

## Homolytic displacement at carbon in organocobaloximes: Part 9<sup>†</sup>—Reactions of organocobaloximes with thiophene 2-sulphonylchloride

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Several allyl (both cyclic and acyclic), allenyl, hexenyl and propargylcobaloximes react regiospecifically with thiophene-2-sulphonyl chloride under thermal and photochemical conditions to give the corresponding sulphones. The reaction is believed to take place by the attack of the sulphur radical on the terminal carbon of the organocobaloxime with the displacement of cobaloxime(II).

The propensity with which organometallic compounds participate in free radical chain substitution reaction ( $S_H2$  and  $S_H2'$ ) is remarkable and has been observed by various groups<sup>1-15</sup>. These reactions not only provide mild protocols for important organic intermediates but also delineate complex organometallic mechanism involving low spin metal radicals. In this paper we present an example of  $S_H2$  and  $S_H2'$  reactions in organocobalt complexes with 2-thiophene sulphonyl chloride under thermal and photochemical stipulations.

### Experimental

The organocobaloximes were available from the previous study and their synthesis has been described earlier<sup>12,13</sup>. The experiments details for thermal and photochemical conditions have also been detailed before<sup>12,13</sup>.

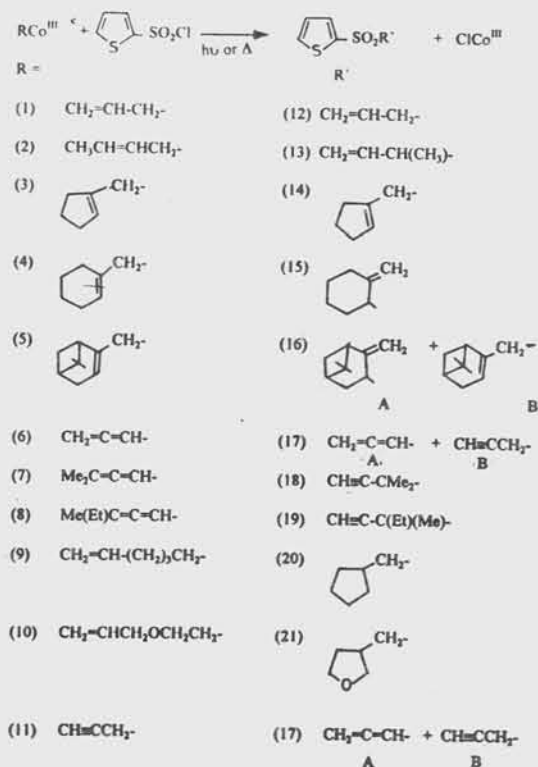
Thiophene-2-sulphonyl chloride was prepared<sup>19,20</sup> by the chlorosulphonation of thiophene at  $-15^\circ\text{C}$  [b.p.  $90^\circ\text{C}/1\text{ mm}$ ,  $^1\text{H NMR}$  ( $\text{CCl}_4$ ). 7.20 (m), 7.93 (m)]. Melting points were measured on Fischer Johns melting point apparatus and are uncorrected.  $^1\text{H NMR}$  NMR spectra were recorded on 80 and 100 MHz NMR spectrometer. IR spectra were recorded on Perkin Elmer (model 377) and 580 IR grating spectrophotometers. The electronic spectra were recorded

on Shimadzu UV 1600 spectrophotometer. Spectral details have been given in Table 1.

### Results and discussion

Organobis(dimethyl glyoximate)pyridine cobalt(III),  $[\text{RCo}^{\text{III}}(\text{dmgH})_2\text{Py}]$ , trivially known as organocobaloximes (**1-11**) were available from previous studies<sup>12,13</sup>. The reactions of organocobaloximes with 2-thiophene sulphonyl chloride in 1:1.1 molar ratio under anaerobic photochemical conditions at  $0^\circ\text{C}$  proceed to completion giving rise to the corresponding sulphones in excellent isolated yields. Chlorocobaloxime,  $[\text{ClCo}^{\text{III}}(\text{dmgH})_2\text{Py}]$  was the only inorganic product in all cases.

