A New Route to Alkoxy Radicals – Photochemical Reactions with (Alkylperoxy)cobaloximes

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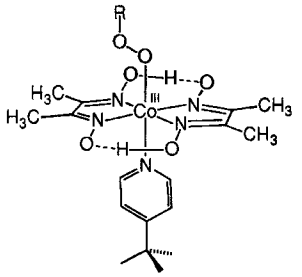
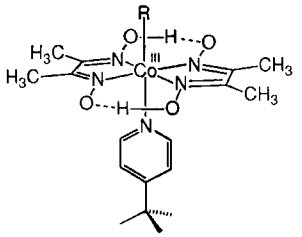
Alkoxy radicals have been generated by photochemical reactions of (alkylperoxy)cobaloximes **1**. The occurrence of alkoxy radicals has been proved by characteristic cyclization and β-scission reactions of the reactive intermediates.

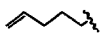
(Alkylperoxy)(pyridine)cobaloximes **1f** have been of interest since their discovery by Gianotti et al.[1]. In contrast to other oxygen-containing cobalt(III) chelates[2] (alkylperoxy)(pyridine)cobaloximes **1f** do not liberate molecular oxygen upon heating or irradiation but yield alcohols and ketones or aldehydes[3].



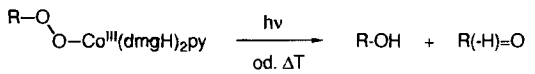


1 ≡ R–O–O–Co^{III}(dmgH)$_2$Bupy **2** ≡ R–Co^{III}(dmgH)$_2$Bupy

dmgH = 2,3-butandione dioxime monoanion
Bupy = 4-tert-butylpyridine

1, 2, 7	R
a	
b	
c	

1, 2	R
d	
e	$(H_3C)_3C$-

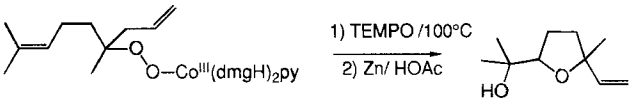


1f

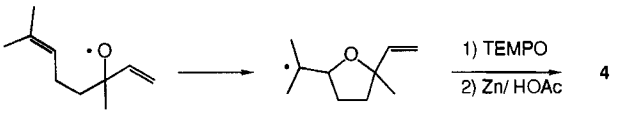
py = pyridine

X-ray crystallography of (alkylperoxy)cobaloximes **1f** provided the coordination of the peroxy group to the cobalt(III) ion[4]. The cobalt(III) metal is bound to one oxygen atom of the alkylperoxy ligand only. The oxygen–oxygen bond length of 1.455 Å, which is quite independent of the nature of the alkyl group R in **1f**, is similar to the one observed in hydrogen peroxide[5].

Recently, Pattenden and co-workers have demonstrated that the thermal reaction of linalool peroxycobaloxime **3** with tetramethylpiperidine *N*-oxide (TEMPO) and reductive workup of the reaction mixture (Zn/HOAc/H_2O) yield linalool oxide (**4**)[6] an ingredient of the Mexican linalool oil[7].



3 **4**



5 **6**

According to our investigation of (alkylperoxy)cobaloximes **1** this reaction very likely proceeds via the alkoxy radical intermediate **5** which cyclizes in a 5-*exo*-*trig* manner. Trapping of **5** by TEMPO followed by zinc reduction of the adduct then leads to linalool oxide (**4**).

