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## PHOTOCHEMICAL SUBSTITUTION REACTIONS OF SOME ALKYLCOBALOXIMES BY HYDROPEROXIDES AND THE CRYSTAL STRUCTURE OF CUMYL PEROXIDE(PYRIDINE) COBALOXIME

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### Summary

Alkyl(pyridine) cobaloximes irradiated with visible light in the presence of tert-butyl or cumyl hydroperoxide give rise to tert-butyl or cumyl peroxide-(pyridine)cobaloxime by photochemical substitution reaction. We report the structure of the cumyl peroxide(pyridine)cobaloxime determined by X-ray diffraction.

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### Introduction

The reactivity of the Co—C bond is of general interest [1] and in previous publications we reported studies of the anaerobic photolysis of some alkyl-cobaloximes [2]. In the present paper we report the photo-induced reactivity of some alkyl(pyridine)cobaloximes (Ia—Ie) with the tert-butyl (III1) and cumyl hydroperoxide (III2) and we describe the possible synthesis of the tert-butyl and cumyl peroxide(pyridine)cobaloximes (II1, II2) by a photo-induced substitution reaction.

### Results and discussion

The irradiation with visible light of a benzene solution of alkyl(pyridine)-cobaloxime (Ia—Ie) and tert-butyl (III1) or cumyl hydroperoxide (III2) gives a green organometallic compound (respectively II1 and II2) and several organic products (Scheme 1). This reaction does not occur in the dark, even under reflux. The reduction of II1 or II2 by excess NaBH<sub>4</sub> gives tert-butanol or 2-phenyl-2-propanol, respectively. Analysis of the organic compounds occurring in the reaction has been performed after reaction of benzyl(pyridine)cobaloxime

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\* This work is a part of the thesis of C. Fontaine.

## SCHEME 1

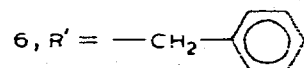
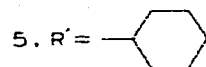
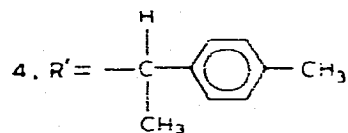
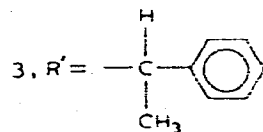
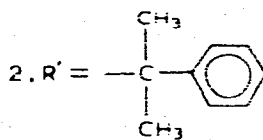
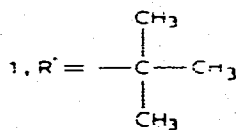
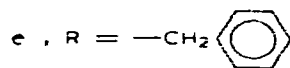
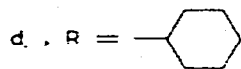
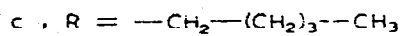
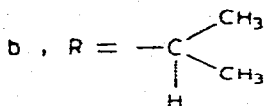
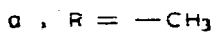
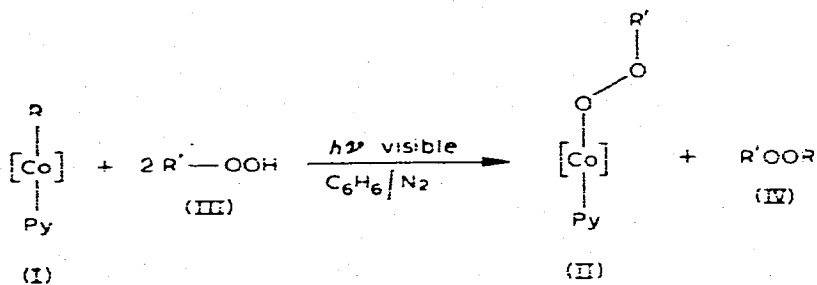
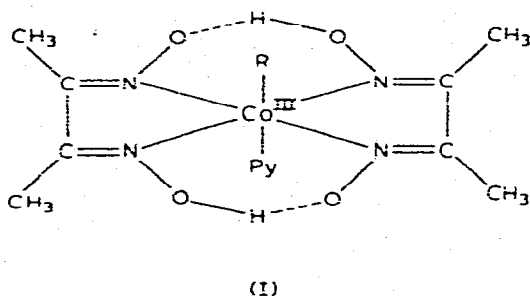


