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Selective homolytic reactions of alkylcobaloxime with nitrogen monoxide

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Abstract

Alkylcobaloxime with an acidic hydrogen atom attached to α-carbon reacted selectively with nitrogen monoxide (NO) to give a high yield of the corresponding oxime, whereas alkylcobaloxime with a less acidic hydrogen atom attached to α-carbon gave an alkyl nitrate and an alcohol. In the reactions of benzylcobaloximes, oxime was predominantly formed at higher temperatures, and alkyl nitrate at lower temperatures. Cobaloxime was converted into nitrocobaloxime in every case.

Introduction

The alkyl-radical generating and radical trapping properties of alkylcobaloxime, alkylbis(dimethylglyoximato)pyridine cobalt(III) **1** have been widely noted [1]. The Co–Cα bond of alkylcobaloxime has been reported [2] to be cloven homolytically by visible light or by heat. We have investigated [3] the reactivity of photoactivated alkylcobaloximes in connection with the reactivity of cobalamine activated by an apoenzyme. It has been reported [1,4] that alkylcobaloxime traps various organic radicals. Alkylcobaloxime has also been reported [5] to react with a paramagnetic gaseous molecule, dioxygen. Although the paramagnetic properties of gaseous nitrogen oxides, abundant in the environment, are well known, the reactions of alkylcobaloxime or related cobalt complex with nitrogen oxides have received only little attention [6]. In addition, some organotransition-metal complexes with NO have been reported [7], but these studies have not yet been applied in organic synthesis.

In this paper, analysis of the products of the reactions of alkylcobaloximes with nitrogen monoxide (NO) is reported and discussed in terms of the reactivity of alkylcobaloxime with paramagnetic gaseous NO.

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Experimental

Measurements

The NMR measurements were carried out with JEOL PMX-60si and Varian XL-300 instruments with tetramethylsilane as an internal standard in deuterochloroform. The IR spectra were recorded with a Hitachi 260-10 infrared spectrophotometer and a Perkin–Elmer 1600 Series FTIR. The mass spectra were recorded with a Perkin–Elmer ITD system.

Materials

Cobaloximes having an alkyl ligand **1a–h** were prepared by the reported method [8], and these cobaloximes were identified by ^{1}H NMR and confirmed by elemental analysis. Alkyl nitrates and alkyl nitrites were prepared according to the reported method [9] as authentic samples for the identification of the reaction products. Solvents were purified in the usual manner. Other chemicals used in this study were of reagent grade.

General procedure

Alkylcobaloxime **1** (1 mmol) and CH_2Cl_2 (10 ml) were placed in a Schlenk tube (120 cm^3). Air in the reaction vessel was purged and replaced with NO by a freeze–pump–thaw technique. The reaction was carried out for 24 h at 35°C with irradiation by a tungsten lamp (400 W) under NO atmosphere. Products were isolated by silica-gel column chromatography, and were identified by ^{1}H NMR, IR, and GC–MS.

NMR data of cobaloximes

^{1}H NMR: **1a**, δ 0.72(t, 3H), 0.95–1.50(m, 2H), 1.23(t, 3H), 1.95(t, 1H), 2.20(s, 12H), 3.99(q, 2H), 7.25–7.50(m, 2H), 7.62–7.95(m, 1H), 8.52–8.71(m, 2H); **1b**, 0.45(d, 3H), 2.20(s, 13H), 5.00(s, 2H), 7.20–7.95(m, 8H), 8.55–8.75(m, 2H); **1c**, 1.93(s, 12H), 2.88(s, 2H), 7.03(s, 5H), 7.30–7.41(m, 2H), 7.60–7.72(m, 1H), 8.54–8.62(m, 2H); **1d**, 0.59(d, 3H), 1.95(s, 12H), 3.58(q, 1H), 6.90–7.40(m, 7H), 7.50–7.70(m, 1H), 8.40–8.60(m, 2H); **1e**, 1.78(s, 12H), 3.36(s, 2H), 7.10–7.90(m, 10H), 8.45–8.65(m, 2H); **1f**, 1.80(t, 2H), 2.10(s, 12H), 2.19(t, 2H), 7.08–7.26(m, 5H), 7.29–7.34(m, 2H), 7.68–7.74(m, 1H), 8.61–8.64(m, 2H); **1g**, 1.27(m, 2H), 1.65(t, 2H), 2.08(s, 12H), 2.51(t, 2H), 7.07–7.24(m, 5H), 7.27–7.32(m, 2H), 7.68–7.72(m, 1H), 8.57–8.59(m, 2H); **1h**, 0.70–1.80(m, 13H), 2.13(s, 12H), 7.20–7.50(m, 2H), 7.60–7.90(m, 1H), 8.58–8.75(m, 2H); **6**, 2.37(s, 12H), 7.18–7.48(m, 2H), 7.65–8.00(m, 1H), 8.27–8.50(m, 2H).

