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Preliminary communication

Synthesis of organocobaloximes: modification of the organic group in organocobaloximes

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Abstract

5-Substituted heteroaromaticmethyl cobaloximes are synthesized by a very simple reaction of arenesulfenyl chloride, ArSCl (Ar = Ph, C_6Cl_5 and 2,4-$(NO_2)_2C_6H_3$) with heteroaromaticmethyl cobaloximes, $RCo^{III}(dmgH)_2Py$ [R = 2- and 3-thienylmethyl, furfuryl] in the dark at 0 °C. As organocobaloximes are susceptible to Co–C bond cleavage by the electrophiles and free radicals, the ring substitution is quite remarkable.

Keywords: Organocobaloxime; Organocobalt

1. Introduction

The initial studies on organocobaloximes, $RCo(dmgH)_2Py$, were focused largely on its role as a model for vitamin B_{12} coenzyme [1–10]. Recent work, however, has shown that its chemistry is so interesting that it has acquired an independent research field [11–16]. These have been used as templates in many organic syntheses [17] and as catalysts in chemical processes [18]. The key feature of these complexes is the weak Co–C bond and, since small structural changes in the molecule have a profound effect on the reactivity of the Co–C bond [9], the synthesis of new complexes continues to interest chemists. Many synthetic routes have been reported and many new ones are still appearing in the literature [10]. Generally, one starts with a Co(I), Co(II) or Co(III) complex to synthesize organocobaloximes. The use of organocobaloximes as precursors for the synthesis of new organocobaloximes, however, does not find an adequate place in the literature. The known examples, though few, have generally employed simple reactions like hydrolysis (both acidic as well as basic) [19,20], acetal hydrolysis [21], cyclisation reactions [22–24], transalkylations [25], σ–π rearrangements [26–28], cycloaddition [29,30] and Diels-Alder reaction [31]. Solid state photoisomerisation of optically active alkyl cobaloximes has also been reported [32].

In this paper we report the synthesis of 5-substituted heteroaromaticmethyl cobaloximes by a simple reaction of the arene sulfenyl chloride, ArSCl (Ar = Ph, C_6Cl_5 and 2,4-$(NO_2)_2C_6H_3$) with heteroaromaticmethyl cobaloximes.

2. Experimental

The synthesis of organocobaloximes (1–3) has been reported earlier [15]. Benzene sulfenyl chloride (A) was prepared [33] by the chlorination of diphenyldisulfide with sulfuryl chloride at ambient temperature (b.p. 46–48 °C/4 mm, lit. 49 °C/2 mm, ^{1}H NMR δ: (CCl_4) 7.4 (s, Ar). Pentachlorobenzenesulfenyl chloride (B) was prepared [34] by the chlorination of pentachlorobenzenethiol with chlorine gas (m.p. 100 °C, lit. 104 °C). The thiol was prepared [35] from hexachlorobenzene, sodium sulfide and sulfur under refluxing conditions. 2,4-Dinitrobenzenesulfenyl chloride (C) was bought from Fluka and used as such.

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3. Results and discussion

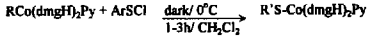
Organocobaloximes (1–3) react with arene sulfenyl chloride, ArSCl (A, B or C) [see Scheme 1] in 1:1 molar ratio in the dark (reaction flask covered with aluminum foil) at 0 °C in dichloromethane. The progress of the reaction is monitored by TLC on silica gel using ethyl acetate. The reaction is generally complete within 3 h. The mixture is then concentrated and poured into solvent ether. The precipitated solid is washed with ether and is further purified by column chromatography on silica gel using a mixture of dichloromethane and ethyl acetate. The combined ether extract after evaporation does not afford any characterizable organic product. Similar reactions when carried out under photochemical conditions (irradiation by 2 × 200 W tungsten lamps) at 0 °C give a complicated mixture of products, both organic as well as organometallic, in each reaction (Table 1).

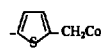
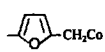
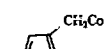
The exclusive formation of the ring-substituted organocobaloximes suggests that we are dealing with a unique class of sigma bonded organo cobalt complexes having an activated arene ring which is susceptible to attack by the electrophilic ArS^+ species. This is justified in view of our earlier observations that the metallomethyl group $-CH_2Co(dmgH)_2Py$ is highly activating, and its activation is even more than that of the methoxy group [16]. As organocobaloximes are susceptible to Co–C cleavage by the electrophiles [16,36–39] and free radicals [11–16], the substitution into the aromatic ring is quite remarkable. This is a rare observation in organocobaloxime chemistry.

One-electron oxidation potential values of the ring-substituted products are comparable to those of the parent cobaloximes and are irreversible in nature.

The ring-substituted organocobaloximes undergo very facile oxygen insertion into the Co–C bond under photochemical conditions ($h\nu$, 0 °C/2 h) (Scheme 1, footnote).

