# What is Different in Photochemical Reactions of Primary and Secondary Alkylcobaloximes with and without Radical Traps?

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Received December 3, 1992

**Key Words:** Cobaloximes, alkyl- / 5-Hexenyl, cyclization to cyclopentylmethyl / Radicals, alkyl / Abstraction of bromine and chlorine

Photochemical cyclization and halogen abstraction reactions of secondary alkylcobaloximes **1b** and **1d** compared to their primary counterparts **1a** and **1c** show an enhanced reactivity of secondary alkylcobaloximes: Thus, cyclohexylcobaloxime **1d** reacts 13 times faster with $CCl_4$ than *n*-hexylcobaloxime **1c**, 6-hepten-2-yl-cobaloxime **1b** rearranges 58 times faster to its cyclopentylmethyl isomer **4b** than 5-hexenylcobaloxime **1a**. Although *free* alkyl radicals are reactive intermediates in photolytic conversions of alkylcobaloximes **1** in organic solvents, the presence of $BrCCl_3$ or bromobenzene in photoreactions of primary alkylcobaloximes **1a** and **1c** seems to cause a more efficient homolytic cleavage of the Co–C bond.

Alkylcobaloximes **1** once introduced as vitamin $B_{12}$ mimics have successfully been employed as sources of *free* carbon-centered radicals in selective organic transformations[1,2]. Several studies demonstrate useful carbon-carbon[3] and carbon-heteroatom[4] bond formation in intra- and intermolecular reactions using photolabile **1** in visible-light induced reactions. In the course of our mechanistic studies of alkylcobalt complexes in organic synthesis we have found that primary alkylcobaloximes are more photostable than secondary derivatives. These results prompted us to perform a series of competition experiments of primary and secondary alkylcobaloximes in organic solvents with and without efficient radical traps[5].

Alkylcobaloximes **1a–e** are prepared from alkyl bromides **3a–d** and nucleophilic cobaloxime(I) **2** in good to excellent yield[6].

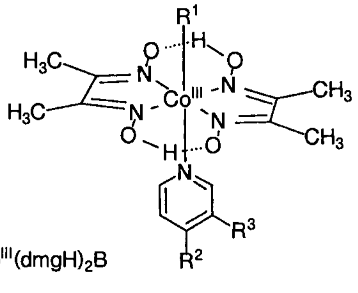
Anaerobic irradiation of benzene solutions of 5-hexenylcobaloxime **1a** and 6-hepten-2-ylcobaloxime **1b** in a falling-film photoreactor[8] gives rise to a mixture of open-chain und cyclic cobaloximes **1** and **4**[7–9]. The relative yields of (cyclopentylmethyl)cobaloximes **4** as determined by $^1H$-NMR analysis are plotted as a function of time. Half-time $\tau_{1/2}$ of the isomerizations **1a** → **4a** and **1b** → **4b** are calculated from the standard first-order isomerization equation which leads to an excellent fit[10]. The data show that 5-hexenyl- to (cyclopentylmethyl)cobaloxime rearrangement **1a** → **4a** (checked for 39 h, $\tau_{1/2} = 403$ min) is 58 times slower than 6-hepten-2-yl- to [(2-methylcyclopentyl)methyl]cobaloxime isomerization **1b** → **4b** (checked for 1 h, $\tau_{1/2} = 7$ min) at $T = 15\,°C$.

Chlorobenzene exerts no influence on the overall rate of the isomerization **1a** → **4a**. However, performing the photoarrangement of **1a** → **4a** in bromobenzene at $T = 15\,°C$

| No. | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| **1a** | 5-hexen-1-yl | $C(CH_3)_3$ | H |
| **1b** | 6-hepten-2-yl | $C(CH_3)_3$ | H |
| **1c** | *n*-$C_6H_{13}$ | $C(CH_3)_3$ | H |
| **1d** | *c*-$C_6H_{11}$ | $C(CH_3)_3$ | H |
| **1e** | 5-hexen-1-yl | $CH_3$ | Br |

$$\underset{\mathbf{2}}{\mathrm{Na[Co^{I}(dmgH)_2B]}} \xrightarrow[\text{- NaBr}]{\text{+ R-Br } \mathbf{3}} \underset{\mathbf{1}}{\mathrm{R\text{-}Co^{III}(dmgH)_2B}}$$

| No. | R |
|---|---|
| **3a** | 5-hexen-1-yl |
| **3b** | 6-hepten-2-yl |
| **3c** | *n*-$C_6H_{13}$ |
| **3d** | *c*-$C_6H_{11}$ |



