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Co–C bond cleavage in the reactions of alkyl, benzyl and heteroaromaticmethyl cobaloximes with arene sulfenyl chloride: Homolytic and heterolytic pathways[1]

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Abstract

The reactions of arene sulfenyl chlorides, ArSCl, (Ar = Ph, C_6Cl_5, 2,4 $(NO_2)_2C_6H_3$) with organocobaloximes, $RCo(dmgH)_2Py$, (R = alkyl, benzyl and heteroaromaticmethyl) were carried out under thermal and photochemical conditions. A variety of organic and organometallic products are formed depending upon the substrate cobaloxime. For 3-methoxybenzyl and heteroaromaticmethyl cobaloximes the results suggest that they represent a unique class of cobaloximes whereby both the aromatic ring as well as the Co–C bond are highly activated towards attack by the arene sulfenyl chloride. Both homolytic as well as heterolytic pathways are operative.

Keywords: Organocobaloximes; Homolytic; Heterolytic cleavage

1. Introduction

Organocobaloximes, $RCo(dmgH)_2Py$ (R = alkyl, benzyl and heteroaromaticmethyl), have been extensively studied [2] ever since Schrauzer first highlighted their importance as models of coenzyme B_{12} [3]. Since then they have outgrown their initial relevance and have gained significance in their own right, mainly because of their rich chemistry [2,4,10]. The Co–C bond is weak and its cleavage has been achieved in many ways. This includes electrophilic, nucleophilic, or free radical attack at the R group, reduction/oxidation of RCo^{III}, modification of the R group, charge transfer interaction of the macrocycle with additional reagents, cleavage by light or heat, and finally by the steric interaction between macrocycle and the R group [5–12]. The actual cleavage process depends on the nature of the R group and is often governed by a combination of parameters. For example, in the electrophilic displacement reactions ([10](a–d), [12]), the organocobaloximes are susceptible to oxidation by some of the electrophiles, therefore a direct heterolytic cleavage of the Co–C bond competes with the electron transfer process. Organocobaloximes are also prone to homolysis and frequently contain traces of cobaloxime(II) which may initiate chain reaction [8,10,11] even when the heterolytic process might otherwise be dominant. Because of these competing reactions, a mixture of products is often formed. Since Co–C cleavage is a very facile process, any transformation of the organic group without affecting the Co–C bond becomes a challenging task. In the preliminary communication [1] we have shown that an exclusive ring substitution

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[1] A preliminary account of this work has been published (B.D. Gupta, V. Dixit, J. Organometal. Chem. 533 (1997) 261).

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into the aromatic ring can be achieved without affecting the Co–C bond leading to the synthesis of modified organocobaloximes.

In the present study, we describe the reactions of arene sulfenyl chlorides, ArSCl, with organocobaloximes under thermal and photochemical conditions. The reason for choosing arene sulfenyl chlorides as the reactive substrate is simply because these can act both as free radicals and/or as electrophiles depending upon the reaction conditions and the substituents on the arene ring [13]. The present study, therefore, has been aimed: (i) at understanding the Co–C cleavage mechanism; and ii) to study the phenomenon of Co–C cleavage vs ring substitution in benzyl and heteroaromaticmethyl cobaloximes.

2. Results

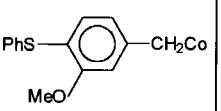
Alkyl cobaloximes (**1**–**9**) react with arene sulfenyl chlorides, ArSCl, [Ar = Ph, C_6Cl_5, 2,4, $(NO_2)_2C_6H_3$ A, B, and C, respectively] in 1:1 molar ratio under photolytic conditions (P1, irradiation by 2 × 200 W tungsten lamp at 0°C) to give exclusively the corresponding alkyl phenyl sulfides (**10**–**30**) in 50–90% yield. The reaction takes 4–20 h depending upon the substrate cobaloxime (Scheme 1). The inorganic product is chlorocobaloxime in all cases.

Benzyl cobaloximes (**31**–**37**) react under similar P1 conditions to form the corresponding sulfides (**38**–**51**) with (A and B). However with (C), some side products, e.g. bibenzyls (**59**–**65**) and benzyl ether of dimethylgly-

$RCo(dmgH)_2Py$ (1-9) R=	ArSCl	RSAr (10-30)	Yield (%)
Me, Et, Pr, ^{i}Pr, ^{n}Bu, ^{n}Hex,	A, C	(10-21)	[50-70]
$PhCH_2CH_2$,* $PhCH_2CH_2CH_2$,*	B	(22-30)	[84-90]
$PhOCH_2CH_2CH_2$ *			

