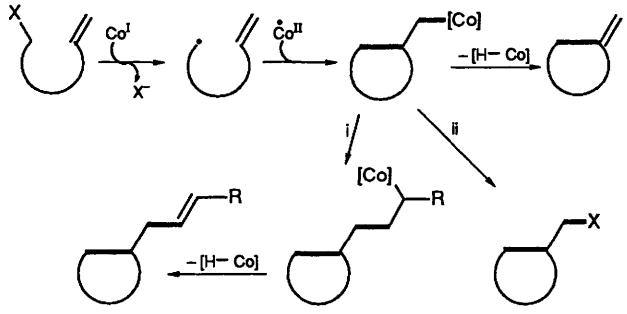
Hydrocobaltation Reactions of 1,3-Dienes. Regioselective Hydroxylation of Myrcene to Geraniol and to (±)-Linalool *via* Allylcobaloxime Intermediates

Amy R. Howell and Gerald Pattenden *
Department of Chemistry, The University, Nottingham NG7 2RD

Hydrocobaltation of myrcene (**3**) by pyridinatocobaloxime leads to a 2:1 mixture of the *E*- and *Z*-allylcobaloxime (**4a**) and (**4b**) in good yield. When a solution of the cobaloximes (**4a**) and (**4b**) in toluene is heated in the presence of tetramethylpiperidine oxide (TEMPO) the hydroxylamines (**7a**) and (**7b**) result, which can be converted into geraniol (**8a**) and nerol (**8b**) by reduction using zinc in acetic acid. By contrast, in the presence of molecular oxygen, the allylcobaloxime (**4**) is converted into the allylperoxycobaloxime (**15**) which on reduction produces (±)-linalool (**16**). In addition, when the cobaloxime (**15**) is heated with TEMPO it undergoes cyclisation to the tetrahydrofuran (**17**), precursor to (+)-linalool oxide (**18**). Whereas the 1,3-dienes (**20**)–(**24**) all failed to undergo hydrocobaltation reactions, both cobaloximes (**27**) and (**28**) were easily obtained from 2-methyl-(**25**) and 2,3-dimethyl-buta-1,3-diene (**26**), respectively. Using similar chemistry to that described for compound (**4**), the allylcobaloxime (**27**) was smoothly converted into the hydroxylamine (**29**) and into the epoxy-TEMPO derivative (**32**).

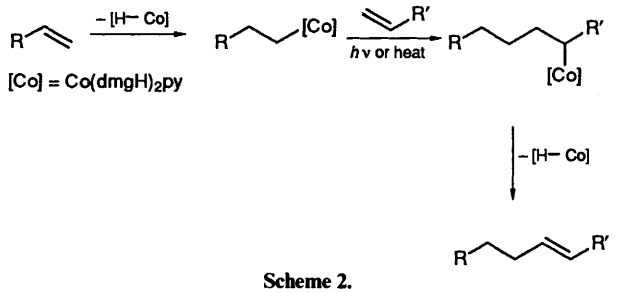
In the accompanying papers and in earlier work we have demonstrated the enormous scope for alkyl-, acyl-, and carbamoyl-cobalt complexes based on Vitamin B_{12}, in the synthesis of a range of functionalised carbo- and hetero-cyclic ring systems *via* inter- and intra-molecular oxidative free radical carbon-to-carbon bond-forming reactions (Scheme 1).[1–3] We



Scheme 1. *Reagents and conditions:* i, heat, *hv*, $RCH{=}CH_2$; ii, heat, *hv*, X•.

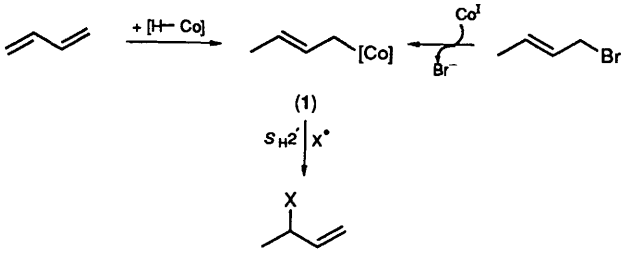
have also shown that homolyses of alkylcobalt salophens in the presence of radical-trapping agents, *e.g.* molecular oxygen, tetramethylpiperidine oxide (TEMPO), nitrogen mono-oxide, diphenyl disulphide, diphenyl diselenide, and bromotrichloromethane, readily leads to the synthesis of oxygen-, nitrogen-, sulphur-, selenium-, and halogen-functionalised carbon radical products.[4] In other investigations we have highlighted the synthesis of functionalised alkenes *via* sp^2–sp^2 cross-coupling reactions between two alkene precursors by 'hydrocobaltation' of one of the alkenes followed by homolysis of the resulting organocobalt reagent in the presence of the second alkene substrate (Scheme 2).[5] We now describe the extensions of these studies with cobalt-mediated radical reactions to an investigation of the selectivity of hydrocobaltation reactions of 1,3-dienes, and the uses of the resulting allylcobalt complexes in the synthesis of specific terpenols.[6]

In comparison with hydrocobaltation reactions of monoenes,[5] studies of the utility and selectivity of hydrocobaltations of 1,3-dienes have received only little attention. The 1,4-hydrocobaltation of buta-1,3-diene itself, by pyridinatocobaloxime, leading to the but-2-enyl derivative (**1**) was reported