**1** ≡ $R\text{-}Co^{III}(dmgH)_2B$

dmgH = 2,3-butanedione dioxime monoanion
B = 4-*tert*-butylpyridine or 3-bromo-4-methyl-pyridine

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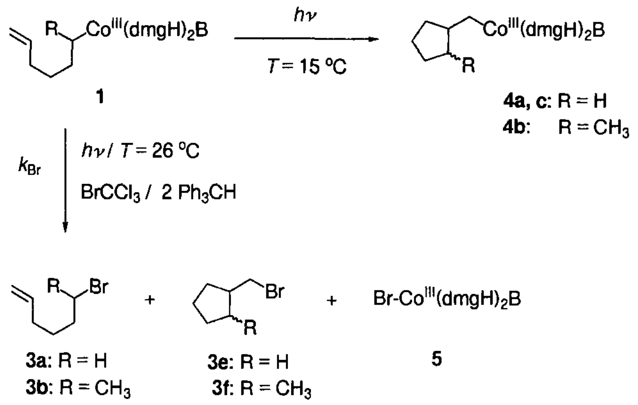


speeds up the overall rate by 2.6 (checked for 6 h, $\tau_{1/2} = 155$ min). The question arose whether a bromine atom incorporated into a cobaloxime derivative of **1a** could have the same rate-enhancing effect as in the solvent bromobenzene. Photolytic conversion of (3-bromo-4-methylpyridine)-5-hexenylcobaloxime (**1e**) to its cyclopentylmethyl isomer **4c** (checked for 6 h, $\tau_{1/2}$ = 310 min) occurs at a rate which is similar to that of the photochemical **1a** → **4a** rearrangement. Obviously, the bromine atom in **1e** is too far away from the reaction site as to increase the reactivity of **1e** towards rearrangement.

Table 1. Products and reactivity data obtained from photolytic conversions of alkyl-cobaloximes **1**

| No. | R | B | Reactivity |
|---|---|---|---|
| 1a → 4a | H | 4-*tert*-butylpyridine | $\tau_{1/2}$ = 403 min (benzene) |
| | | | $\tau_{1/2}$ = 155 min (bromobenzene) |
| 1b → 4b | CH$_3$[a] | 4-*tert*-butylpyridine | $\tau_{1/2}$ = 7 min (benzene) |
| 1e → 4c | H | 3-bromo-4-methyl-pyridine | $\tau_{1/2}$ = 310 min (benzene) |
| 1a → 3a + 3e | H | 4-*tert*-butylpyridine | $k_{Br} = (3.0 \pm 1.2) \cdot 10^8$ l mol$^{-1}$ s$^{-1}$ |
| 1b → 3b + 3f | CH$_3$[b] | 4-*tert*-butylpyridine | $k_{Br} = (1.2 \pm 0.6) \cdot 10^8$ l mol$^{-1}$ s$^{-1}$ |

[a] *cis*:*trans* ratio = 77:23. — [b] *cis*:*trans* ratio = 78:22.