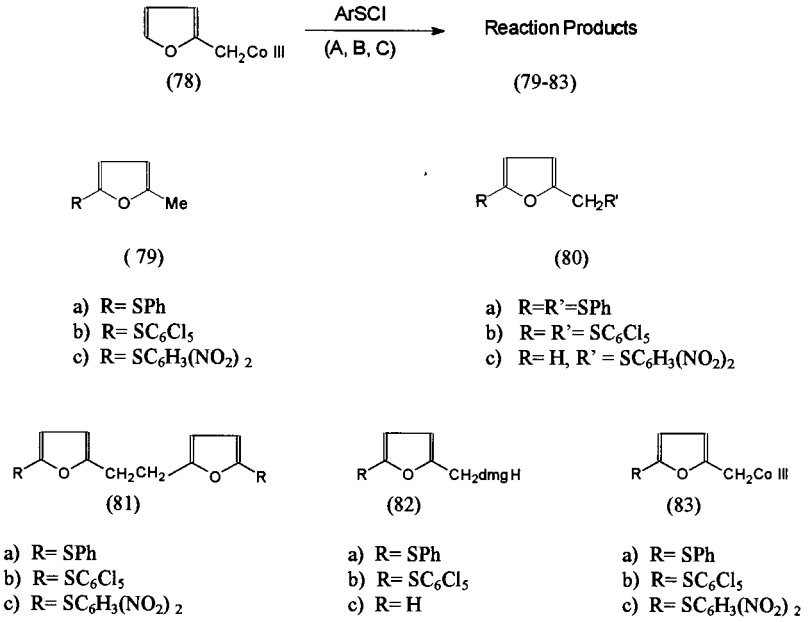
A=PhSCl, B= C_6Cl_5SCl, C= $C_6H_3(NO_2)_2SCl$; P1= 400W tungsten lamp/4-20h /0°C
* Only with B has been done

Scheme 1. Reactions of $RCo^{III}(dmgH)_2Py$ (**1**–**9**) with ArSCl under P1 conditions.

$4R\text{-}C_6H_4CH_2Co^{III}$ (comp. no) R=	ArSCl/ Reaction condtion	$4RC_6H_4CH_2SAr$ comp. no. [yield %]	$4R\text{-}C_6H_4CH_2dmgH$ comp. no. [yield %]	$(4R\text{-}C_6H_4CH_2)_2$ comp. no. [yield %]
H, Me, CMe_3, Cl, CN, NO_2, OMe (31-37)	A/ P1	(38-44) [48-65]	Nil	Nil
	B/ P1	(45-51) [70-80]	Nil	Nil
	C/ P1	(52-58) [50-62]	Nil	(59-65) [15-26]
	Δ	(52-58) [50-72]	(66-72) [10-15]	Nil
$3\text{-}OMeC_6H_4CH_2Co^{III}$ (73)	A / P1	$3\text{-}OMeC_6H_4CH_2SPh$ (74) [32]		
	A/ P2	 (75) [40]		
$PhSCH_2Co^{III}$ (76)	B / P1	$PhSCH_2SC_6Cl_5$ (77) [62]		

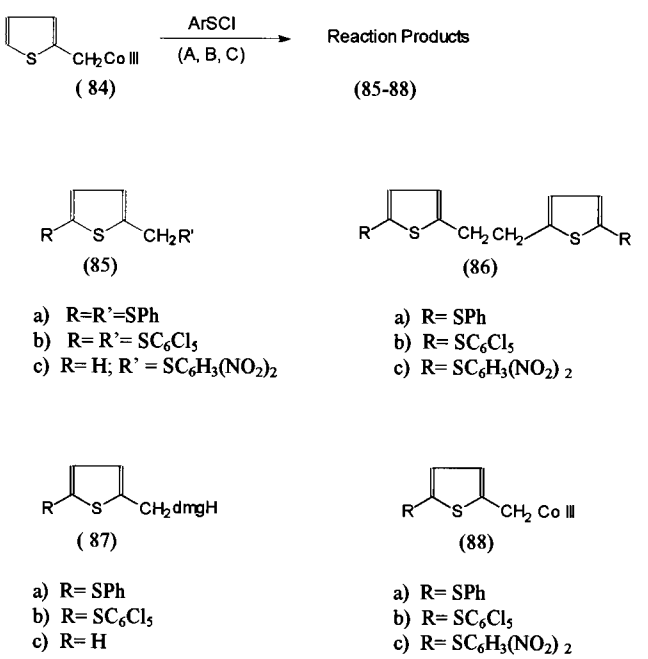
A=PhSCl, B= C_6Cl_5SCl, C= $C_6H_3(NO_2)_2SCl$;
P1= 400W tungsten lamp/ 3-6h /0°C; P2= 0°C/dark/10h; Δ = Refluxing dichloromethane;
Co=$Co(dmgH)_2Py$

Scheme 2. Reaction of $4R\text{–}C_6H_4CH_2Co^{III}(dmgH)_2Py$ (**31**–37, 73 and **76**) with ArSCl.



