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An efficient and convenient method for preparation of disulfides from thiols using air as oxidant catalyzed by Co-Salophen

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Abstract

Disulfides have been synthesized by oxidation of thiols using air as oxidant catalyzed by Co-Salophen with high yields, mild and neutral conditions, and easy procedures of the catalyst. The products were confirmed by ¹H NMR and IR. \bigcirc 2011 Cheng Xia Tan. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

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Disulfides are important intermediates for chemical transformations [1]. They are mostly prepared from the oxidation of thiols. Hydrogen peroxide is the most commonly used oxidant [2]. There are numerous other methods reported for the preparation of disulfides, such as the oxidation of sodium alkyl thiosulfate by hydrogen peroxide [3], reductive coupling of sulfonyl chlorides with piperidinium tetrathiotungstate [4] as well as with sodium cyanoborohydride [5]. Although they are efficient synthesis of disulfides, their use is usually in the laboratory and cannot be applied in industry because these reagents are expensive, provide low yields, or are not environmentally friendly. Recently the oxidation of thiols to disulfides promoted by activated carbon-air system was reported [6].

There has been considerable interest in the synthesis and catalytic activity of Schiff-M (M = metal ion) complexes [7] in past decade because they mimic enzymatic systems. And Cobalt (II) is the good catalyst widespread used in methoxycarbonylation of olefins [8], dimerization of propylene [9] and so on. Cobalt (II)–Schiff base complexes have received attention for a long time, being good catalysts for oxidation with dioxygen. Co-Salophen (N,N'-bis(salicylaldehyde)-1,2-phenylenediimino cobalt (II)) (Fig. 1) is one kind of Schiff-M complex, which is a tetradentate ligand having a stable structure with two oxygen and two nitrogen atoms, and is analogous to metalloporphyrins of cytochrome P450 in structure and catalytic activity. Its catalytic and oxygen-carrying function has widely been recognized [10]. Herein, we report an efficient and convenient preparation of disulfides from thiols using air catalyzed by Co-Salophen (Scheme 1).

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Scheme 1. Synthesis of symmetrical disulfides.

1. Experimental

All materials were obtained from commercial source. Melting points were obtained with a capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on Nicolet Aviatar-370 infrared spectrophotometer in KBr with absorptions in cm⁻¹. ¹H NMR spectra (500 MHz) were determined on Varian 500 instrument using CDCl₃ or DMSO-d6 as the solvent with TMS as an internal standard.

1.1. General procedure for the preparation of Co-Salophen

Salicylide (0.02 mol) and *o*-phenylenediamine (0.01 mol) were solved in 40 mL EtOH stirring at 60 °C for 1 h. Then filtrated, washed with EtOH, dried at 60 °C under vacuum to obtain short columnar yellow crystal Salophen (2.99 g), yield 95%, mp 158–160 °C. Salophen (1.58 g, 5 mmol) and Co(OAc)₂ (0.89 g, 5 mmol) were added under the nitrogen protection, then injected 20 mL EtOH. The reaction was taken at 55–65 °C for 2 h; filtrated at reduced pressure and washed with EtOH, dried at 60 °C under vacuum to obtain dull-red solid (1.70 g), yield 91.0%, mp >300 °C. IR (KBr): 3437 cm⁻¹, 1607 cm⁻¹, 1561 cm⁻¹, 590 cm⁻¹, 420 cm⁻¹.

The products were confirmed by IR. The band emerging at 3437 cm⁻¹ and 1607 cm⁻¹ in the FT-IR spectrum could be assigned to the vibrations of ν (O–H) and the characteristic imido (C=N) band respectively. And bands at 1607 cm⁻¹ and 1520 cm⁻¹ due to ν (C=N) and ν (C–O) vibrations, respectively, in the Schiff-base, which were shifted relative to the free ligand (Schiff-base) (1607 cm⁻¹ and 1561 cm⁻¹). The more or less shifting of these bands indicated that the cobalt ion was bonded to the ligand through the two N and O donor atoms as a tetradentate ONNO functionality. The absorption bands near 590 cm⁻¹ and 420 cm⁻¹ further affirmed the coordination of Schiff-base to cobalt ion through Co-O and Co-N bands.

1.2. General procedure for the preparation of disulfide

Thiols (0.6 mmol), ethanol (8 mL), Co-Salophen (0.006 mmol) were added in flask with a magnetic stirring bar, bubbling air into the solution at 60 °C. The progress of the reaction was monitored by TLC. When the reaction finished, the catalyst were filtered, then the products were separated by column chromatography.

The products were confirmed by ¹H NMR and IR. Di(4-methylphenyl)disulfide (**3a**): ¹H NMR (500 MHz, CDCl₃): δ 7.35 (d, 4H, J = 8.0 Hz), 7.10 (d, 4H, J = 8.0 Hz), 2.31 (s, 6H); IR (KBr): 3019, 1488, 801, 479 cm⁻¹; Di-(2-methylphenyl)disulfide (**3b**): ¹H NMR (500 MHz, CDCl₃): δ 7.36 (m, 2H), 7.06–7.08 (m, 6H), 2.35 (s, 6H); IR (KBr): 2976, 1585, 1465, 1039, 737 cm⁻¹; Di(2-benzothiazyl)disulfide (**3c**): ¹H NMR (500 MHz, DMSO- d_6): δ 8.01 (d, 2H, J = 8.0 Hz), 7.85 (d, 2H, J = 8.0 Hz), 7.54 (d, 2H, J = 7.5 Hz), 7.43 (d, 2H, J = 7.0 Hz). IR (KBr): 2922, 669, 443 cm⁻¹; Diphenyldisulfide (**3d**): ¹H NMR (500 MHz, CDCl₃): δ 7.50 (d, 4H, J = 8.5 Hz), 7.31 (dt, 4H, J = 7.5 Hz), 7.25 (dt, 2H, J = 7.0 Hz). IR (KBr): 3070, 685, 461 cm⁻¹; Di(2-bromophenyl)disulfide (**3e**): ¹H NMR (500 MHz, CDCl₃): δ 7.14–7.59 (m, 8H). IR (KBr): 1588, 1441, 1244, 1036, 740 cm⁻¹; Di(4-methoxyphenyl)disulfide (**3f**): ¹H NMR (500 MHz, CDCl₃): δ 7.48 (d, 4H, J = 8.0 Hz), 6.79 (d, 4H, J = 8.0 Hz), 3.86 (s, 6H); IR (KBr): 2837, 1578,

