# Routes of Formation and Crystal Structure of an Alkylperoxycobaloxime: Bis[dimethylglyoximato(1 −)](4-ethoxycarbonylbut-3-en-2-ylperoxo)(pyridine)cobalt(III)‡

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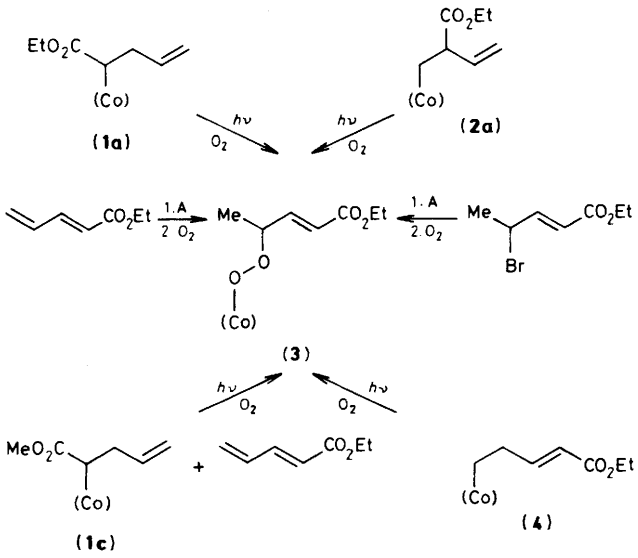
Thermal and photolytic routes from alkylating agents *via* alkylcobaloximes are described leading to the formation of the complex bis[dimethylglyoximato(1 −)](4-ethoxycarbonylbut-3-en-2-ylperoxo)(pyridine)cobalt(III). All the routes converge at the putative intermediate 3-ethoxycarbonyl-1-methylallyl(pyridine)cobaloxime, the Co–C bond of which reacts with dioxygen at room temperature to give the alkylperoxycobaloxime. The formation of the alkylperoxycobaloxime by aerobic photolysis of 2-ethoxycarbonylbut-3-enyl(pyridine)cobaloxime proceeds *via* the 2-ethoxycarbonylbut-3-enyl radical, which rearranges to the 1-ethoxycarbonylbut-3-enyl radical. This radical reacts with cobaloxime(II) to give hydridocobaloxime and 1-ethoxycarbonylbuta-1,3-diene. Recombination of these species yields 3-ethoxycarbonyl-1-methylallyl(pyridine)cobaloxime and hence the alkylperoxycobaloxime. The structure was identified by an *X*-ray determination, final $R$ = 0.049 for 1 652 observed diffractometer-collected reflections. Principal dimensions (average) are Co–O 1.923(4), O–O 1.415(7), Co–N(oxime) 1.896(3) Å, Co–O–O 115.3(3)°, and dihedral angle Co–O–O–C 100.0(4)°.

During studies[1] of rearrangements of 1- and 2-ethoxycarbonylbut-3-enyl(pyridine)cobaloxime {(**1a**) and (**2a**), respectively, cobaloxime = bis[dimethylglyoximato(1 −)]cobalt}, solutions of these cobaloximes in deuteriochloroform were exposed to sunlight. The production of a much more polar cobaloxime (**3**) was monitored by thin-layer chromatography. This compound was also a product of the aerobic photolysis of 4-ethoxycarbonylbut-3-enyl(pyridine)cobaloxime (**4**) and of the attempted preparation of 3-ethoxycarbonyl-1-methylallyl(pyridine)cobaloxime (**5**) from (pyridine)cobaloxime(I) and ethyl 4-bromopent-2-enoate in ethanol. Two more routes to (**3**), which bear on the mechanism of its formation under all sets of conditions (summarised in the Scheme) are described below (see Discussion section).

The $^1$H n.m.r. spectral data for cobaloxime (**3**) indicated the presence of a (pyridine)cobaloxime and an (*E*)-4-ethoxycarbonylbut-3-en-2-yl fragment. The $^{13}$C-{$^1$H} n.m.r. spectrum confirmed these assignments and indicated the presence of a C–O bond. However, neither spectrum permitted a definite identification of (**3**), which was achieved by crystal structure analysis.




