).[12]



(13)

(14)



(15)

(16)

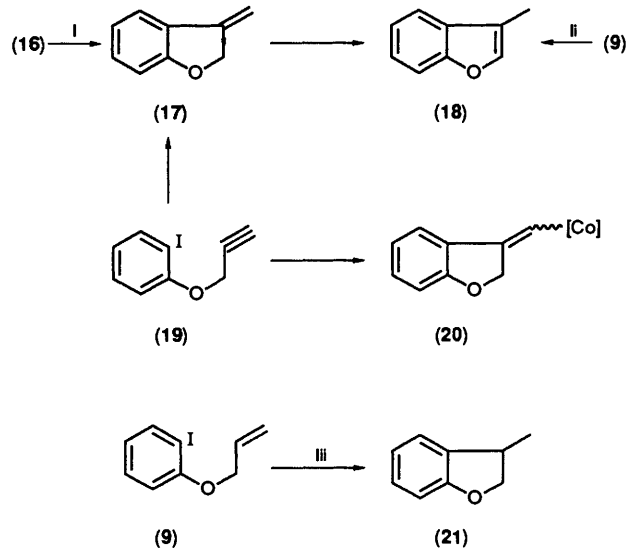
a; [Co] = Co(salen)
b; [Co] = Co(salophen)py

The formation of the complexes (**16a**) and (**16b**) from the iodide (**9**) in the presence of the cobalt(I) reagents is rationalised

* Throughout this paper, benzofuran refers to benzo[*b*]furan.

on the basis of initial electron transfer from the corresponding Co^{I} species to the carbon-to-iodine bond in compound (**9**), followed by loss of the iodide ion leading to an intermediate σ-aryl radical (**13**). 5-*exo*-Trigonal closure onto the proximate olefinic bond in radical (**13**) then produces the product radical (**14**), which is trapped by Co^{II}, leading to the observed products (**16a**) and (**16b**).

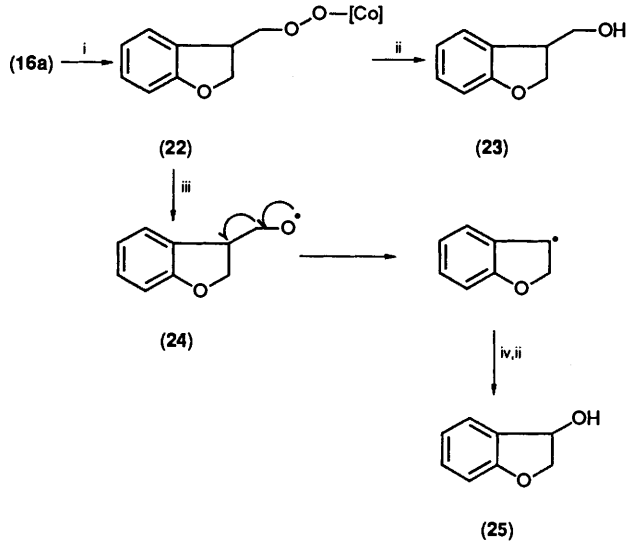
In each of the cyclisations (**9**) ⟶ (**16**) in the presence of reduced complexes (**11**) and (**12**), small amounts of the alkene (**17**), resulting from *in situ* β-elimination of Co–H from the product cobalt complexes, were produced concurrently. Indeed, when solutions of compounds (**16a**) or (**16b**) in benzene or dichloromethane were exposed to light from a 300 W sunlamp or when they were heated under reflux, the only product isolated was the unstable olefin (**17**), which on work-up and chromatography isomerised quantitatively to 3-methylbenzofuran (**18**). Furthermore, the heterocycle (**18**) alone was produced when the aryl iodide (**9**) was treated with Co^{I} salen under normal laboratory light conditions. In addition, a mixture of isomers (**17**) and (**18**), together with a small amount of an unstable complex, tentatively assigned structure (**20**), was obtained when the (*O*-propargyl)iodophenol (**19**) reacted with the Co^{I} species derived from complex (**11**).



Reagents and conditions: i, heat or *hv*; ii, Co^{I}, *hv*; iii, cat. Co^{I}.

Although the use of vitamin B_{12} as an efficient radical initiator has found many applications in electro-organic synthesis,[8] to our knowledge there have been no reports of intramolecular aryl radical cyclisations catalysed by the vitamin. We found that catalytic amounts of Co^{I} salen could be generated at a mercury pool cathode, when a potential of −1.8 V (*vs.* $AgNO_3$) was applied across the electrode of an H-cell containing a solution of complex (**11**) and lithium chlorate in methanol–pyridine as the electrolyte. Addition of the aryl iodide (**9**) followed by electrolysis for 12 h then led to the dihydrobenzofuran (**21**) as the sole product. 3-Methylbenzodihydrofuran (**21**) and its analogues can be obtained more conveniently and in higher yields by treatment of (*O*-allyl)-iodophenols with tributyltin hydride.[13]

In experiments designed to demonstrate further scope for the cobalt-mediated radical initiation–cyclisation–trapping sequence leading to functionalised reduced heterocycles in synthesis, we also examined the interaction between the cobalt complex (**16a**) and molecular oxygen. Thus, when a solution of complex (**16a**) in dichloromethane was irradiated in the presence of oxygen, using light from an ordinary 100 W sunlamp, work-up and chromatography led to the unstable peroxycobalt complex (**22**).[14] Reduction of complex (**22**) using alkaline sodium borohydride then provided the corresponding alcohol (**23**)[15] whose formation was accompanied by that of the alcohol (**25**), which presumably results from a fragmentation reaction *via* the alkoxyl radical (**24**) produced by homolysis of the peroxy complex (**22**).

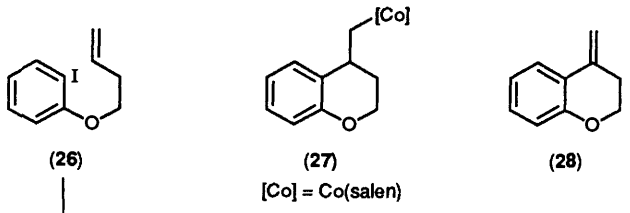


Reagents and conditions: i, *hv*, $^3O_2$; ii, $NaBH_4$; iii, heat; iv, $^3O_2$.

In order to evaluate the use of the cobalt-mediated cyclisation sequence (Scheme 2) in the formation of aryl-fused six-membered *O*-heterocycles, we next examined the cyclisation of the (*O*-butenyl)iodophenol (**26**). Thus, addition of substrate (**26**) to a solution of sodium cobalt(I) salen, in the usual manner, led to the slow discharge of the green colour of the Co^{I} species, and work-up produced dark green crystals of the expected dihydrobenzopyran cobalt(III) complex (**27**) in 45% yield. The alkene (**28**) resulting from *in situ* β-elimination from complex (**27**) together with the butenyl ether (**29**) produced by reduction of the aryl iodide (**26**), accompanied the formation of complex (**27**). The competitive formation of the ether (**29**) could well occur *via* an intramolecular H-abstraction sequence, and demonstrates that the 6-*exo*-cyclisation leading to complex (**27**) occurs far less readily than the aforementioned 5-*exo*-cyclisation synthesis of complex (**16**). Perhaps not too surprising therefore, neither the nitrogen analogue (**30a**) or (**26**) or the allyl ether isomer (**31a**) of (**26**) underwent cyclisation, and only their product of reduction, *i.e.*, (**30b**) and (**31b**), were observed on treatment of these substrates with Co^{I} salen. In addition, we were only able to observe the products of reduction (**32b**) and (**33b**) from treatment of the corresponding aryl iodides (**32a**) and (**33a**) respectively with Co^{I} salen.