We have further studied photoreactions of **1** with polyhalogenated methanes. Alkylcobaloximes **1** react smoothly with CCl$_4$ and BrCCl$_3$ when irridiated with incandescent light to yield alkyl chlorides **6** or bromides **3**[4a,17]. Photolysis of *n*-hexylcobaloxime **1c** or cyclohexylcobaloxime **1d** in CCl$_4$/BrCCl$_3$ mixtures at temperatures between 32 and 72°C according to Giese et al. leads to a mixture of *n*-hexyl halides or cyclohexyl halides[11,12]. Relative rate constants $k_{rel}$ for halogen abstraction in photoreactions of **1c** and **1d** are derived from equation (1). Differences in activation parameters ($\Delta\Delta H^{+} = \Delta H^{\ddagger}_{Cl} - \Delta H^{\ddagger}_{Br}$ and $\Delta\Delta S^{+} = \Delta S^{\ddagger}_{Cl} - \Delta S^{\ddagger}_{Br}$) are calculated from equation (2) (Table 2). A comparison of the data compiled in Table 2 with the values published for free alkyl radicals[11] also provides results for the cyclohexyl case but deviations from photoreactions of *n*-hexylcobaloxime **1c**. Relative rate constants for the reaction of photoexcited **1c** in CCl$_4$/BrCCl$_3$ are almost twice as high as compared to the *free* *n*-hexyl radical while the temperature dependence of $k_{rel}$ yields higher $\Delta\Delta H^{+}$ and higher $\Delta\Delta S^{+}$ values for the latter reaction.

$$k_{rel} = \frac{k_{Br}}{k_{Cl}} = \frac{[R\text{-}Br][CCl_4]}{[R\text{-}Cl][BrCCl_3]} \qquad (1)$$

$$\ln k_{rel} = \frac{\Delta H^{\ddagger}_{Cl} - \Delta H^{\ddagger}_{Br}}{RT} - \frac{\Delta S^{\ddagger}_{Cl} - \Delta S^{\ddagger}_{Br}}{R} \qquad (2)$$

In order to shed more light on these findings, the two parallel-grouped reactions of the competition experiments described are classified into single processes. Absolute rate constants of chlorine atom abstractions of 5-hexenyl- and 6-hepten-2-yl radicals generated from parent alkylcobaloximes **1a** and **1b** have been reported for $T = 26$°C (5-hexenyl radical: $k_{Cl} = 6.9 \cdot 10^3$ l mol$^{-1}$ and 6-hepten-2-yl radical: $2.1 \cdot 10^4$ l mol$^{-1}$ s$^{-1}$)[13,14]. Likewise, $k_{Br}$ values have been estimated from photoreactions of **1a** and **1b** in benzene/BrCCl$_3$ by the radical-clock technique (Table 1)[15]. Moreover, relative rate constants $k_{rel} = k_{Br}/k_{Cl}$ are calculated for the photoreactions of 5-hexenylcobaloxime (**1a** = 43500) and for 6-hepten-2-ylcobaloxime (**1b** = 5700) at $T = 26$°C. The latter value matches nicely with $k_{rel}$ reported for *free* 2-octyl radical at 30°C ($k_{rel}$ = 4400). However, $k_{rel}$(calcd.) = 43500 for **1a** is about 16 times higher as compared to 1-hexyl radical ($k_{rel}$ = 2750 at 30°C)[11] assuming that the anomalies observed in competition experiments arise from the photoreactions of primary alkylcobaloximes with BrCCl$_3$.

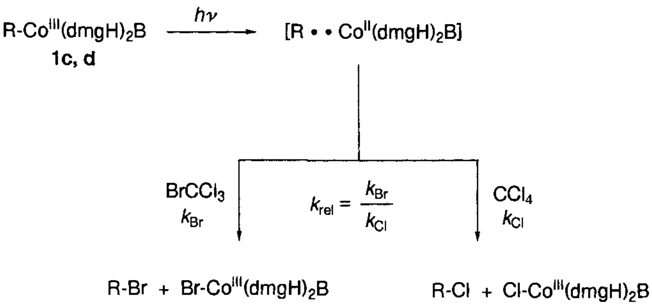
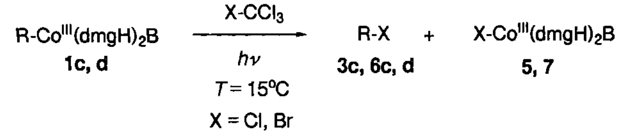