TABLE 1

<sup>1</sup>H NMR CHEMICAL SHIFT OF SOME ALKYL PEROXIDE COBALOXIMES ( $\delta$ , ppm) IN CDCl<sub>3</sub>

Compounds	CH <sub>3</sub> (DMG)	CH <sub>2</sub>	Pyridine		
			H <sub><math>\alpha</math></sub>	H <sub><math>\beta</math></sub>	H <sub><math>\gamma</math></sub>
III1	2.32(s)	0.95(s)	8.40(m)	7.30(m)	7.70(m)
IIIb	2.30(s)	0.86(d)	8.41(m)	7.30(m)	7.70(m)
III2	2.28(s)	1.25(s)	8.40(m)	7.25(m)	7.70(m)
IIIc	2.14(s) 2.23(s)	1.25(s)	8.40(m)	7.20(m)	7.68(r t)

(Ie) into tert-butyl or cumyl hydroperoxide (III1, III2); we obtained compounds (IVE1) and (IVE2), respectively.

The <sup>1</sup>H NMR spectra of the organometallic complexes III1, III2 in comparison with those of ethylphenyl (III3) and isopropyl (IIIb, R = R') peroxide(pyridine)-cobaloxime suggest that two oxygen atoms are attached to the cobalt atom (Table 1) this conclusion is in agreement with the elementary analysis of III1 and III2 (Table 2). The X-ray structure of a crystal of cumyl peroxide(pyridine)-cobaloxime (III2) confirming this hypothesis. The atom labelling scheme is shown in Fig. 1 and Fig. 2 gives a view along the O(5)—Co—N(5) axes. The atomic parameters of the molecule are listed in Tables 3a and 3b; the various lengths and bond angles are reported in Tables 4 and 5.

The four equatorial Co—N bond lengths range from 1.887 to 1.892 Å (average value 1.889(2) Å); the Co—N(pyridine) bond length is 1.994(3) Å and that of O—O 1.454(3) Å, distances which are in agreement with the values found in the crystal structure of 1-methyl-4-ethylphenylperoxidecobaloxime (III4) [3]. The increase of the torsional angle Co—O—O—C to 132° (114° in the previously-quoted structure) is a necessary consequence of steric interactions between the methyl moieties of the cumyl and dimethylglyoxime groupings. The Newman projections along the O(6)—C(9) and C(9)—C(12) bonds are given in Fig. 3.

This photochemical substitution can be explained by the following mechanism: in the presence of hydroperoxide the alkyl(pyridine)cobaloxime gives rise to a cobalt(II) complex which reacts immediately with the tert-butyl or cumyl peroxide(pyridine)cobaloxime (III1, III2). To confirm this point we have synthesised a cobalt(II) complex Py—(Co<sup>II</sup>)—Py (V) [4] and shown that the dark reaction of

(continued on p. 62)

TABLE 2

ELEMENTARY ANALYSIS OF III1 AND III2

Compound	Formula	Analysis found (calcd.)			
		C	H	N	Co
III1	C <sub>17</sub> H <sub>28</sub> N <sub>5</sub> O <sub>6</sub> Co	44.26 (44.64)	6.14 (6.12)	15.35 (15.33)	12.33 (12.69)
III2	C <sub>22</sub> H <sub>30</sub> N <sub>5</sub> O <sub>6</sub> Co	50.49 (50.85)	5.92 (5.78)	13.54 (13.48)	11.02 (11.36)

TABLE 3

## FRACTIONAL ATOMIC COORDINATES WITH THEIR STANDARD DEVIATIONS (in parentheses) AND THERMAL PARAMETERS

$\beta_{ij}$  are the coefficients in the expression:  $\exp [(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . " $\beta_{ii}$ " = the equivalent isotropic thermal factor.