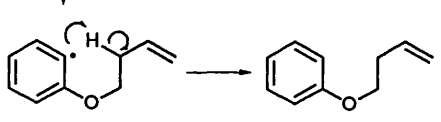
By similar methods to those described for the dihydrofurylmethylcobalt (**16**), irradiation of the dihydropyran cobalt complex (**27**) in the presence of oxygen, followed by reduction of the resulting peroxycobalt, with alkaline borohydride, led to a mixture of the known alcohols (**34**) and (**35**). Finally, further scope for the aforementioned oxidative free-radical cyclisations using cobalt 'salen' was demonstrated when it was found that *N*-allyl-2-iodo-*N*-methylaniline (**36**) gave 1,3-dimethylindole (**37**), in one step, on treatment with compound (**11**) and sodium amalgam.[16]

The aforementioned syntheses of reduced heterocycles fully vindicated the earlier supposition that their preparations can be achieved *via* oxidative free-radical cyclisations using nucleophilic cobalt(I)-reagents (*i.e.*, Scheme 2). As shown, in one

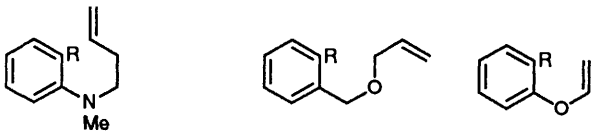


(26) (27) (28)

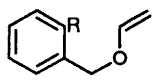
[Co] = Co(salen)



(29)



(30) (31) (32)



(33)

a; R = I
b; R = H

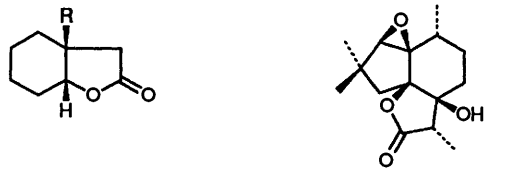
(34) (35)

(36) (37)

procedure the method leads *via* hydrogen-atom loss (*viz.* dehydrocobaltation) to an alkene at the product radical centre. The second method leads, through isolable alkyl and alkylperoxycobalt intermediates, to a hydroxy-group substituent at the same product radical centre. By using a combination of these methods we have also been able to develop novel approaches to the synthesis of γ'-hydroxy-γ-butyrolactone units, *viz.* (**53**), which are present in a range of biologically active natural products. These studies will now be described.

Earlier work by Stork *et al.*[17] has demonstrated that reductive cyclisation of the bromo acetal (**38a**) derived from cyclohex-2-enol in the presence of tributyltin hydride leads to high yields of the *cis*-fused adduct (**39a**), which by hydrolysis and oxidation produces the butyrolactone (**40a**). Later work by ourselves showed that the same general chemistry, using the corresponding enol ether (**38b**), provides an expeditious synthesis of the β-oxy-γ-butyrolactone unit (**40b**) present in

(38) (39)

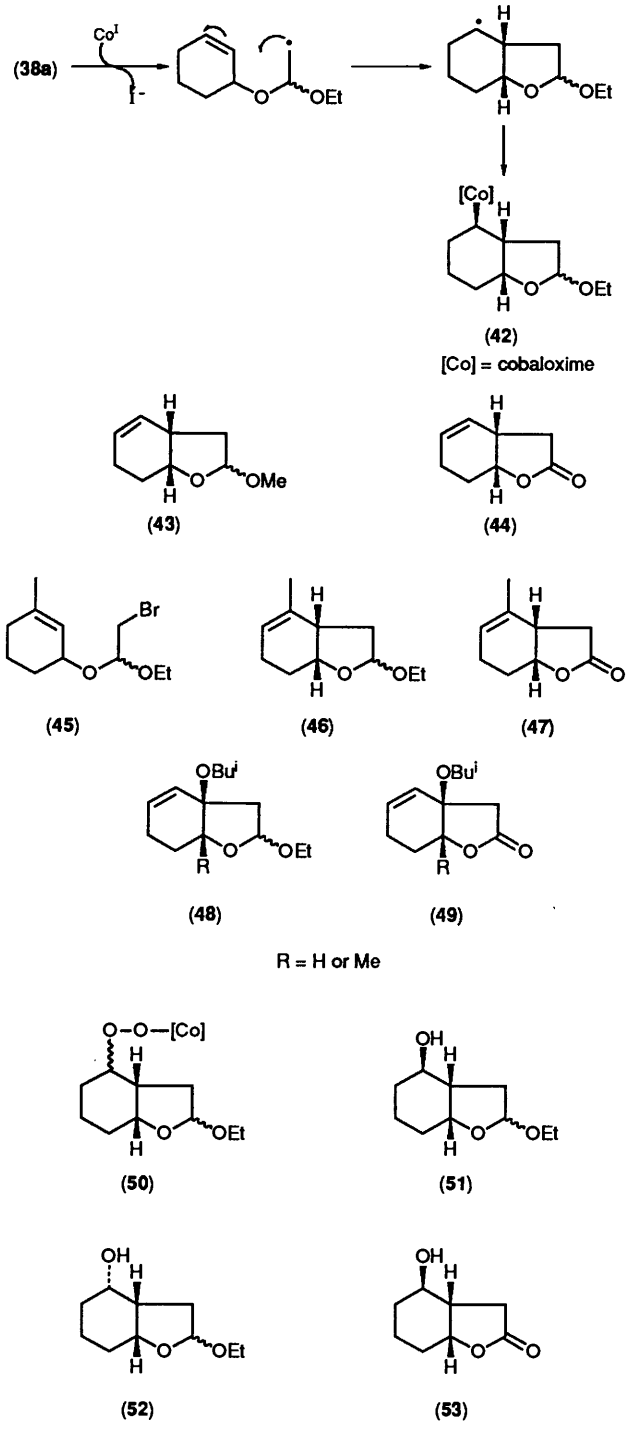


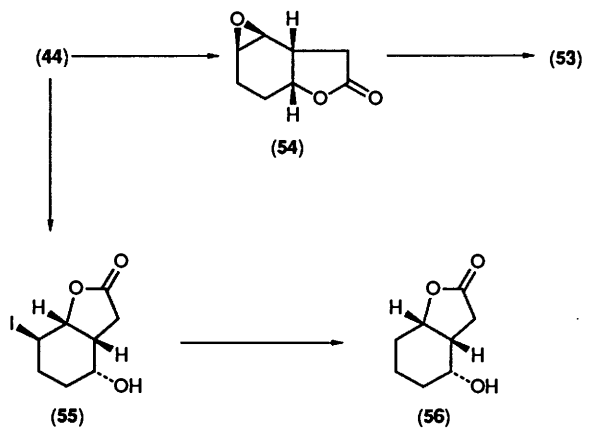
(40) (41)

a; R = H
b; R = Oalkyl

alliacolide (**41**) and related natural products.[18] We have now found that treatment of the acetal (**38a**) under catalytic conditions (~10%) with the Co^{I} species generated by electrochemical reduction of the cobaloxime (**10**) produces a good yield (60–70%) of the *cis*-fused adduct (**43**) containing unsaturation in the six-membered ring. This product, like the alkene (**16**), results from the now familiar sequence of: (i) radical initiation, (ii) 5-*exo*-trig radical cyclisation, (iii) trapping of the product radical centre by Co^{II}, leading to the cobalt complex (**42**), and (iv) dehydrocobaltation (β-elimination). The same product (**43**) can also be produced from the acetal (**38a**) in similar yields, under identical conditions using vitamin B_{12}, but alternative reducing conditions; *e.g.*, ZnHg, aq. MeOH; Zn, aq. MeOH; $NaBH_4$, NaOH, MeOH, using either vitamin B_{12} or the cobaloxime (**10**) led to the unsaturated acetal (**43**) contaminated with small amounts (~20%) of the corresponding *trans*-fused adduct. Hydrolysis and oxidation of the acetal (**43**) in the presence of Jones' reagent then provided the known unsaturated lactone (**44**).[19] In a similar manner, using Co^{I}-catalytic procedures, cyclisation of the bromo acetal (**45**) led almost exclusively to the *endo*-unsaturated acetal (**46**), which could be converted into the lactone (**47**). These observations are consistent with our earlier finding that treatment of the enol ether bromo acetals (**38b**) with the cobalt(I)-reagent generated from compound (**10**) ($NaBH_4$, aq. NaOH), followed by oxidation of the intermediates (**48**), leads to the corresponding unsaturated β-oxy-γ-butyrolactones (**49**) in good overall yields.[18]

When the bromo acetal (**38a**) was treated with cobalt^{I} (1.2 mol equiv.) generated from complex (**10**), chromatography separated the alkylcobaloxime (**42**) (60%) as a heat- and light-sensitive orange powder. Irradiation of the alkylcobaloxime (**42**) in acetonitrile in the presence of oxygen under the same conditions used for photoreaction of complex (**16a**) then led to the corresponding alkylperoxycobalt complex (**50**), which after reduction with sodium borohydride provided a mixture (*ca.* 2:1) of the β- and α-secondary alcohols (**51**) and (**52**). Hydrolysis and oxidation of the β-isomer (**51**) under Grieco's conditions [*m*-chloroperbenzoic acid (MCPBA) in the presence of catalytic boron trifluoride][20] then produced the known β-hydroxy lactone (**53**).[21] The same β-hydroxy lactone (**53**) was also produced from the alkene (**44**) following epoxidation to (**54**) and reduction with sodium cyanoborohydride. Finally, to complete the correlation, the known isomeric α-hydroxy lactone (**56**)[19a] was also prepared from the alkene (**44**) following saponification (aq. NaOH), iodolactonisation (KI, I_2), and reduction of the resulting iodide (**55**) (Bu_3SnH) according to the methods described earlier by Grieco *et al.*[19a]





Experimental

General Details.—M.p.s were recorded on a Kofler hot-stage and are uncorrected. Kugelrohr bulb-to-bulb distillations were performed on a Büchi GKR-50 rotating bulb apparatus. IR spectra were recorded on a Philips PU9706, or a Pye-Unicam SP3-100 spectrometer. Samples were analysed either as thin liquid films on sodium chloride discs (for oils), or as KBr discs, or as solutions in the stated solvent. UV absorption spectra were obtained on a Pye-Unicam SP1700 spectrophotometer for dilute solutions in ethanol.

