Homolytic Displacement at Saturated Carbon in Organocobaloximes.† Part 4

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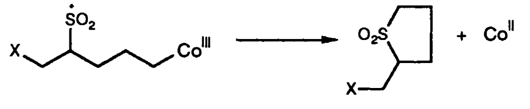
Benzyl and *para*-substituted benzylcobaloximes react with substituted arenesulphonyl chlorides under photochemical and anaerobic conditions at 0 °C to give a variety of products including the sulphones, bibenzyls, and benzyl ethers of dimethylglyoxime in variable yields. However, when the reactions are carried out in the presence of a 1 mol excess of pyridine, the yield of sulphones is increased by at least 20% in each case. The corresponding yield of bibenzyls is decreased and no trace of the benzyl ether of dimethylglyoxime is formed. On the other hand, the reaction of heteroaromatic methyl cobaloximes with arenesulphonyl chlorides form the corresponding sulphones as the exclusive organic product in good yield and with no side products. The reactions are interpreted in terms of a direct attack of the arenesulphonyl radical on the α carbon of the benzyl and heteroaromatic methyl ligand.

The use of transition metal complexes in organic synthesis has seen considerable development in the past ten years. In these reactions, which can be stoicheiometric or catalytic, the organic substrates are most often involved as π ligands which undergo electrophilic or nucleophilic attack by various reagents.[1] Radical reactions of synthetic utility using transition-metal complexes are, by contrast, scarce.[2a] One such reaction is the bimolecular homolytic displacement at a saturated carbon centre generally referred to[2b] as an S_H2 reaction.

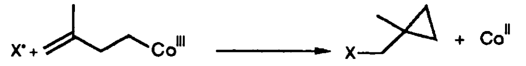
$$X^{\bullet} + RCH_2Y \longrightarrow RCH_2X + Y^{\bullet} \qquad (1)$$

This reaction, however, has rarely been discussed in the literature and has often been described[3] as a highly improbable reaction. The scarcity of this reaction is not because it is not possible, but because other processes usually take precedence.[3] The d^7 low-spin cobaloxime(II) complex has been shown to be a good leaving group and several examples of such reactions have been postulated recently as being the key step in the reactions of diamagnetic σ-bonded organocobaloximes with free radical precursors. The examples include attack of trichloromethyl radicals, arenesulphonyl radicals, and hydroxyalkyl radicals at the carbon of benzylcobaloximes [equation (2)[4]] and the formation of sulpholanes by intramolecular attack of remote sulphonyl radical centres on the α-carbon of substituted alkylcobaloximes [equation (3)[5]]. The formation of cyclopropane derivatives from but-3-enyl compounds may also be considered as a further example of a homolytic substitution at a saturated carbon [equation (4)[6]].

$$X^{\bullet} + PhCH_2Co^{III} \dashrightarrow PhCH_2X + Co^{II} \qquad (2)$$



(3)



(4)

Co = [Co(dmgH)$_2$Py]; dmgH = dimethyl glyoximate (1 −)
$\dot{X}$ = $\dot{C}Cl_3$, $Ar\dot{S}O_2NMe$, $R\dot{S}O_2$, $\dot{C}H_2OH$

Many examples have been described in which closely related S_H2' reactions have been proposed as steps in chain reactions involving organocobaloximes[7] and allyltin(IV) compounds.[8] Recently, metal-for-metal S_H2' reactions of organoiron complexes have also been postulated for the photochemical exchange of a phosphine ligand.[9]

In this paper we describe a number of reactions of benzyl- and *para*-substituted benzylcobaloximes and heteroaromatic methylcobaloximes with arenesulphonyl chlorides under anaerobic and photochemical conditions, in an attempt to identify homolytic displacement reactions at saturated carbon in solution and to develop a useful synthesis of the substituted benzyl aryl and heteroaromatic methyl sulphones.

Results

4-Methylbenzenesulphonyl chloride (A_1) reacts with benzyl cobaloxime (**1**) in 1:1 molar ratio in dichloromethane at 0 °C under anaerobic and photochemical conditions. A smooth reaction takes place and is complete within 2 h to give three products, the sulphone (**7**) bibenzyl (**37**), and benzyl ether of dimethylglyoxime (**43**) in 30, 58, and 8% yields, respectively. The reaction is subject to an induction period, the length of which depends upon the purity of the substrate cobaloxime. Substrate samples contaminated with cobaloxime(II) react faster. The rate of reaction is drastically lowered by added Galvinoxyl and is accelerated by dibenzoyl peroxide. Similar reactions of benzyl cobaloximes (**1**)–(**6**) with 4-methyl-, 4-methoxy-, 4-chloro-, 4-bromo-, and 2,4,5-trichloro-benzenesulphonyl chloride (A_1–A_5, respectively) under identical conditions form the corresponding sulphones (**8**)–(**36**), bibenzyls (**37**)–(**42**), and benzyl ethers of dimethylglyoxime (**43**)–(**48**) in variable yields. Chlorocobaloxime and p-$R'C_6H_4SO_2$-$Co^{III}Py$ (R′ = 4-Me, 4-OMe, 4-Cl, 4-Br, and 2,4,5-Cl$_3$) are the inorganic products isolated in all cases (Scheme 1, Table 1). When the reactions are carried out in the presence of a 1 molar excess of pyridine, the yield of the sulphone is increased by 20% in each case. The corresponding yield of bibenzyl is decreased and no trace of the benzyl ether of the dimethylglyoxime product is observed.