Results

Four organic products (**2**, **3**, **4**, and **5**) derived from the alkyl ligand and nitrocobaloxime **6** were isolated (eq. 1) by the reaction of alkylcobaloxime **1** with NO under irradiation.

$$\underset{\mathbf{1}}{RCH_2\text{-}Co(DH)_2py} \xrightarrow{NO} \underset{\mathbf{2}}{RCH{=}NOH} + \underset{\mathbf{3}}{RCH_2ONO_2} + \underset{\mathbf{4}}{RCH_2OH} + \underset{\mathbf{5}}{RCHO} + \underset{\mathbf{6}}{NO_2Co(DH)_2py} \qquad (1)$$

Table 1

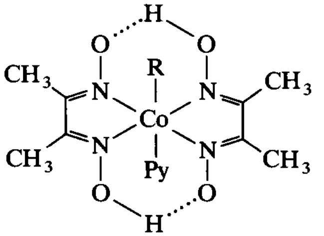
Reaction of alkylcobaloxime with NO under irradiation [a]

Entry	Cobaloxime	Yield of product (%)			
		2	**3**	**4**	**5**
1	**1a**	96	0	0	0
2	**1b**	87	0	0	0
3	**1c**	74	14	6	4
4	**1d**	35	16	8	7
5	**1e**	18	26	13	2
6	**1f**	0	52	12	0
7	**1g**	0	55	28	0
8	**1h**	0	14	14	0

[a] Conditions (**1**): 100 mM in CH_2Cl_2, under NO, at 35°C, for 24 h, under irradiation with tungsten lamp (400 W).

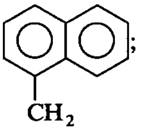
The results are summarized in Table 1. When cobaloxime **1a** or **1b** is reacted with NO, the alkyl ligand is specifically converted into oxime **2** in high yield (Table 1, entries 1 and 2). The cobalt complex is converted into nitrocobaloxime **6**, isolated in 77% yield.

On the other hand, alkyl ligands in cobaloximes (**1f**, **1g**, and **1h**) are converted into alkyl nitrate (**3**) and alcohol (**4**) respectively, without the formation of oximes (**2**) (entries 6–8). In the reaction with NO of cobaloximes having a benzylic ligand (**1c**, **1d**, and **1e**) an intermediate feature is observed, *i.e.*, considerable amounts of oxime **2**, nitrate **3**, and alcohol **4**, and a small amount of aldehyde **5** are obtained (entries 3–5). GC–MS indicated that these are by far the major products.



Alkyl(pyridine)cobaloxime **1**

(**a**, R = CH(Et)COOEt;

e, R =  ;

b, R = $CH(Me)COOCH_2Ph$;

c, R = CH_2Ph;

d, R = CH(Me)Ph;

f, R = CH_2CH_2Ph;

g, R = $CH_2CH_2CH_2Ph$;

h, R = $CH_2(CH_2)_4CH_3$)

Results of some control experiments are summarized in Table 2. The visible light irradiation influences only slightly the reaction of the benzylcobaloxime **1c** with NO (Table 2, entry 10). On the other hand, the effect of irradiation is observed in the case of 2-phenylethylcobaloxime **1f** (entry 15). When the reaction is carried out at a higher temperature, the selectivity for the formation of oxime is

Table 2

Control experiments of the reaction of alkylcobaloxime with NO[a]

Entry	Cobaloxime	Temperature (°C)	Time (h)	Light [b]	Yield of product (%)	
					2	**3**
9	**1c**	35	5	on	51	21
10	**1c**	35	5	off	50	20
11	**1c**	60	5	off	55	5
12	**1c**	0	5	off	0	83
13	**1e**	0	5	off	0	57
14	**1f**	35	24	on	0	52
15	**1f**	35	24	off	0	34

[a] Conditions (**1**): 100 mM in CH_2Cl_2, under NO. [b] on, irradiation with tungsten lamp (400 W); off, dark reaction.

increased (entry 11). Conversely, the alkyl nitrate is produced selectively in good yield under these condition but at lower temperature (entries 12, 13).

