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Homolytic displacements at two reactive centers: organodicobaloximes and organodisulfonyl chloride ☆

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Abstract

The reactions of 1,3 xylylene dicobaloxime with PhSSPh, PhSeSePh, ArSO$_2$Cl at 0°C under irradiation form the corresponding disulfides, diselenide and the disulfones but the 2,5 thiophene dicobaloxime form the methyl substituted mono sulfides, selenides and sulfones. The 3-methylallylcobaloxime with biphenyldisulfonyl chloride and mesitylene disulfonyl chloride forms exclusively the corresponding disulfones whereas 3-thienylmethyl cobaloxime forms a mixture of products. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Homolytic displacements; Organodicobaloximes; Organodisulfonyl chloride
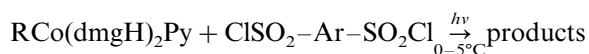
1. Introduction

It is now well established that organocobalt complexes undergo very facile radical chain reactions (S$_{H2}$ and S$'_{H2}$) and provide an excellent handle in the form of a reactive Co–C bond where the organic group has been functionalized by a variety of C, S and N centered radicals [1–6].

$$RCo^{III}(dmgH)_2Py + XY \rightarrow R'Y + XCo^{III}(dmgH)_2Py$$
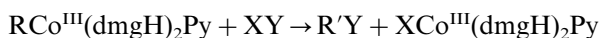
R = allyl, allenyl, benzyl, butenyl, hexenyl etc.; R' = rearranged organic group; XY = BrCCl$_3$, CCl$_3$CN, ArSO$_2$Cl, PhSSPh, PhSeSePh, etc.

All these reactions are free radical in nature and the yield of the product depends upon various factors like the nature of organocobalt substrate, nature of the free radical and the reaction conditions. It is envisaged that the utility of these reactions if extended to two reactive centers, either in the organometallic substrate or in the free radical substrate, will open up ways for the synthesis of many new organic products. With this in mind we have studied (a) the reactions of organobridged dicobaloximes (having two reactive Co–C bonds) with sulfur centered radicals (TsCl, PhSSPh, PhSeSePh) and (b) the reactions of diorganosulfonyl dichloride (having two reactive S–Cl bonds) with organocobaloximes.

$$Co^{III}CH_2ArCH_2Co^{III} + XY \rightarrow products$$

$$XY = TsCl, \ PhSSPh, \ PhSeSePh, \ Co = Co(dmgH)_2Py$$

$$RCo(dmgH)_2Py + ClSO_2-Ar-SO_2Cl \underset{0-5°C}{\overset{hv}{\rightarrow}} products$$

Besides, there has been a continued interest in the synthesis of new organocobaloximes [8] as small structural changes in the molecule have profound influence on the Co–C bond reactivity [7]. Surprisingly, the neutral organobridged dicobaloximes have virtually been unknown in the literature until recently [9].

2. Experimental

The synthesis of 3-methylallyl and 3-thienylmethyl cobaloximes have been reported earlier [10]. Organobridged dicobaloximes **1** and **2** have been synthesized by the reaction of Co^I (dmgH)$_2$Py (3 mmol) with organic dihalide (1 mmol) under strict inert conditions. The former is prepared in situ by the reduction of chlorocobaloxime with NaBH$_4$. The synthesis of organodicobaloximes **1** has been reported earlier by Johnson
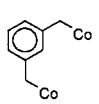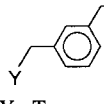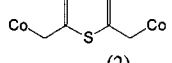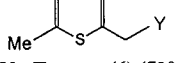
et al. [11] using Schrauzer's disproportionation method, however no yield or NMR were quoted. We have found that using their method a mixture of haloalkylcobaloxime and dicobaloxime is always formed which requires extensive separation on the silica gel column. We have also observed that the synthesis via the chlorocobaloxime is better. The molar ratio of $Co^I(dmgH)_2Py$:dihalide, reaction time and the temperature of the reaction play a crucial role in the formation of the dicobaloximes. (1) Yield (68%), ^{1}H-NMR ($CDCl_3$) δ (ppm): 1.90 (s, dmgH), 2.75 (s, CH_2), 6.65 (m, Ar), [7.26, 7.68, 8.50 (m, Py)], λ_{max} (MeOH) 356, 284, 241; (2) Yield (71%), ^{1}H-NMR ($CDCl_3$) δ (ppm): 2.10 (s, dmgH), 2.96 (s, CH_2), 6.25–6.68 (m, Ar), [7.22,7.56,8.30 (m, Py)], λ_{max} (MeOH) 390, 292, 241.

Biphenyldisulfonyl chloride and mesitylenedisulfonyl chloride were bought from Fluka and used as such.