The reactions of heteroaromatic methylcobaloximes (**49**)–(**52**) with *para*-substituted benzenesulphonyl chlorides (A_1–A_4 and A_6) under identical photochemical conditions at 0 °C form the corresponding sulphones (**53**)–(**72**) as the exclusive organic products in 66–90% yield. No other side product is observed. Chlorocobaloxime(III) is the only inorganic product

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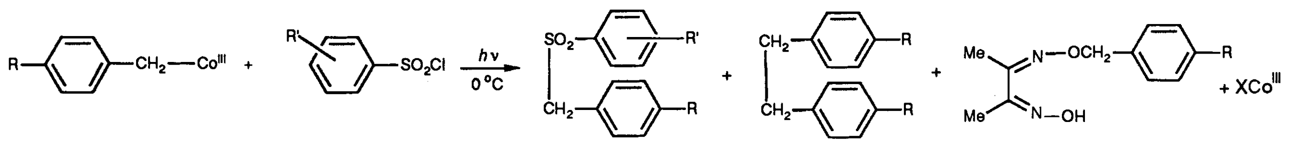
† A preliminary account of this work has been published;[4c] for part 3 see ref 7(*d*).



(**1**) R = H	(**A$_1$**) R′ = 4-Me	(**7**) R = H; R′ = 4-Me	(**37**) R = H	(**43**) R = H
	(**A$_2$**) R′ = 4-OMe	(**8**) R = H; R′ = 4-OMe		
	(**A$_3$**) R′ = 4-Cl	(**9**) R = H; R′ = 4-Cl		
	(**A$_4$**) R′ = 4-Br	(**10**) R = H; R′ = 4-Br		
	(**A$_5$**) R′ = 2,4,5-Cl$_3$	(**11**) R = H; R′ = 2,4,5-Cl$_3$		
(**2**) R = Me		(**12**) R = Me; R′ = 4-Me	(**38**) R = Me	(**44**) R = Me
		(**13**) R = Me; R′ = 4-OMe		
		(**14**) R = Me; R′ = 4-Cl		
		(**15**) R = Me; R′ = 4-Br		
		(**16**) R = Me; R′ = 2,4,5-Cl$_3$		
(**3**) R = Br		(**17**) R = Br; R′ = 4-Me	(**39**) R = Br	(**45**) R = Br
		(**18**) R = Br; R′ = 4-OMe		
		(**19**) R = Br; R′ = 4-Cl		
		(**20**) R = Br; R′ = 4-Br		
		(**21**) R = Br; R′ = 2,4,5-Cl$_3$		
(**4**) R = Cl		(**22**) R = Cl; R′ = 4-Me	(**40**) R = Cl	(**46**) R = Cl
		(**23**) R = Cl; R′ = 4-OMe		
		(**24**) R = Cl; R′ = 4-Cl		
		(**25**) R = Cl; R′ = 4-Br		
		(**26**) R = Cl; R′ = 2,4,5-Cl$_3$		
(**5**) R = CN		(**27**) R = CN; R′ = 4-Me	(**41**) R = CN	(**47**) R = CN
		(**28**) R = CN; R′ = 4-OMe		
		(**29**) R = CN; R′ = 4-Cl		
		(**30**) R = CN; R′ = 4-Br		
		(**31**) R = CN; R′ = 2,4,5-Cl$_3$		
(**6**) R = NO$_2$		(**32**) R = NO$_2$; R′ = 4-Me	(**42**) R = NO$_2$	(**48**) R = NO$_2$
		(**33**) R = NO$_2$; R′ = 4-OMe		
		(**34**) R = NO$_2$; R′ = 4-Cl		
		(**35**) R = NO$_2$; R′ = 4-Br		
		(**36**) R = NO$_2$; R′ = 2,4,5-Cl$_3$		

Scheme 1.

formed in each case (Scheme 2). The characteristics of the products including their NMR, IR, and UV spectroscopic values are given in Tables 2–4. In addition the following observations were made from independent experiments.

(*a*) the reaction of (**49**) with 4-bromobenzenesulphonyl chloride (**A$_4$**) under thermal conditions (refluxing dichloromethane) takes about 12 h. However, there is no change in yield or nature of product as compared with the corresponding photochemical reaction. However, the same reaction at 0 °C, but with no irradiation, does not proceed at all and the starting cobaloxime is recovered after 20 h.

(*b*) The reaction of organocobaloximes with aged samples of arenesulphonyl chlorides contaminated with the corresponding sulphonic acid affords sulphones in lower yields. The decrease in yield depends upon the amount of sulphonic acid present.

(*c*) The reaction of benzylcobaloxime (**1**) with 4-methylbenzenesulphonyl chloride (**A$_1$**) in Srinivasan's photoreactor (irradiation by 400 W medium-pressure mercury lamp) at 25 °C takes only 1 h. However, the yield of the sulphone is much less compared with the corresponding reaction under photochemical conditions at 0 °C. The products formed are (**7**) (9%), (**37**) (62%), and (**43**) (12%) (Scheme 1).