Table 2. Relative rate constants for the formation of alkyl bromides **3c**, **d** versus alkyl chlorides **6c**, **d** from photoreactions of alkylcobaloximes **1c**, **d** in CCl$_4$/BrCCl$_3$

| T [°C] | *n*-Hexylcobaloxime 1c $k_{rel}$ | Cyclohexylcobaloxime 1d $k_{rel}$ |
|---|---|---|
| 30 | 8000 | 3900 |
| 42 | 5699 | 2900 |
| 52 | 5300 | 2500 |
| 62 | 4000 | 1800 |
| 72 | 3000 | - |
| $\Delta\Delta H^{\ddagger}$[a] | 19 kJ mol$^{-1}$ | 22 kJ mol$^{-1}$ |
| $\Delta\Delta S^{\ddagger}$[a] | -9 J mol$^{-1}$ K$^{-1}$ | 5 J mol$^{-1}$ K$^{-1}$ |

[a] Estimated error: ±10% in $\Delta\Delta H^{+}$ and ±20% in $\Delta\Delta S^{+}$.

The product analysis of the photochemical conversion of *n*-hexylcobaloxime **1c** and cyclohexylcobaloxime **1d** in $CCl_4$ to the corresponding alkyl halides **6c**, **6d** and chlorocobaloxime **7** as a function of time shows that secondary alkylcobaloxime **1d** reacts 13 times faster than *n*-hexylcobaloxime **1c**[16]. However, if **1c** is photolyzed in benzene/$BrCCl_3$ solution (the concentration of bromine atom donor is lowered by the factor $k_{rel}$ for free *n*-hexyl radicals compared to neat $CCl_4$) **1c** is converted to 1-hexyl bromide (**3c**) 7 times faster than expected, indicating a more efficient photochemical homolytic cleavage of the Co–C bond in **1c** in the presence of $BrCCl_3$.



$$\underset{\textbf{1c, d}}{\text{R-Co}^{\text{III}}(\text{dmgH})_2\text{B}} \xrightarrow[\substack{h\nu \\ T = 15^\circ\text{C} \\ \text{X = Cl, Br}}]{\text{X-CCl}_3} \underset{\textbf{3c, 6c, d}}{\text{R-X}} + \underset{\textbf{5, 7}}{\text{X-Co}^{\text{III}}(\text{dmgH})_2\text{B}}$$

Table 3. Half-life times of product formation in photoreactions of alkylcobaloximes **1c** and **1d** in $CCl_4$ or $BrCCl_3$ ($T = 15\,^\circ C$)

| R | X | No. | $\tau_{1/2}$ [min][a]<br>R-X | <br>R-Co$^{III}$(dmgH)$_2$ Bupy |
|---|---|---|---|---|
| *n*-$C_6H_{13}$ | Cl[b] | **6c** | 72 | 67 |
| *n*-$C_6H_{13}$ | Br[c] | **3c** | 8 | 13 |
| c-$C_6H_{11}$ | Cl[b] | **6d** | 5 | 6 |

[a] $\tau_{1/2}$ is referred to as the rate of R–X formation and R–Co$^{III}$(dmgH)$_2$Bupy **1** decomposition respectively. – [b] Reaction was performed in neat $CCl_4$. – [c] [$BrCCl_3$] = $2.75 \cdot 10^{-3}$ mol $l^{-1}$ in benzene.

## Conclusions

Photochemical reactions of secondary alkylcobaloximes **1b** and **1d** are faster than those of their primary counterparts **1a** and **1c** no matter whether reactive radical-quenching organic molecules are present or not.

Bromine atom-containing reactants, e.g. the solvent bromobenzene or $BrCCl_3$, are able to accelerate reactions of photochemically excited alkylcobaloximes **1a** and **1c**. The latter phenomenon is not observed in photoreactions of secondary alkylcobaloximes presumably due to faster homolytic cleavage of the Co–C bond. It is tempting to state that the interaction of photolytically excited alkylcobaloxime **1a** or **1c** with either the non-reactive solvent bromobenzene or the bromine atom donor $BrCCl_3$ leads to the observed unexpected high reactivity and hence selectivity in our experiments[17]. The suspected formation of an exciplex between excited **1a** or **1c** and $BrCCl_3$ cannot be confirmed due to lack of fluorescence of both parent alkylcobaloximes **1a** and **1d**[18].