R (**5**) R = CH(Me)CH=CHCO$_2$Et
(Co) (**6**) R = CH(Ph)CH$_2$OH
R• (**1b**) R = CH(CO$_2$Et)CH$_2$CH=CH$_2$
(Co) (**2b**) R = CH$_2$CH(CO$_2$Et)CH=CH$_2$

**Scheme.** (Co) = Co(Hdmg)$_2$, A = (pyridine)cobaloxime(I)

## Experimental

*Preparative Chemistry.*—For general directions see refs. 2 and 3. The preparative methods for 1- and 2-ethoxycarbonylbut-3-enyl(pyridine)cobaloxime [(**1a**) and (**2a**), respectively] were outlined in ref. 1. Further details will be given in the full paper corresponding to this communication.

*Ethyl* (E)-5-(*methanesulphonyloxy*)*pent-2-enoate.* This was prepared by treating the corresponding alcohol with $MeSO_2Cl$–$NEt_3$ in $CH_2Cl_2$,[4] and was isolated as an oil in 58% yield: $\delta_H(CCl_4)$ 1.29 (t, 3 H), 2.65 (q, 2 H, *J* 6.4), 2.96 (s, 3 H), 4.15 (q, 2 H), 4.29 (t, 2 H, *J* 6.4), 5.89 (d, 1 H, $J_{trans}$ 16.1), and 6.82 (dt, 1 H, *J* 6.4, $J_{trans}$ 16.1 Hz); $\nu_{max.}$(film) 3 020w, 1 719s, 1 660m, 1 335s, and 1 175s cm$^{-1}$.

*Ethyl* (E)-4-*bromopent-2-enoate.* This was prepared by allylic bromination[5] of ethyl (*E*)-pent-2-enoate, which was obtained by the Doebner condensation[6] of malonic acid with propionaldehyde followed by esterification. Distillation of the crude product through a short fractionating column afforded

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‡ *Supplementary data available* (No. SUP 56234, 3 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

*Non-S.I. unit employed*: mmHg ≈ 133 Pa.

**Table 1.** Atom co-ordinates ( × $10^4$) for compound (3)

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Co | 4 333·5(7) | 3 356.4(4) | 4 949.1(11) | C(5) | 3 335(5) | 3 317(3) | 7 732(7) |
| N(1) | 5 006(4) | 3 039(2) | 3 223(6) | C(6) | 3 562(5) | 2 727(3) | 7 318(9) |
| N(2) | 4 456(4) | 4 034(2) | 3 724(6) | C(7) | 2 747(6) | 3 484(3) | 9 153(9) |
| N(3) | 3 660(4) | 3 672(2) | 6 700(6) | C(8) | 3 184(6) | 2 242(4) | 8 250(9) |
| N(4) | 4 094(4) | 2 671(2) | 6 082(6) | C(9) | 6 433(5) | 3 043(3) | 6 628(7) |
| N(5) | 5 779(4) | 3 482(2) | 6 181(5) | C(10) | 7 439(6) | 3 113(3) | 7 420(8) |
| O(1) | 5 234(4) | 2 479(2) | 3 133(5) | C(11) | 7 810(6) | 3 656(4) | 7 781(9) |
| O(2) | 4 076(4) | 4 537(2) | 4 168(7) | C(12) | 7 143(6) | 4 106(3) | 7 342(9) |
| O(3) | 3 537(4) | 4 240(2) | 6 866(6) | C(13) | 6 144(5) | 4 007(3) | 6 547(8) |
| O(4) | 4 366(4) | 2 152(2) | 5 548(6) | C(14) | 600(7) | 3 601(4) | 5 237(11) |
| O(5) | 3 036(3) | 3 220(2) | 3 548(5) | C(15) | 1 527(6) | 3 677(3) | 4 250(8) |
| O(6) | 2 103(4) | 3 151(2) | 4 352(6) | C(16) | 1 146(6) | 3 831(3) | 2 549(10) |
| O(7) | 299(5) | 4 224(3) | −680(8) | C(17) | 1 435(6) | 4 297(3) | 1 806(9) |
| O(8) | 1 607(4) | 4 886(2) | −432(6) | C(18) | 1 024(6) | 4 447(4) | 147(10) |
| C(1) | 5 220(5) | 3 387(3) | 2 072(7) | C(19) | 1 339(7) | 5 060(4) | −2 092(10) |
| C(2) | 4 870(5) | 3 977(3) | 2 372(8) | C(20) | 1 924(9) | 5 558(4) | −2 466(14) |
| C(3) | 5 723(6) | 3 210(4) | 606(8) | H(014) | 4 854(68) | 2 208(35) | 4 624(98) |
| C(4) | 4 941(7) | 4 451(3) | 1 213(9) | H(023) | 3 767(58) | 4 460(31) | 5 608(98) |

