

## Photochemical Reactions of Organocobaloximes with Aryldisulfonyl Chloride

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Benzyl, allenyl and heteroaromatic methyl cobaloximes react with 4,4'-biphenyl disulfonyl chloride under photochemical and anaerobic conditions at 0 °C to give a variety of products including the disulphones, dimer and dmGH-ethers in variable yields.

**Key Words:** Photochemical reactions, Organocobaloximes, Aryldisulfonyl chloride.

### INTRODUCTION

The ease with which organometallic complexes participate in free radical reactions is quite remarkable<sup>1-6</sup>. In particular, organobis(dimethylglyoxime) cobalt(III) pyridine complexes, trivially known as organocobaloximes, have been successfully utilized in organic synthesis by many groups<sup>7-14</sup>. Recently, organocobaloximes have been used for the synthesis of symmetrical disulphones<sup>15</sup>.

In this paper we report the reaction of allenyl, benzyl and heteroaromatic methyl cobaloximes with 4,4'-biphenyl disulfonyl chloride under photochemical conditions. The present study therefore has been undertaken to understand the Co-C bond cleavage process in organocobaloximes.

### EXPERIMENTAL

**Synthesis of organic precursors:** 3-Furylbromide was synthesized from propargyl alcohol as outlined by Tada *et al.*<sup>16</sup>. 3-Butyn-1-bromide was brominated with PBr<sub>3</sub> in ether according to the method of Collman<sup>17</sup>. Cinamyl bromide was synthesized by the bromination of cinamyl alcohol with lithium bromide<sup>18</sup>.

**Synthesis of cobaloximes:** All the organocobaloximes were synthesized by the literature procedure from *bis*(dimethylglyoximate)pyridine cobalt(I) and organic halides. Cobaloxime(I) was generated *in situ* by anaerobic disproportionation of cobaloxime(II) in methanol as described by Schrauzer<sup>19</sup>.

**General procedure for the photochemical reaction:** A solution of aryldisulfonyl chloride (1 mmol in 30 mL of dichloromethane) was degassed for 0.5 h and organocobaloximes (2 mmol) was added to it. The reaction mixture was cooled to

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0 °C and irradiated using 2 W × 200 W tungsten lamps. The progress of the reaction was monitored using TLC in ethyl acetate on completion, the mixture was concentrated and the organic compounds were separated by flash chromatography. The organic products were further purified on the silica gel column.

**Disulphone (1a):** White solid, m.p. 162-164 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), 4.67 (s, 4H, CH<sub>2</sub>SO<sub>2</sub>), 7.63 (d, *J* = 8.5, 4H, Ar), 7.70 (d, *J* = 8.3, 4H, Ar), 7.76 (d, *J* = 8.5, 4H, Ar), 7.96 (d, *J* = 8.5, 4H, Ar).

**Disulphone (2a):** White solid, m.p. 238-240 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), 4.52 (s, 4H, CH<sub>2</sub>SO<sub>2</sub>), 7.31 (d, *J* = 7.1, 2H, Ar), 7.36 (t, *J* = 8.1, 4H, Ar), 7.40-7.43 (m, 6H, Ar), 7.64 (d, *J* = 8.4, 4H, Ar), 7.76 (d, *J* = 8.5, 2H, Ar), 7.83 (d, *J* = 8.1, 2H, Ar), 7.86 (d, *J* = 8.1, 2H, Ar).

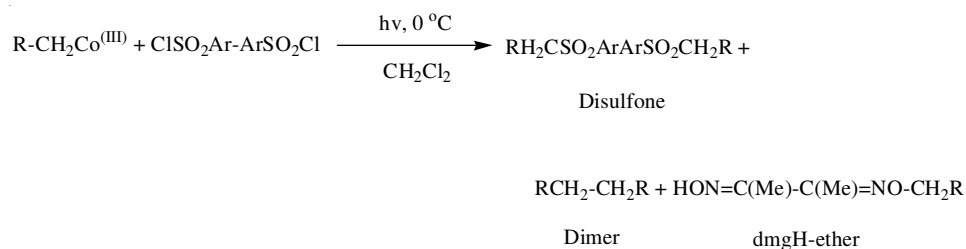
**Disulphone (3a):** White solid, m.p. 226-228 °C; <sup>1</sup>H NMR (500 MHz, DMSO), 5.25 (d, *J* = 16.8, 2H, CH=C), 5.40 (dd, *J* = 9.3, *J* = 10, 4H, CH<sub>2</sub>SO<sub>2</sub>), 6.27 (m, 2H, HC=C), 7.35 (m, 6H, Ar), 7.62 (d, *J* = 7.7, 4H, Ar), 7.80 (d, *J* = 8.1, 4H, Ar), 7.95 (d, *J* = 8.1, 4H, Ar).