(a) HEAVY ATOMS: ALL THE VALUES ARE  $\times 10^4$

Atom	X	Y	Z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	B
C(1)	5335(5)	4721(4)	3230(3)	99	66	59	30	27	19	3.1
C(2)	5268(6)	5995(4)	3158(4)	223	61	108	45	36	12	5.2
C(3)	6357(5)	4328(4)	4061(3)	106	64	51	10	33	4	3.1
C(4)	7514(6)	5157(4)	4917(4)	187	89	92	10	--2	--7	5.4
C(5)	4640(5)	--107(4)	2050(4)	145	57	87	33	42	14	3.9
C(6)	4895(7)	--1367(4)	2054(4)	341	71	131	60	65	33	6.8
C(7)	3569(5)	298(4)	1200(3)	156	69	63	28	30	4	3.8
C(8)	2717(7)	--484(4)	248(4)	350	90	82	23	8	--31	6.8
C(9)	8160(4)	4330(3)	1320(3)	110	78	46	23	20	28	3.1
C(10)	9415(5)	3725(4)	964(3)	167	95	74	41	51	20	4.4
C(11)	6671(5)	4098(3)	462(3)	164	82	52	21	5	18	4.4
C(12)	8884(4)	5578(3)	1727(3)	103	76	44	23	22	24	3.0
C(13)	10138(5)	6003(4)	2579(4)	166	99	62	22	--9	21	4.6
C(14)	10828(6)	7218(5)	2980(4)	212	133	55	--3	--18	5	5.7
C(15)	10285(6)	8124(4)	2516(4)	273	74	69	12	23	--2	5.3
C(16)	9046(6)	7811(4)	1669(4)	218	83	81	39	22	24	5.0
C(17)	8352(5)	6600(4)	1285(3)	141	84	56	32	13	22	3.8
C(18)	1530(4)	2049(3)	2948(3)	96	83	52	34	7	26	3.2
C(19)	224(5)	1874(3)	3450(4)	92	90	78	28	21	26	3.9
C(20)	365(5)	1485(4)	4427(4)	113	95	73	24	43	28	4.0
C(21)	1807(5)	1275(3)	4862(3)	118	90	51	18	29	29	3.5
C(22)	3070(4)	1471(3)	4322(3)	100	65	51	25	6	18	3.0
N(1)	4540(4)	3834(3)	2506(3)	89	65	46	31	16	23	2.7
N(2)	6210(3)	3162(3)	3945(2)	78	76	44	26	10	18	2.8
N(3)	5298(4)	740(3)	2837(3)	102	65	64	35	25	28	3.1
N(4)	3690(4)	1437(3)	1387(3)	119	73	50	28	14	13	3.3
N(5)	2968(3)	1870(2)	3376(2)	94	52	47	22	13	14	2.6
O(1)	3533(3)	4026(2)	1687(2)	121	90	64	51	3	36	3.7
O(2)	7091(3)	2542(2)	4523(2)	130	107	57	49	--6	27	4.0
O(3)	6247(3)	531(2)	3682(2)	130	89	80	56	12	39	4.1
O(4)	2862(3)	1961(2)	683(2)	175	95	53	44	--12	15	4.3
O(5)	6806(3)	2585(2)	2085(2)	177	58	72	23	40	20	3.4
O(6)	7733(3)	3854(2)	2278(2)	111	79	54	11	21	25	3.4
Co	4910(1)	2288(0)	2680(0)	89	55	48	28	14	18	2.6