This work was supported by the *Volkswagen-Stiftung* and the *Swiss National Science Foundation*. We thank Dr. R. *Tampé* for helpful discussions on fluorescence spectroscopy.

## Experimental

NMR: Bruker WM 300, Bruker AC 300 (TMS as internal standard). – MS: Finnigan MAT. – UV/Vis: Beckman UV 5240 and DK2A. – Fluorescence spectroscopy: Perkin Elmer MPF 3 (xenon high-pressure lamp). – IR: Perkin Elmer 325. – GC: Carlo Erba GC 6000 (Vega Series), FID, connected to Spectra Physics integrator 4290; nitrogen at a flow rate of 3 ml/min (equals 120 kPa pressure) was used as carrier gas; injector and detector temperature 250 °C; SE 30 capillary column from Macherey & Nagel. – Preparative column chromatography: Merck silica gel 60 (0.063–0.200 mm). – Purification of solvents: benzene was distilled from sodium benzophenone under nitrogen directly before use. *n*-Hexane was refluxed for several hours with calcium hydride, distilled under nitrogen and stored over molecular sieves (4 Å). Tetrachloromethan was refluxed for 4 h with calcium oxide. The center cut of the distillation was collected, refluxed with potassium permanganate for 4 h, distilled under nitrogen and stored in dark bottles over molecular sieves (4 Å) for periods not exceeding one week. Benzene used for fluorescence spectroscopy was purchased from Merck (fluorescence spectroscopy grade).

The following compounds were prepared according to literature procedures: cyclohexylcobaloxime **1d**[6b], 5-hexenylcobaloxime **1a**[14], 6-hepten-2-ylcobaloxime **1b**[14], 6-bromo-1-heptene (**3b**)[19], bromocobaloxime **5**[20], chlorocobaloxime **7**[20], 3-bromo-4-methylpyridine[21], (bromomethyl)cyclopentane (**3e**)[22], 1-(bromomethyl)-2-methylcyclopentane (**3f**)[23].

1. *Syntheses of Alkylcobaloximes* **1**: 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 the addition of 0.6 ml (4.6 mmol) of 4-*tert*-butylpyridine or 0.8 g (4.6 mmol) of 3-bromo-4-methylpyridine 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 was stirred for an additional 60 min. Alkyl bromide **3** (neat, 5.0 mmol) was added to the black solution at −20 °C and the reaction mixture stirred at 20 °C in the dark for 14 h. The solvent was distilled from the orange solution, then 100 ml of water containing 1 drop of 4-*tert*-butylpyridine or 3-bromo-4-methylpyridine was added to the oily residue, and the precipitated orange crystals of alkylcobaloximes **1** were removed by filtration, dried and stored in amber-colored vials.

*(4-tert-Butylpyridine)bis(dimethylglyoximato)hexylcobalt(III)* (**1c**): Yield 1.75 g (82%), m.p. 166–168 °C (methanol). – $^1H$ NMR ($CDCl_3$): δ = 18.26 (s, 2H, OH), 8.43 (dd, $J$ = 1.5/5.2 Hz, 2 H, B), 7.27 (dd, $J$ = 1.5/5.2 Hz, 2H, B), 2.14 (s, 12H, $CH_3$), 1.62–1.57 (m, 2H, 1-H), 1.28 (s, 9H, $CH_3$), 1.24–1.14 (m, 6H), 0.96–0.86 (m, 2H, 2-H), 0.86–0.78 (m, 3 H, $CH_3$). – $^{13}C$ NMR ($CDCl_3$): δ = 11.99, 14.10, 22.71, 30.27, 30.48, 30.57, 31.70, 32.37, 34.74, 122.30, 148.39, 149.39, 161.59. – MS(FD): $m/z$ = 510/509 [$M^+$]. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (ε) = 418 nm (1410) sh, 377 (2160), 323 (5650) sh, 292 (8480), 235 (30600). – IR (KBr): $\tilde{\nu}$ = 2965 cm$^{-1}$, 2945, 2920, 2880, 2860, 1740, 1610, 1555, 1500, 1420, 1235, 1095.