^{1}H NMR spectra were routinely recorded as pulsed Fourier transform spectra on a Bruker WP80SY PFT spectrometer at 80 MHz. Alternatively, spectra were obtained on a Bruker WM250 PFT or a Bruker AM400 PFT spectrometer at 250 MHz and 400 MHz, respectively, as stated. ^{13}C NMR spectra were also recorded on these Bruker instruments at 20.15 MHz, 60.90 MHz, or at 100.62 MHz respectively as stated. All NMR spectra were obtained for dilute solutions in deuteriochloroform containing tetramethylsilane (TMS) as internal standard, unless otherwise stated, and chemical shifts (δ) are reported downfield from TMS. Line separations (J) are given in Hertz; app refers to apparent multiplicity; except where J modulated spin echo or distortionless enhancement by polarisation transfer (DEPT) pulse sequences have been used in conjunction with broad-band decoupled ^{13}C NMR. In these cases, the number of hydrogen atoms attached to a specific carbon atom can be determined, and are recorded as such.

Mass spectra were recorded on a AEI MS902, or on a VG 7070E instrument using positive electron impact (EI) (ionisation at 70 eV) or fast-atom bombardment (FAB) (thioglycerol or *m*-nitrobenzyl alcohol matrix) techniques. Microanalyses were performed using a Perkin-Elmer 240B elemental C, H, N, analyser. The halogens and sulphur were analysed using Schoniger oxygen flask methods.

The phrases 'evaporated *in vacuo*,' or 'evaporated under reduced pressure' refer to the removal of volatile organic solvents by evaporation at 11 mmHg pressure on a Büchi Rotavapor followed, in the case of non-volatile solids or viscous oils, by evaporation at 0.05 mmHg as appropriate ('*in vacuo*'). All hydrocarbon solvents and dichloromethane for column chromatography were redistilled before use, and light petroleum refers to that fraction boiling in the range 40–60 °C. Silica refers to Kieselgel 60 (230–400 mesh), used for performing column chromatography. Analytical TLC was performed on Polygram SIL G/UV$_{254}$ plastic-backed plates, which were visualised with UV light (254 nm), and then developed with basic potassium permanganate reagent. THF was freshly distilled from sodium wire before use. All other solvents and reagents were purified according to literature procedures, and freshly dried, anhydrous solvents were stored over activated molecular sieves and under nitrogen immediately prior to use. Photolytic reactions were performed using a simple KL 2866 Philips Ultraphil 300W health lamp, with a tungsten filament.

Precursors for Oxidative Free Radical Cyclisations.—The following compounds were synthesized according to literature procedures: allyl 2-iodophenyl ether (**9**) had b.p. 110–120 °C/0.2 mmHg (Kugelrohr) (lit.,[13a] 141–144 °C/18 mmHg); bromotriphenylphosphine cobalt(III) salen (**11**) recrystallised

from ethanol as a black, crystalline solid; m.p. 150–151 °C (lit.,[10c] 151–152 °C); cobalt(II) salophen (**12**) was produced as a black, crystalline solid according to the method of Costa;[11] but-3-enyl 2-iodophenyl ether (**26**) had b.p. 150–155 °C/15 mmHg (Kugelrohr) (lit.,[13a] 146–148 °C/13 mmHg); *N*-allyl-2-iodomethylaniline (**36**) had b.p. 83–85 °C/20 mmHg (lit.,[13a] 108–110 °C/4.5 mmHg); 2-iodophenylpropargyl ether (**19**) showed ν_{max}(film) 2 130w cm^{-1}; δ_H 7.83–6.63 (m, 4 × ArH), 4.7 (d, *J* 2.4 Hz, OCH_2), and 2.5 (t, *J* 2.4 Hz, ≡CH) which data were consistent with the literature;[22] *N*-but-3-enyl-2-iodo-*N*-methylaniline (**30a**) showed δ_H 7.9–6.7 (m, 4 × ArH), 5.8 (m, CH=), 5.0 (m, $=CH_2$), 3.00 (app. t, *J* 7.1 Hz, CH_2NMe), 2.7 (NMe), and 2.3 (m, CH_2C=), consistent with literature data;[13a] allyl *o*-iodobenzyl ether (**31a**) had b.p. 92–94 °C/0.65 mmHg (lit.,[13a] 116–118 °C/3.6 mmHg); *o*-Iodophenyl vinyl ether (**32a**) showed δ_H 7.8–6.7 (m, 4 × ArH), 6.5 (dd, *J* 6.1 and 13.7 Hz, CH=), 4.7 (dd, *J* 1.9 and 13.7 Hz, =C*H*H), and 4.5 (dd, *J* 1.9 and 6.1 Hz, =CH*H*), consistent with literature data;[13a] *o*-iodobenzyl vinyl ether (**33a**) showed δ_H 7.9–6.8 (m, 4 × ArH), 6.6 (dd, *J* 7 and 14 Hz, OCH=), 4.7 (CH_2), 4.32 (dd, *J* 7 and 2.5 Hz, =C*H*H), and 4.1 (dd, *J* 14 and 2.5 Hz, =CH*H*), consistent with literature data.[13a]

Sodium Cobalt(I) N,N′-1,2-*Ethylenebis*(*salicylideimine*) ($NaCo^I$ *Salen*).[10c]—Bromotriphenylphosphine cobalt(III) salen complex (**11**) (1.34 g, 2.00 mmol) was added all at once to sodium amalgam (1%; 20 g) under dry, deoxygenated THF (130 ml) at room temperature, under argon, and the mixture was then stirred for 1.5 h. During this period of time, the colour of the suspension changed from black through light brown and dark brown to emerald green. The mixture was stirred at 25 °C until all the colour of the brown suspension was reduced to give the green solution of $NaCo^I$ salen, and was then transferred by cannulation into a clean flask, under argon. The sodium cobalt(I) salen solution could be stored at 25 °C for several hours under an inert gas (nitrogen or argon).

(2,3-*Dihydrobenzofuran*-3-*yl*)*methylcobalt*(III) *Salen* (**16a**) *and* 2,3-*Dihydro*-3-*methylenebenzofuran* (**17**).—A solution of allyl 2-iodophenyl ether (260 mg, 100 mmol) in dry deoxygenated THF (5 ml) was added during 5 min to a stirred solution of the sodium cobalt(I) salen reagent (2.00 mmol) in dry, deoxygenated THF (125 ml) at 25 °C under nitrogen. The emerald green solution of the $NaCo^I$ salen reagent in THF rapidly changed to brown, and the mixture was stirred at 25 °C under nitrogen and in the dark for 14 h. The solvent was removed *in vacuo* (dark; < 30 °C), and the resulting residue was then diluted with water (100 ml) and extracted with diethyl ether–light petroleum (1:1; 5 × 20 ml). Evaporation of the dried ($MgSO_4$) extracts *in vacuo* followed by microdistillation of the residue (Kugelrohr apparatus) gave the benzofuran (**17**) (23 mg, 18%) as an oil, b.p. 75–80 °C/12 mmHg; ν_{max} 1 640w cm^{-1}; δ_H 7.5–6.8 (m, 4 × ArH), 5.4 (t, *J* 3.2, =C*H*H), 5.1 (t, *J* 2.7, OCH_2), and 5.0 (m, =CH*H*) (Found: M^+, 132.0564. Calc. for C_9H_8O: *M*, 132.0575), which data were consistent with the literature.[23]

Further extraction of the aqueous phase with chloroform (5 × 30 ml) gave a dark green solution, which was dried ($MgSO_4$) and evaporated (dark; < 30 °C) to leave a brown residue. Chromatography [silica; (1:4) $CHCl_3$–EtOAc] gave the alkylcobalt(III) complex (**16a**) as a brown solid (296 mg, 65%), which was recrystallised from chloroform–light petroleum as black crystals, m.p. 77–79 °C (decomp.); ν_{max}($CHCl_3$) 1 605m, 1 440w, 1 310w, 1 120s, and 660s cm^{-1}; δ_H(400 MHz) 8.1 (CH=N), 7.9 (CH=N), 7.7–6.5 (m, 12 × ArH), 4.5 (t, *J* 9.2 Hz, OC*H*H), 4.3 (dd, *J* 6.6 and 9.5 Hz, OCH*H*), 4.0 (m, CH_2N), 3.7 (m, C*H*HN), 3.6 (m, CH*H*N), 3.2 (dd, *J* 6.3 and 2.9, C*H*HCo), 3.1 (dd, *J* 6.3 and 11.1 Hz, CH*H*Co), and 2.77 (m, ArC*H*); δ_C(100.62 MHz) (quaternary) 165.9, 165.8, 159.8, 128.1, 120.2, and 120.0; (CH_2) 79.0, 59.4, 58.9, and 21.0, and (CH) 164.7, 164.5, 134.1–109.4 (12 C), and 43.8; [*m*/*z* (FAB) 458 (M^+, 2%) and 279 (100). $C_{25}H_{23}CoN_2O_3$ requires *M*, 458].