Discussion

An initial step in every case is the formation of a labile nitrosoalkane by the reaction of alkylcobaloxime with NO. The formation of nitrosoalkane has been generally agreed [10] to be the first step of the reaction of an alkyl radical with NO (eq. 2).

$$RCH_2^{\bullet} + NO \rightarrow RCH_2NO \tag{2}$$

Nitrosoalkane has been reported to isomerize to oxime predominantly at temperatures higher than room temperature [11]. The selectivity of oxime formation (Table 1) can be interpreted in terms of the acidity of Cα–H bond. The acidity of the hydrogen atom attached to the α-carbon of **1a** and **1b** is the highest among the cobaloximes used in the present work, since both **1a** and **1b** have an electron-withdrawing group at the β-position to Co. A predicted order of Cα–H bond acidity, **1a** ≃ **1b** > **1c** ≃ **1d** ≃ **1e** > **1f** ≃ **1g** ≃ **1h**, is well correlated with the selectivity of oxime formation. Thus, the alkyl ligand of **1a** and **1b** is specifically converted into oxime **2** through nitrosoalkane isomerization caused by proton migration (eq. 3).

$$RCH_2NO \rightarrow RCHN{=}OH \tag{3}$$

On the other hand, the nitrosoalkane has been reported [10,12] to react with two molecules of NO to give an unstable diazo nitrate which decomposes subsequently to give NO_2 and an alkoxy radical (eq. 4).

$$RCH_2NO + 2NO \rightarrow RCH_2\text{–}N(NO)ONO \rightarrow RCH_2\text{–}N{=}NONO_2 \tag{4a}$$

$$RCH_2\text{–}N{=}NONO_2 \rightarrow RCH_2^{\bullet} + N_2 + NO_3 \tag{4b}$$

$$NO_3 + NO \rightarrow 2NO_2 \tag{4c}$$

$$RCH_2^{\bullet} + NO_2 \rightarrow RCH_2O^{\bullet} + NO \tag{4d}$$

Many products, such as nitroalkane, alkyl nitrate, alkyl nitrite, olefin, aldehyde, alcohol, etc., are expected [12] to be produced by this decomposition. Alkyl nitrite produced by the reaction of alkyl radical with NO_2 or by the reaction of alkoxy radical with NO is consumed by the reaction with alkyl radical (eq. 5) [13].

$$RCH_2^{\bullet} + RCH_2ONO \rightarrow RCH_2O^{\bullet} + RCH_2NO \tag{5}$$

Another route for the decomposition of nitrosoalkane with NO has been reported (eq. 6) [14].

$$RCH_2NO + NO \rightarrow RCH_2O^{\bullet} + N_2O \tag{6}$$

Finally, alkyl nitrate **3** is produced by elimination of dinitrogen from the alkyl diazo nitrate (eq. 7) or by the coupling of alkoxy radical with NO_2 (eq. 8) [12].

$$RCH_2\text{-}N{=}N\text{-}ONO_2 \rightarrow RCH_2ONO_2 + N_2 \tag{7}$$

$$RCH_2O^{\bullet} + NO_2 \rightarrow RCH_2ONO_2 \tag{8}$$

Nitrosoalkanes produced by the reaction with NO of those alkylcobaloximes (**1f–h**) with a less acidic hydrogen atom attached to α-carbon react with excess NO according to eqs. 4–8 to give alkyl nitrates respectively (Table 1, entries 6–8) without the formation of oxime. The considerable yield of alcohol **4** is consistent with the intermediate formation of an alkoxy radical which subsequently abstracts a hydrogen from the solvent. The preferential formation of NO_2 and alkoxy radical during the decompositions of nitrosoalkane (eqs. 4–6) is one reason for the selective formation of alkyl nitrate **3** and alcohol **4**.

Apparently, two types of reactions (eq. 3 and eqs. 4–8) proceed simultaneously in the reaction of alkylcobaloximes (**1c–e**) (Table 1, entries 3–5). Formation of aldehyde **5** is due to the disproportionation of the benzyloxy radical into alcohol and aldehyde (eq. 9) [15].

$$2ArCH_2O^{\bullet} \rightarrow ArCH_2OH + ArCHO \tag{9}$$

Especially in the case of cobaloximes bonded to a benzylic ligand (**1c–e**), the isomerization of nitrosoalkane into oxime (eq. 3) can be accelerated at a higher reaction temperature (entry 11) and depressed at a lower reaction temperature, and the reaction for the formation of nitrate (eqs. 4–8) accelerated by increasing the concentration of dissolved NO (entries 12 and 13).

Nitrocobaloxime **6** is produced according to eq. 10 in every case.

$$RCo(dmgH)_2py + 2NO \rightarrow RNO + Co(dmgH)_2(py)NO \tag{10a}$$

$$Co(dmgH)_2(py)NO + 2NO \rightarrow Co(dmgH)_2(py)NO_2 + N_2O \tag{10b}$$

Initially, divalent cobaloxime is reacted with NO to give nitrosylcobaloxime whose formation has been confirmed in other studies [16]. Nitrosylcobaloxime is known to react with excess NO to give nitrocobaloxime [17].