3. Results and discussion

Organodicobaloxime 1 reacts with tosyl chloride in molar ratio 1:3 under photolytic conditions (irradiation by 2×200 W tungsten lamps) at 0°C and forms the corresponding disulfone 3. The similar reaction of organodicobaloxime 2 with tosyl chloride, however, forms the monomethyl substituted thiophene sulphone 6 in 73% yield. Similar observations are made in the reactions of PhSSPh and PhSeSePh with 1 and 2 and the corresponding organic products 4, 5, 7, 8 are formed (Scheme 1).

On the other hand, the reaction of organodisulfonyl dichloride A and B with 3-methylallyl cobaloxime (9) (Scheme 2) under similar photochemical conditions are

| Co^{III} RCo^{III}	XY^b	Time (h)^a	Product/ yield (%)^c
(1)	TsCl, PhSSPh PhSeSePh	3 1^d 1^d	Y= Ts (3) (30%)* Y= SPh (4) (66%) Y= SePh (5) (62%)
(2)	TsCl, PhSSPh PhSeSePh	2 5^d 2^d	Y= Ts (6) (73%) Y= SPh (7) (56%) Y= SePh (8) (52%)

a = Reaction conditions : 0°C/CH_2Cl_2/3h,
b = molar ratio organodicobaloxime: XY (1:3)
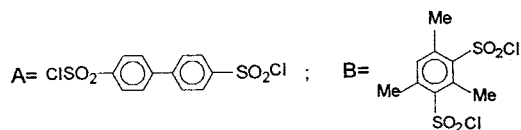c = isolated yield after chromatographic separation ;
d = 18–25 °C/hv
* In addition, a hard material is formed which is little soluble in chloroform, dichloromethane, methanol and ether

Scheme 1. Reaction of organodicobaloximes 1 and 2 with TsCl, PhSSPh, PhSeSePh.
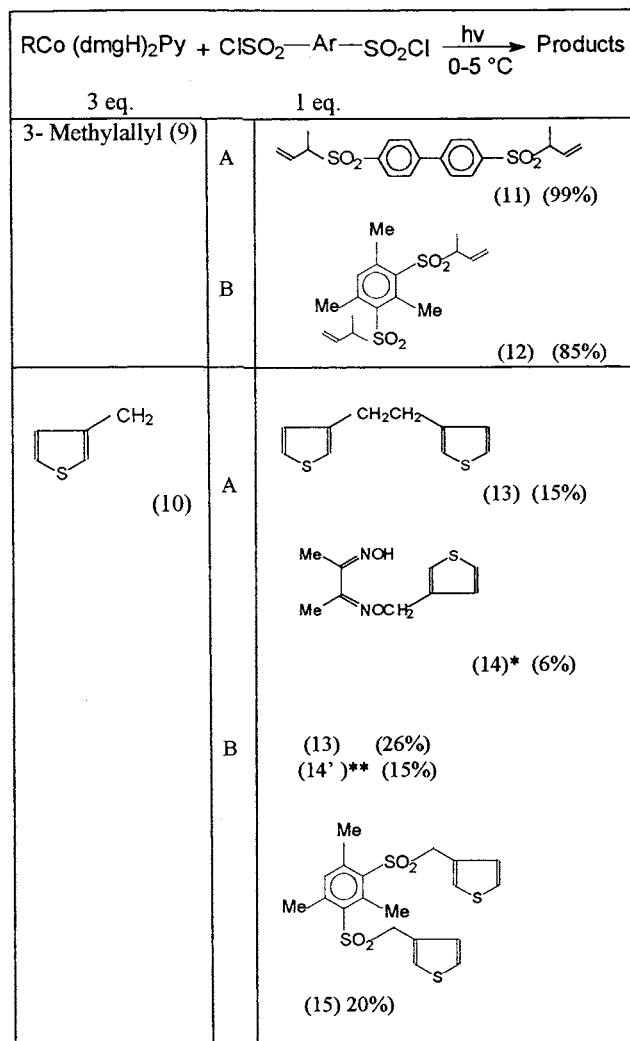
* mixture of two isomers, syn and anti
** same as (14) but only one isomer

Scheme 2. Reaction of organodisulphonyl dichloride A and B with organocobaloximes 9 and 10.

clean and form the corresponding disulfones 11 and 12 in high yield. However, the reaction of 3-thienyl methyl cobaloxime (10) with A and B is complicated and forms a mixture of products 13, 14 and 15. Surprisingly, no disulfone is formed in the reaction with A.

