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A new synthesis and study of diferrocenylsulfide

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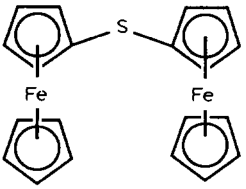
Abstract

Diferrocenylsufide (I) has been prepared in 76% yield via a new simple route involving bromoferrocene and the reactive bis(phenylsulfonyl)sulfide. Cyclic voltammetry of diferrocenylsulfide in CH_2Cl_2 shows two reversible one electron processes at 0.61 V and 0.90 V. The mixed valence diferrocenylsulfide species was prepared by controlled current oxidation and two bands in the visible region at λ_{max} 800 nm (ϵ 442) and λ 410 nm (ϵ 1548) are observed, no near IR band is detected.

Introduction

Sulfur-containing ferrocene derivatives have previously been described in the literature [1–8]. Included in these are two preparations of diferrocenylsulfide [7,8]. The first method reported involves the synthesis of ferrocenylthiol via the reduction of ferrocenesulfonyl chloride by lithium aluminum hydride and subsequent reaction of the thiol with iodoferrocene in the presence of freshly activated copper bronze [7]. The second reported procedure reacts ferrocene with S_8 in the presence of $Fe_3(CO)_{12}$ to obtain a mixture of seven sulfonated products with a total yield of 36%, with diferrocenylsulfide as the main product of the mixture [8].



I

In combination with our studies involving biferrocene derivatives [9], we wish to report a new, simple, alternative synthesis of diferrocenylsulfide that employs bis(phenylsulfonyl)sulfide [10–12]. De Jong and Janssen observed that bis(phenylsulfonyl)sulfide was more reactive than other sulfides commonly used to form dithienyl sulfides [10]. In our efforts we have found that ferrocenyllithium reacts

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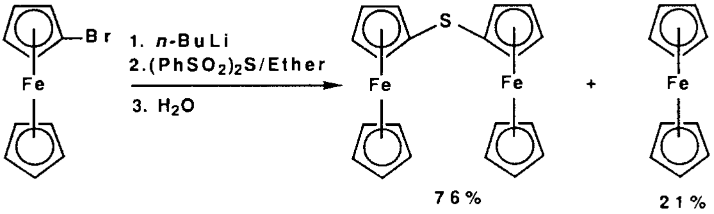
cleanly with bis(phenylsulfonyl)sulfide to produce diferrocenylsulfide in 76% yield. This procedure could be utilized as a convenient and general synthesis for the formation of a series of symmetrical as well as possibly unsymmetrical thioethers.



Results and discussion

When ferrocenyllithium, obtained by a metal–halogen exchange reaction with bromoferrocene [13] and butyllithium was treated with bis(phenylsulfonyl)sulfide, diferrocenylsulfide was formed in 60–76% yield. Ferrocene and biferrocene were obtained as side products with yields of 10–30% and 0–15%, respectively. In one case, the half reacted product, ferrocenylphenylsufonyl sulfide, was isolated in 15% yield and its formation was attributed to a shorter reaction time. This result affords the possibility, by changing the ratio of equivalents of the reactants, of forming ferrocenylphenylsulfonyl sulfide as the main product and, via subsequent reactions with alkyl and aryl lithiated species, form a series of unsymmetrical thioethers. Use of bis(phenylsulfonyl)sulfide also inhibits formation of disulfide derivatives which often are prevalent in sulfide and thio ether syntheses.

In connection with our earlier study of diferrocenyl ketone [14], we also investigated what effect a Barbier type of addition would have on this synthesis. Simultaneous addition of bromoferrocene and bis(phenylsulfonyl)sulfide to the alkyllithium reagent did not improve the yield, but decreased it considerably. Products isolated from this reaction include diferrocenyl sulfide in low yields (16%), biferrocene (13%), and recovered bromoferrocene (68%). Overall conversion of bromoferrocene to the desired diferrocenyl sulfide was ~ 50%; however, in general the Barbier type of addition was not as successful as generation of the ferrocenyl lithium compound followed by addition of the sulfide reagent.