We have shown by radical cyclization and β-scission reactions that (alkylperoxy)cobaloximes **1** yield alkoxy radicals[8] upon irradiation. **1** may be synthesized in two different ways, depending on the nature of the alkyl ligand attached to the dioxy group[4a,9,10]. Primary and secondary (alkylperoxy)cobaloximes such as **1a–d** are readily obtained from their parent alkylcobaloximes **2a–c** by photolysis in the presence of air. The alkylcobaloximes **2a–c** are prepared according to the one-pot procedure of Schrauzer[11] from 5-pentenyl bromide (**7a**), cyclohexyl bromide (**7b**), or *cis*-4-*tert*-butylcy-

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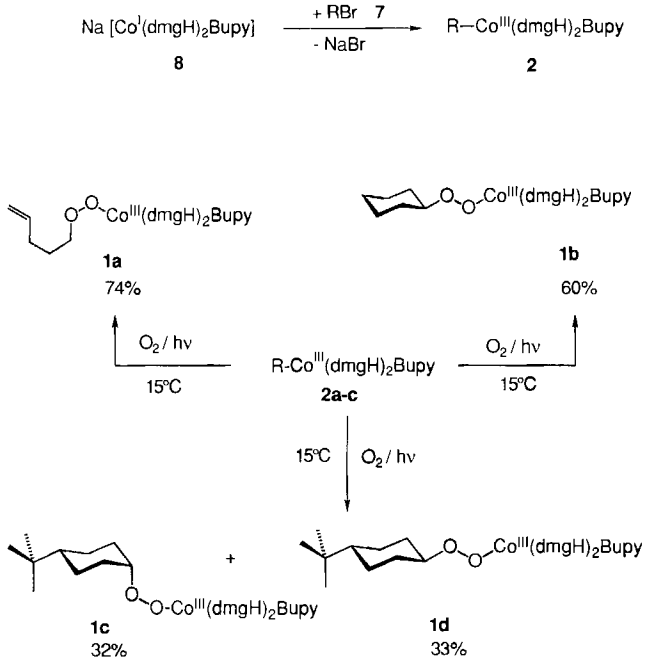
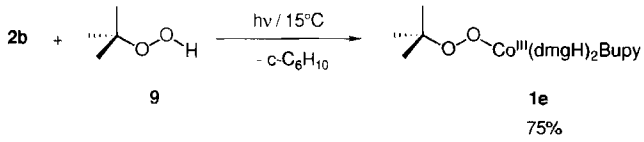
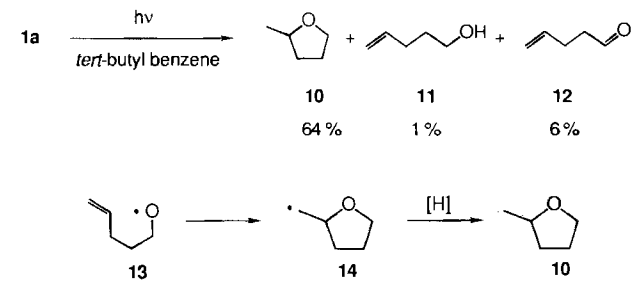
clohexyl bromide (**7c**)[12] and cobaloxime(I) **8**. The reaction between *cis*-bromide **7c** and cobalt(I) nucleophile **8** leads exclusively to *trans*-(4-*tert*-butylcyclohexyl) cobaloxime **2d**, the photoreaction of which yields the *cis*/*trans* isomers of **1c** (olive-green crystals) and **1d** (brown crystals) in almost equal amounts.



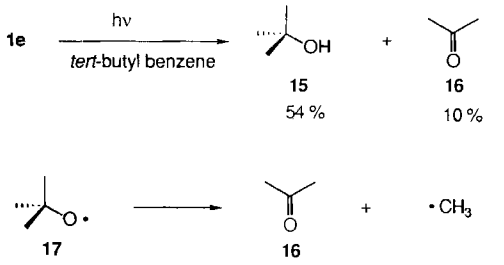
(*tert*-Butylperoxy)(4-*tert*-butylpyridine)cobaloxime (**1e**) is obtained by photolysis of cyclohexylcobaloxime **2b** with *tert*-butyl hydroperoxide (**9**). Irradiation of **2b** in the absence of an efficient radical trap yields cyclohexene and cobaloxime(II)[13]. The latter is converted by **9** into the (*tert*-butylperoxy)cobaloxime **1e**.