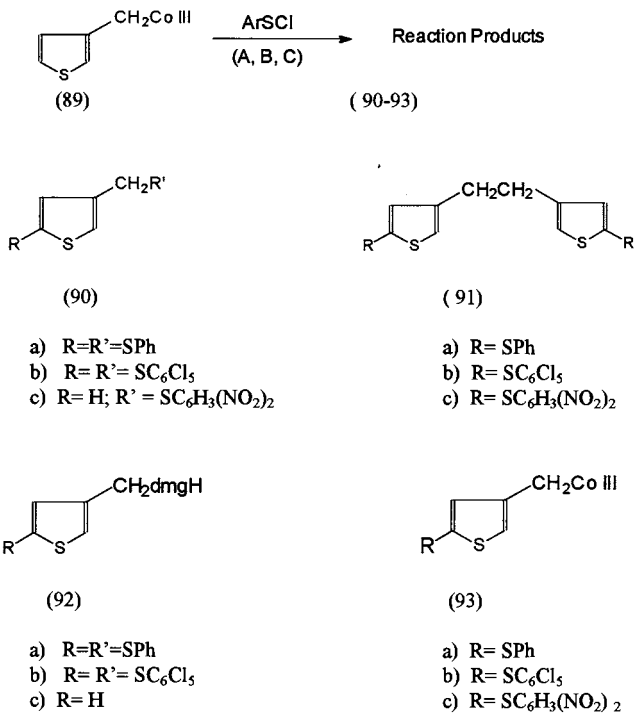
Scheme 3.

oxime (**66**–**72**) are also formed in addition to the arene sulfides (**52**–**58**). Thermal reactions are slow in general, for example, the reaction of benzyl cobaloxime (**31**) with (B) at room temperature in the dark remains incomplete even after 40 h. The only organic product isolated is the corresponding sulfide (**45**). 3-Methoxybenzyl cobaloxime (**73**), on the other hand, forms the ring substituted organometallic product (**75**) with (A) in the dark whereas under P1 it forms 3-methoxybenzyl sulfide (74) (Scheme 2). Similarly $PhSCH_2Co(dmgH)_2Py$ (**76**) forms the corresponding sulfide (**77**) with B in 62% yield.



Scheme 4.

The reactions of heteroaromaticmethyl cobaloximes (**78**, **84** and **89**) with (A, B or C) are relatively fast and finish within 1.5 h under all conditions, whether thermal or photochemical. Both organic and organometallic products are formed in each reaction (Schemes 3–5). The yield and nature of the product depend upon the substrate cobaloxime and the reaction conditions (Scheme 6). The change in solvent from dichloromethane to acetic acid does not make any



Scheme 5.

RCo^{III}	ArSCl	Reaction Conditions	Organic/organometallic products Product no. (%)
(78)	A	1	79a(20), 80a(25), 81a(18), 82a(15)
		2	83a(64)
	B	1	79b(35), 80b(15), 81b(10)#, 82b(5)#, 83b(27)
		2	83b(60)
	C	1	79c(16), 80c(57), 81c(5)
		2	83c(55)
(84)	A	1	85a(40), 86a(24), 87a(25)
		2	88a (50)
	B	1	85b(18), 86b(16)#, 88b(29)
		2	88b(70)
	C	1	85c(58), 86c(5)
		2	88c(28)*
(89)	A	1	90a(38), 91a(27), 92a(19)
		2	93a(52)
	B	1	90b(24), 91b(16)#, 92b(10)#, 93b(28)
		2	93b(58)
	C	1	90c(58), 91c(5)
		2	93c(27)*

1 = P1/ 20-80 min; 2= dark/ 0°C/ 30-60 min; * incomplete; yield based on nmr integeration only

Scheme 6. Reaction products of RCo^{III} (**78**, **84**, **89**) with ArSCl.

significant difference in the nature of the products, though the ratio is changed in certain cases.

The characteristics of all the products are given in Tables 1–5 [24].

3. Discussion

Arene sulfenyl chlorides can act both as sources of free radicals and/or as electrophiles depending upon the reaction conditions and the substituents on the arene ring [13].

If ArSCl reacts with organocobaloximes in a free radical manner, it may do so in a number of ways [7,8] (i) Co–C bond homolysis and subsequent reactions of the generated R; and (ii) S_H2 reactions at the carbon centre displacing cobaloxime(II); (iii) electron transfer from RCo(III) complex to ArSCl followed by attack of $ArS^{\cdot}$ on the intermediate organocobalt (IV) species.

However, if ArSCl acts as an electrophile, then in principle, it may attack the organometallic complex at a number of sites: (a) attack may take place at the aromatic ring (benzyl and heteroaromaticmethyl cobaloximes) leading to substitution [1,14] and/or to metal carbon bond cleavage [15]; (b) attack at the metal centre [16] may lead to products from reductive elimination and from the nucleophilic displacement of the α carbon; (c) attack may take place at the ligand leading to a variety of products including those from insertion process [17,18] (ligand migration); and (d) attack may also occur at the α carbon (on the C–M bond orbital [19]b. Reactions of each of these types is known and the path followed is certainly a function of the particular electrophile, its interaction with the HOMO of the complex, and the nature of the reaction medium. In all cases a certain degree of electron transfer occurs [7,19].