ethyl (*E*)-4-bromopent-2-enoate, 6.40 g (88%), b.p. 98 °C at 15 mmHg (lit.,[7] b.p. 78—79 °C at 12 mmHg): $\delta_H(CCl_4)$ 1.30 (t, 3 H), 1.83 (d, 3 H, *J* 6.8), 4.16 (q, 2 H), 5.66 (dq, 1 H, $J_1$ 6.8, $J_2$ 7.8 Hz), 5.85 (d, 1 H, $J_{trans}$ 15.6), and 6.95 (dd, 1 H, $J_2$ 7.8, $J_{trans}$ 15.6 Hz); $\nu_{max.}$(film) 1 722s, 1 653m, and 725m $cm^{-1}$.

*Ethyl* (E)-*penta*-2,4-*dienoate*. To a round bottom flask (100 $cm^3$) was added ethyl (*E*)-2-bromopent-4-enoate (1.65 g, 7.97 mmol), acetone (15 $cm^3$), and triethylamine (5 $cm^3$). The reaction mixture was stirred at 55 °C for 5.5 h during which time $NHEt_3Br$ precipitated as a white solid. The reaction mixture was cooled to room temperature and filtered through a sintered-glass funnel before removing the solvent at the pump. In order to remove all the remaining triethylammonium bromide, the product was dissolved in diethyl ether (10 $cm^3$) and filtered through a short column (*ca.* 10 cm) of silica gel. The solvent was removed (< 30 °C), to give ethyl (*E*)-penta-2,4-dienoate, 0.82 g (82%): $\delta_H(CCl_4)$ 1.29 (t, 3 H), 4.18 (q, 2 H), 5.46 (d, 1 H, *J* 10.7), 5.59 (d, 1 H, *J* 17), 5.85 (d, 1 H, *J* 15.5), 6.44 (dt, 1 H, $J_1$ 10.7, $J_2$ 17), and 7.19 (dd, 1 H, $J_1$ 10.7 $J_2$ 17 Hz) (*cf.* analysis of parent acid in ref. 8); $\nu_{max.}$(film) 3 100—3 000w, 1 715s, 1 647m, and 1 603m $cm^{-1}$.

(*E*)-4-*Ethoxycarbonylbut*-3-*enyl*(*pyridine*)*cobaloxime* (**4**). This was prepared in the usual manner[9] from the following quantities of reagents: bromo(pyridine)cobaloxime (448 mg, 1 mmol), sodium tetrahydroborate (80 mg, 2.1 mmol), and ethyl (*E*)-5-(methanesulphonyloxy)pent-2-enoate (2.5 g, 11.3 mmol) in ethanol (50 $cm^3$). Chromatography [silica gel, elution with methanol–dichloromethane (10:90)] of the crude product and recrystallisation (dichloromethane–pentane) gave the title compound as orange-red *crystals*: $\delta_H$ 1.25 (t, 3 H), 1.50 (t, 2 H, *J* 8), 1.77 (q, 2 H), 2.12 (s, 12 H), 4.13 (q, 2 H), 5.72 (d, 1 H, *J* 16.4 Hz), 6.87 (dt, 1 H), and pyridine H resonances; $\nu_{max.}$(KBr) 3 420br, 3 100—3 000w, 1 708s, 1 649m, 1 605w, 1 565s, 1 235s, 1 092s, and 519m $cm^{-1}$. A combustion analysis was obtained for the corresponding methyl ester, prepared analogously (Found: C, 47.35; H, 5.7; N, 14.25. Calc. for $C_{19}H_{28}CoN_5O_6$: C, 47.4; H, 5.85; N, 14.55%).