o-(*Allyloxy*)*benzenediazonium Tetrafluoroborate*.—The diazonium salt was prepared according to the procedure described by Beckwith[12] and was obtained (61%) as crystals, m.p. 81–83 °C (from Et_2O–EtOH); ν_{max}(KBr) 3 400w, 2 250s, 1 590s, 1 565m, 1 490s, 1 300s, 1 265m, 1 070s, and 775m cm^{-1}; δ_H[$(CD_3)_2SO$] 8.5 (m, ArH), 8.2 (m, ArH), 7.7 (d, *J* 9 Hz, ArH), 7.4 (t, *J* 4 Hz, ArH), 6.1 (m, CH_2CH=), 5.4 (m, $=CH_2$), and 5.1 (d, *J* 3.5 Hz, OCH_2) [Found: C, 43.3; H, 3.7; N, 11.4%; *m*/*z* (FAB) $(M - BF_4)^+$ 161. Calc. for $C_9H_9BF_4N_2O$: C, 43.6; H, 3.7; N, 11.3%. $C_9H_9N_2O$ requires *M*, 161].

2,3-*Dihydro*-3-(*iodomethyl*)*benzofuran* (**15**).[12]—Sodium iodide (10.89 g, 0.0726 mol) was added portionwise to a solution of *o*-(allyloxy)benzenediazonium tetrafluoroborate (9.00 g, 0.0363 mol) in deoxygenated acetone (250 ml) at room temperature; a vigorous evolution of nitrogen ensued. The solution was then heated under reflux for 30 min, then evaporated *in vacuo*, diluted with water (200 ml), and extracted with diethyl ether (5 × 50 ml). The combined, dried ($MgSO_4$) extracts were evaporated *in vacuo* to leave an oil, which was then purified by passage through a short pad of silica (5 cm; light petroleum) to give the iodide (8.35 g, 88.5%) as an oil; ν_{max}(film) 2 900m, 1 600s, 1 580s, 1 460s, 1 320w, 1 160m, 1 100w, and 970 cm^{-1}; δ_H 7.2 (m, 2 × ArH), 6.8 (m, 2 × ArH), 4.6 (dd, *J* ~9.3 Hz, OC*H*H), 3.8 (m, ArC*H*), 3.5 (dd, *J* 4.4 and 9.9 Hz, C*H*HI), and 3.2 (dd, *J* ~9.9 Hz, CH*H*I); δ_c(20.1 MHz) 160.0 and 128.6 (C); 129.1, 124.2, 120.4, 110.1, and 44.6 (CH); 77.4 and 9.0 (CH_2) (Found: M^+, 259.9689. Calc. for C_9H_9IO: *M*, 259.9698).

(2,3-*Dihydrobenzofuran*-3-*yl*)*methylcobalt*(III) *Pyridine Salophen* (**16b**).—A solution of sodium borohydride (7.76 g, 0.21 mol) in water (10 ml) was added dropwise during 20 min to a stirred and cooled suspension (ice–H_2O) of cobalt(II)salophen (**12**) (18.60 g, 0.0499mol) in deoxygenated methanol (450 ml) under nitrogen. A vigorous evolution of gas was observed accompanied by the formation of a green mixture. The mixture was stirred at room temperature for a further 30 min, and then a solution of 2,3-dihydro-3-(iodomethyl)benzofuran (**15**) (11.79 g, 0.0454 mol) in deoxygenated methanol (5 ml) was added, in one aliquot, at room temperature. The green colour was almost immediately discharged and the mixture was stirred at 25 °C, under nitrogen and in the dark, for a further 22.5 h before being evaporated *in vacuo* (dark; < 30 °C) to one-third of its original volume and was then diluted with water (60 ml) whereupon a black solid precipitated. The precipitate was filtered off, then washed successively with (1:1) water–MeOH (2 × 10 ml) and diethyl ether (30 ml) and finally dried under high vacuum (25 °C; 0.05 mmHg; dark). Pyridine (300 ml) was added to the black solid (26.50 g) and the mixture was then filtered. Water was added (80 ml) to the filtrate and the solution was then kept at 25 °C in the dark for *ca.* 1 day. The solution was filtered and the insoluble solid was dried (25 °C; 0.05 mmHg; dark) to give the cobalt salophen complex (14.7 g, 55.4%) as a black, crystalline solid; m.p. 193–198 °C (decomp.); ν_{max}($CHCl_3$) 2 940s, 1 600s, 1 570s, 1 430s, 1 370s, 1 330s, 1 150s, 1 130s, 950s, and 920s cm^{-1}; λ_{max}(EtOH) 194 (ε 39.716) and 252 nm, (38.106); δ_H(250 MHz) 8.7 (CH=N), 8.6 (CH=N), 8.5 (m, 2 × pyH), 8.0–7.9 (m, ArH), 7.9–7.9 (m, ArH), 7.6 (tt, *J* 7.6 and 1.7 Hz, pyH), 7.4–7.2 (m, 8 × ArH and 2 × pyH), 7.0–6.9 (app. t, *J* 7.9 Hz, ArH), 6.9 (app. d, *J* 7.4 Hz, ArH), 6.7–6.6 (m, 4 × ArH), 4.6 (t, *J* 9.1 Hz, OC*H*H), 4.4 (dd, *J* 6.9 and 9.5 Hz, OCH*H*), 3.2 (dd, *J* 6.7 and 11.5 Hz, C*H*HCo), 2.9 (dd, *J* 2.9 and 6.8 Hz, CH*H*Co), and 2.8 (m, ArC*H*; δ_C(100.6 MHz) 168.7, 168.5, 159.8, 144.4, 144.0, 131.0, and 119.5 (C); 154.6, 154.5, 135.9, 134.8, 134.4, 127.3,

126.9, 124.6, 124.3, 119.7, 114.9, and 114.5 (CH); and 79.3 and 28.3 (CH_2) [Found: C, 69.8; H, 4.9; N, 7.5%; *m/z* (FAB) (MH − py)$^+$, 507. $C_{35}H_{28}CoN_2O_3$ requires C, 69.7; H, 4.98; N, 7.2%; $C_{30}H_{23}CoNO_3$ requires *M*, 507].

3-*Methylbenzofuran* (**18**).—*Method* (i). A catalytic quantity of trifluoroacetic acid (TFA) (2 μl) was added to a stirred solution of 2,3-dihydro-3-methylenebenzofuran (10 mg) in dry chloroform (10 ml) at 25 °C under nitrogen and the mixture was stirred at room temperature for 2 h and was then evaporated *in vacuo* to leave an oil, which after microdistillation (Kugelrohr) gave the methylbenzofuran (**18**) (9.8 mg, 98%) as an oil; b.p. 120–130 °C/11 mmHg (lit.,[24] b.p. 196–197 °C/742 mmHg); ν_{max}($CHCl_3$) 1 590w cm^{-1}; δ_H 7.5–7.2 (m, 5 × ArH) and 2.25 (d, *J* 1.3 Hz, Me) (Found: M^+, 132.0564. Calc. for C_9H_8O: *M*, 132.0575).

Method (ii). A water-cooled solution of (2,3-dihydrobenzofuran-3-yl)methylcobalt(III) salen (**16a**) (100 mg, 0.21 mmol) in dry, deoxygenated benzene (40 ml) under nitrogen was irradiated through Pyrex glass with a 400 W high-pressure UV mercury lamp (*d* 2 cm) for 8 h. The solvent was evaporated off *in vacuo*, and the residue was then purified by chromatography [silica; (1:20) diethyl ether–light petroleum] to give the benzofuran (**18**) (27.5 mg, 95.4%) as an oil whose chromatographic and spectroscopic data were identical with those described above.

2,3-*Dihydro*-3-*methylenebenzofuran* (**17**) *and* 3-*Methylbenzofuran* (**18**).—2-Iodophenyl propynyl ether (**19**) (250 mg, 1.00 mmol) was treated with sodium cobalt(I) salen (2.00 mmol), by the general procedure, to give a mixture of the furans (**17**) and (**18**) (53.0 mg, 40%) as an oil (eluted first), whose spectral data were identical with those obtained previously, and the starting iodide (67 mg, 26% recovery) (eluted second).