| | | | | |
|---|---|---|---|---|
| $C_{23}H_{40}CoN_5O_4$ (509.5) | Calcd. | C 54.22 | H 7.91 | N 13.74 |
| | Found | C 54.04 | H 8.05 | N 13.70 |

*(3-Bromo-4-methylpyridine)bis(dimethylglyoximato)-5-hexenylcobalt(III)* **1e**: Yield 2.08 g (91%), m.p. 158–162 °C (dec) (methanol). – $^1H$ NMR ($CDCl_3$): δ = 18.22 (s, 2H, OH), 8.58 (s, 1H, B), 8.38 (d, $J$ = 5.6 Hz, 1H, B), 7.19 (d, $J$ = 5.6 Hz, 1H, B), 5.71 (ddt, $J$ = 6.8/10.1/17.0 Hz, 1H, 5-H), 4.94–4.83 (m, 2H, 6-H, 6′-H), 2.39

(s, 3H, $CH_3$), 2.13 (s, 12H, $CH_3$), 1.96 (q, $J = 7.0$ Hz, 2H, 4-H), 1.64–1.59 (m, 2H, 1-H), 1.27 (quint, $J = 7.4$ Hz, 2H, 3-H), 0.96–0.85 (m, 2H, 2-H). – $^{13}C$ NMR ($CDCl_3$): $\delta = 12.03$, 22.33, 29.50, 30.03, 31.78, 33.52, 113.74, 126.85, 126.93, 139.33, 148.09, 149.19, 149.36, 150.99. – MS (FD): $m/z = 545/543$ [$M^+$]. – UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 490 nm (175) sh, 420 (1490), 327 (2600) sh, 299 (9110). – IR (KBr): $\tilde{\nu} = 3080$ $cm^{-1}$, 3030, 2970, 2910, 2850, 1750, 1630, 1590, 1550, 1480, 1430, 1410, 1370, 1225, 1090.

$C_{20}H_{31}BrCoN_5O_4$ (544.3) Calcd. C 44.13 H 5.74 N 12.87
Found C 43.86 H 5.74 N 12.81

2. *Visible Light Photolysis of 5-Hexenylcobaloxime* **1a**, **1e** *and 6-Hepten-2-yl-cobaloximes* **1e** *in the Absence of Radical Traps:* Anaerobic photolysis (argon, incandescent light: Osram Concentra®, R 95 Natura, 300 W PAR 56), of 1.0 mmol of alkylcobaloxime **1** dissolved either in benzene, chlorobenzene, or bromobenzene in a falling-film photoreactor at $T = 15\,°C$ yields a purple solution which was quickly removed from the reaction vessel and concentrated in vacuo in the dark. Purification of the oily residue (silica gel, ethyl acetate, $R_f = 0.4$) yielded either pure (cyclopentylmethyl)cobaloximes **4** or a mixture of **1** and **4** as orange crystals.

*(3-Bromo-4-methylpyridine)(cyclopentylmethyl)bis(dimethylglyoximato)cobalt(III)* (**4c**): Reaction time 39 h, yield 0.09 g (16%), m.p. 179–182°C (dec.) (methanol). – $^1H$ NMR ($CDCl_3$): $\delta = 18.23$ (2, 2H, OH), 8.57 (s, 1H, B), 8.38 (d, $J = 5.5$ Hz, 1H, B), 7.18 (d, $J = 5.5$ Hz, 1H, B), 2.38 (s, 3H, $CH_3$), 2.13 (s, 12H, $CH_3$), 1.77 (d, $J = 6.2$ Hz, 2H, 6-H), 1.65–1.61 (m, 2H), 1.59–1.26 (m, 5H), 0.99–0.88 (m, 2H). – $^{13}C$ NMR ($CDCl_3$): $\delta = 12.07$, 22.30, 25.30, 34.61, 40.09, 41.89, 124.34, 126.98, 147.98, 149.31, 150.91. – MS (FD): $m/z = 545/543$ [$M^+$].