(*d*) The change of equatorial ligand in organocobaloximes does not affect the nature and yield of the reaction product. For example, the reaction of 2-thienylmethylbis(cyclohexylglyoxime)pyridinecobalt(III) with 4-methylbenzenesulphonyl chloride (**A$_1$**) under photochemical conditions forms sulphone (**54**) in a yield identical with that of reaction of (**49**) with (**A$_1$**).

(*e*) 2-Benzofurylmethylcobaloxime reacts rather slowly (>6 h) with 4-methylbenzenesulphonyl chloride (**A$_1$**) under photochemical conditions to form the corresponding sulphone, 2-benzofuryl 4-methyltolyl sulphone in 60% yield, m.p. 178 °C, δ(CDCl$_3$; 400 MHz) 7.72–7.71 (m, 8 H, ArH), 6.68 (s, 1 H), 4.56 (s, CH$_2$), and 2.44 (s, CH$_3$); *m*/*z* 286 (6%), 221 (3), and 131 (100); λ_{max} 278, 270, and 250 nm.

Discussion

It is believed that all the reactions described in this paper are free radical in nature. Since Co–C cleavage is a key feature of these reactions, the tendency of the organocobaloximes to undergo unimolecular homolysis merits examination. It is well established that the thermolysis and photolysis of Co–C bond in organocobaloximes is very facile even at wavelengths greater than 360 nm.[10] This is consistent with the low Co–C bond energy which falls in the range 17–25 kcalmol^{-1} * in such substrates.[11] Tungsten lamps and glass apparatus are, therefore, adequate enough for preparative photolysis experiments in the present study. Cobaloxime(II), a d^7 species, formed on the homolysis of Co–C bond has been observed to be a good leaving group in many such similar reactions.[4–7] Arenesulphonyl chlorides have previously been identified as chain-propagating species in many organic reactions of alkenes and its potential as a free-radical precursor is well established in literature.[12]

The nature of products and the influence of initiators and

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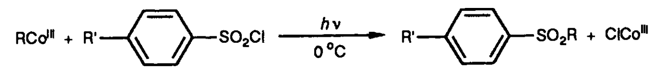
* 1 cal = 4.184 J.



(49) R = 2-Thienylmethyl
(50) R = Furfuryl
(51) R = 3-Thienylmethyl
(52) R = 3-Furylmethyl

(A_6) R′ = H
(A_1) R′ = Me
(A_2) R′ = OMe
(A_3) R′ = Cl
(A_4) R′ = Br

(53) R = 2-Thienylmethyl; R′ = H
(54) R = 2-Thienylmethyl; R′ = Me
(55) R = 2-Thienylmethyl; R′ = OMe
(56) R = 2-Thienylmethyl; R′ = Cl
(57) R = 2-Thienylmethyl; R′ = Br
(58) R = Furfuryl; R′ = H
(59) R = Furfuryl; R′ = Me
(60) R = Furfuryl; R′ = OMe
(61) R = Furfuryl; R′ = Cl
(62) R = Furfuryl; R′ = Br
(63) R = 3-Thienylmethyl; R′ = H
(64) R = 3-Thienylmethyl; R′ = Me
(65) R = 3-Thienylmethyl; R′ = OMe
(66) R = 3-Thienylmethyl; R′ = Cl
(67) R = 3-Thienylmethyl; R′ = Br
(68) R = 3-Furylmethyl ;R′ = H
(69) R = 3-Furylmethyl ;R′ = Me
(70) R = 3-Furylmethyl ;R′ = OMe
(71) R = 3-Furylmethyl ;R′ = Cl
(72) R = 3-Furylmethyl ;R′ = Br

Scheme 2.

Table 1. Organic products from the reaction of benzylcobaloximes **(1)**–**(6)** with benzenesulphonyl chlorides (A_1–A_5).

Cobaloxime	*p*-$RC_6H_4SO_2Cl$	Organic products and % yields *
(1)	(A_1)	**(7)** 30, **(37)** 58, **(43)** 8
	(A_2)	**(8)** 40, **(37)** 43
	(A_3)	**(9)** 31, **(37)** 59
	(A_4)	**(10)** 30, **(37)** 55, **(43)** 5
	(A_5)	**(11)** 55, **(37)** 35
(2)	(A_1)	**(12)** 46, **(38)** 21, **(44)** 24
	(A_2)	**(13)** 45, **(38)** 15
	(A_3)	**(14)** 37, **(38)** 43, **(44)** 8
	(A_4)	**(15)** 33, **(38)** 32, **(44)** 20
	(A_5)	**(16)** 67, **(38)** 25
(3)	(A_1)	**(17)** 36, **(39)** 57
	(A_2)	**(18)** 45, **(39)** 22
	(A_3)	**(19)** 30, **(39)** 55, **(45)** 5
	(A_4)	**(20)** 32, **(39)** 23, **(45)** 16
	(A_5)	**(21)** 61, **(39)** 21, **(45)** 8
(4)	(A_1)	**(22)** 39, **(40)** 48
	(A_2)	**(23)** 47, **(40)** 29
	(A_3)	**(24)** 33, **(40)** 49, **(46)** 8
	(A_4)	**(25)** 39, **(40)** 27, **(46)** 18
	(A_5)	**(26)** 64, **(40)** 26, **(46)** 5
(5)	(A_1)	**(27)** 41, **(41)** 9, **(47)** 9
	(A_2)	**(28)** 40, **(41)** 5, **(47)** 5
	(A_3)	**(29)** 15, **(41)** 35, **(47)** 15
	(A_4)	**(30)** 27, **(41)** 31, **(47)** 17
	(A_5)	**(31)** 59, **(41)** 22, **(47)** 8
(6)	(A_1)	**(32)** 20, **(42)** 17, **(48)** 8
	(A_2)	**(33)** 32, **(42)** 20, **(48)** 5
	(A_3)	**(34)** 8, **(42)** 38, **(48)** 6
	(A_4)	**(35)** 15, **(42)** 28, **(48)** 9
	(A_5)	**(36)** 45, **(42)** 30, **(48)** 5