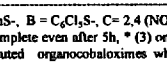
We also observe a remarkable difference in the reactivity of 3- and 4-methoxybenzyl cobaloximes [15] with arene sulfenyl chloride. For example, the cleavage of the Co–C bond occurs in the 4-OMe case with 4-$OMeC_6H_4CH_2SPh$ as one of the many products: ^1H



R=	*RCo(III)	ArSCl (ZCl) Z=	Product (Product no)	Yield (%)
	(1)	A,B,C	Z 	
			Z=A (4)	64
			B (5)	60
			C (6)	55
	(2)	A,B,C	Z 	
			Z= A (7)	50
			B (8) $	70
			C (9)	28#
	(3)	A,B,C	Z 	
			Z= A (10)	52
			B (11)	58
			C (12)	27#

A = PhS-, B = C_6Cl_5S-, C= 2,4 $(NO_2)_2$ C_6H_3S-

Incomplete even after 5h, * (3) on reaction with Cl_2 or Br_2 at 0°C in dark forms the 5-halo substituted organocobaloximes whereas (1) and (2) lead to the cleavage of the Co-C bond [15]. $ (8) with molecular oxygen under photochemical conditions forms



[^1H NMR ($CDCl_3$), 2.3(s), 4.26(s), 6.3-6.7(dd), 7.20, 7.56, 8.24 (m)]

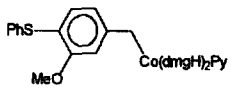
Scheme 1.

Table 1
Characteristics of the organocobaloximes (1–3) and ring-substituted products (4–12)

Product No.	^{1}H NMR (chemical shifts) δ				UV–vis	CV values [a]				
	dmgH	CH_2	Heteroaromatic	Py/aromatic	λ_{max} (nm) (CH_3OH)	$E_{1/2}$ vs. SCE (V)	Anal. Found (Calc.) (%) [b]			
							C	H	N	S
1	2.05 (s)	3.00 (s)	6.65, 7.00 (dd)	7.20, 7.65, 8.50	385, 281, 240	0.950	[c]			
2	2.00 (s)	2.40 (s)	6.00, 7.40 (dd)	7.30, 7.75, 8.60	383, 284, 239	0.931	[c]			
3	2.00 (s) 2.10 (s)	2.85 (s)	6.65, 7.20 (dd)	7.30, 7.70, 8.50	359, 277, 239	0.950	[c]			
4	2.06 (s)	2.60 (s)	6.02–6.40 (dd)	7.20, 7.60, 8.40 7.10	379, 240, 208	0.825	50.12 (50.26)	4.82 (4.88)	12.18 (12.21)	11.10 (11.16)
5	2.00 (s)	2.50 (s)	5.96–6.40 (dd)	7.20, 7.50, 8.35	382, 217	0.834	38.58 (38.63)	3.01 (3.08)	9.32 (9.38)	8.55 (8.58)
6	2.06 (s)	2.50 (s)	5.95–6.50 (dd)	7.20, 7.60, 8.40 7.66 (s), 7.40 (s) 8.20 (d), 8.90 (d) 9.00 (d)	299, 239, 207	0.915	43.35 (43.43)	3.85 (3.92)	14.68 (14.78)	9.60 (9.65)
7	1.96 (s)	2.75 (s)	6.50–6.80 (dd)	7.20, 7.40, 8.35 7.04–7.10 (m)	380, 286, 243 208	0.899	51.62 (51.70)	5.91 (5.02)	12.08 (12.13)	5.68 (5.74)
8	1.90 (s)	2.80 (s)	6.60–6.90 (dd)	7.20, 7.60, 8.40	385, 290, 219	0.846	39.41 (39.47)	3.14 (3.15)	7.50 (7.59)	4.32 (4.38)
9	2.18 (s)	3.00 (s)	6.80–7.08 (dd)	7.34, 7.80, 8.52 7.60 (s), 7.40 (s) 8.30 (d), 8.35 (d) 9.10 (d)	308, 241, 206	1.071	44.82 (44.85)	3.95 (4.04)	15.10 (15.26)	4.88 (4.98)
10	1.96 (s)	2.76 (s)	6.70–6.80 (dd)	7.20, 7.50, 8.40 7.20 (m)	367, 244, 209	0.884	50.28 (50.26)	4.80 (4.88)	12.18 (12.21)	11.10 (11.16)
11	2.01 (s)	2.95 (s)	6.65–6.85 (dd)	7.20, 7.50, 7.85	380, 237, 218	0.958	38.59 (38.63)	3.02 (3.08)	9.35 (9.38)	8.50 (8.58)
12	2.01 (s)	2.56 (s)	6.7–7.0 (m)	7.60 (s), 7.40 (s) 7.70 (m), 8.10 (d) 8.25 (d), 9.10 (d)	306, 242, 206	1.01	43.30 (43.43)	3.88 (3.92)	14.79 (14.78)	9.64 (9.65)

[a] Oxidation potential.
[b] (5) Cl, 23.72 (23.80); (8) Cl, 24.21 (24.33); (11) Cl, 23.70 (23.80).
[c] Taken from Ref. [15].

NMR ($CDCl_3$) δ: [3.86 (s, $-CH_2S$), 7.10, 6.50–7.00 (dd, Ar), 3.70 (s, OMe–)]; m.p. 75 °C, λ_{max} (MeOH) 265, 231, whereas ring substitution is the facile process in 3-methoxybenzyl cobaloxime.



Yield 40%. ^{1}H NMR ($CDCl_3$) δ: 1.98 (s, dmgH), 2.98 (s, $-CH_2$), 3.72 (s, –OMe), 6.60–7.20 (m, Ar and Py), 7.48, 8.40 (m, Py); λ_{max} (MeOH) 344, 246, 212.

Acknowledgements

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