



Synthesis of Dibenzylsulfoxide using Tris[1,10-Phenanthroline] Iron(II) Perchlorate

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Abstract : The availability of selective oxidants to use for selective synthesis of organic compounds is of obvious importance to research in organic chemistry. The importance of organic sulfides and sulfoxides as reductants in biological systems is well known. Electron Transfer reaction¹⁻³ is highly sensitive to the structure of aromatic sulfide as well as the structure of the ligand of the Fe(III)-polypyridyl complexes. In the present study, the detailed literature survey for the synthesis of dibenzylsulfoxide using DBS as substrate and Fe(Phen)₃³⁺ as oxidant. The oxidation procedure is very simple and the products are easily isolated in 92% yields.

Key words : Electron Transfer(ET), Dibenzyl Sulfide(DBS).

Introduction

Sulfoxide synthesis constitutes an important research area⁴⁻¹¹ as they are versatile building blocks in organic synthesis.^{9,10} A great number of oxidizing agents can affect the conversion of sulfides into sulfoxides.¹⁴⁻¹⁸ However, the susceptibility of sulfoxide to further oxidation narrows the choice of reagents for the oxidation of sulfides to sulfoxides. Introduction of new oxidants for the transformation of sulfides to sulfoxides under mild condition is of importance in synthetic organic chemistry.

Experimental

Preparation of [Fe(Phen)₃]³⁺ Complexes

Step-I :Tris(1,10-phenanthroline)iron(II) perchlorate

AnalaR grade ferrous ammonium sulfate (1 g, 2.5 mM) is dissolved in 20ml of water containing 1 ml of 0.01N H₂SO₄. 1,10-phenanthroline (1.6 g, 7.5 mM) is dissolved in 60ml of hot water containing 2 ml of 1 M HClO₄. To this hot solution, ferrous ammonium sulfate solution is added slowly with stirring followed by sodium perchlorate solution. The reaction mixture is allowed to remain in a water bath for half an hour for

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digestion, cooled and then filtered. Red crystals of tris(1,10-phenanthroline)iron(II) perchlorate are obtained. The crystals are washed with ethanol and water and dried in vacuum. The absorption spectrum of the complex in 1 M HClO₄ shows a maximum at 510 nm which is the value reported by Ford-Smith and Sutin.¹⁹

Step-II :Tris(1,10-phenanthroline)iron(III) perchlorate

To the already prepared tris(1,10-phenanthroline)iron(II) perchlorate, 40ml of 1M H₂SO₄ is added and cooled in ice. Then excess of PbO₂ is added. Oxidation takes place and a blue solution is formed. The solution when kept for 30 min, the precipitate of tris(1,10-phenanthroline)iron(III) perchlorate is formed. The precipitate is filtered, washed with ethanol in ice-cold water and dried in vacuum. The absorption spectrum of the complex in HClO₄ shows a maximum at 602 nm.

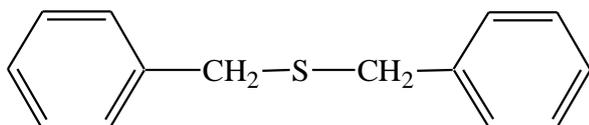
The wavelength of maximum absorption (λ_{\max}) and molar extinction coefficients (ϵ) estimated from the absorption spectra (Figures 1- 2) and IR spectra of [Fe(Phen)₃]³⁺ complex are collected in Table 1.

Table 1: λ_{\max} & ϵ values of polypyridyl complex of iron(II) and iron(III)

Complex	λ_{\max} (nm)		ϵ (cm ⁻¹ M ⁻¹)	IR* cm ⁻¹
	Found	Literature ¹⁹⁻²²		
[Fe(phen) ₃] ²⁺	510	510	11100	
[Fe(phen) ₃] ³⁺	600	602	870	470

Preparation of Dibenzyl Sulfide

The structures of the substrate used in the present study is



Dibenzyl sulfide

A solution prepared from 25.8 g (0.2 M) of benzyl chloride and 75ml of 95% ethanol contained in a 250ml round bottom flask equipped with an efficient bulb condenser and a magnetic stirrer was brought to gentle reflux by means of a heating mantle. Sodium sulfide nona hydrate (36g, 0.15 M) was added with stirring and heating over a four hour period through a dropping funnel. The solution was heated at reflux for three days, after which the ethanol was removed by distillation at atmospheric pressure.