TABLE 3

(b) ATOMIC COORDINATES ( $\times 10^3$ ) OF THE HYDROGEN ATOMS

Atom	X	Y	Z	B
H(2A)	624	664	332	5.1
H(2B)	446	615	265	5.1
H(2C)	500	519	372	5.1
H(4A)	815	582	470	5.0
H(4B)	720	583	524	5.0
H(4C)	826	484	533	5.0
H(6A)	392	-199	191	6.4
H(6B)	521	-161	281	6.4
H(6C)	515	-143	149	6.4
H(8A)	314	-103	-18	5.9
H(8B)	222	-118	25	5.9
H(8C)	245	-4	-32	5.9
H(10A)	881	268	89	4.5
H(10B)	971	393	26	4.5
H(10C)	1051	411	153	4.5
H(11A)	707	443	-25	4.1
H(11B)	612	318	28	4.1
H(11C)	584	465	66	4.1
H(13)	1055	532	293	4.4
H(14)	1172	747	360	5.2
H(15)	1082	901	285	4.7
H(16)	871	851	133	4.9
H(17)	743	636	66	3.5
H(18)	144	232	221	2.8
H(19)	-85	204	308	3.6
H(20)	-60	139	484	3.5
H(21)	190	98	559	3.3
H(22)	414	131	460	2.8
H(02)	688	160	427	4.1
H(04)	303	286	103	4.3

TABLE 4

## BOND LENGTHS (Å)

C(1)—C(2)	1.475(6)	C(16)—C(17)	1.379(6)
C(1)—C(3)	1.458(6)	C(18)—C(19)	1.364(6)
C(1)—N(1)	1.297(5)	C(18)—N(5)	1.347(5)
C(3)—C(4)	1.468(6)	C(19)—C(20)	1.378(6)
C(3)—N(2)	1.296(5)	C(20)—C(21)	1.367(6)
C(5)—C(6)	1.502(6)	C(21)—C(22)	1.363(6)
C(5)—C(7)	1.459(6)	C(22)—N(5)	1.345(5)
C(5)—N(3)	1.299(6)	N(1)—O(1)	1.336(4)
C(7)—C(8)	1.465(6)	N(1)—Co	1.887(3)
C(7)—N(4)	1.293(5)	N(2)—O(2)	1.344(4)
C(9)—C(10)	1.516(6)	N(2)—Co	1.890(3)
C(9)—C(11)	1.520(6)	N(3)—O(3)	1.342(5)
C(9)—C(12)	1.525(5)	N(3)—Co	1.892(3)
C(9)—O(6)	1.462(5)	N(4)—O(4)	1.343(4)
C(12)—C(13)	1.380(6)	N(4)—Co	1.887(3)
C(12)—C(17)	1.378(6)	N(5)—Co	1.994(3)
C(13)—C(14)	1.388(7)	O(5)—O(6)	1.455(3)
C(14)—C(15)	1.377(7)	O(5)—Co	1.909(3)
C(15)—C(16)	1.368(7)		

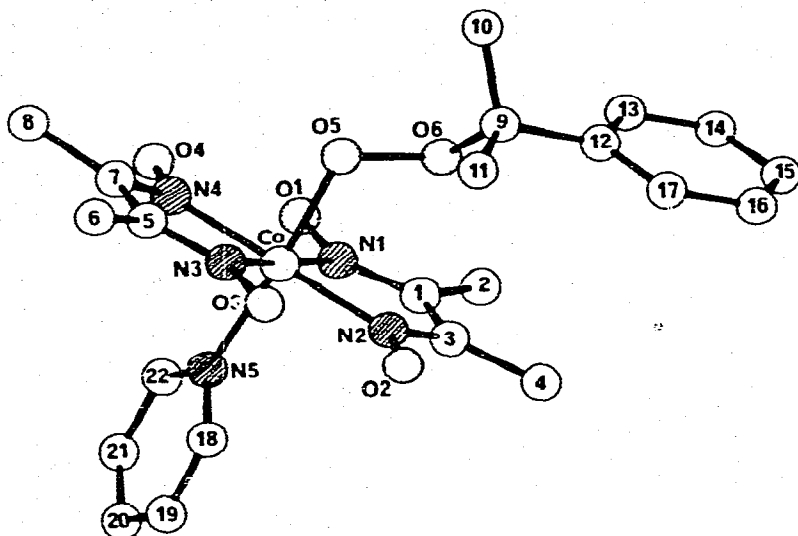


Fig. 1. A view of the molecule showing the numbering of the atoms. The hydrogen atoms are omitted.

this complex with *tert*-butyl or cumyl hydroperoxide rapidly gives the corresponding peroxides (III1) and (III2).