4-*Ethoxycarbonylbut*-3-*en*-2-*ylperoxocobaloxime* (**3**). This was prepared as follows.

(*i*) From ethyl (*E*)-4-bromopent-2-enoate (207 mg, 1 mmol) by the procedure[9] using bromo(pyridine)cobaloxime (448 mg, 1 mmol) and $NaBH_4$ (76 mg, 2 mmol), which gave the title compound (53 mg, 11%) as a dark brown *solid*: $\delta(CDCl_3)$ 1.00 (d, *J* 7, *Me*CH), 1.26 (t, *Me*$CH_2$), 2.30 (s, 4 Hdmg *Me*), 3.86 (dq, *J* 7 and 7, MeC*H*), 5.23 (d, *J* 16, CHCO), 6.73 (dd, *J* 7 and 16 Hz, C*H*=CHCO) and pyridine H resonances; $\delta_C(CDCl_3)$ 12.30 (4 Hdmg *Me*), 14.08 (ester Me), 18.19 (*Me*CH), 59.83 (ester $CH_2$), 78.05 (CHO), 120.80 (*C*HCO), 125.05 (2 py $C^3$), 138.08 (py $C^4$), 149.78 (*C*H=CHCO), 150.78 (2 py $C^2$), 151.40 and 151.52 (4 C=NO, two diastereotopic pairs), and 166.30 (CO); $\nu_{max.}$(KBr) 3 450br, 3 120—3 000w, 1 722s, 1 658m, 1 640w, 1 605w, 1 568s, 1 242s, 1 092s, and 514 $cm^{-1}$; $\lambda_{max.}$(EtOH) 310 nm (ε 7 500 × $10^3$ $cm^2$ $mol^{-1}$) (no absorption at $\lambda_{max.}$ *ca.* 450 nm); $R_f$ of 0.45 (**1a**), 0.45 (**2a**), and 0.22 (**3**) on silica gel $F_{254}$, with $CH_2Cl_2$–MeOH–pyridine (96:3:1) as eluant. A satisfactory combustion analysis was not obtained for this compound, although its n.m.r. spectra showed no impurities and it was chromatographically homogeneous.

(*ii*) From photolysis of cobaloxime (**1a**), (**2a**), or (**4**) in deuteriochloroform or [$^2H_4$]methanol. Typically, a *ca.* 2 mol $dm^{-3}$ solution of the cobaloxime in a well stoppered n.m.r. tube was exposed to sunlight or a 150-W electric light bulb for various times, the progress of reaction being monitored by $^1H$ n.m.r. spectroscopy. At the end of the photolysis, the contents of the tube were flash chromatographed on silica gel 60, eluting with dichloromethane–pyridine–methanol (95:1:5) to give the alkylperoxycobaloxime (**3**) as the major product.

*Crystal Structure Analysis*.—$C_{20}H_{30}CoN_5O_8$, *M* = 527.4, monoclinic, space group $P2_1/n$, *a* = 12.553(2), *b* = 23.456(5), *c* = 8.260(1) Å, β = 96.00(1)°, *U* = 2 418.9(7) $Å^3$, $D_m$ = 1.43 g $cm^{-3}$, *Z* = 4, $D_c$ = 1.45 g $cm^{-3}$, λ(Mo-$K_\alpha$) = 0.710 69 Å, μ(Mo-$K_\alpha$) = 7.58 $cm^{-1}$, *F*(000) = 1 104, *T* = 290 K.

Single crystals obtained from ethanol were reddish brown laths. Data were collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 52°, with a scan range ±0.9° (2θ) around the $K_{\alpha1}$–$K_{\alpha2}$ angles, scan speed 3—29° $min^{-1}$, depending on the intensity of a 2-s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. All reflections in the range 2θ 3—45° were measured, but from 45 to 52° only those above a preset level on an 8-s prescan were collected. Three standard reflections were monitored every 200 reflections, and showed no changes during data collection. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 14 high-angle reflections. Of the total 6 573 reflections, 2 888 with $I/\sigma(I) > 2.5$ were used in the initial refinement, reduced to 1 652 in the final cycles, and corrected for Lorentz, polarisation, and absorption effects, the last by the Gaussian method; maximum transmission factors were 0.965 and 0.906. The crystal dimensions were 0.06 × 0.04 × 0.20 mm.