All the reactions are free radical in nature. All the organodicobaloximes are stable in solution and no decomposition takes place. The formation of the disulfone in 1 and monomethyl sulfone in 2 suggests that the mechanism of their formation is different in these two cases. The low yield of the disulfone is probably because of the tendency of the benzylic radicals to dimerization. The formation of a hard material (see Scheme

1) supports this viewpoint. In view of the drastic yield difference in the reaction of tosyl chloride and diphenyldisulfide with **1** and **2** , it seems the electrophilicity of the free radical plays a significant role. The mechanism of the formation of monomethyl products **6**, **7** and **8** is not fully understood at the moment, however, the hydrogen required in its formation does not come from the solvent since the same product is formed when benzene is used as a solvent instead of dichloromethane. It may be coming from the equatorial dimethylglyoxime, as observed earlier [4f,12]. The studies are underway to confirm this.

The formation of **13** and **14** in the reaction of 3-thienylmethyl cobaloxime (**10**) with **A** and **B** suggests that some ancillary competing processes are also operative in addition to the S_{H2} process and these become the main process in the reaction with **A** as there is a complete absence of the disulfone in this reaction. The formation of the dimer **13** in such high yield is surprising considering that these complexes are stable and decomposition in blank reaction in the absence of disulfonyldichloride is found to be negligible. In contrast, the reaction of **10** with $ArSO_2Cl$ under identical conditions form exclusively the corresponding organosulfones [4a]. The regiospecificity observed in the reaction of 3-methylallylcobaloxime (**9**) with **A** and **B** is similar to our earlier observations [4c,13].

The present results suggests that the S_{H2} reaction at two reactive centers in the same molecule is very facile in the allyl system but not in the thienylmethyl system and these provide the first examples of this kind in this area.

3.1. Characteristics of organic products

(**3**) ^{1}H-NMR (CDCl$_3$) δ: 4.24(s, CH$_2$), 7.00–7.57 (m, Ar); m.p. 240°C (decomp.), λ_{max}(nm) (CH$_3$OH) 260, 271; (**4**) ^{1}H-NMR (CDCl$_3$) δ: 4.00 (s, CH$_2$), 7.10 (m, Ar) m.p. 72°C, λ_{max}(nm) (CH$_3$OH) 256 nm; (**5**) ^{1}H-NMR (CDCl$_3$) δ: 3.90 (s, CH$_2$), 6.90–7.80 (m, Ar), m.p. 118°C, λ_{max}(nm) (CH$_3$OH) 236; (**6**) ^{1}H-NMR (CDCl$_3$) δ: 4.36 (s, CH$_2$), 6.50(s), 7.10–7.60 (dd, Ar), m.p. 135°C, λ_{max}(nm) (CH$_3$OH) 238, 242; (**7**) ^{1}H-NMR (CDCl$_3$) δ: 3.34 (s, CH$_2$), 4.06(s), 6.26–6.50(m), 7.00(m) (Ar), λ_{max}(nm) (CH$_3$OH) 254, 208; (**8**) ^{1}H-NMR (CDCl$_3$) δ: 2.40 (s, CH$_2$), 4.20(s), 6.50(s), 7.10–7.80(m) (Ar), oil, λ_{max}(nm) (CH$_3$OH) 238; (**11**) ^{1}H-NMR (CDCl$_3$) δ: 1.50 (d, Me, $J = 7$ Hz), 3.53–4.03(m, SO$_2$CH), 4.97–6.17 (m, CH$_2$=CH), 7.47–8.27 (m, Ar) , m.p. 107°C, λ_{max}(nm) (CH$_3$OH) 268.2; (**12**)

^{1}H-NMR (CDCl$_3$) δ: 1.57 (d, Me, $J = 8$ Hz), 2.73 (s, Me), 3.10 (s, Me), 3.70–4.23 (m, SO$_2$CH), 4.97–6.20 (m, CH$_2$=CH), 7.13 (s, Ar); m.p. 94°C, λ_{max}(nm) (CH$_3$OH) 283, 290.8; (**13**) ^{1}H-NMR (CDCl$_3$) δ: 2.86(t, CH$_2$, $J = 4$ Hz), 6.70–7.20 (m, Ar), oil; (**14**) ^{1}H-NMR (CDCl$_3$) δ: 1.90(s, Me), 1.96(s, Me), 2.06(s, Me), 2.13(s, Me), 5.10(s, CH$_2$), 5.16(s, CH$_2$), 7.00–7.30 (m, Ar); m.p. 80–82°C, λ_{max}(nm) (CH$_3$OH) 244.8; (**14′**) ^{1}H-NMR (CDCl$_3$) δ: 1.96 (s, Me), 2.10 (s, Me), 5.10 (s, OCH$_2$), 7.00–7.30 (m, Ar), m.p. 74–76°C, λ_{max}(nm) (CH$_3$OH) 244.8; (**15**) ^{1}H-NMR (CDCl$_3$) δ: 2.30 (s, Me), 2.85 (s, Me), 4.40 (s, CH$_2$), 6.75–7.30 (m, Ar); m.p. 162–164°C (decomp.) λ_{max}(nm) (CH$_3$OH) 245.6.

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