To attempt to extend this reaction to other organic hydroperoxides we synthesized the cyclohexyl and benzyl hydroperoxides [5] (III5, III6) but the photolysis of alkyl(pyridine)cobaloximes (Ia–Ie) with (III5) or (III6) gives no corresponding peroxide (pyridine)cobaloximes (II5) and (II6). The photosubstitution reaction only occurs with very stable hydroperoxides which give rise during the photolysis to long-living free radicals which can react with other free radicals arising from the photolysis of alkyl(pyridine)cobaloximes. In confirmation of this point, the photolysis of alkyl(pyridine)cobaloximes with the di-*tert*-butyl peroxide gives no photoproducts.

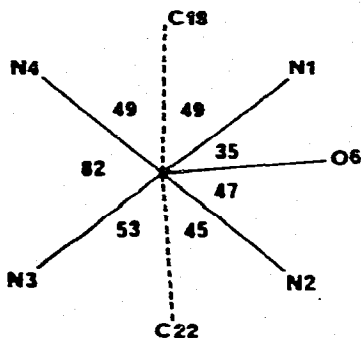


Fig. 2. Arrangement of the atoms viewed down the O(5)—Co—N(5) axes (angles in degrees).

TABLE 5  
VALENCY ANGLES (degrees)

C(2)—C(1)—C(3)	124.8(4)	C(1)—N(1)—Co	116.1(3)
C(2)—C(1)—N(1)	122.2(4)	O(1)—N(1)—Co	122.9(2)
C(3)—C(1)—N(1)	112.8(4)	C(3)—N(2)—O(2)	121.4(3)
C(1)—C(3)—C(4)	124.4(4)	C(3)—N(2)—Co	115.8(3)
C(1)—C(3)—N(2)	113.2(4)	O(2)—N(2)—Co	122.4(2)
C(4)—C(3)—N(2)	122.3(4)	C(5)—N(3)—O(3)	121.5(4)
C(6)—C(5)—C(7)	125.2(4)	C(5)—N(3)—Co	115.8(3)
C(6)—C(5)—N(3)	121.4(4)	O(3)—N(3)—Co	122.7(3)
C(7)—C(5)—N(3)	113.4(4)	C(7)—N(4)—O(4)	120.2(3)
C(5)—C(7)—C(8)	125.0(4)	C(7)—N(4)—Co	116.8(3)
C(5)—C(7)—N(4)	112.4(4)	O(4)—N(4)—Co	123.0(2)
C(8)—C(7)—N(4)	122.6(4)	C(18)—N(5)—C(22)	117.3(3)
C(10)—C(9)—C(11)	110.7(3)	C(18)—N(5)—Co	121.3(2)
C(10)—C(9)—C(12)	112.1(3)	C(22)—N(5)—Co	121.2(2)
C(10)—C(9)—O(6)	108.2(3)	O(6)—O(5)—Co	111.7(2)
C(11)—C(9)—C(12)	113.3(3)	C(9)—O(6)—O(5)	110.3(2)
C(11)—C(9)—O(6)	111.4(3)	N(1)—Co—N(2)	81.9(1)
C(12)—C(9)—O(6)	100.8(3)	N(1)—Co—N(3)	179.2(1)
C(9)—C(12)—C(13)	119.0(4)	N(1)—Co—N(4)	98.0(1)
C(9)—C(12)—C(17)	123.2(4)	N(1)—Co—N(5)	90.1(1)
C(13)—C(12)—C(17)	117.7(4)	N(1)—Co—O(5)	93.9(1)
C(12)—C(13)—C(14)	121.0(4)	N(2)—Co—N(3)	98.6(1)
C(13)—C(14)—C(15)	120.2(5)	N(2)—Co—N(4)	177.6(1)
C(14)—C(15)—C(16)	119.3(5)	N(2)—Co—N(5)	91.3(1)
C(15)—C(16)—C(17)	120.2(4)	N(2)—Co—O(5)	88.7(1)
C(12)—C(17)—C(18)	121.6(4)	N(3)—Co—N(4)	81.6(1)
C(19)—C(18)—N(5)	122.5(4)	N(3)—Co—N(5)	90.6(1)
C(18)—C(19)—C(20)	119.1(4)	N(3)—Co—O(5)	85.4(1)
C(19)—C(20)—C(21)	119.1(4)	N(4)—Co—N(5)	91.2(1)
C(20)—C(21)—C(22)	119.1(4)	N(4)—Co—O(5)	88.9(1)
C(21)—C(22)—N(5)	122.9(3)	N(5)—Co—O(5)	175.9(1)
C(1)—N(1)—O(1)	121.0(3)		