Cyclisation using Electrogenerated Catalytic Cobalt(I) *Reagents. General Procedure.*—A divided electrochemical H-cell consisting of a mercury pool cathode and a graphite rod anode was used. The cell was filled with 0.2M-lithium perchlorate electrolyte in the chosen dry solvent (methanol, pyridine, or acetonitrile). The reference electrode consisted of a solution of silver nitrate (10 mg) in dry solvent (5 ml). The cell was then connected to a potentiostat and the electrolyte was deoxygenated (N_2/Ar) and pre-electrolysed (at the potential to be used in the reaction) simultaneously for 1–1.5 h. The cobalt catalyst [Co^{II} salophen (**12**); $BrCo(salen)PPh_3$ (**11**); $ClCo(dmgH)_2py$ (**10**), or Vitamin B_{12} (**1a**)] (10–12%) was added to the catholyte. Application of the desired potential (1.800–2.100 V) caused an initial increase in cell current and the formation of a green-black solution in the cathode department. A solution of the substrate (1.00 mmol) in deoxygenated solvent (*ca.* 2 ml) was injected into the catholyte; this caused a discharge of the green colour followed by a dramatic increase in the cell current. Electrolysis was continued until all the starting substrate was consumed [determined by (i) TLC analysis, (ii) the drop in cell current to a constant low value, and (iii) the regeneration of the green-black colour].

2,3-*Dihydro*-3-*methylbenzofuran* (**21**).—By the general procedure allyl 2-iodophenyl ether (**9**) (260 mg, 1.00 mmol) and Co^{II} salen (**11**) (40 mg, 0.12 mmol), in the presence of dry pyridine (0.5 ml), were electrolysed at −1.800 V for 12 h. The electrolyte was quenched in dil. hydrochloric acid (130 ml) and extracted with diethyl ether (5 × 30 ml). The extracts were then washed with water (2 × 15 ml), dried ($MgSO_4$), and evaporated *in vacuo* to leave an oil. The oily residue was subjected to column chromatography (silica; light petroleum) to give the title furan (60 mg, 45%) as an oil; ν_{max}(film) 2 960s, 1 590s, and 1 580s cm^{-1}; δ_H 7.1 (m, 2 × ArH), 6.8 (m, 2 × ArH), 4.7 (dd, *J* ~8.7 Hz, OC*H*H), 4.1 (dd, *J* 7.4 and 8.5 Hz, OCH*H*), 3.5 (m, ArC*H*), and 1.3 (d, *J* 6.8 Hz, Me); δ_C(60.9 MHz) 158.8 and 132.3 (C); 128.0, 123.8, 120.4, 109.5, and 36.5 (CH); 78.5 (CH_2); 19.3 (Me) (Found: M^+, 134.0724. Calc. for $C_9H_{10}O$: *M*, 134.0732), which data were consistent with the literature.[25]

Control experiment. Allyl 2-iodophenyl ether (**9**) (130 mg, 0.50 mmol) was electrolysed by the general procedure in the absence of catalytic Co^{II} salen at a potential of −2.200 V. After 21 h the cell current had fallen to a constant low level, and the catholyte was then evaporated *in vacuo*. The residue was diluted with water (20 ml) and then extracted with diethyl ether (3 × 30 ml). The combined, dried ($MgSO_4$) extracts were evaporated and the residue was purified by chromatography (silica; light petroleum) to give allyl phenyl ether (30 mg, 44.5%) as an oil; δ_H 7.3 (m, 2 × ArH), 6.9 (m, 3 × ArH), 6.0 (m, CH=C), 5.5–5.2 (m, $=CH_2$), and 4.5 (m, OCH_2), consistent with the literature data.[26]

Preparation of Alcohols by Insertion of Dioxygen into Carbon–Cobalt Bonds. General Procedure.—A solution of the alkylcobalt complex (1.00 mmol) in oxygenated dichloromethane (110 ml) was irradiated, under reflux, with a 300 W sunlamp (*d* 15 cm), whilst oxygen was bubbled through the solution for 20–24 h. The solvent was evaporated off *in vacuo* (dark; < 30 °C) and the resulting brown, solid residue was then dissolved in methanol (100 ml). Aqueous sodium hydroxide (10M; 1.5 ml) was added to the stirred mixture, followed by portionwise addition of sodium borohydride (2.05 g, 54 mmol) during 0.5 h, at 25 °C. The dark green mixture was stirred for 20–30 h and then the solvent was evaporated off *in vacuo*. The residual brown solid was dissolved in water (25 ml) and then extracted with diethyl ether (3 × 15 ml). The combined, dried ($MgSO_4$) extracts were evaporated *in vacuo*, and the residue was then purified by chromatography.

(2,3-*Dihydrobenzofuran*-3-*yl*)*methanol* (**23**) *and* 2,3-*Dihydrobenzofuran*-3-*ol* (**25**).—A solution of the alkylcobalt(III) salophen complex (**16b**) (400 mg, 0.68 mmol) in dichloromethane (75 ml) was irradiated under reflux in the presence of oxygen for 16 h. The crude peroxide (**22**) was then reduced with sodium borohydride, as described in the general procedure, to give, after purification by chromatography [silica; (1:2) diethyl ether–light petroleum]; (i) the methanol (**23**) (23.2 mg, 25%) (eluted first) as an oil; ν_{max}(film) 3 400br s and 1 600s cm^{-1}; δ_H 6.8–7.5 (m, 4 × ArH), 4.6 (dd, *J* 8.3 and 9.4 Hz, OC*H*H), 4.4 (dd, *J* 5.1 and 9.4 Hz, OCH*H*), 3.7 (m, CH_2OH), 3.6 (m, CH), and 1.7 (br, OH); δ_C(20.1 MHz) 160.3 and 127.3 (C); 128.8, 124.7, 120.4, 109.7, and 44.5 (CH); and 74.0 and 64.7 (CH_2) (Found: M^+, 150.0674. Calc. for $C_9H_{10}O_2$: *M*, 150.0681), consistent with literature data,[27] and (ii) the lower homologue (**25**) (23.0 mg, 24%) (eluted second) as an unstable oil; ν_{max}($CHCl_3$) 3 580m and 3 380br m, cm^{-1} (lit.,[28] 3 400 cm^{-1}); δ_H 7.5–7.2 (m, 2 × ArH), 7.0–6.8 (m, 2 × ArH), 5.4 (m, C*H*OH), 4.6 (dd, *J* 11 and 14, C*H*H), 4.5 (dd, *J* 11 and 12, CH*H* and OC*H*H), and 4.5 (d, *J* 1.2 Hz, OCH*H*) (Found: M^+, 136.0508. Calc. for $C_8H_8O_2$: *M*, 136.0524).

(3,4-*Dihydro*-2H-1-*benzofuran*-4-*yl*)*methylcobalt*(III) *Salen* (**27**), 3,4-*Dihydro*-4-*methylene*-2H-1-*benzopyran* (**28**), *and But*-3-*enyl Phenyl Ether* (**29**).—A solution of but-3-enyl 2-iodophenyl ether (**26**) (274 mg, 1.00 mmol) in dry, deoxygenated THF (5 ml) was injected into a stirred solution of sodium cobalt(I) salen (4.00 mmol) in dry, deoxygenated THF (120 ml) at 25 °C under nitrogen. The mixture was stirred in the dark at room temperature for 18 h during which time the green colour persisted for *ca.* 5 h. The solvent was evaporated off *in vacuo* (dark; < 30 °C) and the solid brown residue was then diluted with water (80 ml) and extracted with diethyl ether–light

petroleum (1:1; 3 × 30 ml). Evaporation of the dried ($MgSO_4$) extracts *in vacuo*, followed by distillation of the residue, gave an oil [b.p. 100–130 °C/8 mmHg (Kugelrohr)], which was shown to contain two components. Purification of the oil by chromatography (silica; light petroleum) gave: (i) but-3-enyl phenyl ether (**29**) (20 mg, 13.5%) (eluted first) as an oil; $\nu_{max}(CHCl_3)$ 2 910w and 1 600s cm^{-1}; δ_H 7.3 (m, 2 × ArH), 6.9 (m, 2 × ArH), 5.9 (m, 1 H, CH=), 5.2 (m, 2 H, $=CH_2$), 4.0 (t, *J* 6.3 Hz, OCH_2), and 2.5 (br q, *J* 6.3 Hz, CH_2C=), consistent with literature data,[13a] and (ii) the *benzopyran* (**28**) (9.0 mg, 6%) (eluted second) as an oil; ν_{max}(film) 2 900m, 1 635m, 1 605m, 1 490s, 1 315s, 1 260s, 1 225s, 1 060s, 890m, and 760s cm^{-1}; δ_H 7.6 (app. d, *J* 7.8 Hz, ArH), 7.2 (m, ArH), 6.9 (m, 2 × ArH), 5.5 (br s, =C*H*H), 4.9 (br s, =CH*H*), 4.2 (t, *J* 5.5 Hz, CH_2O), and 2.7 (tt, *J* 1.3 and 5.5 Hz, CH_2) (Found: M^+, 146.0721. $C_{10}H_{10}O$ requires *M*, 146.0732).