These results are representative of a mechanism that may favor an organometallic pathway rather than a radical pathway. Synthesis of the organolithium species is advantageous to the yield of diferrocenyl sulfide and *in situ* formation of ferrocenyl lithium in the presence of bis(phenylsulfonyl)sulfide does not favor the completion of the reaction. It is reasonable that generation of the ferrocenyl lithium species first is necessary as this eliminates competition between bromoferrocene and bis(phenylsulfonyl)sulfide for the alkyl lithium reagent. Once the organolithium species is formed, it can cleanly react with the sulfide to produce diferrocenyl sulfide. The radical mechanism represented in the diferrocenyl ketone [14] synthesis is in part due to the presence of ketyl radicals generated from the presence of carbonyl compounds. This is clearly not the case with the sulfide reagent and the presence of the sulfide reagent in an *in situ* formation of the ferrocenyl lithium species serves only to interfere with the ferrocenyl lithium production and thus the diferrocenyl sulfide formation.

This work has provided a new, simple, high yielding synthesis of diferrocenyl sulfide from readily available precursors. The reactive bis(phenylsulfonyl)sulfide has been shown to be a useful reagent that inhibits the formation of disulfide derivatives that can be problematic in sulfide and thioether synthesis. It has also been shown that the half reacted ferrocenyl(phenylsulfonyl)sulfide can be formed. It is therefore plausible that other phenylsulfonyl sulfide derivatives can be prepared and provide new routes to both symmetrical and unsymmetrical sulfides.

Cyclic voltammetry data in CH_2Cl_2 for diferrocenylsulfide are presented in Table 1. Potentials are referenced to a saturated calomel electrode in a 0.2 *M* solution of $TBABF_4/CH_2Cl_2$. Two reversible single-electron waves are presented, with the difference in oxidative and reductive peak potentials (E_{pa}–E_{pc}) somewhat higher than the theoretical limit of 60 mV for a reversible one-electron process. However, high (E_{pa}–E_{pc}) values and decreasing peak currents on successive sweeps are known for ferrocene systems in CH_2Cl_2 [15]. It should be noted that the effect a ferrocenyl moiety has on an adjacent ferrocenyl unit is that of an electron-donating group, and therefore results in a lower oxidation potential when compared to an unsubstituted ferrocene molecule. For example, a lower oxidation potential is observed for biferrocene with respect to ferrocene. The effect a thioferrocenyl substituent has on an adjacent ferrocene unit is that of an electron-withdrawing group, thereby resulting in a higher oxidation potential when compared to ferrocene. The difference in the half-wave potentials between the first and second oxidations ($\Delta E_{1/2}$) can represent the extent of electronic interaction between the subunits. The larger $\Delta E_{1/2}$ value suggests a higher degree of interaction for biferrocene as compared to diferrocenylsulfide which contains a bridging ligand. Although the sulfur bridging ligand allows for some interaction between the subunits, it is logical that there should be a decrease in this interaction. It should also be noted that in the case of hetero-atoms, a large $\Delta E_{1/2}$ value can be representative of a through ligand inductive effect (due to the hetero-atoms' polarizability) instead of an intramolecular interaction [16]. This explains why the electronic spectra of the oxidized species of diferrocenylsulfide show no new transition in the near-IR region as is the case for the mixed valent biferrocene species. There are also two bands in the visible region at 800 nm (442) and 410 nm (1548). The absorption at 800 nm is consistent with the red shifted ligand-to-metal transition of the ferrocenium portion of the hetero-containing monocation [16].