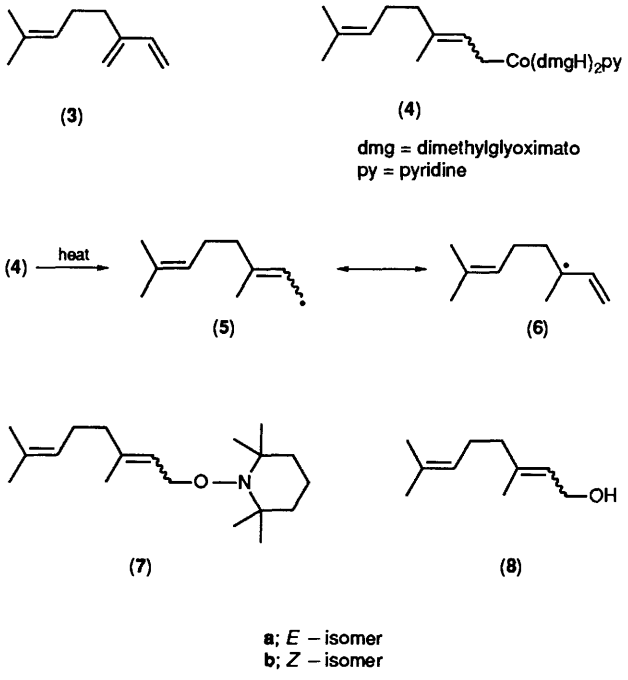
Scheme 2.

as early as 1966,[7] but since this time most researchers have preferred to synthesise allylcobalt complexes like (**1**) using the more traditional method, *viz.* reaction of the corresponding allyl halide with cobaloxime(I).[8] Perhaps in contrast to their formation from 1,3-dienes, some of the *chemistry* of allylcobaloximes has been studied in detail, particularly by Gaudemer and Johnson and their respective colleagues.[8,9] These two research groups have demonstrated that allyl- and most simple allyl-substituted-cobaloximes undergo smooth S_H2' reaction with a range of sulphur-, nitrogen-, and carbon-centred electrophilic radicals, leading to a variety of interesting products (**2**) (Scheme 3). Using the terpene hydrocarbon myrcene (**3**) as a convenient substrate, we have now examined the possibilities for regioselective hydroxylations of 1,3-dienes,



(**2**) X = $CR(CO_2Et)_2$, CHBrCN, $ArSO_2$, $ArSO_2NMe$

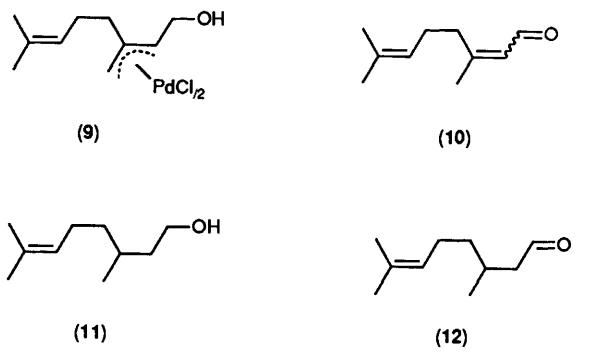
Scheme 3.



leading to specific allyl alcohols *via* hydrocobaltation reactions, and allylcobaloxime intermediates. Here we show how this chemistry can be combined to provide useful and interesting conversions of myrcene into geraniol (**8**), (±)-linalool (**16**), and linalool oxide (**18**).

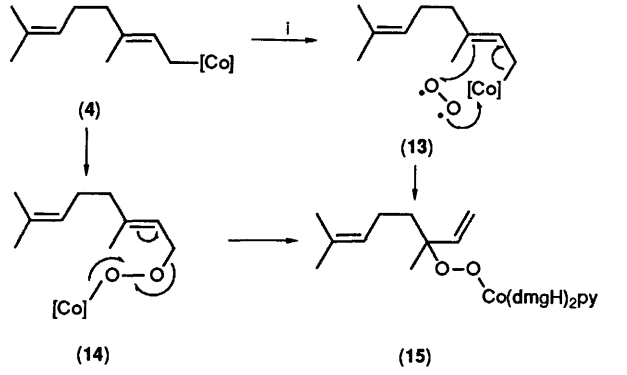
Thus, hydrocobaltation of myrcene (**3**), using cobalt dimethylglyoxime in the presence of hydrogen,[5] proceeded in a regioselective 1,4-addition fashion, and gave rise to a 2:1 mixture of geranyl (**4a**) and neryl cobaloximes (**4b**) which was isolated as a stable orange solid, m.p. 85 °C, in 60–70% yield.[9,10] The two isomers were clearly distinguished in the ^{1}H NMR spectrum where the 3-Me group in the *E*-isomer (**4a**) was deshielded (δ 1.25) compared with the same Me group in the corresponding *Z*-isomer (**4b**) (δ 1.16). When a solution of the orange solid in toluene was heated under reflux for 15 min in the presence of tetramethylpiperidine oxide (TEMPO), work-up and chromatography led to a 2:1 mixture of the corresponding *E*-(**7a**) and *Z*-hydroxylamine (**7b**) in a combined yield of 55%.[4] The hydroxylamines (**7**) thus result from selective trapping by TEMPO at the primary radical centre (**5a**) or (**5b**) in the intermediate allyl radical produced on thermal homolysis of the complexes (**4**). Reduction of the mixture of hydroxylamines (**7**), using zinc dust in 50% aq. acetic acid at 100 °C, finally gave geraniol (**8a**) and nerol (**8b**) in a combined yield of 60%. This easy conversion of myrcene into geraniol–nerol *via* hydrocobaltation–oxidation compares quite favourably with a related method using palladium(II) complexes. Thus, Suzuki and co-workers[11] have shown that when myrcene is treated with water in hexamethylphosphoric triamide in the presence of $PdCl_2$·$(MeCN)_2$ chromatography separates the η^3-allylpalladium complex (**9**) in 75% yield. Reduction of complex (**9**) in the presence of methoxide or hydroxide anion then led to largely nerol (**8b**) whose formation was accompanied by smaller amounts of citral (**10**; *Z*/*E*), citronellol (**11**), and citronellal (**12**).