Further extraction of the aqueous layer with chloroform (3 × 50 ml) followed by evaporation at reduced pressure (dark; < 30 °C) of the dried ($MgSO_4$) extracts and then purification by chromatography [silica; (1:4) $CHCl_3$–EtOAc] gave the *alkylcobalt*(III) *salen complex* (**27**) (200 mg, 42%), which was recrystallised from chloroform–light petroleum as dark green crystals, m.p. 79–82 °C (decomp.); $\nu_{max}(CHCl_3)$ 2 910w, 1 600s, 1 450s, 1 350m, 1 330m, 1 100w, 955w, and 905w cm^{-1}; δ_H(400 MHz) 8.1 (CH=N), 7.9 (CH=N), 7.7–6.6 (m, 12 × ArH), 4.1 (m, OC*H*H), 4.0 (m, C*H*HN), 3.9 (m, CH*H*N), 3.8 (dt, *J* 2.2 and 11.5 Hz, OCH*H*), 3.7 (m, C*H*HN), 3.6 (m, CH*H*N), 3.3 (dd, *J* 10.5 and 5.8 Hz, C*H*HCo), 3.1 (d, *J* 5.9 Hz, CH*H*Co), 2.5 (d, *J* 16.6 Hz, C*H*HCH$_2$O), 1.9 (m, CH*H*CH$_2$O), and 1.8 (m, ArC*H*); δ_C(100.62 MHz) 165.4 (2 × C), 154.6, 123.5, 120.7, and 120.3 (C); 63.3, 59.7, 58.9, and 26.4 (CH_2); and 164.8 (164.7), 134.0, 133.1, 132.3, 132.2, 132.1, 130.2, 128.7, 128.6, 127.2, 123.4 (123.3), 120.1, 117.0, 116.1, and 116.0 (CH) [Found: M^+, (FAB) 472. $C_{26}H_{25}CoN_2O_3$ requires *M*, 472].

Electrochemical Control Experiment leading to 2,3-*Dihydro*-4-*methyl*-2H-1-*benzopyran*.—By the general procedure but-3-enyl 2-iodophenyl ether (**26**) (274 mg, 1.00 mmol) was electrolysed in the presence of a trace of dry pyridine (0.5 ml) and a catalytic quantity of Co^{II} salen (32.5 mg, 0.10 mmol) at −1.800 V for 72 h. The methanol was evaporated off *in vacuo* and the residue was diluted with water (80 ml), and then extracted with diethyl ether (5 × 40 ml). The combined, dried ($MgSO_4$) extracts were evaporated and the oily residue was then purified by chromatography (silica; light petroleum) to give: (i) but-3-enyl phenyl ether (eluted first) (7.6 mg, 5.0%) as an oil whose spectral data were identical with those obtained previously, (ii) 4-methyl-2*H*-1-benzopyran (eluted second) (5.0 mg, 3.4%) as an oil whose spectral data were identical with those obtained previously, and (iii) the title dihydro-2*H*-benzopyran (eluted third) (56.0 mg, 37.8%) as an oil; δ_H 7.2–7.0 (m, 2 × ArH), 6.9–6.7 (m, 2 × ArH), 4.2 (t, *J* 5.3 Hz, OCH_2), 3.9 (m, C*H*Ar), 2.3–1.5 (m, CH_2), and 1.3 (d, *J* 7.0 Hz, Me) (Found: M^+, 148.0884. Calc. for $C_{10}H_{12}O$: *M*, 148.0888), which data were consistent with the literature.[13a]

4-*Methyl*-2H-1-*benzopyran*.—A solution of 3,4-dihydro-4-methylene-2*H*-1-benzopyran (**28**) (9.5 mg, 65.1 μmol) in dry chloroform (8 ml) containing a catalytic amount of TFA (*ca.* 2 μl) was stirred at 25 °C under nitrogen for 20 h. Evaporation of the solvent *in vacuo* and chromatography [silica; (1:10) diethyl ether–light petroleum] of the residue gave the isomerised pyran (7.2 mg, 75%) as an oil; $\nu_{max}(CHCl_3)$ 1 600w cm^{-1} (lit.,[29] 1 653 cm^{-1}); δ_H 7.2–6.7 (m, 4 × ArH), 5.6 (m, 1 H, OCH_2CH=), 4.7 (m, OCH_2), and 2.0 (d, *J* 1.7 Hz, Me) (Found: M^+, 146.0713. Calc. for $C_{10}H_{10}O$: *M*, 146.0732).

N-*But*-3-*enyl*-N-*methylaniline* (**30b**).—*N*-Butenyl-2-iodo-*N*-methylaniline (**30a**) (287 mg, 1.00 mmol) was treated with the cobalt(I) salen reagent (4.00 mmol), by the general procedure, to give the *title dehalogenated* aniline (48 mg, 31%) as a pale yellow oil; δ_H 7.3–6.6 (m, Ph), 6.0–5.4 (m, CH=), 4.9–5.2 (m, C=CH_2), 3.5–3.3 (m, NCH_2), 2.9 (NMe), and 2.4–2.0 (m, allylic CH_2), consistent with the literature data.[13a]

Allyl Benzyl Ether (**31b**).—Allyl 2-iodobenzyl ether (**31a**) (247 mg, 1.00 mmol) was treated with the cobalt(I) salen reagent (2.00 mmol), by the general procedure, to give the benzyl ether (**31b**) (51 mg, 34.2%) as an oil; ν_{max}(film) 2 875s and 1 500w cm^{-1}; δ_H 7.3 (m, Ph), 6.1–5.7 (m, CH_2CH=), 5.4–5.1 (m, $=CH_2$), 4.5 ($ArCH_2$), and 4.0 (dt, *J* 5.4 and 1.3 Hz, OCH_2C=), consistent with the literature data.[30]

Phenyl Vinyl Ether (**32b**).—2-Iodophenyl vinyl ether (**32a**) (180 mg, 0.732 mmol) was treated with the cobalt(I) salen reagent (2.00 mmol), by the general procedure, to give the title ether (33.6 mg, 28%); δ_H 7.4–6.7 (m, Ph), 6.55 (ABX system, *J* 1.5, 6.0, and 13.5 Hz, OC*H*=CH_2), 4.6 (m, =C*H*H), and 4.3 (m, =CH*H*), which were consistent with the literature data.[13e]

Benzyl Vinyl Ether (**33b**).—2-Iodobenzyl vinyl ether (**33a**) (260 mg, 1.00 mmol) was treated with the cobalt(I) salen reagent (2.00 mmol), by the general procedure, to give the title ether (45 mg, 34%) as an oil; δ_H 7.3 (br s, Ph), 6.5 (dd, *J* 6.9 and 14.3 Hz, CH=), 4.3 (dd, *J* 7 and 2.5 Hz, =C*H*H), and 4.1 (dd, *J* 14 and 2.5 Hz, =CH*H* and $ArCH_2$), which were consistent with the literature data.[31]

(3,4-*Dihydro*-2H-1-*benzopyran*-4-*yl*)*methanol* (**34**) *and Chroman*-4-*ol* (**35**).—A solution of the alkylcobalt(III) salen (**27**) (150 mg, 0.32 mmol) in dichloromethane (35 ml) was irradiated under oxygen for 24 h, and then reduced by the general procedure. The mixture was purified by column chromatography [silica; (1:5) diethyl ether–light petroleum] to give: (i) the chromanol (**35**) (15.8 mg, 33%) (eluted first) as white platelets, m.p. 39–41 °C (from Et_2O–light petroleum) (lit.,[32] 41 °C); $\nu_{max}(CHCl_3)$ 3 350 br s, 1 605m, and 1 580s cm^{-1}; δ_H 7.3 (m, 2 × ArH), 6.9 (m, 2 × ArH), 4.8 (t, *J* 4.0 Hz, C*H*OH), 4.3 (dd, *J* 5.4 and 6.6 Hz, OCH_2), 2.0 (m, $CHCH_2$), and 1.7 (br s, OH) (Found: M^+, 150.0669. Calc. for $C_9H_{10}O_2$: *M*, 150.0681), and (ii) the alcohol (**34**) (3.2 mg, 6%) (eluted second) as an oil; $\nu_{max}(CHCl_3)$ 3 500br, m, 2 900s, 1 605w, and 1 580m cm^{-1}; δ_H 7.1 (m, 2 × ArH), 6.8 (m, 2 × ArH), 4.2 (m, OCH_2), 3.9 (dd, *J* 5.0 and 10.9 Hz, C*H*HOH), 3.8 (dd, *J* 8.0 and 10.9 Hz, CH*H*OH), 3.0 (m, ArC*H*), 2.1 (m, OCH_2CH_2), and 1.6 (br s, OH) (Found: M^+, 164.0834. Calc. for $C_{10}H_{12}O_2$: *M*, 164.0837), which data were consistent with the literature.[33]