The nature of the organic product is crucially determined by the parent cobalt complex (Table 2). Thus in the case of allyl cobalt complexes (**1-4**); the corresponding sulphones (**12-15**) are the regiospecific rearranged organic products. In case of  $\alpha$ -pinenyl cobalt complex (**5**) two products are formed (**16A**, **16B**). The endo methylene sulphone (**16B**) probably arises from 1, 3 sigmatropic rearrangement of the exo methylene product (**16A**) as described earlier<sup>15</sup>. Unsubstituted allenyl and propargyl cobalt complexes (**6**) and



<sup>†</sup> For part 8, see ref. 15

Table 1—Spectral characteristics of the sulphones (12-21)

Product No.	<sup>1</sup> H NMR (CDCl <sub>3</sub> ) Chemical shift δ (ppm) [J]	UV(MeOH) λ <sub>max</sub> (nm)	IR, ν (cm <sup>-1</sup> )	Mass, M/e <sup>+</sup> (% abundance)
(12)	5.08, 5.36(d, CH <sub>2</sub> = [10], 5.82(m, =CH), 3.86(d, -CH <sub>2</sub> SO <sub>2</sub> )[8], 7.73, 7.18(m, Th)	234,250	1355,1315 1157	147(43.31), 124(67.33) 41(100)...(A+B)
(13)	5.10, 5.35(d, CH <sub>2</sub> = [9], 5.90(m, =CH), 3.80(m, -CHSO <sub>2</sub> ), 1.48(d, Me)[8], 7.75, 7.20(m, Th)	232,252	1322,1149 1139	202(5.82), 147(11.28), 138(36.41) 137(53.06), 83(13.27), 559(100)...(A+B)
(14)	5.27(bs, HC =), 3.98(t, -CH <sub>2</sub> SO <sub>2</sub> ) 1.42-1.97(bm, cp), 1.97-2.42(bm, cp) 7.13, 7.66(m, Th)	231,247	1338, 1297 1130, 1115	228(7.25), 163(62.50), 81(20), 80(100)...(C')
(15)	4.53, 4.96(t, =CH <sub>2</sub> ), 3.75(d, CHSO <sub>2</sub> ) 1.20-1.44(m, ch), 1.44-2.13(m, ch), 2.22 (m, ch), 2.65(m, ch), 7.10, 7.62(m, Th)	233, 249	1340, 1300 1155, 1135	242(0.91), 178(18.82) 149(6.99), 95(100) 94(79.57)...(A+C)
(16)A	1.80-2.65(bm, cycloalk), 3.99-4.41(m, CHSO <sub>2</sub> ), 5.01, 5.81(d, =CH)[8], 0.57 1.22(s.gem Me), 7.11, 7.66(m, Th)	234,250	1317,1300 1149,1135	282(0.13), 147(14.37), 135(36.48) 119(56.41), 106(23.08), 91(100)...(D)
(16)B	1.80-2.65(bp, cycloalk), 3.76(s, CH <sub>2</sub> SO <sub>2</sub> ) 5.40(bs, vinyl), 0.85, 1.31(s.gem Me) 7.11, 7.66(m, Th)	234,250	1317,1300 1149, 1135	same as (16)A
(17)A	5.50(d, CH <sub>2</sub> = [7], 6.60(t, =CHSO <sub>2</sub> )[4] 7.83, 7.12(m, Th)	234,252	1972,1928 1348,1305	186(2.14), 147(100), 122(97.96) 83(43.37)...(A+B)
(17)B	2.46(s, CH=C), 4.06(s, CH <sub>2</sub> SO <sub>2</sub> ) 7.83,7.12(m, Th)	232,251	3285,1329 1306,1150	186(5.97), 147(40.7) 39(100)...(B)
(18)	2.48(s, CH=C), 1.66(s, Me) 7.84,7.26 (m, Th)	231,250	3280,1138 1305,1158 1121	214(14.29), 149(47.89), 150 (12.49), 67(100)...(B)
(19)	2.56(s, CH=C), 1.70-2.20(m), 1.90 (CH <sub>2</sub> , t, Et), 1.56(s, Me), 7.75, 7.16(m,Th)	233,253	3275,1340 1314,1153 1125,1110	228(9.73),149(45.30) 147(60.5), 81(100)...(B)
(20)	0.73-2.70(bm,ch), 3.30(d, CH <sub>2</sub> SO <sub>2</sub> ) [8], 7.20, 7.70 (m, Th)	230,247		231(8.77), 147(51.5) 83(100)...(B)
(21)	1.50-2.00, 2.00-2.55, 2.55-3.05(all m thf), 3.36(d, CH <sub>2</sub> SO <sub>2</sub> )[6], 3.66-4.05 (m, thf), 7.25, 7.86 (m, Th)	231, 249		