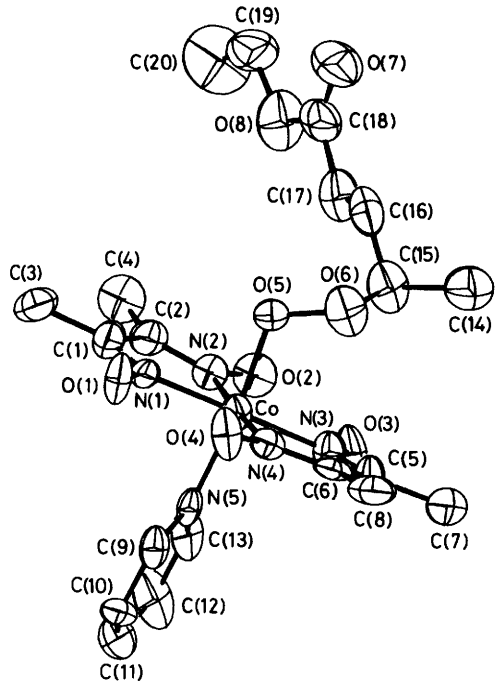


**Figure.** The title compound, showing the atomic numbering

The structure was initially believed to be triclinic with $Z = 4$ and was solved and refined on this basis, with two Co atoms located by Patterson techniques and light atoms found by successive Fourier syntheses. Refinement gave a 'final' $R$ value of 0.055. The cell reduction program of Clegg[10] then became available and revealed the correct monoclinic unit cell and symmetry, which was used for the final refinement. Hydrogen atoms in defined positions were inserted and held fixed. For all methyl groups, the H-atom positions were calculated using the dihedral angles of the strongest single hydrogen peak; the methyl groups were then refined as rigid units. The oxime protons [H(014), H(023)] were visible on the penultimate Fourier difference synthesis, clearly associated with O(2) and O(4), respectively. They were refined for one cycle, which led to a shift in H(023) towards O(3). However, the standard deviations were too large for these proton positions to be very informative.

Refinement was done by least-squares methods, in cascaded large blocks. On a final difference synthesis a few peaks > 0.3 e $Å^{-3}$ remained near the Co atom, but the map was otherwise featureless. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.0007$ was used. This was shown to be satisfactory by a weight analysis. The final $R$ value was 0.049. Computing was done with the SHELXTL system[11] on a Data General NOVA3. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 12. Final atomic co-ordinates are given in Table 1, bond lengths and angles in Table 2.

## Discussion

*Crystal Structure of Compound* (3).—The asymmetric unit contains one molecule of the alkylperoxycobaloxime (3) (Figure). The molecular dimensions (Table 2) are largely as expected. The positions of the oxime protons [H(014), H(023)] are of interest. They appear clearly on Fourier difference syntheses and are asymmetrically located [one associated with each oxime, on O(2) and O(4)], although they have relatively large positional estimated standard deviations (e.s.d.s). The

**Table 2.** Selected bond lengths (Å) and angles (°)

| | | | |
|---|---|---|---|
| Co–N(1—4) (oxime) | 1.896(3)* | O(1)···O(4) | 2.493(7) |
| | | O(2)···O(3) | 2.495(8) |
| Co–N(5) | 2.007(5) | O(3)–H(014) | 1.51(9) |
| Co–O(5) | 1.923(4) | O(4)–H(014) | 1.03(9) |
| N(1—4)–O(1—4) (oxime) | 1.347(4)* | O(2)–H(023) | 1.30(8) |
| | | O(3)–H(023) | 1.22(8) |
| N(1—4)–C(1,2,5,6) (oxime) | 1.289(5)* | | |
| | | N(1,3)–Co–N(2,4) | 81.7(1)* |
| C(1,2)–C(5,6) (oxime) | 1.471(7)* | N(1,2)–Co–N(3,4) | 98.4(1)* |
| | | Co–N(1—4)–C(1,2,5,6) | 116.1(3)* |
| O(5)–O(6) | 1.415(7) | N(1)–Co–O(5) | 84.0(2) |
| O(6)—C(15) | 1.428(8) | N(2)–Co–O(5) | 86.0(2) |
| C(14)–C(15) | 1.500(12) | N(3)–Co–O(5) | 96.2(2) |
| C(15)–C(16) | 1.480(10) | N(4)–Co–O(5) | 89.3(2) |
| C(16)–C(17) | 1.322(10) | Co–O(5)–O(6) | 115.3(3) |
| C(17)–C(18) | 1.457(11) | O(5)–O(6)–C(15) | 108.2(5) |

* Averaged over equivalent values.