1,3-*Dimethylindole* (**37**).—A solution of *N*-allyl-2-iodo-*N*-methylaniline (**36**) (273 mg, 1.00 mmol) in dry, deoxygenated THF (5 ml) was added to a green solution of $NaCo^I$ salen (2.00 mmol) in dry, deoxygenated THF (130 ml) at room temperature, under nitrogen. The green colour was gradually discharged during 2 h, and the mixture was stirred for a further 19 h in the dark at 25 °C. The solvent was evaporated off *in vacuo* (dark; < 30 °C), and the solid brown residue was then diluted with water (80 ml), and extracted with diethyl ether–light petroleum (1:1; 3 × 30 ml). Evaporation of the dried ($MgSO_4$) organic extracts *in vacuo*, followed by chromatography (silica; light petroleum) of the residue gave the dimethylindole (**37**) (46 mg, 32%) as a pale yellow oil; ν_{max}(film) 1 615w cm^{-1}; δ_H 7.5 (m, ArH), 7.2 (m, 3 × ArH), 6.8 (br s, indole 2-H), 3.7 (NMe), and 2.3 (Me) (Found: M^+, 145.0885. Calc. for $C_{10}H_{11}N$: *M*, 145.0891), consistent with the literature data.[34] [The ^1H NMR spectrum of the crude reaction mixture

indicated the co-formation of the corresponding dihydro-3-methyleneindole isomer; $\delta_H(CDCl_3)$ 5.3 (app. t, *J* 3.2 Hz, =C*H*H), 4.9 (app. t, *J* 3.2 Hz, =CH*H*), 4.0 (app. t, *J* 3.2 Hz, CH_2NMe), and 2.7 (NMe)].

Electrochemical Control Experiment leading to 1,3-*Dimethylindoline*.—By the general procedure *N*-allyl-2-iodo-*N*-methylaniline (**36**) (273 mg, 1.00 mmol), cobalt(II) salen (40 mg, 0.12 mmol), and pyridine (0.5 ml) were electrolysed at −1.800 V for 40 h. The solvent was evaporated off *in vacuo* and the solid residue was then diluted with water (10 ml) and extracted with diethyl ether (4 × 10 ml). The combined, dried ($MgSO_4$) extracts were evaporated *in vacuo* and the residue was then subjected to chromatography (silica; light petroleum) to give the indoline (44.1 mg, 30%) as an unstable oil; $\delta_H(CDCl_3)$ 7.0 (m, 2 × ArH), 6.6 (m, 2 × ArH), 3.7–3.1 (m, 2 H, NC*H*H and CH), 2.9–2.7 (m, CH*H*), 2.7 (NMe), and 1.3 (d, *J* 6.5 Hz, 3-Me) (Found: M^+, 147.1046. Calc. for $C_{10}H_{13}N$: *M*, 147.1048), consistent with the literature data.[13a]

3-(2-*Bromo*-1-*ethoxyethoxy*)*cyclohexene* (**38a**).—A solution of bromine (1.9 ml) in dichloromethane (5 ml) was added to a stirred solution of ethyl vinyl ether (2.6 g, 0.036 mol) in dichloromethane, maintained at < −60 °C. Addition of more ethyl vinyl ether (1–2 ml) resulted in a pale yellow solution. A solution of dimethylaniline (5 ml) and cyclohex-2-enol (2.6 g, 0.026 mol) in dichloromethane (15–20 ml) was added while the reaction temperature was kept <40 °C and the stirred mixture was then allowed to warm slowly to room temperature overnight. The reaction mixture was diluted with dichloromethane and the solution was then washed successively with water, 10% aq. hydrochloric acid, saturated aq. sodium hydrogencarbonate, and brine. The dichloromethane extract was dried ($MgSO_4$), filtered, and then evaporated *in vacuo*, leaving a brown-green oil. The residue was purified by chromatography on silica gel, with light petroleum–diethyl ether (60:1) as eluant, to give the bromoacetal (**38a**) (5.85 g, 91%)[17] as a pale yellow oil; ν_{max}(film) 1 640, 1 040, and 740 cm^{-1}; δ_H 5.8 (m, *H*C=CH), 4.8 (t, *J* 7 Hz, OCHO), 4.1 (m, OCH), 3.6 (m, OCH_2), 3.3 (d, *J* 7 Hz, CH_2Br), 2.1–1.6 (6 H, m), and 1.2 (t, *J* 8 Hz, Me); δ_C (mixture of diastereoisomers) 131.3, 127.7, 127.3, 100.9, 100.3, 71.0, 70.8, 62.4, 61.6, 32.4, 31.9, 28.8, 25.1, 19.2, 18.9, 15.3, and 15.2 (Found: *m/z* 150.9545. Calc. for C_4H_8BrO: *m/z*, 150.9756).

2,3,3aα,6,7,7aα-*Hexahydro*-2-*methoxybenzofuran* (**43**).—*Method* 1. Both compartments of a standard H-electrochemical cell were filled with 0.1M-lithium perchlorate in methanol. The cathodic solution also contained 3-(2-bromo-1-ethoxyethoxy)-cyclohexene (**38a**) (0.50 g, 2.0 mmol). A stirred mercury pool was used for the cathode, and a graphite rod was used for the anode; the reference electrode comprised a silver wire in 0.01M-methanolic silver nitrate. The cathodic solution was degassed with nitrogen at −1.8 V until the current fell to 0.5 mA. Vitamin B_{12} (80 mg, 0.06 mmol) was added to the cathodic section, and electrolysis at a potential of −1.8 V was continued for 24 h. Over the course of the reaction, the reaction mixture went from red-purple to brown-green. The cathodic solution was then removed, diluted with water (25 ml), saturated with sodium chloride, and extracted with diethyl ether (3 × 25 ml). The combined extracts were dried, and the solvent was removed *in vacuo*, leaving the *title product* (283 mg, 90%) as a pale yellow, fruity smelling oil, ν_{max}(film) 1 440, 1 350, and 1 200 cm^{-1}; δ_H 5.8 (dm, *J* ~9 Hz, =CH), 5.5 (dm, *J* ~9 Hz, =CH), 5.0 (dd, *J* 5 and 2 Hz, OCHO), 4.3 (dt, *J* 9 and 4 Hz, CHO), 3.4 and 3.38 (2 × s, 3 H, Me anomers), 2.8 (1 H, m), and 2.2–1.7 (m, 6 H); δ_C 128.4, 127.0, 104.6, 75.2, 54.8, 39.5, 36.4, 25.8, and 20.5 (Found: M^+, 154.1019. $C_9H_{14}O_2$ requires *M*, 154.0994).

Method 2. As in method 1 (above) 3-(2-bromo-1-ethoxyethoxy)cyclohexene (**38a**) (0.38 g, 1.6 mmol) was placed in the cathodic solution of a standard H-electrochemical cell. Following degassing and pre-electrolysis, chloropyridine cobaloxime (80 mg, 0.2 mmol) was added to the cathodic compartment. After 48 h, the reaction mixture was worked up as in method 1, and the product (172 mg, 66%) was isolated as a yellow oil, identical with previously characterised 2,3,3,aα,6,7,7aα-hexahydro-2-methoxybenzofuran.

Method 3. Ammonium chloride (2.4 g, 45 mmol) was added to a stirred solution of 3-(2-bromo-1-ethoxyethoxy)cyclohexene (**38a**) (0.49 g, 2.00 mmol) in methanol–water (1:1; 30 ml), followed by the addition of activated zinc dust (0.4 g, 6.1 mmol). The reaction mixture was deoxygenated by bubbling nitrogen directly through it for 15 min. Vitamin B_{12} complex (40 mg, 0.029 mmol) was then added, and the reaction mixture became purple. After the mixture had been stirred overnight under nitrogen more (0.9 g) activated zinc dust was added to the red-brown reaction mixture, and the mixture was stirred for 4 h, resulting in a dark green colour. The reaction mixture was filtered, and upon exposure to air the solution went from green to red. The filtrate was extracted with diethyl ether (3 × 50 ml), and the combined extracts were washed with water and dried ($MgSO_4$). The ether was removed *in vacuo*, leaving the product (220 mg, 66%) as a slightly yellow oil.