$C_{20}H_{31}BrCoN_5O_4$ (544.3) Calcd. C 44.13 H 5.74 N 12.87
Found C 43.95 H 5.81 N 12.74

*(4-tert-Butylpyridine)bis(dimethylglyoximato)[cis- and trans-(2-methylcyclopentyl)methyl]cobalt(III)* (**4b**): Reaction time 1 h; *cis*- and *trans*-**4b** were isolated as a mixture of isomers (*cis*:*trans* = 78:22); yield 0.29 g (55%). – MS (FD): $m/z = 522/521$ [$M^+$].

$C_{24}H_{40}CoN_5O_4$ (521.5) Calcd. C 55.27 H 7.73 N 13.43
Found C 55.05 H 7.87 N 13.53

*(4-tert-Butylpyridine)bis(dimethylglyoximato)[cis-(2-methylcyclopentyl)methyl]cobalt(III):* $^1H$ NMR ($CDCl_3$): $\delta = 18.27$ (s, 2H, OH), 8.45–8.40 (m, 2H, B), 7.30–7.25 (m, 2H, B), 2.14 (s, 6H; $CH_3$), 2.13 (s, 6H, $CH_3$), 1.85–0.83 (m, 10H), 1.27 (s, 9H, $CH_3$), 0.65 (d, $J = 7.1$ Hz, 3H, $CH_3$). – $^{13}C$ NMR ($CDCl_3$): $\delta = 12.00$, 14.65, 22.19, 30.24, 31.31, 33.31, 33.64, 34.52, 37.46, 45.00, 122.26, 148.61 or 148.98, 149.28, 161.50.

*(4-tert-Butylpyridine)bis(dimethylglyoximato)[trans-(2-methylcyclopentyl)methyl]cobalt(III):* $^1H$ NMR ($CDCl_3$): $\delta = 18.27$ (s, 2H, OH), 8.45–8.40 (m, 2H, B), 7.30–7.25 (m, 2H, B), 2.14 (s, 6H, $CH_3$), 2.13 (s, 6H, $CH_3$), 1.85–0.83 (m, 10H), 1.27 (s, 9H, $CH_3$), 0.79 (d, $J = 7.1$ Hz, 3H, $CH_3$). – $^{13}C$ NMR ($CDCl_3$): $\delta = 11.99$, 15.79, 24.13, 30.24, 33.97, 34.52, 34.78, 38.75, 42.47, 49.41, 122.26, 148.61 or 148.98, 149.28, 161.50.

3. *Photoreactions of Alkylcobaloximes* **1** *in the Presence of Radical Traps*

3.1 *Visible-Light Photolysis of Alkylcobaloximes* **1c** *and* **1d** *in the $CCl_4/BrCCl_3$ Competition System:* A solution of 1.0 mmol of alkylcobaloxime **1** and 20–40 mmol of $BrCCl_3$ in about 7 mol of degassed $CCl_4$ was photolyzed under argon at temperatures between 32 and 72°C for 5 h. Cobalt complexes were removed by adsorptive filtration on a short silica gel column. Alkyl halides are eluted with 50 ml of *n*-hexane and the clear, colorless eluate obtained was subjected to GC analysis ($T = 50\,°C$ for *n*-hexyl halides **3c**, **6c** or 60°C cyclohexyl halides **3d**, **6d**). Results at highest and lowest reaction temperatures were checked by 3 independent runs. Isolated yields: 1-chlorohexane (**6c**) 0.10 g (86%), 1-bromohexane (**3c**) 0.16 g (96%), chlorocyclohexane (**6d**) 0.11 g (96%), bromocyclohexane (**3d**) 0.12 g (74%), bromocobaloxime **5** 0.46–0.49 g (91–97%), chlorocobaloxime **7** 0.34–0.38 g (74–82%).