In contrast to the outcome of the reaction between the cobaloxime (**4**) and TEMPO, when a solution of complex (**4**) in dichloromethane containing dissolved oxygen was left at 25 °C for 48 h, chromatography[1,4] separated the corresponding linalool peroxycobaloxime (**15**) as a green powder, m.p. 185 °C

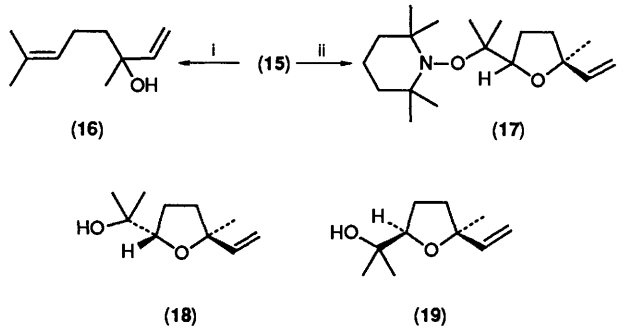


in 35% yield. When the peroxycobaloxime (**15**) was then reduced with sodium borohydride in methanolic sodium hydroxide, (±)-linalool (**16**) was obtained in *ca.* 30% yield.

The linalool peroxycobaloxime (**15**) is produced from complex (**4**) by 'insertion' of triplet oxygen between the cobalt centre and the tertiary allyl carbon centre in complex (**4**). This



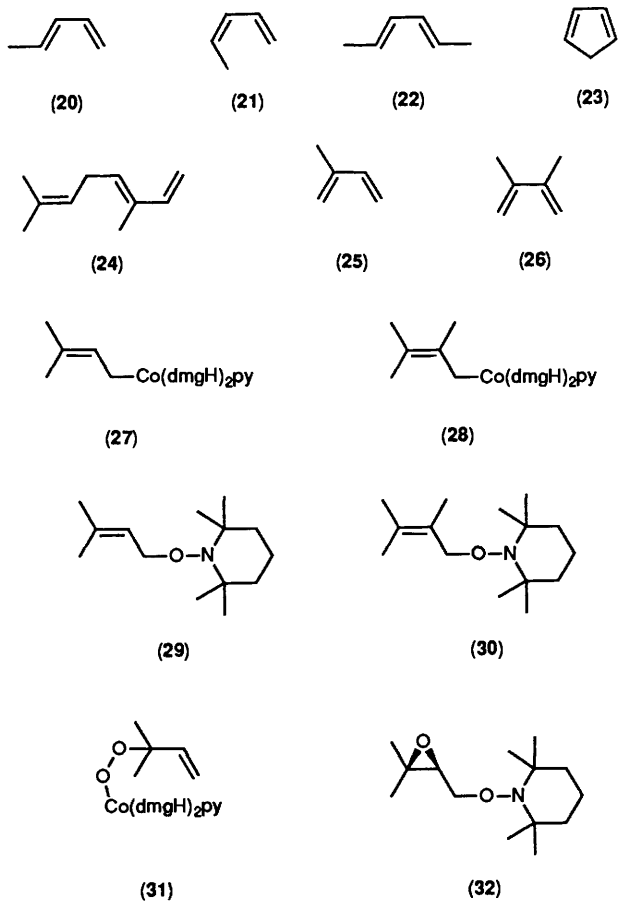
Scheme 4. *Reagents and conditions:* i, heat, $^3O_2$.



Reagents and conditions: i, Zn, HOAc; ii, TEMPO, heat.

conversion could possibly take place *via* the discrete tertiary radical (**6**) or through a six-centred transition state, *i.e.* (**13**), using a radical equivalent of a cobalt-ene reaction, or alternatively through rearrangement of an initially formed geranyl/neryl peroxycobaloxime complex (**14**) (see Scheme 4).[12] The dichotomy in reactivity between the cobaloxime (**4**) and TEMPO or O_2 no doubt reflects, in part, the relative steric demands of the two reagents, with the larger TEMPO reagent precluding attack at the tertiary radical centre in the isomers (**5**)/(**6**).

Interestingly, when a solution of the peroxycobaloxime (**15**) in toluene was heated at 100 °C in the presence of TEMPO for 15 min, chromatography separated the diastereoisomers of the 1:1 mixture of tetrahydrofuranylmethanol–TEMPO adducts



(**17**) (46%).[13] Reduction of each of the adducts, using zinc dust in acetic acid, then produced (+)-linalool oxide (**18**) (60%) and the corresponding *syn*-diastereoisomer (**19**).[14]

As a corollary to these studies with myrcene, we also examined the potential for hydrocobaltation reactions of a variety of other substituted 1,3-dienes. The results were disappointing, since none of the dienes (**20**)–(**24**) containing substituents at their terminal centres underwent hydrocobaltation to produce the corresponding allylcobaloximes.[10] Only the dienes (**25**) and (**26**) gave rise to allylcobaloxime products, *viz.* (**27**) and (**28**), respectively.[15] It is tempting to suggest that the differing ease of hydrocobaltation amongst the 1,3-dienes (**20**)–(**26**) has its origin in the steric effects of the 1,4-substituents. Similar to the allylcobaloxime (**4**), the cobaloximes (**27**) and (**28**) derived from 2-methylbuta-1,3-diene and 2,3-dimethylbuta-1,3-diene respectively, both reacted with TEMPO to afford the 'primary' hydroxylamines (**29**) and (**30**), respectively. In addition, the allylcobaloxime (**27**) produced the corresponding peroxycobaloxime (**31**) in the presence of molecular oxygen, which gave rise to the epoxide derivative (**32**) when heated in the presence of TEMPO.