The hot aqueous solution was poured with stirring into a 250 ml beaker half filled with chipped ice. After the ice had melted, the resulting yellow solid was filtered on a buckner funnel and washed with 50ml of water. After air drying, the solid was distilled under reduced pressure (b.pt. 120°C/0.15 mm) to give 17.6 g of dibenzyl sulfide. Recrystallisation from 70% ethanol gave a pure sample with an m.pt of 47°C. The reported m.pt was 46-48°C.²³⁻²⁵

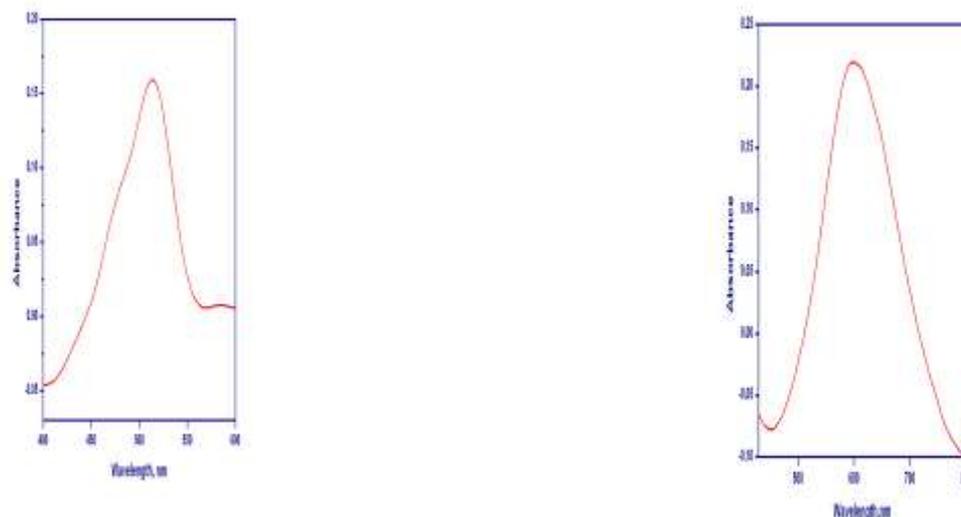
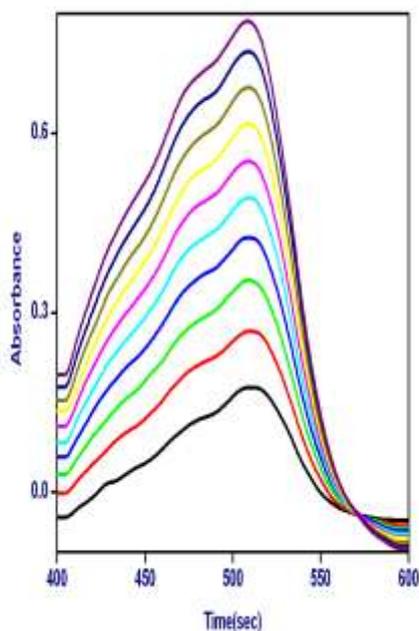


Fig. 1 & 2: Absorption spectra of $[\text{Fe}(\text{phen})_3]^{2+}$ and $[\text{Fe}(\text{phen})_3]^{3+}$

Rate measurements

ELICO UV-Vis double beam spectrophotometer (Model SL-164) was employed to record the absorption spectra of iron(II) and iron(III)-phenanthroline complex used in the present study (Figure 3) and to follow the kinetics of ET reactions of $[\text{Fe}(\text{phen})_3]^{3+}$.

The studies were carried out under pseudo first order conditions with dibenzyl sulfide, $[\text{Fe}(\text{phen})_3]^{3+}$ complex ratio of at least 15:1. The substrate DBS with all additives except the oxidant was allowed to attain the experimental temperature by keeping them separately in the constant temperature bath. A known volume of $[\text{Fe}(\text{phen})_3]^{3+}$ complex was then transferred to the reaction mixture at zero time and shaken well. The rate of formation of $[\text{Fe}(\text{NN})_3]^{2+}$ complex was followed using the UV-Vis spectrophotometer by measuring the change in the absorbance at wavelengths 510nm corresponding to $[\text{Fe}(\text{phen})_3]^{2+}$.¹⁷ The $[\text{Fe}(\text{NN})_3]^{2+}$ complex had molar extinction coefficients of the order of $\sim 1 \times 10^4 \text{ cm}^{-1}\text{M}^{-1}$ (Table 1) in the observed region while the corresponding iron(III) complex was practically transparent at this wavelength region. The reaction was followed at definite time intervals by following the increase in absorbance of $[\text{Fe}(\text{phen})_3]^{2+}$ till maximum absorbance (A_∞) was reached. The Figure 3 indicate the increase in the absorbance of iron(II) complex with time to show the progress of the reaction.