3.1. Alkyl cobaloximes

The experimental observations point to the free radical nature of these reactions. The alkyl sulfides are formed by a direct displacement of cobaloxime(II) by attack of the $ArS^{\cdot}$ radical on the α carbon of the alkyl group. A trace of cobaloxime(II) present as impurity in all organocobaloximes is sufficient to generate $ArS^{\cdot}$ radical by the abstraction of $Cl^{\cdot}$ from the ArSCl. We do not prefer the alternative route where $R^{\cdot}$, formed by the unimolecular homolysis of RCo^{III}, attacks the sulfur centre of ArSCl to form ArSR. As the alkyl radicals are known to dimerise fast and have the tendency to ab-

Table 1
Characteristics of alkyl sulphides (**16**–**30**)

Comp. No	^{1}H-NMR chemical shift δ, $CDCl_3$ (ppm)				MP (°C)	λ_{max} CH_3OH (nm)	Anal. found (calc.) (%)			
	CH_2S	$(CH_2)_n$ (m)	Me	Aromatic[a]			C	H	N	S
(**16**)	2.35 (s)	—	—	7.31–8.78	126	335, 270, 210	28.19 28.33	0.95 1.01	—	10.71 10.79
(**17**)	3.0 (q)	—	2.36 (t)	7.32–8.78	88	335, 270, 211	31.12 30.91	1.56 1.61	—	10.38 10.30
(**18**)	2.8 (t)	1.7	1.16 (t)	7.32–8.80	80	335, 272, 210	33.17 33.28	2.14 2.16	—	9.80 9.86
(**19**)	3.56 (m)	—	1.5 (d)	7.4–8.85	95	336, 271, 211	33.20 33.28	2.01 2.16	—	9.82 9.86
(**20**)	2.8 (t)	1.55	0.82 (bm)	7.25–8.78	65	335, 272, 210	35.18 35.45	2.60 2.66	—	9.39 9.45
(**21**)	2.85 (t)	1.6	0.8 (bm)	7.26–8.78	74	336, 270, 221	39.21 39.29	3.47 3.55	—	8.68 8.73
(**22**)	2.33 (s)	—	—	—	65	295,214	39.39 39.25	2.77 2.80	12.98 13.08	14.90 14.95
(**23**)	2.9 (q)	—	2.33 (t)	—	66	296, 214	42.01 42.10	3.49 3.51	12.30 12.28	14.01 14.03
(**24**)	2.83 (t)	1.5	1.0 (t)	—	59	297, 213	44.62 44.63	4.12 4.13	11.52 11.57	13.19 13.22
(**25**)	3.46 (m)	—	1.23 (d)	—	55	298, 213	44.58 44.63	4.07 4.13	11.51 11.57	13.16 13.22
(**26**)	2.9 (t)	1.5	0.97 (bm)	—	72	296,213	46.93 46.88	4.60 4.69	10.87 10.94	12.57 12.50
(**27**)	2.8 (t)	1.5	0.86 (bm)	—	76	300, 213	50.78 50.70	5.58 5.63	9.89 9.86	11.25 11.27
(**28**)	2.6–3.3 (m)	2.6–3.3	—	7.03	64	297, 220	55.21 55.26	3.81 3.95	9.25 9.21	10.63 10.53
(**29**)	2.5—3.0 (m)	1.6–2.1	2.5–2.9 (m)	6.5–7.4	65	290, 222	56.74 56.60	4.36 4.40	8.69 8.80	10.01 10.06
(**30**)	3.0–3.3 (t)	1.8–2.2	3.6–4.3 (m)	6.5–7.2	60	284, 219	53.83 53.89	4.12 4.19	8.18 8.28	9.61 9.58

[a] Multiplet.

stract halogen from ArSCl, a complete absence of both the products, i.e. R–R and RCl supports the above viewpoint. Evidence for both these processes has been provided in the literature ([13]d, [25]).

3.2. Benzyl cobaloximes

A similar argument as above is extended for the results for (A) and (B) and the benzyl sulfides are formed by the direct displacement of cobaloxime(II) by the attack of $ArS^{\cdot}$ radical on the α carbon of the benzyl group.

The product distribution in case of (C), however, suggests that the mechanism is different under thermal and photochemical conditions. For example, the formation of bibenzyl (**59**–**65**) under P1 conditions is indicative of the presence of benzyl radicals as intermediates whereas the formation of benzyl ethers of dimethylglyoximes (**66**–**72**) under thermal conditions points to the existence of RCo^{IV} as an intermediate in solution. Recently, such similar ether products have been observed as side products in many electrophilic, free radical and oxidation reactions of organocobaloximes ([7,8]a, [10,20]) and RCo^{IV} species is shown to be present as an intermediate in such reactions.

Interestingly, 3-methoxybenzyl cobaloxime (**73**) undergoes a facile ring substitution with (A) suggesting that the ring is highly activated. Its chemistry resembles with the heteroaromaticmethyl cobaloximes and is discussed later.