Experimental

For general experimental details see ref. 1.

3,7-*Dimethylocta*-2,6-*dienylpyridinatocobaloxime* (**4**).—A stirred suspension of cobalt(II) chloride hexahydrate (1.90 g, 8.00 mmol), dimethylglyoxime (1.86 g, 16.0 mmol), and methanol (40 ml) was degassed by bubbling nitrogen for 30 min at room temperature. Pyridine (0.63 g, 8.00 mmol) was added (the reaction mixture went brown), followed by the addition of aq. 10M-sodium hydroxide (3 ml), and a black solution resulted. Degassing with nitrogen was continued for 10 min, and then the nitrogen was exchanged for hydrogen. After 5 min freshly distilled myrcene (**3**) (0.55 g, 4.00 mmol) was added, and the mixture was then stirred for 3 h at room temperature under hydrogen, before being poured into water (50 ml). The resulting orange, solid cobaloxime (1.22 g, 60%) (decomp. >85 °C) was filtered off, and the residue was then washed successively with water and hexane and dried under vacuum. Spectroscopic data showed that the cobaloxime was a 2:1 mixture of the *E*- and *Z*-isomer, $\nu_{max}(CHCl_3)$ 3 350 (OH), 2 920, 1 600 (C=C), 1 560, 1 100 cm^{-1} (C–O); δ_H(*E*-isomer) 8.5 (dd, *J* 6.2 and 1.2 Hz, pyr. CH), 7.7 (m, pyr. CH), 7.3 (m, pyr. CH), 5.1 (m, =CH), 5.0 (m, =CH), 2.4 (d, *J* 9.5 Hz, CH_2Co), 2.1 (4 × Me), 2.0 (m, CH_2), 1.65 (Me), 1.6 (m, CH_2), 1.55 (Me), and 1.25 (Me); δ_H(*Z*-isomer) 2.4 (d, *J* 9.5 Hz, CH_2Co), 2.11 (4 × Me), 1.6 (Me), and 1.16 (Me); *m/z* (FAB) 463, 426 (M^+ − pyr.), 339, 290 [$Co(dmgH)_2$ + 1], and 289.

(E/Z)-3,7-*Dimethyl*-1-(2,2,6,6-*tetramethylpiperidin*-1-*yloxy*)-*octa*-2,6-*diene* (**7**).—Dry toluene (25 ml) was deoxygenated by bubbling nitrogen for 1 h. (*E*/*Z*)-3,7-Dimethylocta-2,6-dienyl(pyridinato)cobaloxime (**4**) (0.50 g, 0.99 mmol) and TEMPO (0.31 g, 2.0 mmol) were added, and the resulting brown solution was then submerged in an oil-bath (100 °C) and stirred under nitrogen for 15 min. The solution was allowed to cool to room temperature, when it was extracted with water (25 ml). The aqueous phase was extracted with diethyl ether (2 × 15 ml). The combined toluene and ethereal phases were dried ($MgSO_4$), and the solvents were then removed *in vacuo*. The residue was preloaded on silica gel, and the product was then eluted with light petroleum–diethyl ether (99:1). The oily TEMPO adduct (**7**) (0.12 g, 41%) was isolated as a mixture of *E* and *Z* isomers, which showed $\nu_{max}(CHCl_3)$ 1 650, 1 350, and 990 cm^{-1}; δ_H 5.3 (m, =CH), 5.1 (m, =CH), 4.3 (m, CH_2O), 2.1 (4 H, m), 1.7 (Me), 1.64 (Me), 1.61 (3 H, s, Me, *Z*-isomer), 1.6 (Me), 1.5–1.2 (6 H, m), 1.2 (2 × Me), and 1.1 (2 × Me); *m/z* (EI) 156 (M^+ − $C_9H_{18}NO$), 142, 137 ($C_{10}H_{17}$), 93, 81, and 69 (Found: C, 78.0; H, 11.8. $C_{19}H_{35}NO$ requires C, 77.8; H, 12.0%).

Geraniol/*Nerol* (**8**).—Activated zinc dust (0.57 g, 8.7 mmol) was added to a stirred solution of compound (**7**) (0.17 g, 0.58 mmol) in 50% aq. acetic acid (8 ml). The mixture was submerged in an oil-bath (100 °C) and heated for 1 h. After cooling to room temperature the mixture was diluted with water (8 ml) and extracted with diethyl ether (3 × 8 ml). The combined extracts were neutralised with saturated aq. sodium hydrogen carbonate, then dried ($MgSO_4$) and evaporated *in vacuo*. The residue was purified by chromatography on silica gel, with light petroleum–diethyl ether (97:3) as eluant, to give geraniol/nerol (**8a** and **b**) (41 mg, 46%; ratio 2:1 by ^1H NMR analysis) as a liquid, identical with authentic geraniol/nerol.