In addition, the difference of Co–Cα bond dissociation energies in various alkylcobaloximes reflects the initial homolytic substitution of alkylcobaloxime **1** by NO. The labile alkylcobaloximes (**1a–e**) have little need for the Co–Cα bond to be activated by irradiation for the substitution, but such activation is effective in the case of alkylcobaloximes (**1f–h**) whose Co–Cα bond dissociation energies are relatively high (Table 2, entries 10 and 15).

Conclusion

The reactivity of alkylcobaloximes towards paramagnetic NO was investigated through the reactions of various alkylcobaloximes with NO. The course of reaction of the unstable nitrosoalkane was found to be controlled by the nature of alkyl ligands (Table 1) and the reaction conditions (Table 2). We would like to mention additionally that this study could enable reaction conditions to be developed so that reactions of alkylcobaloximes with NO would be better controlled and have higher yields.

References

1 M.D. Johnson, Acc. Chem. Res., 16 (1983) 343; B. Giese, Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds, Pergamon, Oxford, 1986; G. Pattenden, Chem. Soc. Rev., 17 (1988) 361.
2 J.M. Pratt and B.R.D. Whitera, J. Chem. Soc. A, (1971) 252; D.N. Ramakrishna and M.C.R. Symons, J. Chem. Soc., Faraday Trans. 1, 80 (1984) 423.
3 M. Kijima, K. Miyamori and T. Sato, J. Org. Chem., 52 (1987) 706; M. Kijima, K. Miyamori and T. Sato, ibid., 53 (1988) 1719; M. Kijima, K. Miyamori, T. Nakamura and T. Sato, Bull. Chem. Soc. Jpn., 63 (1990) 2549.
4 M. Veber, K.N.V. Duong and A. Gaudemer, J. Organomet. Chem., 177 (1979) 231; S. Roy, B.D. Gupta and S. Chaklanobis, ibid., 269 (1984) 201; C. Gianotti, C. Fontaine, A. Chiaroni and C. Riche, ibid., 113 (1976) 57; A. Bury and M.D. Johnson, J. Chem. Soc., Chem. Commun., (1980) 498.
5 C. Gianotti, C. Fontaine and B. Septe, J. Organomet. Chem., 71 (1974) 107; C. Bied-Charreton and A. Gaudemer, ibid., 124 (1977) 299.
6 T. Okamoto, K. Kobayashi, S. Oka and S. Tanimoto, J. Org. Chem., 52 (1987) 5089; V.F. Patel and G. Pattenden, J. Chem. Soc., Perkin Trans. 1, (1990) 2703.
7 J.A. McCleverty, Chem. Rev., 79 (1979) 53; A.R. Middleton and G. Wilkinson, J. Chem. Soc., Dalton Trans., (1980) 1888; M.D. Seidler and R.G. Bergman, J. Am. Chem. Soc., 106 (1984) 6110; A. Goldhaber, K.P.C. Vollhardt, E.C. Walborsky and M. Wolfgruber, ibid., 108 (1986) 516.
8 G.N. Schrauzer, Inorg, Synth., 11 (1968) 61.
9 B. Prager, P. Jacobsen, P. Schmidt and D. Stern, Beilsteins Handbuch Der Organischen Chemie, Band 6, System No. 528, Springer-Verlag, Berlin, 1923, p. 439.
10 Y. Rees and G.H. Williams, Adv. Free-Radical Chem., 3 (1969) 199.
11 L. Batt and B.G. Gowenlock, Trans. Faraday Soc., 56 (1960) 682.
12 O.P. Strausz and H.E. Gunning, Can. J. Chem., 41 (1963) 1207; L.G. Donaruma and D.J. Carmody, J. Org. Chem., 22 (1956) 635.
13 B. Bromberger and L. Phillips, J. Chem. Soc., (1961) 5302; M.L. Poustma, in J.K. Kochi (Ed.), Free Radicals, Wiley, New York, Vol. 2, 1973.
14 T. Johnston and J. Heicklen, J. Phys. Chem., 70 (1966) 3088.
15 Y. Takegami, Y. Fujimura and H. Ishii, Kogyo Kagaku Zasshi, 68 (1965) 196; A.G. Goble, A.G. Lidstone and P.J.S. Pauwels, Chem. Ind., (1959) 1489.
16 M. Tamaki, I. Masuda and K. Shinra, Bull. Chem. Soc. Jpn., 45 (1972) 171; W.C. Trogler and L.G. Marzilli, Inorg. Chem., 13 (1974) 414.
17 D. Gwost and K.G. Caulton, Inorg. Chem., 13 (1974) 414.