3.3. Heteroaromaticmethyl cobaloximes

The reactions, in general, are complicated and a mixture of products, both organic and organometallic, are formed in each reaction. The product distribution suggests that these reactions proceed by a mixture of mechanisms. In general, the following useful information emerges out of the study.

(a)In the reactions of (**78**, **84**, **89**) with (A) or (B), all the products formed, organic or organometallic, are the ring substituted products. This suggests that the ring substitution is the primary process followed by Co–C bond cleavage [10]a. The exclusive formation of the ring substituted product in the dark lends support to this viewpoint. It looks as if we are dealing with a unique class of organocobaloximes having a highly activated aromatic ring. This may be justified considering the highly activating nature of the $CH_2Co(dmgH)_2Py$ group [10]a. The formation of the dimer (**81**, **86** and **91**) and the heteroaromaticmethyl ether of dimethylglyoxime (**82**, **87** and **92**) can be explained by the electron transfer process as discussed above for benzyl case. The disulfides (**80**, **85** and **90**)

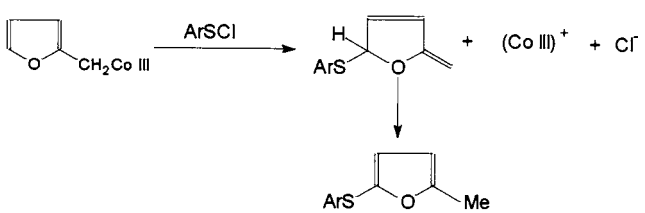
Table 2
Characteristics of benzyl sulphides (**45**–**58** and **77**)

Comp. No	^{1}H-NMR chemical shift δ, (ppm)			MP (°C)	λ_{max} CH_3OH (nm)	Anal. found (calc.) (%)			
	CH_2S (s)	Aromatic	Others			C	H	N	S
(**45**)	4.05	7.13 (s)		75	237, 217	41.80 41.88	1.84 1.88	—	8.55 8.59
(**46**)	4.06	7.03 (s)	2.25	76	237, 216	43.40 43.46	2.29 2.33	—	8.22 8.28
(**47**)	4.06	7.03–7.36 (m)	1.27	73	258, 213	47.62 47.61	3.46 3.50	—	7.42 7.47
(**48**)	4.05	7.13 (s)	—	114	363, 217	38.21 38.33	1.44 1.47	—	7.74 7.86
(**49**)	4.08	7.20–7.44 (m)	—	145	221, 217	42.29 42.32	1.45 1.51	3.49 3.53	8.00 8.06
(**50**)	4.15	7.29–8.04 (dd)	—	135	262, 215	37.28 37.36	1.38 1.44	3.31 3.35	7.60 7.66
(**51**)	4.03	6.68–7.06 (dd)	3.73	152	225, 216	41.71 41.74	2.19 2.24	—	7.90 7.95
(**52**)	4.30	7.4–9.10 (m)		130	332, 269	53.71 53.79	3.34 3.44	9.61 9.66	11.10 11.03
(**53**)	4.20	7.2—9.10 (m)	2.30	121	334, 270, 230	55.21 55.26	3.87 3.95	9.12 9.21	10.43 10.53
(**54**)	4.20	7.0–9.10 (m)	1.32	122	335, 270, 230	58.79 58.96	5.12 5.20	8.12 8.09	9.12 9.25
(**55**)	4.15	7.1–8.9 (m)	1.26	124	332, 265, 221	48.10 48.07	2.71 2.77	8.61 8.63	9.78 9.86
(**56**)	4.60	7.74–9.12 (m)	—	128	334, 265, 233	53.29 53.33	2.76 2.86	13.35 13.33	10.00 10.16
(**57**)	4.68	7.65–9.15 (m)	—	138	335, 278, 211	46.43 46.57	2.66 2.69	12.39 12.54	9.51 9.55
(**58**)	4.30	6.9–9.10 (m)	3.80	125	335, 272, 230	52.39 52.50	3.69 3.75	8.62 8.75	9.98 10.00
(**74**)	3.90	3.66–7.18 (m)	3.60	120	338, 272, 228	73.00 73.04	6.01 6.09	—	13.84 13.91
(**77**)	4.30	7.28 (s)	—	88	217.5	38.50 38.57	1.69 1.73	—	15.78 15.82

may arise either by the direct S_E2 or S_H2 process at the α carbon of the ring substituted product. It is however very difficult to pin point the exact pathway at this stage.

The reactivity of (C) however is different from (A) and (B) since the ring substitution as well as the cleavage of the Co–C bond in the parent cobaloxime (**78**, **84** and **89**) occur simultaneously.

(b) The formation of the ring substituted methyl furan (**79**) is quite novel as it is rarely seen in such studies. The following mechanism is proposed for its formation. A similar mechanism was proposed by us to explain the formation of the ring halogenated toluene in the halogenation of 4-methoxybenzyl cobaloxime [10]a.