DBS vs $[\text{Fe}(\text{phen})_3]^{3+}$

Fig. 3: Increase in absorbance $[\text{Fe}(\text{phen})_3]^{2+}$ at 10 seconds time intervals for the $[\text{Fe}(\text{phen})_3]^{3+}$ oxidation of DBS

Stoichiometry

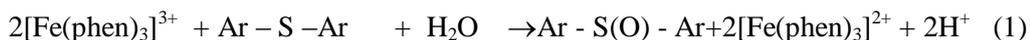
The stoichiometry of the reaction was determined by taking different ratios of oxidant and substrate concentrations. The investigation was first carried out with the oxidant, tris(1,10-Phenanthroline)iron(III) and the substrate, dibenylsulfide. A known excess of $[\text{Fe}(\text{phen})_3]^{3+}$ was mixed with a known concentration of dibenylsulfide under the experimental conditions of $[\text{H}^+] = 0.5\text{M}$ in 50% aqueous CH_3OH at 305K. The reaction was followed by measuring the change of absorbance of $[\text{Fe}(\text{phen})_3]^{2+}$ at 510nm. The amount of $[\text{Fe}(\text{phen})_3]^{2+}$ formed must be equal to the amount of $[\text{Fe}(\text{phen})_3]^{3+}$ consumed during the reaction. After the reaction was complete, the concentration of the product, $[\text{Fe}(\text{phen})_3]^{2+}$ was calculated from its absorbance maximum and the known value of molar extinction coefficient and this gave the amount of $[\text{Fe}(\text{phen})_3]^{3+}$ consumed in the reaction. The results are presented in Table 2.

Table 2: Stoichiometry of the reaction

$[\text{Fe}(\text{phen})_3]^{3+}$ $\times 10^3, \text{M}$	$[\text{DBS}]$ $\times 10^4, \text{M}$	$[\text{Fe}(\text{phen})_3]^{3+}]_{\text{reac}}$ $\times 10^4, \text{M}$	$\frac{[\text{Fe}(\text{phen})_3]^{3+}]_{\text{reac}}}{[\text{DBS}]_{\text{initial}}}$
1.0	1.0	2.04	2.04
2.0	1.0	1.96	1.96
2.0	2.0	4.16	2.08

$[\text{H}^+] = 0.5 \text{ M}$; solvent = 80% CH_3OH – 20% H_2O (v/v); temp. = 32° C

These results indicate that one mole of Dibenzyl sulfide was consumed per two moles of $[\text{Fe}(\text{phen})_3]^{3+}$. All these studies confirm the above conclusion that one mole of substrate was consumed per two moles of oxidant, $[\text{Fe}(\text{NN})_3]^{3+}$ in accordance with the eq. 1.



where



Cyclic voltammetry

The oxidation potentials of DBS and the reduction potentials of $[\text{Fe}(\text{Phen})_3]^{3+}$ complex was determined using EG and G 273A Princeton Applied Research Potentiostat / Galvanostat equipped with a X-Y-t-recorder. The stock solutions of the metal complex and dibenzylsulfide for the electrochemical studies were prepared in aqueous CH_3OH (v/v). The supporting electrolyte was 0.1 M t-butylammonium perchlorate. A two compartment three electrode cell was used to record the cyclic voltammograms. A glassy carbon working electrode (area = 0.07 cm^2), 1 cm^2 platinum plate counter electrode and a standard calomel reference electrode (SCE) were used in the electrochemical experiments. Cyclic voltammograms were recorded after purging the solution with nitrogen gas for 30 min. The redox potential values measured in the present study are in close agreement with the reported values.²⁶⁻²⁹ The redox potentials of $[\text{Fe}(\text{Phen})_3]^{3+}$ complex with dibenzylsulfide is as 1.60 V. A sample cyclic voltammogram is shown in Figure 4.