* Refers to isolated yields after chromatographic separation.

inhibitors on the rates of reaction point to the free-radical nature of these reactions and we believe that a chain reaction is involved in which arenesulphonyl radicals, $Ar\dot{S}O_2$, and cobaloxime(II) are the chain-carrying species (Scheme 3). However, the formation of a mixture of products such as bibenzyls, sulphones, and benzyl ethers of dimethylglyoxime suggests that the reaction of benzylcobaloximes with arenesulphonyl chlorides under thermal and photochemical conditions proceeds by a mixture of mechanisms, for example (*i*) the formation of a substantial amount of bibenzyl in each reaction is indicative of the presence, as intermediates, of benzyl radicals, which are known to dimerise rapidly[4b] [equation (9)], (*ii*) the sulphone, may arise by an S_H2 attack of $Ar\dot{S}O_2$ at the α carbon of the benzylcobaloxime [equation (7)] to generate cobaloxime(II) which forms part of a chain reaction by abstracting a chlorine atom from the arenesulphonyl chloride to give another propagating species $Ar\dot{S}O_2$ [equation (6)], and (*iii*) the formation of the benzyl ether of dimethylglyoxime points to the intermediate formation of organocobalt(IV) species in solution (Scheme 4).

Initiation

$$RCH_2Co^{III}(dmgH)_2Py \rightleftharpoons \dot{R}CH_2 + Co^{II}(dmgH)_2Py \quad (5)$$

Propagation

$$Co^{II}(dmgH)_2Py + ArSO_2Cl \rightleftharpoons ClCo^{III}(dmgH)_2Py + Ar\dot{S}O_2 \quad (6)$$

$$Ar\dot{S}O_2 + RCH_2Co^{III}(dmgH)_2Py \longrightarrow ArSO_2CH_2R + Co^{II}(dmgH)_2Py \quad (7)$$

Termination

$$Ar\dot{S}O_2 + \dot{R}CH_2 \longrightarrow RCH_2SO_2Ar \quad (8)$$

$$\dot{R}CH_2 + \dot{R}CH_2 \longrightarrow RCH_2CH_2R \quad (9)$$

$$Co^{II}(dmgH)_2Py + Ar\dot{S}O_2 \longrightarrow ArSO_2Co^{III}(dmgH)_2Py \quad (10)$$

Scheme 3.

$$RCH_2Co^{III}(dmgH)_2Py \underset{+Py}{\overset{-Py}{\rightleftharpoons}} RCH_2Co^{III}(dmgH)_2 \overset{Ar\dot{S}O_2}{\rightleftharpoons} RCH_2Co^{IV}(dmgH)_2SO_2Ar \rightleftharpoons \dot{R}CH_2 + Co^{III}(dmgH)_2SO_2Ar \underset{-Py}{\overset{+Py}{\rightleftharpoons}} PyCo^{III}(dmgH)_2SO_2Ar$$

Scheme 4.

Evidence for $Ar\dot{S}O_2$ radical and cobaloxime(II) as the propagating species in equations (6) and (7) comes from the earlier studies.

Table 2. Characteristics of the benzyl sulphones **(7)**–**(36)**.