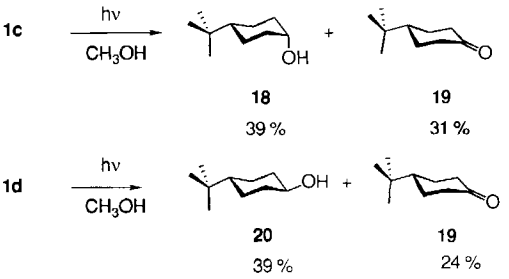
Photolysis of (4-pentenylperoxy)cobaloxime **1a** in methanol gives 2-methyltetrahydrofuran (**10**) as the main product with small amounts of the uncyclized alcohol **11** and aldehyde **12**. The formation of the cyclic ether **10** is in accord with a 5-*exo*-*trig* cyclization of the alkoxy radical **13** → **14**[8]. Subsequent hydrogen abstraction yields **10**.



Other evidence for the occurrence of alkoxy radicals as intermediates is provided by experiments with (*tert*-butylperoxy)cobaloxime **1e**. The photolysis of **1e** leads to *tert*-butyl alcohol (**15**) and acetone (**16**). The formation of both products points to the *tert*-butoxy radical (**17**) as intermediate which either abstracts a hydrogen atom or undergoes β-bond cleavage to give acetone and methyl radicals.

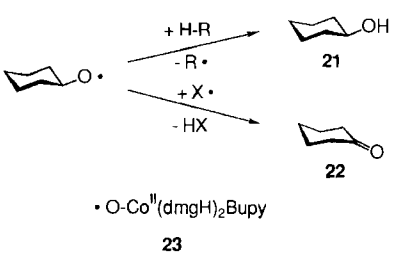


Experiments with the *cis* and *trans* isomers of **1c** and **1d** show that the C–O bond remains intact during the reaction. Thus, photolysis of **1c** and **1d** leads with complete stereospecificity to *cis*- and *trans*-4-*tert*-butylcyclohexanols (**18** and **20**, respectively).



Reactions of (cyclohexylperoxy)cobaloxime **1b** in different solvents demonstrate that in the presence of good hydrogen donors the formation of alcohols increases. Thus, in toluene cyclohexanol (**21**) and cyclohexanone (**22**) are formed in equal amounts whereas in benzene cyclohexanone (**22**) is the main product. Moreover, bibenzyl is obtained in small yields if toluene is used as solvent. It is therefore highly likely that

solvent:			
	benzene	9 %	46 %
	toluene	33 %	33 %
	tetrahydrofuran	24 %	23 %



the solvent acts at least as one of the hydrogen donors to give the alcohols.

The respective ketones are presumably formed by hydrogen abstraction of the corresponding radicals. One of the possible radicals could be the cobaltoxy radical **23**.

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Experimental

NMR: Bruker WM 300, Bruker AC 300 (TMS as internal standard). – MS: Finnigan MAT 311 A. – UV/VIS: Beckman UV 5240 and DK 2A. – IR: Perkin-Elmer 325.– Gas-liquid chromatography: Carlo Erba GC 6000 (Vega Series), FID, connected to Spectra Physics Integrator 4290; OV 17/01 capillary column from Macherey & Nagel. – Preparative column chromatography: Merck silica gel 60 (0.063–0.200 mm).

A) *Syntheses of Alkyl(4-tert-butylpyridine)cobaloximes* **2**: All cobaloximes containing the axial ligand 4-*tert*-butylpyridine are new compounds, cyclohexyl- and *trans*-(4-*tert*-butylcyclohexyl)-(pyridine)cobaloxime have already been prepared[10,14].