3.2 *Photolysis of Hexyl-* **1c** *and Cyclohexylcobaloxime* **1d** *in Tetrachloromethane and Bromotrichloromethane:* Solutions of 1.0 mmol of alkylcobaloxime **1** in about 250 ml of degassed anhydrous solvent (either neat $CCl_4$ or definite amounts of $BrCCl_3$ in benzene) were photolyzed at 15°C for a given time in a falling-film photoreactor. The brown solution was removed from the reaction chamber and poured onto a short silica gel column to free the solution from cobalt complexes. Alkyl halides were eluted with 50 ml of *n*-hexane (GC analysis). Cobalt complexes were quickly eluted with ethyl acetate to yield an orange band of alkylcobaloxime **1** and a brown band of halogenocobaloxime **5** or **7**. Isolated yields: *n*-hexyl chloride (**6c**) 0.10 g (86%), *n*-hexyl bromide (**3c**) 0.16 g (96%), cyclohexyl chloride (**6d**) 0.11 g (96%), cyclohexyl bromide (**3d**) 0.15 g (91%), bromocobaloxime **5** 0.46–0.49 g (91–97%), chlorocobaloxime **7** 0.34–0.38 g (74–82%).

3.3 *Photolysis of Hexenyl-* **1a** *and 6-hepten-2-ylcobaloxime* **1b** *in $BrCCl_3$/Benzene:* Solutions of 1.0 mmol of alkylcobaloxime **1** in about 100 ml degassed anhydrous solvent (definite amounts of $BrCCl_3$ in benzene) containing 2.0 mmol of triphenylmethane were photolyzed at $T = 26\,°C$ (argon, incandescent light) for 5 h until **1** had completely been consumed. The progress of the reaction was accompanied by a gradual change in color from orange to brown. Cobalt complexes were removed by adsorptive filtration on a short silica gel column. Alkyl bromides were subjected to GC analysis ($T = 60\,°C$, for **3a** $t_R = 2.1$ min, **3e** $t_R = 2.7$ min, **3b** $t_R = 3.4$ min, **trans-3f** $t_R = 4.2$ min, **cis-3f** $t_R = 5.1$ min).

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[17] Due to control experiments bromocobaloxime **5**, which is formed in photoreaction of **1** in $BrCCl_3$ in excellent yields, cannot act as a competitive and more efficient bromine atom donor.

[18] 5-Hexenylcobaloxime **1a** and cyclohexylcobaloxime **1d** were analyzed at 20°C in a fluorescence spectrometer (**1a**: $c = 2.93 \cdot 10^{-5}$ mol l$^{-1}$; the sample was irradiated in oxygen-free benzene solutions at three different wavelengths: 420, 370, and 340 nm; **1d**: $c = 3.61 \cdot 10^{-5}$ mol l$^{-1}$; the sample was irradiated in oxygen-free benzene solutions at three different wavelengths: 430, 390, and 330 nm). Neither of the runs showed fluorescence emissions between 340 and 600 nm. – For photochemistry of cobalt(III) complexes see A. Adamson, G. Satori, *Adv. Inorg. Chem. Radiochem.* **1972**, *17*, 1–57; J. F. Endicott, G. J. Ferraudi, J. R. Barber, *J. Phys. Chem.* **1975**, *79*, 630–643; A. Adamson, A. H. Sporer, *J. Am. Chem. Soc.* **1958**, *80*, 3865–3870; W. L. Waltz, R. G. Sutherland, *Chem. Soc. Rev.* **1972**, *1*, 241–258; A. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, R. D. Lindholm, *Chem. Rev.* **1968**, *68*, 541–585; V. Balzani, L. Moggi, V. Carasitti, *Ber. Bunsenges. Phys. Chem.* **1968**, *72*, 288–295; G. N. Schrauzer, L. P. Lee, J. W. Sibert, *J. Am. Chem. Soc.* **1972**, *92*, 2997–3005.

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