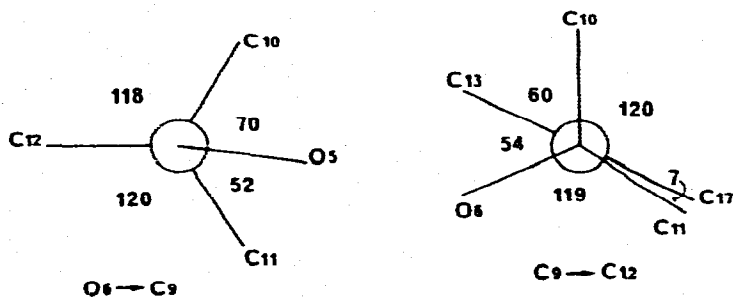


Fig. 3. Newman projections along the O(6)—C(9) and C(8)—C(12) bonds; torsional angles are in degrees.

### Experimental methods

The  $^1\text{H}$  NMR spectra were taken in  $\text{CDCl}_3$  solution on a Varian T 60 model instrument with tetramethylsilane as internal reference, s, singlet; d, doublet; m, multiplet.

We used the silicagel GF 254 (Merck) for the thin layer chromatographic

separation, and a 2 : 2 : 1 mixture of chloroform, ethyl acetate and methanol for elution.

### General photolysis

Alkyl(pyridine)cobaloximes (Ia–Ie) were synthesized according to Schrauzer et al. methods [6]. A well deoxygenated yellow benzene solution of alkyl-(pyridine)cobaloximes ( $2 \times 10^{-3} M$ ) and commercial tert-butyl or cumyl hydroperoxide ( $1 \times 10^{-2} M$ ) was irradiated with visible light produced by an OSRAM model XBF-Xe 2.5 kW arc lamp. A copper sulfate solution was used as a filter [7]. After the irradiation the solution became deep green. The solvent was removed under vacuum. The green mixture was chromatographed on thin layer apparatus (a) giving a large green band ( $R_f$  0.6) from which we obtained a 75% yield of green needles. Compounds (II1) and (II2) were characterised by their  $^1H$  NMR spectra (Table 1) and their elementary analysis (Table 2). Crystals of cumyl peroxide(pyridine)cobaloxime (II2) suitable for X-ray study were grown by slow evaporation of ether/methanol solution.

The organic products are described in the case of the photolysis of the benzyl-(pyridine)cobaloxime (Ie).

### X-ray methods

For the crystal structure determination, the intensities of 2084 independent reflexions ( $I > 3\sigma(I)$ ) have been collected by the  $\theta - 2\theta$  technique out off  $\theta = 24^\circ$  on a Philips PW 1100 diffractometer. Crystallographic data for II2 are: mol. wt. 519.4; triclinic space group  $P\bar{1}$ , cell dimensions:  $a = 8.596(3)$ ,  $b = 11.382(5)$ ,  $c = 12.987(7)$  Å,  $\alpha = 95.04(3)$ ,  $\beta = 98.56(3)$ ,  $\gamma = 103.78(3)^\circ$ , two molecules in the unit cell ( $Z = 2$ ),  $D_c$  1.42, (Mo- $K_\alpha$ ) 0.7107 Å.