In a typical procedure 1.0 g (4.2 mmol) of cobalt(II) chloride hexahydrate and 1.0 g (8.4 mmol) of 2,3-butanedione dioxime (dimethylglyoxime) were stirred in 25 ml of degassed methanol under nitrogen at −20°C. 1.0 ml of 50% aqueous degassed sodium hydroxide solution was added dropwise to the reaction mixture followed by addition of 0.6 ml (4.2 mmol) of 4-*tert*-butylpyridine and 0.2 g (5.3 mmol) of $NaBH_4$, dissolved in 1–2 ml of methanol. The reaction mixture was allowed to warm to room temp. and stirred for a further 60 min. Alkyl bromide **7** (neat) was added dropwise to the black solution at −20°C and the reaction mixture stirred for ca. 12 h at 20°C. The solvent was distilled from the orange solution, 100 ml of water was added to the oily residue, and the precipitating orange crystals of alkyl cobaloxime **2** were filtered off under suction, dried, and stored in amber-colored vials.

(4-tert-Butylpyridine)bis(dimethylglyoximato)(4-pentenyl)cobalt(III) (**2a**): Yield 54%, m.p. 182–185°C (dec.) (methanol). – ^{1}H NMR ($CDCl_3$): δ = 18.27 (s, 2H, OH), 8.42 (dd, *J* = 1.5, 5.3 Hz, 2H, Bupy), 7.27 (dd, *J* = 1.5, 5.3 Hz, 2-H, Bupy), 5.71 (ddt, *J* = 7.1, 10.2, 16.9 Hz, 1-H, 4-H), 4.90–4.78 (m, 2H, 5-H), 2.14 (s, 12H, CH_3), 1.94 (d, *J* = 7.1 Hz, 2-H, 3-H), 1.61–1.55 (m, 2-H, 1-H), 1.28 [s, 9H, $C(CH_3)$], 1.07–0.96 (m, 2H, 2-H). – MS (FD): *m/z* = 494/493 [M^+]. – UV/VIS (CH_2Cl_2): λ_{max} (ε) = 480 nm (186) sh, 421 (1370) sh, 371 (2590) sh.

$C_{22}H_{36}CoN_5O_4$ (493.5) Calcd. C 53.55 H 7.35 N 14.19
Found C 53.02 H 7.34 N 14.01

(4-tert-Butylpyridine)(cyclohexyl)bis(dimethylglyoximato)cobalt(III) (**2b**): Yield 54%, m.p. 158–160°C (dec.) (methanol). – ^{1}H NMR ($CDCl_3$): δ = 18.10 (s, 2H, OH), 8.40 (dd, *J* = 1.5, 5.3 Hz, 2H, Bupy), 7.23 (dd, *J* = 1.5, 5.3 Hz, 2-H, Bupy), 2.15 (s, 12H, CH_3), 1.82 (tt, *J* = 3.5, 11.3 Hz, 1H, 1-H_{ax}), 1.72 (dq, *J* = 3.5, 11.5 Hz, 2H, 2-H_{eq}), 1.55–1.38 (m, 3-H, 3-H_{eq}, 4-H_{eq}), 1.27 (qt, *J* = 3.5, 11.5 Hz, 2-H, 3-H_{ax}), 1.26 [s, 9H, $C(CH_3)$], 1.10 (qt, *J* = 13.5 Hz, 11.5 Hz, 1H, 4-H_{ax}), 0.85 (qd, *J* = 3.5, 11.5 Hz, 2-H, 2-H_{ax}). – ^{13}C NMR ($CDCl_3$): δ = 12.10, 27.37, 29.62, 30.22, 34.74, 36.78, 50.25, 122.17, 149.26, 161.36. – UV/VIS (CH_2Cl_2): λ_{max} (ε) = 430 nm (1479) sh, 332 (6160) sh, 290 (8755) sh, 244 (30500).