Table 1 The effects of amount of catalyst, reaction time and temperature on yield.^a

Entry	Catalyst/mmol	Time/h	Temp./°C	Yield ^c /mol%
1	0.003	3	60	56
2	0.006	3	60	96
3	0.015	3	60	96
4	None	3	60	Trace
5	0.006 ^b	3	60	11
6	0.006	0.5	60	35
7	0.006	1	60	65
8	0.006	2	60	85
9	0.006	3	60	96
10	0.006	4	60	96
11	0.006	3	20	24
12	0.006	3	40	75
13	0.006	3	80	80

^a All reactions were run with *p*-methylbenzenethiol (0.6 mmol), ethanol (8 mL).

^b Co(OAc)₂.

Table 2

^c Isolated yields based on *p*-methylbenzenethiol.

1473, 1270, 1238, 1059, 1036, 1021, 740 cm⁻¹; Di(4-chlorophenyl)disulfide (**3g**): ¹H NMR (500 MHz, CDCl₃): δ 7.24 (d, 4H, J = 8.0 Hz), 7.45 (d, 4H, J = 8.0 Hz); IR (KBr): 1568, 1471, 1386, 1112, 1010, 815 cm⁻¹; Di(2-chlorophenyl)disulfide (**3h**): ¹H NMR (500 MHz, CDCl₃): δ 7.11–7.52 (m, 8H); IR (KBr): 1564, 1448, 1247, 1028, 746 cm⁻¹; Dibenzyldisulfide (**3i**): ¹H NMR (500 MHz, CDCl₃): δ 7.02–7.28 (m, 10H), 2.45 (s, 4H); IR (KBr): 3020, 2900, 1595, 1490, 1445, 710, 690 cm⁻¹.

2. Results and discussion

Using *p*-methylbenzenethiol as substrate the reaction was optimized by experimenting with various reaction conditions (solvent, amount of catalyst, reaction time and temperature). Results are shown in Table 1. Among the solvents tested, ethanol gave the best results. To examine the catalytic activity of Co-Salophen, we explore the oxidation of thiol in the presence of 0.5%, 1.0%, 2.5%, no Co-Salophen and 1.0% Co(OAc)₂. According to Table 1, 1.0% of Co-Salophen was enough and efficient for this reaction, and an excessive amount of the catalyst did not increase the yields (Table 1, entries 1–3). It was found that the oxidation of thiol did not occur in the absence of Co-Salophen (Table 1, entry 4) and Co(OAc)₂ could not promote the reaction very well (Table 1, entry 5). It was interesting in the yield of the oxidation at 80 °C (Table 1, entry 13) was lower than at 60 °C (Table 1, entry 9). It may be that higher temperature results in reduction of the catalytic and oxygen-carrying activity (Table 1, compare entries 11–13). Our results show that the optimum condition for the oxidation of *p*-methylbenzenethiol is with 1.0 mmol% of the catalyst Co-Salophen, 3 h at 60 °C in ethanol.

Compound	Time/h	Yield ^b /mol%	Mp/°C	Lit/mp/°C
3 a	3	96	47–48	48 [5]
3b	3	95	36–37	37-38 [11]
3c	3	94	177–178	177-179 [12]
3d	3	95	59-60	59-60 [13]
3e	3	92	97	97–98 [11]
3f	3	96	118–119	120 [11]
3g	3	94	70-71	72 [5]
3h	3	96	86-87	87-88 [11]
3i	4	90	70–71	71 [14]

Aerobic oxidative coupling of thiols to disulfides catalyzed by Co-Salophen.^a

^a The reactions were carried out with 0.6 mmol of substrates with 1% Co-Salophen at 60 °C and bubbling of air into the solution.

^b Yields based on the thiols.



Fig. 2. Mechanism of oxidation of thiols to disulfides.

With optimized conditions in hand, we explored the scope of the reaction, including aromatic and alkyl thiols (Table 2). To our delight, the catalytic oxidation occurred smoothly with excellent selectivity and yield. Co-Salophen was recycled, reused four times, and the yields are 95%, 90%, 82% and 51% respectively. It was shown that recycled Co-Salophen still had catalytic activity.

It is possible that different metal ions keeps appearing. The mechanism of oxidation of thiols to disulfides by Co-Salophen may be as follow [15]: the thiols were oxidized into disulfides by the active oxygen with the help of CoSalophen (II) (Fig. 2).

3. Conclusions

In summary, we have developed an experimentally simple Co-Salophen catalyzed aerobic oxidation of thiols into disulfides using air as oxidant. This catalytic oxidation system is clean, selective and very effective. Further oxidation reactions using this system are in progress in our laboratory.

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