Product No.	M.p./°C	δ_H(ppm) [J/Hz][a] Aromatic	CH_2	Others	m/z[b] (% Relative abundance)	λ_{max}/nm[d] (CH_3OH)
(7)	135	7.0–7.70 (m)	4.29 (s)	2.39 (Me)	247 (15), 183 (47), 182 (75), 91 (100) (A)	224
(8)	83	6.86 (d), 7.45 (d), 6.92–7.30 (m) [9]	4.16 (s)	3.72 (OMe)	262 (66), 199 (50), 198 (99), 91 (100) (A)	240
(9)	118	7.0–7.80 (m)	4.31 (s)	—	268 (0.5), 266 (0.6), 181 (2), 91 (100) (B)	229
(10)	152	7.0–7.70 (m)	4.33 (s)	—	312 (0.1), 310 (3), 181 (11), 91 (100) (B)	233
(11)	115	7.73 (s), 7.56 (s), 7.02–7.33 (m)	4.49 (s)	—	334 (4), 181 (20), 91 (100) (B)	236, 213
(12)	150	7.72 (d), 7.43 (d), 7.29 (s) [9]	4.39 (s)	2.58, 2.70 (Me) (Me)	260 (2), 195 (0.3), 105 (100) (A)	222
(13)	98	6.87 (d), 7.55 (d), 6.02–7.15 (m) [8]	4.22 (s)	2.30, 3.82 (OMe) (Me)	276 (19), 212 (18), 105 (100) (A)	241, 223
(14)	131	6.79–7.22 (m), 7.30–7.70 (m)	4.24 (s)	2.30 (Me)	282 (0.1), 280 (0.1), 215 (0.1), 105 (100) (A)	226
(15)	152	6.97–7.30 (m), 7.40–7.75 (m)	4.23 (s)	2.33 (Me)	326 (0.2), 324 (0.4), 209 (11), 105 (100) (B)	231
(16)	184	7.55 (s), 7.72 (s), 6.91–7.06 (m)	4.42 (s)	2.21 (Me)	(C)	213, 235
(17)	165	7.03 (d), 7.23–7.58 (m) [9]	4.22 (s)	2.42 (Me)	(C)	231
(18)	144	6.86 (d), 7.50 (d), 7.20–7.40 (m) [8]	4.09 (s)	3.86 (OMe)	(C)	237
(19)	155	7.02 (d), 7.25–7.65 (m) [8]	4.24 (s)	—	(C)	226
(20)	136	7.03 (d), 7.30–7.90 (m) [9]	4.28 (s)	—	(C)	231
(21)	199	7.26 (s), 7.52 (s), 6.75 (d), 7.06 (d) [9]	4.12 (s)	—	(C)	226, 212
(22)	152	7.03 (d), 7.56 (d), 7.20–7.44 (m) [9]	4.23 (s)	2.39 (Me)	280 (5), 279 (14), 216 (1), 215 (0.4), 125 (100) (A)	225
(23)	151	6.90 (d), 7.48 (d), 7.30 (d), 7.05 (d) [8] [9]	4.16 (s)	3.86 (OMe)	298 (5), 296 (14), 232 (22), 125 (100) (A)	226, 239
(24)	143	7.03 (d), 7.85 (d), 7.45–7.70 (m) [9]	4.26 (s)	—	(C)	226
(25)	148	7.10 (d), 7.40 (d), 7.52–7.80 (m) [9]	4.26 (s)	—	(C)	231
(26)	205	7.92 (s), 7.69 (s), 7.10–7.40 (m)	4.59 (s)	—	(C)	216, 230
(27)	198	7.12–7.36 (m), 7.45–7.67 (m)	4.30 (s)	2.39 (Me)	271 (28), 207 (8), 116 (100) (A)	232
(28)	112	6.92 (d), 7.21 (d), 7.42–7.82 (m) [9]	4.30 (s)	3.78 (OMe)	287 (4), 223 (0.8), 116 (100) (A)	233
(29)	159	7.28 (d), 7.65 (d), 7.40–7.60 (m)	4.37 (s)	—	293 (1), 291 (3), 231 (3), 116 (100) (B)	235
(30)	138	7.27 (d), 7.45–7.78 (m) [9]	4.35 (s)	—	337 (1), 335 (1), 231 (5), 116 (100) (B)	235
(31)	140	7.96 (s), 7.75 (s), 7.20–7.65 (m)	4.63 (s)	—	361 (1), 359 (1), 231 (4), 116 (100) (B)	232
(32)	157	7.22 (d), 7.40–7.80 (m) [9]	4.33 (s)	—	(C)	220, 263
(33)[c]		7.0–8.2 (m)	4.70 (s)	4.10 (OMe)	—	—
(34)[c]		7.0–8.1 (m)	4.55 (s)	—	—	—
(35)[c]		7.1–8.2 (m)	4.50 (s)	—	—	—
(36)[c]		7.2–8.1 (m)	4.65 (s)	—	—	—

[a] All spectra were run on an EM 390 (90 MHz) spectrometer. [b] (A) refers to M^+, $M - SO_2$, R, or M^+, $M - SO_2$, $M - SO_2 - H$,R; (B) refers to M^+, (R–R) $-$ H,R; (C) refers to no clear pattern. [c] Slightly impure. [d] IR absorptions for all compounds were to within 1 160 and 1 180 cm^{-1} (ν_{sym}) and 1 275 and 1 350 cm^{-1} (ν_{sym}).

(*a*) The ^1H and ^{13}C NMR spectra of allyl cobaloxime in $CDCl_3$ both show a dynamic equilibrium which is the result of the cobalt-for-cobalt displacement [reaction (11)]. The dynamic character begins to increase as cobaloxime(II) forms in solution through the homolysis of the Co–allyl bond. The addition of trace of tosyl chloride to such a solution causes a

Table 3. Characteristics of HON=C(Me)–C(Me)=NO–CH$_2$R (**43**)–(**48**).