(79)

(c) The oxidation potentials of the ring substituted organocobaloximes (**83**, **88** and **93**) are comparable to the parent cobaloximes and are reversible in nature.

(d) The ring substituted organocobaloximes undergo very facile oxygen insertion into the cobalt carbon bond under photochemical conditions, for example (**83b**) forms the inserted product within 2 h at 0°C under irradiation. [^{1}H-NMR ($CDCl_3$), 2.3 (s), 4.26 (s), 6.3–6.70 (dd), 7.20, 7.56, 8.24 (m).

(e) The reaction of (**83b**) with tosyl chloride under P1 forms the corresponding sulphone [^{1}H-NMR ($CDCl_3$), 4.16 (s), 2.36 (s), 6.33–6.50 (m)] and the dmgH ether product (**82b**). In contrast the same reaction with (**78**) forms the sulphone exclusively [8]a.

(f) All efforts to put the second group into the aromatic ring have failed. It seems that a combined effect of $-CH_2Co(dmgH)_2Py$, (a conjugatively electron releasing group) and –SAr (an electron withdrawing group) does not make the heteroaromatic ring activated enough towards ring substitution.

(g) The mass spectral data has been collected only on certain representative cases. The fragmentation does not show any clear-cut pattern but the fragments like SPh, SC_6Cl_5, SC_6Cl_4, SC_6Cl_3, $SC_6H_3(NO_2)_2$, $SC_6H_3(NO)$, furfurylmethyl, thienylmethyl, etc. are distinctly seen and the compounds are clearly identified. The base peak in the dimers corresponds to the monomer.

4. Conclusions

The present study clearly shows that both homolytic as well as heterolytic pathways are equally important in the cleavage of Co–C bond in organocobaloximes. Different reaction pathways have been observed with the same reacting substrate-arene sulfenyl chloride. Bimolecular homolytic displacement, S_H2, is the dominant pathway for alkyl and benzyl cobaloximes with the electron transfer process occurring in the latter as a competitive process. The reaction of heteroaromaticmethyl cobaloximes are quite complex in nature because of the simultaneous participation of a number of

Table 3
Characteristics of organic compounds (**79–82**), (**85–87**) and (**90–92**)

Comp. No.	^{1}H-NMR chemical shift, δ, $CDCl_3$ (ppm)				λ_{max} CH_3OH (nm)	MP (°C)	Anal. found (calc.) (%)			
	CH_2[a]	Hetero-aromatic	Aromatic	Other[a]			C	H	N	S
(79a)	—	5.92(d), 6.41 (d)	7.0–7.1 (m)	2.15	242, 209	84	69.43 69.47	5.21 5.26	—	16.76 16.84
(79b)	—	5.83 (d), 6.5 (d)	—	2.25	221	114	36.45 36.41	1.05 1.10	—	8.78 8.83
(79c)	—	6.1(d), 6.7(d)	6.8–8.8 (m)	2.3	310, 245	134	47.05 47.14	2.81 2.86	9.89 10.00	11.42 11.43
(80a)	3.92	5.92–6.41 (dd)	7.0–7.2 (m)	—	245	70	68.39 68.46	4.66 4.70	—	21.41 21.47
(80b)	3.90	5.88–6.50 (dd)	—	—	216.5	180	31.70 31.73	0.55 0.62	—	9.80 9.95
(80c)	4.24	6.26(m), 7.26(m)	7.52–8.93 (m)	—	329, 268	130	47.01 47.14	2.78 2.86	10.12 10.00	11.35 11.43
(81a)	2.92	5.92–6.40 (dd)	7.0–7.2 (m)	—	243.8	100	69.91 69.84	4.70 4.76	—	16.90 16.93
(81b)	2.8	5.88–6.50 (dd)	—	—	[b]	[b]	—	—	—	—
(81c)	2.33	6.10–6.60 (dd)	6.76–8.3 (m)	—	313, 249, 241	124	47.23 47.31	2.55 2.51	10.19 10.04	11.40 11.47
(82a)	5.0	6.30–6.52 (dd)	7.1–7.3 (m)	1.95	307, 240	Oil	58.79 59.21	5.11 5.26	9.04 9.21	10.32 10.53
(82b)	4.98	6.65–7.00 (dd)	—	2.2	[b]	[b]	—	—	—	—
(82c)	5.14	6.40–7.58 (m)	6.40–7.58 (m)	2.28, 2.32	222	106	55.18 55.10	6.02 6.12	14.19 14.29	—
(85a)	4.10	6.85–7.30 (m)	6.85–7.3 (m)	—	241.8	80	64.92 64.97	4.40 4.46	—	30.51 30.56
(85b)	4.10	6.45–6.90 (dd)	—	—	217.5	135	30.99 30.96	0.60 0.61	—	14.51 14.57
(85c)	4.40	6.80–7.26 (m)	7.5–8.96 (m)	—	332, 269	119	44.66 44.59	2.62 2.70	9.41 9.46	21.56 21.62
(86a)	3.14	6.56–7.08 (m)	6.56—7.08 (m)	—	242	98	64.31 64.39	4.43 4.39	—	31.25 31.22
(86b)	2.90	6.38–6.60 (dd)	—	—	[b]	[b]	—	—	—	—
(86c)	2.80	6.56–7.10 (m)	7.4 (s), 7.5 (m)	—	324	120	44.68 44.75	2.33 2.37	7.01 7.12	21.63 21.69
(87a)	5.10	6.76–7.40 (m)	6.76–7.4 (m)	2.0	244	Oil	55.91 56.25	4.78 5.00	8.53 8.75	19.81 20.00
(87b)	4.99	6.86–7.10 (m)	—	1.99	[b]	[b]	—	—	—	—
(87c)	5.10	6.9–7.0 (m)	6.9–7.0 (m)	2.0	—	—	50.89 50.94	5.59 5.66	13.26 13.21	15.11 15.09
(90a)	4.00	6.85–7.30 (m)	6.85–7.3 (m)	—	288, 248	84	64.90 64.97	4.41 4.46	—	30.47 30.56
(90b)	4.15	6.76–7.0 (dd)	—	—	299, 218	140	30.89 30.96	0.60 0.61	—	14.50 14.57
(90c)	4.10	6.86–7.20 (m)	7.38–8.88 (m)	—	333, 269, 230	124	44.49 44.59	2.59 2.70	9.43 9.46	21.61 21.62
(91a)	2.30	6.70–7.70 (dd)	6.7–7.7 (dd)	6.99	352, 247	102	64.32 64.39	4.40 4.39	—	31.16 31.22
(91b)	3.00	6.74–7.10 (dd)	—	6.99	[b]	[b]	—	—	—	—
(91c)	2.90	6.60–7.0 (m)	7.38–8.86 (m)	—	325, 235	128	44.68 44.75	2.31 2.37	7.10 7.12	21.60 21.69
(92a)	5.00	6.80–7.2 (m)	6.8–7.2 (m)	1.98	244	Oil	55.80 56.25	4.81 5.00	8.50 8.75	19.74 20.00
(92b)	5.10	6.86–7.10 (m)	—	1.99	[b]	[b]	—	—	—	—
(92c)	5.10	6.9–7.0 (m)	6.9–7.0 (m)	2.0		—	50.88 50.94	5.615.66	13.23 13.21	15.01 15.09