Linalylperoxy(*pyridinato*)*cobaloxime* (**15**).—A solution of (*E*/*Z*)-3,7-dimethylocta-2,6-dienyl(pyridinato)cobaloxime (**4**) (2.7 g, 5.3 mmol) in dichloromethane (100 ml) was left in the dark until, based on TLC (silica gel; EtOAc), the starting material had disappeared. The solvent was removed, and the residue was then purified by chromatography on a short pad of silica, with ethyl acetate–light petroleum (70:30) as eluant, to give the *title peroxycobalt species* (**15**) (1 g, 35%) as a green powder, m.p. 185 °C (decomp.); $\nu_{max}(CHCl_3)$ 3 350 (OH), 2 900, 1 605, 1 560, and 1 090 cm^{-1}; δ_H 8.3 (m, 2 × pyr. CH), 7.6 (m, pyr. CH), 7.1 (m, 2 × pyr. CH), 5.7 (dd, *J* 18 and 11 Hz, =CH), 4.9 (m, =CH), 4.8 (dd, *J* 11 and 1.8 Hz, =CH), 4.7 (dd, *J* 18 and 1.8 Hz, =CH), 2.2 (4 × Me), 1.6 (m, CH_2), 1.5 (MeC=), 1.5 (MeC=), 1.2 (m, CH_2), and 0.9 (Me); δ_C 150.9 (q), 150.7 (CH), 143.8 (CH), 137.7 (CH), 130.2 (q), 124.8 (CH), 124.7 (CH), 111.3 (CH_2), 80.9 (q), 38.4

(CH_2), 25.1 (CH_3), 22.3 (CH_2), 20.8 (CH_3), 17.1 (CH_3), and 12.0 (CH_3); *m/z* (FAB) 538 ($M^+ + 1$), 463, 462, 368 ($M^+ - C_{10}H_{17}O_2$), 290 [Co(dmgH)$_2$ + 1], and 289 (Found: C, 51.1; H, 6.8; N, 12.8. $C_{23}H_{36}CoN_5O_6$ requires C, 51.4; H, 6.8; N, 13.0%).

Linalool (**16**).—Aq. 10M-sodium hydroxide (0.4 ml) was added to a stirred solution of linalylperoxy(pyridinato)cobaloxime (**15**) (0.33 g, 0.61 mmol) in methanol (30 ml), followed by portionwise addition of sodium borohydride (0.17 g, 4.6 mmol) during 20 min. The reaction mixture was stirred overnight. The solvent was removed at reduced pressure, and the residue was then dissolved in water (20 ml) and extracted with diethyl ether (3 × 10 ml). The extract was dried ($MgSO_4$) and evaporated, and the residue was then purified by chromatography on silica gel, with light petroleum–diethyl ether (92:8) as eluant, to give the alcohol (**16**) (24 mg, 26%) as an oil; δ_H 5.9 (dd, *J* 17 and 11 Hz, =CH), 5.2 (dd, *J* 17 and 1.3 Hz, =C*H*H), 5.1 (m, =CH), 5.05 (dd, *J* 11 and 1.3 Hz, =CH*H*), 2.0 (m, CH_2), 1.7 (Me), 1.5–1.6 (Me), 1.6 (m, CH_2), 1.3 (Me); δ_C 145.0 (CH), 132.0 (q), 124.3 (CH), 111.7 (CH_2), 73.5 (q), 42.0 (CH_2), 27.9 (CH_3), 25.7 (CH_3), 22.8 (CH_2), and 17.7 (CH_3), identical with authentic material.

N-[1-(5-*Ethenyltetrahydro*-5-*methylfuran*-2-*yl*)-1-*methylethoxy*]-2,2,6,6-*tetramethylpiperidine* (**17**).—Sodium-dried toluene (50 ml) was deoxygenated by bubbling nitrogen for 1 h. Linalylperoxy(pyridinato)cobaloxime (**15**) (1.0 g, 1.7 mmol) and TEMPO (0.34 g, 2.2 mmol) were added, and the resulting brown solution was then submerged in an oil-bath (100 °C) and stirred under nitrogen for 15 min. The solution was allowed to cool to room temperature, when it was extracted with water (40 ml); the separated aq. phase was then extracted with diethyl ether (2 × 25 ml). The combined toluene and ether extracts were dried ($MgSO_4$), and the solvents were then removed *in vacuo*. The residue was preloaded on silica gel, and the diastereoisomeric TEMPO adducts (**17**) (0.17 g, 35%) (1:1 ratio) products were then eluted with light petroleum–diethyl ether (99:1) to give: (i) the anti-*isomer* (eluted first) as an oil, ν_{max}($CHCl_3$) 1 350, 1 190, 1 010, and 920 cm^{-1}; δ_H 5.8 (dd, *J* 17 and 11 Hz, =CH), 5.2 (dd, *J* 17 and 1.7 Hz, =C*H*H), 5.0 (dd, *J* 11 and 1.7 Hz, =CH*H*), 4.1 (t, *J* 7.1 Hz, CHO), 2.0–2.8 (3 H, m), 1.6 (1 H, m), 1.5 (4 H, m), 1.35 (2 H, m), 1.33 (Me), 1.31 (Me), 1.22 (Me), 1.16 (Me), 1.10 (Me), 1.08 (Me), and 1.05 (Me); δ_C 144.0 (CH), 111.0 (CH_2), 84.3 (CH), 83.0 (q), 80.0 (q), 59.2 (q), 59.0 (q), 41.0 (CH_2), 37.1 (CH_2), 35.0 (CH_3), 27.0 (CH_3), 26.0 (CH_2), 23.1 (CH_3), 22.0 (CH_3), 20.5 (CH_3), 20.2 (CH_3), and 17.0 (CH_2) (Found: *m/z*, 156.1392 and 153.1279. $C_9H_{18}NO$ requires *m/z*, 156.1389; $C_{10}H_{17}O$ requires *m/z*, 153.1280. Found: C, 74.1; H, 11.8; N, 4.2. $C_{19}H_{35}NO_2$ requires C, 73.7; H, 11.4; N, 4.5%); and (ii) the *syn*-isomer (eluted second) as an oil, ν_{max}($CHCl_3$) 2 880, 1 640w, 1 450, 1 370, 1 140, and 1 020 cm^{-1}; δ_H 6.0 (dd, *J* 17 and 11 Hz, =CH), 5.2 (dd, *J* 17 and 1.5 Hz, =C*H*H), 5.0 (dd, *J* 11 and 1.5 Hz, =CH*H*), 4.2 (t, *J* 7.1 Hz, CHO), 2.0 (m, CH_2), 1.7 (m, CH_2), 1.5 (4 H, m), 1.36 (m, CH_2), 1.34 (Me), 1.30 (m, CH_2), 1.28 (Me), 1.2 (Me), 1.15 (Me), 1.12 (Me), 1.08 (Me), and 1.06 (Me); δ_C 144.4 (CH), 111.1 (CH_2), 84.0 (CH), 83.0 (q), 80.3 (q), 59.5 (q), 59.2 (q), 41.0 (CH_2), 38.1 (CH_2), 35.1 (CH_3), 26.4 (CH_2), 25.3 (CH_3), 23.4 (CH_3), 22.3 (CH_3), 21.0 (CH_3), 20.4 (CH_3), and 17.2 (CH_2) (Found: *m/z*, 156.1398 and 153.1294. $C_9H_{18}NO$ requires *m/z*, 156.1389; $C_{10}H_{17}O$ requires *m/z*, 153.1280. Found: C, 73.6; H, 11.7; N, 4.3%).