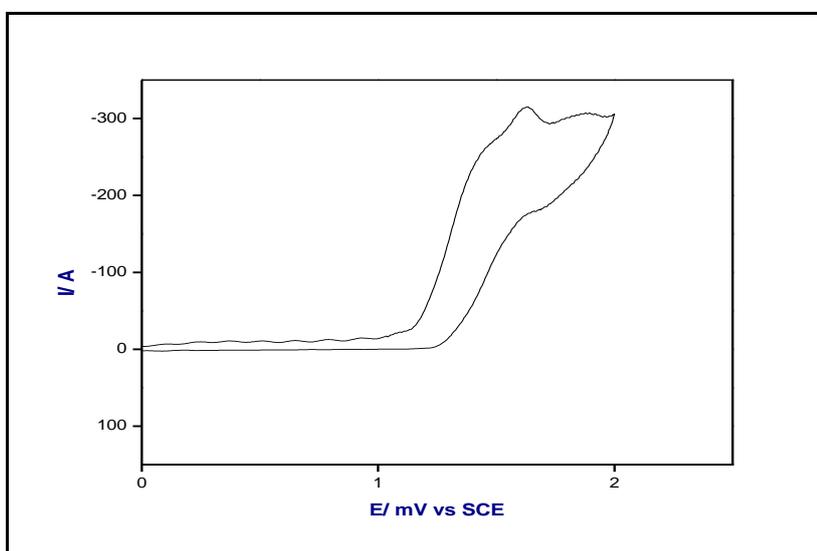


Fig. 4: Cyclic voltammogram of DBS in CH_3OH

Product analysis

Tris(1,10-Phenanthroline)iron(III) complex and dibenzylsulfides were mixed in the ratio of 1:15 under the experimental conditions. The reaction was followed by measuring the absorbance of $[\text{Fe}(\text{NN})_3]^{2+}$. The reaction was complete when the absorbance reaches a maximum and the reaction mixture was shaken with ether. The ether extract was concentrated and the product separated out. It was repeatedly washed with alcohol and dried in vacuum. The IR spectrum of the product was recorded and it was found to be identical with that of dibenzylsulfoxide, having S=O stretching frequency in the characteristic region $1090\text{-}1030 \text{ cm}^{-1}$ (Figure 5). This study of product analysis demonstrates that sulfoxide is the only product formed under the present reaction conditions.

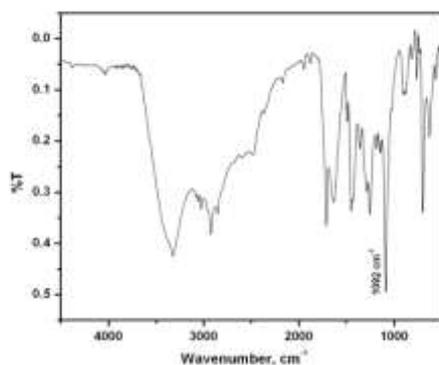


Fig. 5: IR Spectrum of dibenzylsulfoxide

^1H NMR, GC-MS techniques were used for the analysis of the products obtained during the course of the reaction. For ^1H NMR spectrum, CDCl_3 is used as the solvent. In Figure 6, the product of the peak at $\delta 3.63$ ppm corresponds to $-\text{CH}_2$ groups of sulfoxides.³⁰ The aromatic region is informative as the aromatic protons of sulfoxides appear as multiplets centered at δ values 7.26 and 7.38 ppm respectively. Similarly the presence of $\text{S}(\text{O})$ stretching frequency at 1082 cm^{-1} confirms that the sulfoxide is the only product in the reaction.

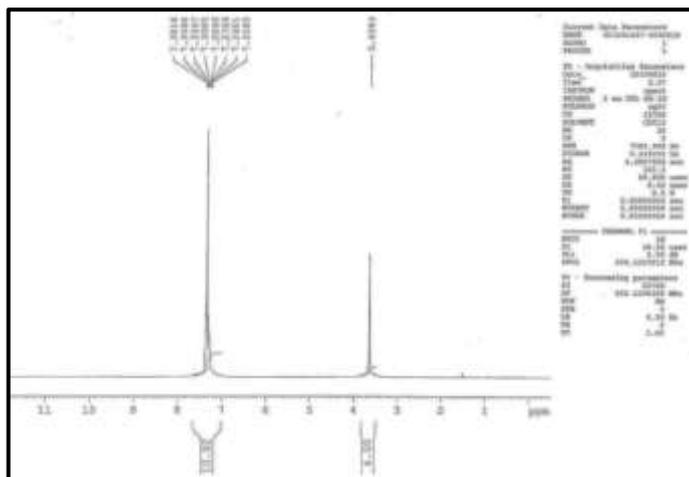


Fig.6: Dibenzylsulfoxide NMR Spectrum

Based on GC analysis, the percentage yield of sulfoxide was found to be 92%.

Conclusion

The present work aims at developing a new process to selectively synthesize sulfoxide from sulfides using one electron oxidant $[\text{Fe}(\text{phen})_3]^{2+}$. Dibenzyl sulfide (DBS) has been taken as a reactant. The rate of the reaction was followed by monitoring the increase in concentration of $[\text{Fe}(\text{NN})_3]^{2+}$ complexes spectrophotometrically. It was observed that the periodic addition of stoichiometric ratio of DBS and $[\text{Fe}(\text{phen})_3]^{2+}$ is 1:2. The maximum conversion achieved in the present work was 92% with sulfone formation being only 2% indicating 98% selectivity for the desired product i.e. sulfoxides.

The oxidation probably involves the one electron oxidant with the sulfide atom. Moreover, this oxidation system is operationally simple and the yields of the products are high, so the oxidation method is suitable for practical synthesis.

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