Product No.	M.p./°C	δ_H(CDCl$_3$;Me$_4$Si) dmgH	CH$_2$	Aromatic	m/z[b] (% Relative abundance)	λ_{max}/nm (CH$_3$OH)
(**43**)	90–92	1.95	5.10	7.23	—	—
(**44**)	85	2.00, 2.08	5.12	7.16	220 (2), 105 (100)	228
(**45**)[a]	100	A 1.90, 2.30	5.14	7.12, 7.32	285 (2), 170 (100)	220
		B 2.22, 2.35	5.10	7.12, 7.32		
(**46**)	98	1.90, 2.30	5.16	7.20	239 (1.5), 124 (100)	226
(**47**)	95	1.95, 2.04	5.16	7.40, 7.52	231 (10), 116 (100)	235
(**48**)[a]	99	A 2.05, 2.35	5.25	7.50, 8.20	283 (2), 168 (100)	217, 230
		B 2.18, 2.22	5.10	7.50, 8.20		260

[a] A and B refer to two different isomers by ^{1}H NMR spectroscopy only. However, they could not be separated by chromatography. The melting point and spectral characteristics correspond to the mixture in these cases. [b] Values refer to M^+ and $(M - \text{dmgH})^+$, however, for (**46**) and (**48**), the values refer to $(M - \text{H})^+$ and $(M - \text{H} - \text{dmgH})^+$.

Table 4. Characteristics of the heteroaromatic methyl sulphones (**53**)–(**72**).

Product No.	M.p./°C (% yield)	δ_H(ppm) [J/Hz] Heteroaromatic	Aromatic	CH$_2$	Other	m/z (% Relative abundance)[b]	λ_{max}/nm (CH$_3$OH)
(**53**)[a]	82 (60)	7.20 (m), 6.84 (m), 6.76 (d) [4]	7.42 (m), 7.54 (m), 7.64 (m)	4.46 (s)	—	238 (8), 173 (10), 97 (100) (A)	237, 217
(**54**)	125 (61)	7.23 (m), 6.85 (m), 6.76 (d) [4]	7.55 (d), 7.23[c] (m) [4]	4.49 (s)	2.39 (Me)	252 (5), 187 (5), 97 (100) (A)	226
(**55**)	120 (69)	7.23 (m), 6.70–6.85[d] (m)	7.56 (d), 6.85[d] (m) [9]	4.42 (s)	3.62 (OMe)	268 (4), 203 (2), 97 (100) (A)	225
(**56**)	94 (73)	7.21 (m), 6.76–6.85 (m)	7.55 (d), 7.37 (d) [7]	4.43 (s)	—	272 (0.2), 193 (4), 97 (100) (B)	229
(**57**)[a]	105 (75)	7.28 (m), 6.84 (m), 6.78 (m)	7.46 (d), 7.54 (d) [7]	4.46 (s)	—	318 (1), 193 (15), 97 (100), 316 (1) (B)	233
(**58**)	58 (80)	6.27 (d), 7.30 (s) [5]	7.45–7.81 (m)	4.39 (s)	—	222 (10), 157 (3), 81 (100) (A)	220
(**59**)	100 (65)	6.28 (d), 7.30 (s) [5]	7.51 (d), 7.30 (d)[d]	4.35 (s)	2.39 (Me)	236 (8), 171 (4), 81 (100) (A)	223
(**60**)	81 (70)	6.29 (d), 7.33 (s) [5]	6.97 (d), 7.64 (d) [9]	4.39 (s)	3.89 (OMe)	252 (5), 187 (1), 81 (100) (A)	241
(**61**)	113 (73)	6.33 (d), 7.32 (s) [5]	7.51 (d), 7.71 (d) [9]	4.40 (s)	—	256 (2), 161 (50), 81 (100) 258 (1) (B)	226
(**62**)[a]	127 (63)	6.30 (d), 7.31 (s) [5]	7.52 (d), 7.60 (d) [3.3]	4.38 (s)	—	300 (2.5), 161 (3), 81 (100) 302 (2.5) (B)	233
(**63**)	115 (60)	6.92 (m), 7.04 (d), 7.24 (m) [2]	7.46–7.83 (m)	4.39 (s)	—	238 (5), 173 (3), 97 (100) (A)	216, 232
(**64**)	88 (62)	6.92 (m), 7.03 (d), 7.21 (m) [2]	7.21[b] (m), 7.52 (d) [6]	4.33 (s)	2.43 (Me)	252 (10), 187 (5), 97 (100) (A)	224
(**65**)[a]	79 (67)	6.92 (m), 7.04 (d), 7.26 (m) [2]	6.92[b] (m), 7.50 (d) [8]	4.34 (s)	3.84 (OMe)	268 (0.5), 203 (5), 97 (100) (A)	239
(**66**)[a]	107 (69)	6.92 (m), 7.06 (d), 7.28 (m) [2]	7.42 (d), 7.58 (d) [8]	4.38 (s)	—	272 (7), 193 (2), 97 (100) 274 (3) (B)	226
(**67**)[a]	118 (74)	6.90 (m), 7.04 (d), 7.26 (m) [2]	7.52 (d), 7.64 (d) [4]	4.39 (s)	—	316 (10), 193 (98), 97 (100) 318 (11) (B)	234
(**68**)	88 (81)	6.26 (s), 7.23 (s), 7.36 (s)	7.40–7.90 (m)	4.19 (s)	—	222 (2), 158 (15), 81 (100) (A)	216
(**69**)[a]	103 (90)	6.33 (s), 7.22 (s), 7.38 (s)	7.30 (d), 7.62 (d) [7]	4.16 (s)	2.43 (Me) 3.89	236 (2), 172 (7), 81 (100) (A)	222
(**70**)	77 (72)	6.25 (s), 7.23 (s), 7.33 (s)	6.93 (d), 7.67 (d) [9]	4.16 (s)	(OMe)	252 (1), 188 (29), 81 (100) (A)	240
(**71**)	87 (87)	6.28 (s), 7.23 (s), 7.34 (s)	7.48 (d), 7.68 (d) [7]	4.23 (s)	—	256 (8), 192 (14), 81 (100) 258 (2.5), 194 (4) (A)	224
(**72**)	102 (79)	6.27 (s), 7.21 (s), 7.33 (s)	7.65 (s)	4.19 (s)	—	300 (4), 236 (12), 81 (100) 302 (5), 238 (11) (A)	234