(trans-5-*Ethenyltetrahydro*-5-*methylfuran*-2-*yl*)*propan*-2-*ol* (**18**).—Activated zinc dust (0.12 g, 1.8 mmol) was added to a stirred solution of the *anti*-TEMPO adduct (**17**) (0.035 g, 0.12 mmol) in 50% aq. acetic acid (4 ml), and the mixture was then submerged in an oil-bath (100 °C) for 1 h. After cooling to room temperature the mixture was diluted with water (5 ml) and was then extracted with diethyl ether (3 × 5 ml). The combined extracts were neutralised with saturated aq. sodium hydrogen carbonate, then dried ($MgSO_4$), and evaporated *in vacuo*. The residue was purified by chromatography on silica gel, with light petroleum–diethyl ether (92:8) as eluant, to give the alcohol (**18**)[14] (10 mg, 55%) as an oil, δ_H 5.9 (dd, *J* 17 and 11 Hz, =CH), 5.2 (dd, *J* 17 and 1.5 Hz, =C*H*H), 5.0 (dd, *J* 11 and 1.5 Hz, =CH*H*), 4.0 (t, *J* 7.1 Hz, CHO), 2.2 (OH), 1.8 (3 H, m), 1.7 (1 H, m), 1.3 (Me), 1.2 (Me), and 1.1 (Me); δ_C 144.0 (CH), 111.4 (CH_2), 86.0 (CH), 83.1 (q), 71.2 (q), 38.0 (CH_2), 27.3 (CH_3), 27.0 (CH_3), 26.4 (CH_2), and 24.3 (Me); *m/z* (EI) 155 ($M^+ - CH_3$), 111 ($M^+ - C_3H_7O$), 94, 93, and 59 ($C_3H_7O^+$).

(cis-5-*Ethenyltetrahydro*-5-*methylfuran*-2-*yl*)*propan*-2-*ol* (**19**).—The *syn*-TEMPO adduct (**17**) (69 mg, 0.22 mmol) was reduced by the same procedure as that employed for the isomeric TEMPO adduct, to give the corresponding alcohol (**19**)[14] (16 mg, 44%) as an oil, δ_H 6.0 (dd, *J* 17 and 11 Hz, =CH), 5.2 (dd, *J* 17 and 1.2 Hz, =C*H*H), 5.0 (dd, *J* 11 and 1.5 Hz, =CH*H*), 3.9 (t, *J* 7 Hz, CHO), 2.1 (OH), 2.0–1.8 (4 H, m), 1.3 (Me), 1.2 (Me), and 1.1 (Me); δ_C 144.4 (CH), 111.6 (CH_2), 85.6 (CH), 82.8 (q), 71.2 (q), 37.9 (CH_2), 27.5 (CH_3), 26.5 (CH_2), 26.0 (CH_3), and 24.3 (Me); *m/z* (EI) 155 ($M^+ - CH_3$), 111 ($M^+ - C_3H_7O$), 94, 93, and 59 ($C_3H_7O^+$).

3-*Methylbut*-2-*enyl*(*pyridinato*)*cobaloxime* (**27**).[15]—A stirred suspension of cobalt(II) chloride hexahydrate (7.6 g, 32 mmol), dimethylglyoxime (7.4 g, 64 mmol), and methanol (160 ml) in a flask equipped with a reflux condenser was degassed for 30 min at room temperature by bubbling nitrogen. Pyridine (2.5 g, 32 mmol) was added (the reaction mixture went brown), followed by the addition of aq. 10M-sodium hydroxide (12 ml). A black solution resulted. Degassing was continued for 10 min, and then the nitrogen was exchanged for hydrogen. After 5 min the hydrogen flow was changed from being directly into the solution to being a stream above the solution, and isoprene (**25**) (1.6 g, 24 mmol) was added. The mixture was stirred for 4 h at room temperature under hydrogen before being poured into water (150 ml). The product, an orange solid (5.27 g, 50%) (decomp. >85 °C), was isolated by filtration, washed with water, and dried *in vacuo*; it showed ν_{max}($CHCl_3$) 3 350, 2 920, 1 600, 1 550, 1 190, and 1 080 cm^{-1}; δ_H 8.5 (m, 2 × pyr. CH), 7.7 (m, pyr. CH), 7.3 (m, 2 × pyr. CH), 5.0 (m, =CH), 2.4 (d, *J* 9.3 Hz, CH_2Co), 2.1 (4 × Me), 1.2 (Me), and 1.1 (Me); δ_C 149.5 (CH), 149.0 (q), 137.0 (CH), 131.0 (CH), 130.0 (q), 125.0 (CH), 27.0 (CH_3), 26.2 (CH_2), 18.0 (CH_3), and 11.4 (CH_3); *m/z* (FAB) 438 ($M^+ + 1$), 358 (M^+ – pyr.), 290 [Co(dmgH)$_2$ + 1], 289, 205, 154, and 117 (Found: C, 49.1; H, 6.6; N, 16.1. Calc. for $C_{18}H_{28}N_5O_4Co$: C, 49.4; H, 6.4; N, 16.0%).