$C_{23}H_{38}CoN_5O_4$ (507.5) Calcd. C 54.43 H 7.55 N 13.80
Found C 54.30 H 7.57 N 13.81

trans-(4-tert-Butylcyclohexyl)(4-tert-butylpyridine)bis(dimethylglyoximato)cobalt(III) (**2d**): Yield 28%, m.p. 158–163°C (dec.) (methanol). – ^{1}H NMR ($CDCl_3$): δ = 18.14 (s, 2H, OH), 8.42 (dd, *J* = 1.6, 5.2 Hz, 2H, Bupy), 7.23 (dd, *J* = 1.6, 5.2 Hz, 2-H, Bupy), 2.14 (s, 12H, CH_3), 1.88 (dq, *J* = 2.9, 10.8 Hz, 2H, 2-H_{eq}), 1.75 (tt, *J* = 2.9, 10.8 Hz, 1H, 1-H_{ax}), 1.56 (dq, *J* = 2.9, 10.8 Hz, 2H, 3-H_{eq}), 1.26 [s, 9H, $C(CH_3)$], 1.02 (dq, *J* = 2.9, 10.8 Hz, 2H, 3-H_{ax}), 0.89 (tt, *J* = 2.9, 10.8 Hz, 1H, 4-H_{ax}), 0.86 (qd, 2.9, 10.8 Hz, 2H, 2-H_{ax}), 0.76 [s, 9H, $C(CH_3)$]. – ^{13}C NMR ($CDCl_3$): δ = 12.10, 27.59, 30.25, 30.26, 32.05, 34.76, 36.62, 48.52, 49.71, 122.17, 149.27, 149.28, 161.33. – UV/VIS (CH_2Cl_2): λ_{max} (ε) = 429 nm (1350) sh, 334 (5950) sh, 294 (8205) sh, 244 (29200).

$C_{27}H_{46}CoN_5O_4$ (563.6) Calcd. C 57.54 H 8.23 N 12.43
Found C 57.35 H 8.26 N 12.53

B) *Syntheses of (Alkylperoxy)(4-tert-butylpyridine)cobaloximes* **1a–d**: The photolysis of primary and secondary alkyl cobaloximes in the presence of air was carried out in a falling-film photoreactor because otherwise the reaction mixture would quickly darken upon irradiation leading to long reaction periods and a large amount of decomposition products of initially formed (alkylperoxy)cobaloxime **1**. In a typical procedure 2.0 g of alkylcobaloxime **2** was dissolved in 250 ml of aqueous ethanol (95%) and vigorously stirred while purged with air. The photoreaction was achieved by irradiation (1–2 h) with a sun lamp (Osram Power Star HQI®, 250 W) and monitored by TLC: R_f (alkylcobaloxim **2**) = 0.5, orange spot; R_f(**1a,b,d**) = 0.2, R_f(**1c**) = 0.4, brown spots (SiO_2 plates, F_{254}, Merck, eluent AcOEt).

Subsequently, the dark brown reaction mixture was evaporated to dryness and the residue chromatographed on silica gel with ethyl acetate as eluent. The brown fraction was collected, and the brown crystals obtained upon distillation of the solvent were recrystallized from water/methanol (1:1) to yield **1a–d** as monohydrates or semihydrates.

(4-tert-Butylpyridine)bis(dimethylglyoximato)(4-pentenylperoxy)cobalt(III) (**1a**): Yield 74%, m.p. 124–127°C (dec.). – ^{1}H NMR ($CDCl_3$): δ = 18.40 (s, 2H, OH), 8.20 (dd, *J* = 1.5, 5.5 Hz, 2H, Bupy), 7.17 (dd, *J* = 1.5, 5.5 Hz, 2-H, Bupy), 5.75 (ddt, *J* = 6.6, 10.3, 17.0 Hz, 1-H, 4-H), 4.98–4.87 (m, 2H, 5-H), 3.22 (t, *J* = 6.8 Hz, 2H, 1-H), 2.32 (s, 12H, CH_3), 1.94 (d, *J* = 7.2 Hz, 2-H, 3-H), 1.39 (quint, *J* = 7.2 Hz, 2H, 2-H), 1.24 [s, 9H, $C(CH_3)$]. – MS (FD): *m/z* = 526/525 [M^+]. – UV/VIS (CH_2Cl_2): λ_{max} (ε) = 547 nm (196), 304 (8750), 249 (21700). – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 2930, 1740, 1640, 1565, 1470, 1235, 835 (O–O).