3aα,6,7aα-*Tetrahydrobenzofuran*-2(3H)-*one* (**44**).—Conc. sulphuric acid (6.1 ml, 110 mmol) was carefully added to a stirred solution of chromium trioxide (7 g, 70 mmol) in water (50 ml) at 0 °C. This freshly prepared Jones' reagent (1.95 ml, 10 mol equiv.) was added dropwise to a cooled and rapidly stirred solution of 2,3,3aα,6,7,7aα-hexahydro-2-methoxybenzofuran (**43**) (55 mg, 0.33 mmol) in acetone (3 ml). After the starting material had disappeared (15 min), the mixture was quenched cautiously with propan-2-ol (0.5 ml). The upper organic layer was separated, and the green residue was then washed with acetone (2 × 2 ml). The combined acetone extracts were evaporated *in vacuo*, and the residue was then dissolved in diethyl ether (20 ml). The extract was washed with 5% aq. sodium hydrogen carbonate (2 × 5 ml), dried ($MgSO_4$), and then evaporated *in vacuo* to give the lactone (**44**) (27 mg, 60%)[19] as a viscous, yellow oil; ν_{max}(film) 2 920, 1 785, 1 190, and 1 160 cm^{-1}; δ_H 5.8 (m, *J* ~9 Hz, =CH), 5.5 (dm, *J* ~8 Hz, =CH), 4.7 (dt, *J* 5 and 2 Hz, CHOCO), 3.0 (m, =CHC*H*, 2.8 (dd, *J* 8 and 5 Hz, COC*H*H), 2.3 (dd, *J* 8 and 2 Hz, COCH*H*), and 2.5–1.8 (4 H, m); δ_C 177.0, 128.6, 126.0, 78.2, 35.9, 24.6, and 19.2 (Found: C, 69.7; H, 7.6%; *M*, 138.0653. Calc. for $C_8H_{10}O_2$: C, 69.5; H, 7.3; *M*, 138.0680).

3-(2-*Bromo*-1-*ethoxy*)-1-*methylcyclohexene* (**45**).—The title compound was prepared from 3-methylcyclohex-2-enol (2.9 g, 0.026 mol) by the same prodecure which had been used to synthesize 3-(2-bromo-1-ethoxyethoxy)cyclohexene. After chromatography the product (6.2 g, 89%) was isolated as a pale yellow oil; ν_{max} 2 980, 2 940, 1 445, 1 110, 1 070, and 1 035 cm^{-1}; δ_H 5.6 (m, =CH), 4.8 (t, *J* 7 Hz, OCHO), 4.2 (m, CHO), 3.7 (m, OCH_2Me), 3.4 (d, *J* 7 Hz, CH_2Br), 2.1–1.6 (m, 3 × CH_2), 1.7 (=CMe), and 1.3 (t, *J* 7 Hz, OCH_2Me).

3aα,6,7,7aα-*Tetrahydro*-4-*methylbenzofuran*-2(3H)-*one* (**47**).—Ammonium chloride (2.4 g, 45 mmol) was added to a stirred solution of 3-(2-bromo-1-ethoxyethoxy)-1-methylcyclohexene (**45**) (0.50 g, 2.0 mmol) in methanol–water (1:1; 30 ml), followed by the addition of activated zinc dust (1.3 g). The reaction mixture was deoxygenated by bubbling nitrogen directly through it for 15 min. Vitamin B_{12} complex (40 mg, 0.029 mmol) was then added, and the mixture became purple. After being stirred for 24 h under nitrogen the reaction mixture

was filtered, and the filtrate was saturated with sodium chloride and extracted with diethyl ether (3 × 30 ml). The combined extracts were dried ($MgSO_4$), and the ether was removed *in vacuo*, leaving the acetal (**46**) (280 mg, 80%) as a pale yellow oil; ν_{max} 2 940, 1 445, 1 110, 1 055, 1 020, and 915 cm^{-1}.

Freshly prepared Jones' reagent was added dropwise to a cooled, rapidly stirred solution of 2-ethoxy-2,3,3aα,6,7,7aα-hexahydro-4-methylbenzofuran (**46**) (31 mg, 0.17 mmol) in acetone (4 ml) until, based on TLC, the starting cyclic acetal had disappeared. The mixture was poured into water, and the aqueous mixture was then saturated with sodium chloride, and extracted with light petroleum–diethyl ether (4:1). The combined extracts were dried ($MgSO_4$), and the solvents were evaporated off *in vacuo* to give the *title product* (10 mg, 40%) as a yellow oil; ν_{max} 2 900, 1 755, 1 415, 1 145, 1 020, 975, and 915 cm^{-1}; δ_H 5.6 (m, =CH), 4.8 (dt, *J* 6.3 and 3.4 Hz, OCH), 2.8 (m, =CCH), 2.8 (dd, *J* 17 and 9 Hz, COC*H*H), 2.4 (dd, *J* 17 and 5 Hz, COCH*H*), 2.3–1.6 (m, 2 × CH_2), and 1.7 (d, *J* 1.3 Hz, CMe) (Found: M^+, 152.0854. $C_9H_{12}O_2$ requires *M*, 152.0837).

(2-Ethoxyoctahydrobenzofuran-4-yl)peroxypyridinatocobaloxime (**50**).—A stirred suspension of cobalt(II) chloride hexahydrate (1.73 g, 7.27 mmol), dimethylglyoxime (1.69 g, 14.6 mmol), and methanol (11 ml) was degassed for 30 min at room temperature by bubbling nitrogen. The mixture was cooled in an ice-bath, and then 10M-aq. sodium hydroxide (1.5 ml) was added, resulting in a black solution. Pyridine was introduced and the mixture was stirred for 0.5 h, followed by the addition of 3-(2-bromo-1-ethoxyethoxy)cyclohexene (**38a**) (0.90 g, 5.8 mmol). The mixture was stirred for an additional 3 h under nitrogen and was then poured into water. The alkylperoxycobalt species precipitated in water, but the entire mixture was extracted with benzene (4 × 50 ml). The combined extracts were dried ($MgSO_4$), and the solvent was removed *in vacuo*. The remaining red-brown solid was recrystallised from ethyl acetate–light petroleum to give the cobalt complex (**42**) (1.1 g, 56% based on 3.64 mmol of Co^I derived from disproportionation) as an orange powder, δ_H 8.5 (m, 2 H), 7.7 (m, 1 H), 7.3 (m, 2 H), 5.0 (m, 1 H), 3.7 (m, 1 H), 3.4 (m, 1 H), 2.1 and 2.2 (4 × =CMe), and 1.1–1.6 (m, 14 H).

A cooled (propan-2-ol–liquid nitrogen) solution of (2-ethoxyoctahydrobenzofuran-4-yl)pyridinatocobaloxime (**42**) (2.0 g, 3.7 mmol) in dry acetonitrile (300 ml) was irradiated for 24 h with a steady stream of oxygen bubbling through the solution. The reaction mixture was purged with nitrogen; then the solvent was removed *in vacuo*. The residual brown solid was purified by chromatography on silica gel, with gradient elution [neat $CHCl_3$ (9:1) $CHCl_3$–MeOH] as eluant, to give the title product (1.1 g, 50%) as a sand-brown powder; ν_{max}(solution) 2 940, 1 630, 1 560, and 1 100 cm^{-1}; *m/z* (FAB) 570 (M^+ + 1), 541, 462, 368, 290 [Co(dmgH)$_2$ + 1], and 289.

Isomeric 4-Hydroxy-3aα,4,5,6,7,7aα-hexahydrobenzofuran-2(3H)-ones (**53**) *and* (**56**).—Sodium borohydride (60 mg, 1.6 mmol) was added to a stirred solution of (2-ethoxyoctahydrobenzofuran-4-yl)peroxypyridinatocobaloxime (**50**) (0.30 g, 0.52 mmol) in basic methanol [10M-sodium hydroxide (0.1 ml) in methanol (12 ml)]. After the mixture had been stirred for 24 h, the solvent was removed, and the residue was partitioned between water and ethyl acetate. The organic layer was separated and the aqueous layer was further extracted with ethyl acetate. The combined organic phases were washed successively with saturated aq. sodium hydrogen carbonate, brine, and water, dried ($MgSO_4$), and then the solvent was removed *in vacuo*. The residue was purified by chromatography on silica gel, with light petroleum–ethyl acetate (1:1) as eluant, to give the isomeric alcohols (**51**) and (**52**) as viscous oils.

Oxidation of compound (**51**) with MCPBA in the presence of boron trifluoride, according to the method of Grieco,[20] then led to the known β-hydroxy lactone (**53**), m.p. 66–68 °C.[21] The same β-hydroxy lactone was also produced from the alkene (**44**) following epoxidation to compound (**54**) with MCPBA and reduction of the oxirane (**54**) with sodium cyanoborohydride. The known oily isomeric α-hydroxy lactone (**56**) was produced from alkene (**44**) *via* the procedure described by Grieco.[19a]

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