2,2,6,6-*Tetramethyl*-N-(3-*methylbut*-2-*enyloxy*)*piperidine* (**29**).—Dry toluene (25 ml) was deoxygenated by bubbling nitrogen for 1 h. 3-Methylbut-2-enyl(pyridinato)cobaloxime (**27**) (0.50 g, 1.1 mmol) and TEMPO (0.32 g, 2.0 mmol) were added, and the resulting brown solution was then submerged in an oil-bath (100 °C) and stirred under nitrogen for 15 min. The solution was allowed to cool to room temperature and was then poured into water (30 ml). The aq. layer was removed and further extracted with diethyl ether (2 × 25 ml). The combined ethereal and toluene phases were dried ($MgSO_4$), and the solvents were then removed *in vacuo*. The residue was preloaded on silica gel, and the product was then eluted with light petroleum–diethyl ether (99:1). The *TEMPO adduct* (**29**) (0.15 g, 57%) was isolated as an oil; ν_{max}($CHCl_3$) 2 880, 1 670w, 1 450, 1 370, 1 360, 1 130, and 990 cm^{-1}; δ_H 5.3 (m, =CH), 4.5 (d, *J* 7.0 Hz, CH_2O), 1.74 (MeC=), 1.66 (MeC=), 1.5–1.3 (6 H,

m), 1.2 (2 × Me), and 1.1 (2 × Me); δc 136.0 (q), 120.5 (CH), 74.3 (CH_2), 60.0 (q), 40.0 (CH_2), 33.1 (CH_3), 26.0 (CH_3), 20.2 (CH_3), 18.3 (CH_3), and 17.2 (CH_2); *m/z* (EI) 156 ($M^+ - C_5H_9$), 142, 123, and 69 ($C_5H_9^+$) (Found: C, 75.0; H, 12.0; N, 6.1. $C_{14}H_{27}NO$ requires C, 75.0; H, 12.1; N, 6.2%).

(2-*Methylbut*-3-*en*-2-*yl*)*peroxy*(*pyridinato*)*cobaloxime*(**31**).—A solution of 3-methylbut-2-enyl(pyridinato)cobaloxime (**27**) (0.98 g, 2.2 mmol) in dichloromethane (25 ml) was left in the dark until, based on TLC (silica gel; EtOAc), the starting material had disappeared. The solvent was removed, and the residue was then purified by chromatography on a short pad of silica, with ethyl acetate–light petroleum (90:10) as eluant, to give the *peroxycobalt species* as a green powder (0.60 g, 58%) (slow decomp. >180 °C); $\nu_{max}(CHCl_3)$ 3 350, 2 920, 1 610, 1 560, and 1 090 cm^{-1}; δ_H 8.3 (m, 2 × pyr. CH), 7.6 (m, pyr. CH), 7.2 (m, 2 × pyr. CH), 5.9 (dd, *J* 18 and 11 Hz, =CH), 4.9 (dd, *J* 18 and 1.6 Hz, =C*H*H), 4.8 (dd, *J* 11 and 1.6 Hz, =CH*H*), 2.3 (4 × Me), and 1.0 (2 × Me); δ_C 151.4 (CH), 151.2 (q), 145.1 (CH), 138.1 (CH), 125.1 (CH), 111.0 (CH_2), 79.4 (q), 24.5 (CH_3), and 12.6 (CH_3); *m/z* (FAB) 577 (M^+ + thiol matrix), 368 ($M^+ - C_5H_9O_2$), 290 [Co(dmgH)$_2$ + 1], and 289 (Found: C, 46.2; H, 6.2; N, 15.1. $C_{18}H_{28}CoN_5O_6$ requires C, 46.1; H, 6.0; N, 14.9%).

N-(2,3-*Epoxy*-3-*methylbutoxy*)-2,2,6,6-*tetramethylpiperidine* (**32**).—Dry toluene (25 ml) was deoxygenated by bubbling nitrogen for 1 h. The peroxycobalt species (**31**) (0.29 g, 0.66 mmol) and TEMPO (0.24 g, 1.6 mmol) were added, and the resulting dark green solution was then submerged in an oil-bath (100 °C) and stirred under nitrogen for 30 min. The brown solution was allowed to cool to room temperature and was extracted with water (20 ml); the separated aq. phase was then extracted with diethyl ether (2 × 20 ml). The combined ethereal and toluene phases were then evaporated *in vacuo*. The residue was preloaded on silica gel, and the product was then eluted with light petroleum–diethyl ether (95:5). The *TEMPO adduct* (**32**) (73 mg, 46%) was isolated as an oil; $\nu_{max}(CHCl_3)$ 2 980, 2 940, 1 470, 1 455, 1 380, 1 135, and 1 040 cm^{-1}; δ_H 4.0 (dd, *J* 10 and 4.5 Hz, C*H*HO), 3.8 (dd, *J* 10 and 6.2 Hz, CH*H*O), 2.9 (dd, *J* 6.2 and 4.5 Hz, CH_2CHO), 1.4 (4 H, m), 1.34 (MeCO), 1.28 (MeCO), 1.2–1.1 (2 H, m), 1.2 (Me), 1.16 (Me), 1.1 (2 × Me); δ_C 75.3 (CH_2), 60.3 (CH), 59.0 (q), 58.8 (q), 56.4 (q), 39.0 (CH_2), 32.1 (CH_3), 31.8 (CH_3), 23.7 (CH_3), 19.1 (CH_3), 18.1 (CH_3), and 16.1 (CH_2) (Found: C, 69.9; H, 11.6; N, 5.6%; M^+, 241.2046. $C_{14}H_{27}NO_2$ requires C, 69.7; H, 11.3; N, 5.8%; *M*, 241.2043).