The crystal structure was solved by the direct method [8] and refined by full-matrix least-squares procedure [9]. The minimized function was  $\sum w(F_o - F_c)^2$ , where  $w = 1/\sigma^2(F)$  and derived from  $\sigma(I)$ . All the hydrogen atoms were located on a difference map and included in the refinement of experimental positions. They were assigned the equivalent isotropic thermal factor of the bonded carbon atoms. Scattering factors were taken from Doyle and Turner [10] for the Co, C, N and O atoms and from Stewart, Davidson and Simpson [11] for the H atoms. The applied corrections for the anomalous scattering of Co were  $\Delta f' = 0.4$  and  $\Delta f'' = 1.0$ . No correction for absorption was made. The final  $R$  factor was 0.033.

A table of structure factors can be obtained from the authors.

### Photolysis of benzyl(pyridine)cobaloxime

(a) *With tert-butyl hydroperoxide.* When the photolysis is carried out with the benzyl(pyridine)cobaloxime (Ie) in presence of tert-butyl hydroperoxide (IV1), we obtained the corresponding tert-butyl peroxide(pyridine)cobaloxime(II1) and tert-butyl benzyl peroxide(IVe1)  $^1H$  NMR  $\delta$  (ppm): t-butyl 1.30 (s, 9H);  $-\text{CH}_2-$  5.0 (s, 2H);  $\text{C}_6\text{H}_5-$  7.50 (s, 5H); elementary analysis Found: C, 73.47; H, 8.36.  $\text{C}_{11}\text{H}_{14}\text{O}_2$  calcd.: C, 73.33; H, 8.88%. We also isolated the dibenzyl  $\text{C}_{12}\text{H}_{14}$ .  $^1H$  NMR  $\delta$  (ppm):  $-\text{CH}_2\text{CH}_2-$  2.95 (s, 4H);  $\text{C}_6\text{H}_5-$  7.75 (s, 10H); m.p. 51–52°C.

(b) *With cumyl hydroperoxide.* The photolysis of benzyl(pyridine)cobaloxime (Ie) with cumyl hydroperoxide (IVe) gave the corresponding cumyl peroxide-



(pyridine)cobaloxime (II2) and cumyl benzyl peroxide (IVe).  $^1\text{H NMR } \delta$  (ppm):  $2\text{CH}_3$ — 1.30 (s, 6H);  $\text{CH}_2$ — 4.95 (s, 2H);  $2\text{C}_6\text{H}_5$ — 7.20 (m, 10H); elementary analysis: found: C, 79.15; H, 7.31.  $\text{C}_{16}\text{H}_{18}\text{O}_2$  calcd.: C, 79.33; H, 7.43%. Also was found acetophenone:  $^1\text{H NMR } \delta$  (ppm):  $-\text{C}(=\text{O})\text{CH}_3$  2.5 (s, 3H);  $\text{C}_6\text{H}_5$ — 7.30 (m, 3H), 7.95 (m, 2H); carbonyl band in IR at  $1700\text{ cm}^{-1}$ .

*Reduction of II.* Tert-butyl peroxide(pyridine)cobaloxime (III1) 0.5 mmol was dissolved in 50 ml of methanol at  $-10^\circ\text{C}$ , with nitrogen bubbled through the solution. Solid sodium borohydride was added in two 5 mmol portions.

The solution turned dark green. We allowed the temperature to rise to room temperature, added 10 ml of distilled water and extracted with ether. The ether layer was dried over sodium sulfate and yielded 0.4 mmol of tert-butanol identified by  $^1\text{H NMR}$  and IR. In the case of the reduction of cumyl peroxide(pyridine)cobaloxime (II2) we obtained 2-phenyl-2-propanol.

The synthesis of III5, III6 and V were carried out according to the literature [4,5].

*Reactions with cyclohexyl and benzyl hydroperoxide (III5, III6).* A well-deoxygenated benzene solution of alkyl(pyridine)cobaloximes ( $2 \times 10^{-3}\text{ M}$ ) and hydroperoxide (III5 or III6) ( $1 \times 10^{-2}\text{ M}$ ) was irradiated following the above procedure. We observed only decomposition of the alkylcobaloximes (Ia—Ie).

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