**Disulphone (5a):** White solid, m.p. 132-134 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), 2.17 (s, 6H, C-CH<sub>3</sub>), 3.67 (s, 4H, CH<sub>2</sub>SO<sub>2</sub>), 7.86 (d, *J* = 8.3, 4H, Ar), 8.19 (d, *J* = 8.3, 4H, Ar).

**Disulphone (6a):** White solid, m.p. 217-219 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), 4.19 (s, 4H, CH<sub>2</sub>SO<sub>2</sub>), 6.89 (s, 2H, furyl-H), 7.53 (dd, *J* = 2.46, *J* = 5.86 Hz, 2H, furyl-H), 7.7 (dd, *J* = 3.3, *J* = 5.6 Hz, 2H, furyl-H), 7.77 (d, *J* = 8.4 Hz, 4H, Ar), 8.04 (d, *J* = 8.4, 4H, Ar).

## RESULTS AND DISCUSSION

Organocobaloximes are reacted with 4,4'-biphenyl disulfonyl chloride in 2:1 molar ratio in dichloromethane at 0 °C under anaerobic and photolytic conditions. A smooth reaction takes place and is complete within 3 h to give a mixture of products, disulphone, dimer and O-organodimethyl glyoxime (dmgH ether) (eqn. 1).



Cinamylcobaloxime (**3**) on reaction with 4,4'-biphenyl disulfonyl chloride forms disulphone (**3a**) and dmgH-ether (**3c**) in 73 and 25 % yield, respectively. 4-Bromobenzylcobaloxime (**1**) reacts with aryldisulphone chloride to give disulphone (**a**) in 20 % yield. A similar reaction occurs with naphthylcobaloxime (**2**) to yield disulphone (**2a**), dimer (**2b**) and dmgH-ether (**2c**) in 27, 48 and 10 % yield, respectively.

The 4,4'-biphenyldisulfonyl chloride reacts with allenylcobaloxime (**5**) to yield the disulphone (**5a**) and dimer in 40 and 35 % yield, respectively. A similar reaction with 3-cynaobenzylcobaloxime gives bibenzyl (70 %) is the only product (Table-1). Aryldisulfonyl chloride reacts with 3-furyl cobaloxime (**6**) to yield disulphone and dmgH-ether in 65 and 15 % yield, respectively.

TABLE-1  
ORGANIC PRODUCTS FROM REACTION OF ORGANOCOBALOXIMES  
WITH 4,4'-BIPHENYLDISULFONYL CHLORIDE

Entry	RCH <sub>2</sub> Co(III)	Disulfone (yield %) ( <b>1a-6a</b> )	Dimer (yield %) ( <b>1b-6b</b> )	dmgH ether (yield %) ( <b>1c-6c</b> )
1	R = 4-BrC <sub>6</sub> H <sub>4</sub>	20	52	28
2	R = 1-naphthyl	27	48	10
3	R = PhCH=CH	73	4	15
4	R = 3-CNC <sub>6</sub> H <sub>4</sub>	–	70	–
5	R = CH <sub>3</sub> -C≡C	40	35	–
6	R = 3-furyl	65	–	15

ClCo(III)(dmgH)<sub>2</sub>Py is the main inorganic product isolated in these reactions and no attempt has been made to characterize the other water soluble inorganic products. The reactions do not proceed in dark. All the organocobaloximes are stable in solution under inert atmosphere in the absence of aryldisulfonyl chloride.

All the reactions are free radical in nature as inferred from the experimental observations and the nature of products formed. Since the Co-C bond in organocobaloximes is weak (17-30 Kcal mol<sup>-1</sup>) and photolabile, it can be cleaved even at wavelength above 360 nm<sup>11,20</sup>. Tungsten lamp and glass apparatus are, therefore adequate for preparative photolysis experiments. Arene sulfonyl chlorides have previously been identified as chain-propagating species in many organic reactions of alkenes as well as in the reaction with organocobaloximes<sup>21</sup>. Cobaloxime(II), a d<sup>7</sup> species, formed during the homolysis of Co-C bond has been observed to be a good leaving group<sup>21c, 21d</sup>.

The general characteristics of the reaction of organocobaloximes **1-7** with 4,4'-biphenyldisulfonyl chloride are similar to the reaction of the similar substrates with arylsulfonyl chloride described earlier by Gupta<sup>15</sup>.

### Conclusion

Symmetrical disulphones are formed in the reaction of organocobaloximes with aryldisulfonyl chloride. The reactions are more complicated as compared to the reaction of the same organocobaloximes with monosulfonyl chlorides<sup>17</sup>.

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