2,3-*Dimethylbut*-2-*enyl*(*pyridinato*)*cobaloxime* (**28**).—A stirred suspension of cobalt(II) chloride hexahydrate (5.7 g, 24 mmol), dimethylglyoxime (5.6 g, 48 mmol), and methanol (129 ml) in a flask equipped with a reflux condenser was degassed for 30 min at room temperature by bubbling nitrogen. Pyridine (1.4 g, 24 mmol) was added (the reaction mixture went brown), followed by the addition of aq. 10M-sodium hydroxide (9 ml). A black solution resulted. Degassing was continued for 10 min and then the nitrogen was exchanged for hydrogen. After 5 min the hydrogen introduction was changed from being directly into the solution to being a stream above the solution, and 2,3-dimethylbuta-1,3-diene (**26**) (1.3 g, 16 mmol) was added. The reaction mixture was stirred for 4 h at room temperature under hydrogen before being poured into water (129 ml). The *title product*, an orange solid (2.54 g, 35%) (decomp. >145 °C), was isolated by filtration, washed with water, and dried *in vacuo*; it showed $\nu_{max}(CHCl_3)$ 2 900, 1 603, 1 560, and 1 090 cm^{-1}; δ_H 8.6 (m, 2 × pyr. CH), 7.7 (m, pyr. CH), 7.3 (m, 2 × pyr. CH), 2.1 (4 × Me and CH_2Co), 1.6 (Me), 1.15 (Me), and 1.13 (Me); δ_C 150.2 (q), 149.1 (CH), 137.3 (CH), 135.5 (q), 126.0 (q), 125.5 (CH), 34.3 (CH_2), 22.6 (CH_3), 21.8 (CH_3), 20.5 (CH_3), and 11.9 (Me) (Found: C, 50.4; H, 6.8; N, 15.5. $C_{19}H_{30}CoN_5O_4$ requires C, 50.6; H, 6.7; N, 15.5%).

N-(2,3-*Dimethylbut*-2-*enyloxy*)-2,2,6,6-*tetramethylpiperidine* (**30**).—Dry toluene (29 ml) was deoxygenated by bubbling nitrogen for 1 h. 2,3-Dimethylbut-2-enyl(pyridinato)cobaloxime (**28**) (0.25 g, 0.55 mmol) and TEMPO (0.16 g, 1.02 mmol) were added, and the resulting brown solution was submerged in an oil-bath (85 °C) and stirred under N_2 for 15 min. The solution was allowed to cool to room temperature, and was then poured into water (20 ml). The aq. layer was removed and further extracted with diethyl ether (2 × 25 ml). The combined ether and toluene phases were dried ($MgSO_4$), and the solvents were then removed *in vacuo*. The residue was preloaded on silica gel, and the product was then eluted with light petroleum–diethyl ether (99:1). The TEMPO adduct (**30**) (30 mg, 23%) was isolated as an oil, $\nu_{max}(CHCl_3)$ 2 860, 1 435, 1 355, 1 180, 1 130, 985, 970, and 955 cm^{-1}; δ_H 4.8 (OCH_2), 1.8 (=CMe), 1.73 (=CMe), 1.70 (=CMe), 1.6–1.2 (3 × CH_2), 1.2 (2 × Me), and 1.11 (2 × Me); δ_C 129.0 (q), 125.2 (q), 77.5 (CH_2), 59.8 (q), 39.8 (CH_2), 33.2 (CH_3), 20.7 (CH_3), 20.6 (CH_3), 20.2 (CH_3), 17.2 (CH_2), and 17.1 (CH_3); *m/z* 157 ($M^+ - C_6H_{10}$), 156, 142, 83, and 82.

(2,3-*Dimethylbut*-3-*en*-2-*yl*)*peroxy*(*pyridinato*)*cobaloxime*.—A solution of 2,3-dimethylbut-2-enyl(pyridinato)cobaloxime (**28**) (0.24 g, 0.53 mmol) in dichloromethane (15 ml) containing dissolved oxygen was left in the dark until, based on TLC (silica gel; EtOAc), the starting material had disappeared. The solvent was removed, and the residue was then purified by chromatography on a short pad of silica, with ethyl acetate–light petroleum (80:20) as eluant, to give the *title peroxycobalt species* (0.11 g, 43%) as a green powder (slow decomp. >170 °C); $\nu_{max}(CHCl_3)$ 3 680, 3 620, 3 000, 1 420, 1 220, 1 190, 1 045, and 930 cm^{-1}; δ_H 8.4 (m, 2 × pyr. CH), 7.7 (m, pyr. CH), 7.2 (m, 2 × pyr. CH), 4.65 (br s, =C*H*H), 4.6 (br s, =CH*H*), 2.3 (4 × Me), 1.6 (d, *J* 0.5 Hz, =CMe), 1.0 (2 × Me); δ_C 151.5 (q), 151.3 (q), 151.2 (CH), 138.1 (CH), 125.2 (CH), 108.6 (CH_2), 30.9 (q), 24.2 (CH_3), and 19.2 (CH_3) (Found: C, 46.7; H, 6.4; N, 14.5. $C_{19}H_{30}N_5O_6$ requires C, 47.2; H, 6.3; N, 14.5%).

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