cp = cyclopentyl, ch = cyclohexyl, Th = thiophene, thf = tetrahydrofuran,

<sup>+</sup> Mass spectral fragmentation follows the following patterns

A: M<sup>+</sup>, M<sup>+</sup>SO<sub>2</sub>, R (base peak)

B: M<sup>+</sup>, M<sup>+</sup>-R, R (base peak)

C: M<sup>+</sup>, M<sup>+</sup>-R, M<sup>+</sup>RSO<sub>2</sub>, R (base peak), RH

D: M<sup>+</sup>, M<sup>+</sup>-R, R, R-CH<sub>3</sub>, R-C<sub>2</sub>H<sub>5</sub>, R-C<sub>3</sub>H<sub>8</sub> (base peak)

(11) also give rise to mixtures of sulphones (17A) and (17B). This is in line with our earlier observations with arene sulphonyl chlorides<sup>13</sup>. 3, 3-Disubstituted allenyl cobalt complexes (7) and (8) however, yield only one product, i.e. (18) and (19) respectively. The above results can be interpreted very well with the bimolecular homolytic displace-

ment mechanism established earlier by us<sup>12,13</sup>. The attack of the sulphonyl radical is always at the terminal unsaturated carbon in the organic appendage. However, S<sub>H</sub>2' promoted intramolecular cyclisation is observed in complexes (9) and (10) wherein the corresponding cyclopentylmethyl and tetrahydrofuryl methyl sulphones (20) and (21)

Table 2—Organic products and characteristics from the reaction of thiophene 2-sulphonyl chloride with  $\text{RCo}^{\text{III}}$  (1-11) under photochemical conditions (irradiation by  $2 \times 200\text{W}$  tungsten lamps)

$\text{RCo}^{\text{III}}$	Product no.	Reaction time(h)	Isolated yield(%)	Isomeric <sup>†</sup> ratio	-M.P. (°C)
(1)	(12)	2.5	91	a	oil
(2)	(13)	1.5	96	a	oil
(3)	(14)	0.5	97	a	53
(4)	(15)	0.5	98	a	94
(5)	(16A+16B)	1.6	88	80:20	oil
(6)	(17A+17B)	5.0	43	30:70	oil
(7)	(18)	4.0	52	a	oil
(8)	(19)	5.0	57	a	oil
(9)	(20)	22.7	54	a	oil
(10)	(21)	22.0	62	a	oil
(11)	(17A+17B)	6.0	41	50:50	oil

<sup>a</sup> Only one isomer

<sup>†</sup> From  $^1\text{H}$  NMR integration only

have been obtained. This is in line with the earlier observations<sup>16-18</sup>.

The present study once again demonstrates the ability of organometallic complexes to participate as stoichiometric reagents in free radical reactions. By suitable tuning of the organic appendage, one can get the desired product in excellent yield via this protocol.

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