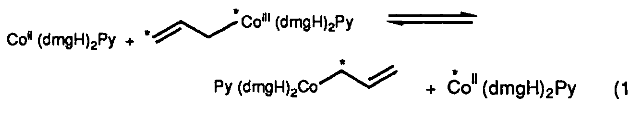
[a] 400 MHz spectra (the rest were taken on 90 MHz machine). [b] Partly obscured. For (**63**) to (**67**), the doublet is well resolved only in the 400 MHz spectrum. [c] A = M^+, $M - \text{SO}_2 - \text{H,R}$; B = M^+, R − R − H, R.

marked decrease in the extent of the dynamic character, which again becomes evident in the NMR spectra when the added tosyl chloride has been consumed.[13a]

(*b*) The reaction of cobaloxime(II) with tosyl chloride gives good yield of chlorocobaloxime and tosyl cobaloxime.[13b]

Thus, the decrease in the dynamic character of the allyl cobaloxime can be directly ascribed to the removal of cobaloxime(II) by tosyl chloride [similar to equation (6) in Scheme 3].

Though we believe that the S_H2 process is the main factor



(11)

responsible for the formation of sulphones in these reactions, we cannot rule out the presence of some ancillary processes in which the sulphones may arise from coupling of benzyl radicals and sulphonyl radicals [equation (8)]. The formation of $RSO_2Co^{III}(dmgH)_2Py$ [equation (10)] and bibenzyl [equation (9)] in each reaction supports this viewpoint. However, it is very difficult to assess the relative contribution of these two processes in the formation of benzyl sulphones. Since the observed reactions are chain reactions and the rate of the propagation step must cover more than the termination step in these reactions, the formation of benzyl sulphones by the coupling process should make only a small contribution.

The significant increase in the yield of sulphone when the reaction is carried out in the presence of an excess of pyridine (see the Results) is ascribed to the fact that the six co-ordinate complex is the reactive species which may (*i*) enhance the rate of reaction of equation (7), (*ii*), partially or completely, prevent the alternative pathway (Scheme 4), in which the free radical $Ar\dot{S}O_2$ attacks the five co-ordinate metal, to form benzyl radicals which in turn increase the formation of bibenzyl by way of equation (9).*

The exclusive formation of sulphones in the reaction of heteroarylmethylcobaloximes (**49**)–(**52**) with arenesulphonyl chlorides supports the above viewpoint. The reactions are much cleaner in these cases because (*i*) the Co–C bond is more nucleophilic compared with the Co–benzyl bond,[14] hence the rate of reaction of equation (7) is higher, (*ii*) RCo^{III}–RCo^{IV} potentials are high compared with the benzyl case, hence the intermediate RCo^{IV} is not formed,[14] (*iii*) the axial base ligand, pyridine, is much less labile and remains in contact with the cobalt,[14] with the result the attack of $Ar\dot{S}O_2$ on the intermediate five co-ordinate species is prevented.

The lowering of the yields in the reactions with aged samples of arenesulphonyl chloride contaminated with the corresponding sulphonic acid impurity is attributed to the fact that one of the propagating species, $Co^{II}(dmgH)_2Py$ decomposes almost instantaneously in the presence of acids to give a Co^{II}(aq.) complex.[15]

The formation of benzyl ethers of dimethylglyoxime in certain reactions and its complete absence in other reactions performed in an excess of pyridine suggests that the six co-ordinate organocobaloxime is the predominant reactive species and that ether formation must be an artefact of the oxidation process on the intermediate five co-ordinate organocobaloxime complex. Its formation has been discussed in earlier papers.[16,17]

The reactions described in this paper have some bearing on recent work carried out on sulphur dioxide insertion reactions.[18] One of the key steps proposed in the reaction scheme is attack of the sulphonyl radical, $R\dot{S}O_2$, formed by capture of an organic radical $R^{\bullet}$ by SO_2, on the organometallic substrate, thereby regenerating the organic radical $R^{\bullet}$ [equation (13)]. The present results indicate that such a process does not

$$R\dot{S}O_2 + RCo^{III}(dmgH)_2Py \longrightarrow RSO_2Co^{III}(dmgH)_2Py + R^{\bullet} \quad (13)$$

take place other than to a minor extent since $R\dot{S}O_2$ preferentially attacks the carbon centre and $RSO_2Co^{III}(dmgH)_2Py$ is formed only as a trace product.