[a] Singlet, [b] not pure.

Table 4
Characteristics of the ring substituted organocobaloximes products (**83abc**, **88abc** and **93abc**)

Comp. No.	dmgH (s)	^{1}H-NMR (chemical shifts), δ			UV-VIS λ_{max} (nm)	CV values[a] $E_{1/2}$ vs SCE	Anal. found (calc.) %			
		CH_2 (s)	Heteroaromatic (dd)	Py/Aromatic	(CH_3OH)	(V)	C	H	N	S
83a	2.06	2.60	6.02–6.40	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)
83b	2.00	2.50	5.96–6.40	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)
83c	2.06	2.50	5.95–6.50	7.20, 7.60, 8.40 7.40–9.00 (m)	299, 239, 207	0.915	43.35 (43.43)	3.85 (3.92)	14.68 (14.78)	9.60 (9.65)
88a	1.96	2.75	6.50–6.80	7.20, 7.40, 8.35 7.04–7.10 (m)	380, 286, 243, 208	0.899	51.62 (51.70)	4.91 (5.02)	12.08 (12.13)	5.68 (5.74)
88b	1.90	2.80	6.60–6.90	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)
88c	2.18	3.00	6.80–7.08	7.34, 7.80, 8.52 7.40–9.10 (m)	308, 241, 206	1.071	44.82 (44.85)	3.95 (4.04)	15.10 (15.26)	4.88 (4.98)
93a	1.96	2.76	6.70–6.80	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)
93b	2.01	2.95	6.65–6.85	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)
93c	2.01	2.56	6.7–7.0 (m)	7.40–9.10 (m)	306, 242, 206	1.01	43.40 (43.43)	3.88 (3.92)	14.79 (14.78)	9.64 (9.65)

a Oxidation potential, (**83b**) Cl, 23.72 (23.80), (**88b**), Cl, 24.21(24.33), (**93b**) Cl, 23.70(23.80)

processes. The electrophilic substitution into the aromatic ring being the key feature of these reactions and this is quite remarkable as the Co–C bond is susceptible to cleavage by electrophiles and free radicals. The preference of one process over the other is guided by many factors like the nature of the substrate cobaloxime, arene sulfenyl chloride and the reaction conditions. We believe that it is very difficult to assess precisely the relative contribution of each of these process until a more detailed study is undertaken.