O···O distances [mean 2.495(5) Å] are significantly longer than in $[Ni(Hdmg)_2]$ [2.453(6) Å],[13] which has symmetrical hydrogen bonds. This difference is apparently sufficient to cause a shift towards asymmetry. The change in O···O distance itself must arise because of the shorter Ni–N distance [1.874(4) Å][13] compared to Co–N [1.896(3) Å]. It is also of interest that the modest amount of asymmetry in the molecule arising from the pyridine and the alkylperoxy-group is sufficient to produce ordered rather than disordered hydrogen bonds.

A significant parameter for all peroxides is the R–O–O–R′ dihedral angle. This has a value of 100.0(4)° in the present compound. Strikingly similar values have been reported for two other alkylperoxycobaloximes.[14,15] Evidently, the same minimisation of lone pair–lone pair interactions that governs the structure of hydrogen peroxide[16] ($\varphi_{HOOH}$ 112°) is the dominant factor for the alkylperoxycobaloximes, notwithstanding the increased steric interactions in the preferred rotamer, compared to the *anti* rotamer.

*Mechanism of Formation of Compound* (3).—For all modes of production of compound (3) (*cf.* Scheme) we propose that the key step is the reaction of dioxygen with the hypothetical intermediate 3-ethoxycarbonyl-1-methylallyl(pyridine)cobaloxime (5). The insertion of dioxygen into an alkylcobaloxime precursor is favoured when the alkyl group can exist as a relatively stable radical[17] (*e.g.* alkyl = 1-phenylethyl) and proceeds by homolytic dissociation of the Co–C σ bond to give a cobaloxime(II) radical pair which is captured by dioxygen.[17–19] We presume that reaction of (pyridine)cobaloxime(I) with ethyl 4-bromopent-2-enoate gives cobaloxime (5), which on exposure to dioxygen in the work-up procedure yields cobaloxime (3). Formation of cobaloxime (3) from (1a) probably occurs *via* photoinduced cleavage of its Co–C bond to give a cobaloxime(II) radical pair (1b) that β-eliminates. The resulting 1-ethoxycarbonylbuta-1,3-diene and hydrido(pyridine)cobaloxime recombine to form (5) or a cobaloxime(II) radical pair corresponding to (5). Insertion of dioxygen then yields (3). A similar pathway explains the formation of (3) from (4). Photoinduced cleavage of the Co–C bond of compound (2a) gives a cobaloxime(II) radical pair (2b), which may rearrange to a cobaloxime(II) radical pair (1b) *via* a cobaloxime(II)–(ethoxycarbonyl)cyclopropylcarbinyl radical pair.[1]

Support for the proposed mechanisms of formation of cobaloxime (3) was obtained from the following experiments. (*i*) 2-Hydroxy-1-phenylethyl(pyridine)cobaloxime[20] (6) in $CDCl_3$ containing 1-ethoxycarbonylbuta-1,3-diene was heated to

45 °C; at this temperature (**6**) decomposes to phenylethanal and hydrido(pyridine)cobaloxime, which reacts with the diene to give (**5**). At this point, the $^1$H n.m.r. spectrum of the reaction solution showed resonances tentatively assigned to (**5**). Resonances for compound (**3**) were only observed after exposure of this solution to air. (*ii*) The methyl ester (**1c**) was irradiated with an equimolar amount of 1-ethoxycarbonylbuta-1,3-diene. This gave a fraction from chromatography containing a *ca.* 1:1 mixture of (**3**) and the corresponding methyl ester, according to $^1$H n.m.r. spectroscopic analysis.

Alkylperoxycobaloximes can be converted into alcohols [17] or aldehydes (ketones).[19] The routes discovered for preparing (**3**) suggest methods for achieving synthetically useful modifications of dienes and allyl halides. These are under investigation.

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