The work described in the present study is significant in view of (*a*) a number of examples of S_H2 reactions in literature, (*b*) their implication on the recently reported SO_2 insertion reactions, and (*c*) ready formation of a wide range of benzyl and heteroaryl methyl sulphones from readily available aryl halides.

Experimental

Material and Instruments.—Benzenesulphonyl chloride, 4-methyl-, 4-methoxy-, 2,4,5-trichloro-benzenesulphonyl chlorides, thiophene, 3-methylthiophene, furfuryl alcohol, benzyl bromide, *N*-bromosuccinimide, cobalt chloride, dimethylglyoxime, pyridine *etc.* were all commercial materials (mostly Aldrich) and were distilled or recrystallised before use. Melting points were determined on a Fisher Johns melting point apparatus and are uncorrected. IR spectra were recorded on Perkin-Elmer model 377 and 580 IR grating spectrophotometers. Electronic spectra were recorded on Shimadzu UV 190 and Carey 17D double-beam spectrophotometers. ^1H NMR spectra were measured at 80, 90, 100, and 400 MHz on Bruker WP 80, Varian EM-390, Varian HA 100, and Bruker WH 400 instruments. Mass spectra were measured on a VG micro mass 7070F mass spectrophotometer. Elemental analysis were carried out at the central microanalytical laboratory, I.I.T. Kanpur and at Regional Sophisticated Instruments Centre, Lucknow.

Synthesis of Organic Precursors.—2-Chloromethylthiophene[19] was prepared by the chloromethylation of thiophene whereas 3-methylthiophene was brominated with *N*-bromosuccinimide to give 3-bromomethylthiophene.[20] Furfuryl alcohol was brominated with PBr_3 in ether according to the method of Zanetti.[21] Since pure furfuryl bromide is very unstable, its ether solution was used in the cobaloxime preparation. 3-Furyl bromide was synthesized from propargyl alcohol as outlined by Tada *et al.*[22] 4-Methyl-, 4-cyano-, 4-chloro-, and 4-nitro-benzyl halides were prepared by literature methods.[23] 4-Chloro- and 4-bromo-benzenesulphonyl chloride were prepared from chlorosulphonic acid and the corresponding halobenzene as outlined by Vogel.[24]

Synthesis of Organocobaloximes.—All the organocobaloximes were synthesized by the literature procedure from bis(dimethylglyoximato)pyridine cobalt(I) and organic halides. Cobaloxime(I) was generated *in situ* by anaerobic disproportionation of cobaloxime(II) in methanol as described by Schrauzer.[25] All the organocobaloximes obtained were pure and were used as such.

Reaction of Organocobaloximes with Organosulphonyl Chloride.—The reactions were carried out in a specially designed all-glass apparatus with an external water-cooling facility. Pyridine (5 drops), organocobaloxime (2 mmol) and organosulphonyl chloride (2.5–5.0 mmol) were successfully added to degassed dichloromethane (50 cm^3). The solution was irradiated by 2 × 200 W tungsten lamps placed 10 cm apart from the reaction vessels, while the temperature was maintained at 0 °C with a Julabo refrigerator, circulator model UC 20. The reaction was monitored for cobaloxime by TLC on silica gel using ethyl acetate as the eluant. On completion of the reaction (1–3 h), the mixture was concentrated *in vacuo* and subjected directly to flash chromatography using dichloromethane–light petroleum (4:1 v/v) as the eluant. After the organic product had eluted, the eluant mixture was changed to dichloromethane–acetone (1:4) mixture when the inorganic product was eluted out. The organic product was further

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* The formation of benzyl ethers of dimethylglyoxime in each reaction supports Scheme 4 and is indicative of the intermediate formation of RCo^{IV} species in solution since such a product is a characteristic decomposition product of benzylcobalt(IV) species in solution.[4,7,15]

purified by preparative TLC using chloroform–light petroleum (4 : 1 v/v) as the eluant.

Thermal Reaction.—The procedure adopted was similar to the above method except that the mixture of organocobaloxime, organosulphonyl chloride, and pyridine in dichloromethane was heated to reflux on a water bath under nitrogen. The reaction took longer (>4 h) in all cases.

Photochemical Reaction via Irradiation with a 400 W *Medium-pressure Mercury Lamp.*—A mixture of organocobaloxime (2 mmol), organosulphonyl chloride (3 mmol) and pyridine (5 drops) in dry dichloromethane (45 cm^3) was thoroughly degassed with nitrogen which was bubbled through it. The mixture was placed inside the quartz tubes of a photoreactor and was irradiated with a 400 W mercury lamp* while the temperature was maintained at 25 °C by cold water which circulated through the outer jacket of the photoreactor. The reaction took far less time compared with the photochemical reaction or the thermal reaction. The monitoring and work-up procedure were similar to the method described above.

Acknowledgements

We thank the Department of Science and Technology, New Delhi, for financial assistance. We also thank the Regional Sophisticated Instrumentation Centre, Lucknow for providing the NMR, MS and elemental analysis facilities.

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Paper 8/01491D
Received 15th *April* 1988
Accepted 7th *July* 1989

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* Watt medium-pressure mercury lamps emit radiations at predominantly 365 nm with smaller amounts in UV region 297, 303, 313, and 334 nm as well as significant amounts in the visible region at 404–408, 436, 546, and 577 nm.