5. Experimental

All the organocobaloximes and the organic precursors used in this study were synthesised by the procedures outlined in our earlier papers [10]. Benzene sulfenyl chloride (A) was prepared [21] by the chlorination of diphenyldisulfide with sulfuryl chloride at ambient temperature (b.p. 46–48°C/4 mm), lit. 49°C/2 mm [21], ^{1}H-NMR (CCl_4) 7.4 (s, Ar), Pentachlorobenzene sulfenyl chloride was prepared [22] by the chlorination of pentachlorobenzenethiol with chlorine gas (m.p. 100°C), lit. 104°C [22]. The thiol was prepared [23] from hexachlorobenzene, sodium sulfide and sulfur under refluxing condition.

Table 5
Mass spectra of the organic products from the reaction alkyl, benzyl and heteroaromaticmethyl cobaloximes with ArSCl

Comp. no	Mass (m/e) [% relative abundance]
(**22**)[a]	296 (2.86)
(**23**)[a]	310 (3.05)
(**24**)[a]	324 (4.36), 43 (100)
(**25**)[a]	324 (3), 43 (88)
(**26**)[a]	338 (2.7), 57 (100)
(**27**)[a]	366 (4.4), 85 (100)
(**45**)[a]	372 (3.55), 91 (100)
(**46**)[b]	385 (6.19), 281 (8.7), 105 (100)
(**47**)[c]	428 (11.7), 147 (100)
(**48**)[a]	407 (4.2), 126 (100)
(**49**)[b]	396 (1.52), 117 (100)
(**50**)[b]	416 (12.45), 136 (100)
(**51**)[b]	401 (0.5), 117 (100)
(**79a**)	190 (42.8), 109 (100), 218 (74)
(**79b**)	366 (82.5), 298 (59), 114 (100)
(**79c**)	280 (3.9), 183 (24), 152 (25), 113 (24)
(**80a**)	298 (3.9), 189 (100), 109 (95.5)
(**80b**)	643 (6.3), 362 (100), 281 (12.9), 246 (25.7)
(**81a**)	378 (23.2), 189 (100), 109 (97.5)
(**81b**)	279 (74.8), 183 (20.2), 125 (45.1)
(**82a**)	304 (10.9), 218 (38.1), 204 (89), 189 (43.4), 109 (100)
(**85a**)	314 (6.2), 205 (93.1), 171 (57.2)
(**85b**)	659 (2.4), 378 (30.4), 342 (100), 246 (80.1), 177 (88)
(**86a**)	410 (89.1), 301 (10.7), 205 (100)
(**86c**)	296 (17), 183 (12), 109 (27.9)
(**87a**)	320 (50.6), 220 (76.6), 205 (100)
(**90a**)	314 (10.1), 205 (100), 109 (16.8), 128 (10.5)
(**90b**)	378 (47.3), 342 (100), 246 (79.1), 177 (99.6)
(**91a**)	320 (62), 205 (100)
(**91c**)	296 (17.9), 201(22.1), 183 (13.1), 109 (21.2)
(**92a**)	320 (40.5), 220 (56.6), 205 (100)

[a] Values refer to ($M^+ + 2$) and (M-SC_6Cl_5).
[b] Values refer to ($M^+ + H$) and (M-SC_6Cl_5).
[c] Values refer to (M^+) and (M-SC_6Cl_5).

5.1. Reaction of arene sulfenyl chloride with organocobaloximes: general procedure

5.1.1. Photochemical reaction (P1)

All reactions are carried out in a specially designed glass apparatus with external water cooling system. Organocobaloxime and arene sulfenyl chloride (1 mmol each) are added to deaerated dichloromethane (25 ml). The solution is irradiated with 2×200 tungsten lamps placed at a distance of 10 cm from the reaction vessel while the temperature was maintained at 0°C by a Julabo refrigerated circulator. The progress of the reaction is monitored for cobaloxime by silica gel using ethyl acetate as the solvent. On completion the reaction mixture is concentrated in vacuo and flash chromatographed using dichloromethane as the eluant. Once the organic product has eluted, the solvent is changed to ethyl acetate when the ring substituted organometallic product elutes out. Finally the inorganic product is taken out with acetone. The organic and the organometallic products are chromatographed further to obtain the pure products.

5.1.2. Thermal reaction (P2)

A similar procedure as above is adopted except that the reaction is carried out either under dark at 0°C or under reflux in diffused light. The reaction vessel is covered with Al foil or with a piece of cloth.

Physical measurements and instruments: ^{1}H-NMR spectra are recorded on Jeol JNM-PMX 60 and Varian 400 spectrometers. The elemental analysis and mass spectra are done at Regional sophisticated Instrumentation Centre at Lucknow. The UV-VIS absorption spectra are recorded on Shimadzu 160A model. The cyclic voltammetric studies are done on BAS model CV-27 polarographic analyser utilizing the three electrode configuration, glassy carbon (working electode), platinum wire (auxillary electrode) and Ag/AgCl (reference electrode). An omnigraphic 100 XY recorder is used to record the current voltage output. A scan rate of 100 mV s^{-1} is used in all cases and dry dichloromethane is used as the solvent medium. The measurements are also made with the scan rate of 50 mV s^{-1} in certain cases.

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