$C_{22}H_{36}CoN_5O_6 \cdot 0.5\,H_2O$ (534.5)
Calcd. C 49.44 H 6.98 N 13.10
Found C 49.45 H 6.81 N 13.27

(4-tert-Butylpyridine)(cyclohexylperoxy)bis(dimethylglyoximato)cobalt(III) (**1b**): Yield 60%, m.p. 169°C (dec.). – ^{1}H NMR ($CDCl_3$): δ = 18.15 (s, 2H, OH), 8.20 (dd, *J* = 1.5, 5.5 Hz, 2H, Bupy), 7.17 (dd, *J* = 1.5, 5.5 Hz, 2-H, Bupy), 3.03 (tt, *J* = 3.9, 10.0 Hz, 1H, 1-H_{ax}), 2.31 (s, 12H, CH_3), 1.86–1.40 (m, 5H, 2-H_{eq}, 3-H_{eq}, 4-H_{eq}), 1.24 [s, 9H, $C(CH_3)$], 1.18–1.02 (m, 3H), 0.92 (qd, *J* = 3.5, 12.2 Hz, 2H). – MS (FD): *m/z* = 540/539 [M^+]. – UV/VIS (CH_2Cl_2): λ_{max} (ε) = 558 nm (208), 309 (9850), 246 (24100). – IR (KBr): $\tilde{\nu}$ = 2980 cm^{-1}, 2860, 1620, 1565, 1275, 1230, 830 (O–O).

$C_{23}H_{38}CoN_5O_6 \cdot H_2O$ (557.5) Calcd. C 49.55 H 7.23 N 12.56
Found C 49.56 H 6.96 N 12.90

cis-(4-tert-Butylcyclohexylperoxy)(4-tert-butylpyridine)bis(dimethylglyoximato)cobalt(III) (**1c**): Yield 32%, m.p. 137–138°C (dec.). – ^{1}H NMR ($CDCl_3$): δ = 18.33 (s, 2H, OH), 8.21 (dd, *J* = 1.5, 5.5 Hz, 2H, Bupy), 7.16 (dd, *J* = 1.5, 5.5 Hz, 2-H, Bupy), 3.32–3.10 (m, 1H, 1-H_{eq}), 2.30 (s, 12H, CH_3), 1.77–1.66 (m, 2H), 1.27–0.77 (m, 7H), 1.22 [s, 9H, $C(CH_3)$], 0.75 [s, 9H, $C(CH_3)$]. – MS (FD): *m/z* = 596/595 [M^+]. – UV/VIS (CH_2Cl_2): λ_{max} (ε) =

558 nm (213), 311 (9000), 247 (23300). – IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 1730, 1620, 1560, 840 (O–O).

$C_{27}H_{46}CoN_5O_6 \cdot H_2O$ (613.6) Calcd. C 52.85 H 7.88 N 11.41
Found C 52.81 H 7.75 N 11.25

trans-(4-tert-Butylcyclohexylperoxy)(4-tert-butylpyridine)bis-(dimethylglyoximato)cobalt(III) (**1d**): Yield 33%, m.p. 122–124°C (dec.). – ^{1}H NMR ($CDCl_3$): δ = 18.40 (s, 2H, OH), 8.21 (dd, *J* = 1.5, 5.5 Hz, 2H, Bupy), 7.17 (dd, *J* = 1.5, 5.5 Hz, 2-H, Bupy), 2.90 (tt, *J* = 3.9, 11.0 Hz, 1H, 1-H_{ax}), 2.30 (s, 12H, CH_3), 1.82–1.72 (m, 2H), 1.65–1.57 (m, 2H), 1.23 [s, 9H, $C(CH_3)$], 0.89–0.69 (m, 5H), 0.80 [s, 9H, $C(CH_3)$]. – MS (FD): *m/z* = 596/595 [M^+]. – UV/VIS (CH_2Cl_2): λ_{max} (ε) = 562 nm (199), 322 (8690), 246 (22800). – IR (KBr): $\tilde{\nu}$ = 2980 cm^{-1}, 1730, 1560, 1240, 845 (O–O).

$C_{27}H_{46}CoN_5O_6 \cdot H_2O$ (613.6) Calcd. C 52.85 H 7.88 N 11.41
Found C 53.02 H 7.70 N 11.45

C) *(tert-Butylperoxy)(4-tert-butylpyridine)bis(dimethylglyoximato)cobalt(III)* (**1e**): To 200 ml of degassed dry benzene containing 1.0 g (2.0 mmol) of (4-*tert*-butylpyridine)(cyclohexyl)cobaloxime **2b** was added at 15°C 3.3 ml (10 mmol) of a 3 M solution of *tert*-butyl hydroperoxide (**9**) in 2,2,4-trimethylpentane. Anaerobic photolysis (light source: 250-W discharge lamp Osram Power Star HQI®) of the reaction mixture for 1.5 h yielded a green solution. The solvent was removed in vacuo and the green residue taken up in 3 ml of ethyl acetate. Column chromatography (ethyl acetate) of the crude product and removal of the solvent in vacuo from the isolated green fraction yielded 0.74 g (75%) of **1e** as green crystals of m.p. 118–120°C. – ^{1}H NMR ($CDCl_3$): δ = 18.40 (s, 2H, OH), 8.22 (dd, *J* = 1.4, 5.5 Hz, 2H, Bupy), 7.16 (dd, *J* = 1.4, 5.5 Hz, 2-H, Bupy), 2.31 (s, 12H, CH_3), 1.24 [s, 9H, $C(CH_3)$], 0.92 [s, 9H, $C(CH_3)$]. – MS (FD): *m/z* = 514/513 [M^+]. – UV/VIS (CH_2Cl_2): λ_{max} (ε) = 600 nm (317), 300 (10700) sh, 248 (23310). – IR (KBr): $\tilde{\nu}$ = 2980 cm^{-1}, 1730, 1610, 1570, 1240, 840 (O–O).

$C_{21}H_{36}CoN_5O_6$ (513.5) Calcd. C 49.12 H 7.07 N 13.04
Found C 48.64 H 7.07 N 13.37

D) *General Procedure for the Photochemical Decomposition of (Alkylperoxy)cobaloximes* **1**: A solution of 0.4 mmol of **1** in 25 ml of degassed solvent was photolyzed at 15°C (incandescent light: Osram Power Star HQI®/250 W) until **1** is completely consumed (18–24 h). The cobalt-free products, which are known compounds, were analysed by gas-liquid chromatography. The yields of the products are given in the reaction schemes.

CAS Registry Numbers

1a: 130351-47-2 / **1b**: 130351-48-3 / **1c**: 118916-56-6 / **1d**: 118799-76-1 / **1e**: 130377-75-2 / **2a**: 130351-45-0 / **2b**: 130351-46-1 / **2d**: 118799-76-1 / **7a**: 1119-51-3 / **7b**: 108-85-0 / **7c**: 5009-36-9 / **8**: 130351-49-4 / **10**: 96-47-9 / **12**: 2100-17-6 / **13**: 23127-65-3 / **15**: 75-65-0 / **16**: 67-64-1 / **17**: 3141-58-0 / **18**: 937-05-3 / **19**: 98-53-3 / **20**: 21862-63-5 / cyclohexanoxy radical: 3384-35-8

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