Table 1

Cyclic voltammetry, 0.2 *M* $TBABF_4/CH_2Cl_2$ vs SCE

Compound	$E_{1/2}(1)$ (V vs SCE)	$E_{1/2}$ (V vs Fc /Fc$^+$)	($E_{pa}-E_{pc}$) (mV)	$E_{1/2}$ (2) (V vs SCE)	$E_{1/2}$ (V vs Fc /Fc$^+$)	($E_{pa}-E_{pc}$) (mV)	$\Delta E_{1/2}$- (2−1) (mV)
Ferrocene	0.530	0.00	85				
Biferrocene	0.500	−0.030	90	0.85	0.32	80	350
Diferrocenyl-sulfide	0.610	0.080	100	0.90	0.37	100	290

Experimental

All reactions were carried out under prepurified argon. Solvents were dried and purified by distillation from sodium. Infrared spectra were recorded on a Mattson Instruments Polaris Nu-10000 FT-IR spectrometer with a IR-12050 detector; ^1H NMR spectra were obtained on a Varian XL-400 (400 MHz) spectrometer with tetramethylsilane as an internal standard. Near-IR and UV–Vis spectra were obtained on a Cary 14 spectrometer and Cary 219 spectrometer, respectively. Low-resolution mass spectra were obtained on a VG Instruments 70-S gas chromatograph/mass spectrometer. Cyclic voltammograms were obtained using a PAR 175 Universal Programmer as a sweep generator and a PAR 173 Potentiostat for potential control. Preparative oxidations were completed on a PAR 179 Digital Coulometer. A standard three-electrode configuration was employed consisting of a platinum button or platinum basket (Beckman) working electrode, a silver or nickel counter electrode and a saturated calomel (SCE) reference electrode. The reference electrode was connected to the electrolysis compartment via a salt bridge containing electrolytic solution. Solvents for electrochemical studies were dried by passing through a column of activated neutral alumina and stored under argon. Tetrabutylammonium tetrafluoroborate ($^nBu_4NBF_4$) was purchased from Southwestern Analytical Chemicals, Inc., Austin, TX, and was used without further purification. Monocations for electronic spectroscopy were prepared by controlled-current oxidation. Samples for absorption spectra were transferred via syringe to a septum-sealed quartz cell.

Preparation of diferrocenylsulfide

Sublimed bromoferrocene (1.33 g, 5 mmol) was dissolved into 15 ml of dry, freshly distilled ether and cooled to −20 °C in a 250 ml, three-neck, round-bottom flask equipped with stir bar, gas adapter, and septum. BuLi (2 ml, 2.5 *M*, 5 mmol) was added dropwise via syringe over 5 min and the temperature maintained at −15 °C for 45 min. The reaction mixture was cooled to −78 °C and the metal–halogen exchange was allowed to continue for an additional 2 h. Bis (phenylsulfonyl)sulfide (0.77 g, 2.5 mmol) was dissolved into dry ether (80 ml) and slowly added dropwise via a syringe to the ferrocenyllithium solution. The reaction was allowed to continue at −78 °C for an additional 3 h and slowly warmed to 0 °C. Distilled water (10 ml) was added and the reaction mixture stirred for 10 min. A thick, light yellow precipitate formed and was filtered and washed several times with ether. The ether filtrate was extracted with water (3 ×, 30 ml) and the combined aqueous layers were back extracted with ether (45 ml). The combined ether layers were dried over sodium sulfite, filtered, and the solvent removed *in vacuo* to yield yellow-orange crystals. The precipitate and the crystals were combined and subjected to flash chromatography. Elution began with a 90% hexanes/10% CH_2Cl_2 solvent system and the polarity slowly increased to 100% CH_2Cl_2. The first band yielded 0.20 g (21%) of ferrocene and the second band afforded 0.76 g (76%) of the desired diferrocenylsulfide; m.p. 160–161 °C (lit [7,8] m.p., 161–162 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 4.27 (4H, t), 4.19 (10 H, s), 4.14 (4H, t); IR (solid sample) 3107, 1414, 1389, 1171, 1106, 886, 864, 822, 596 cm^{-1}; MS m/z (relative intensity) M^+ 401.95 (100.00), 399.98 (12.82), 335.94 (6.54), 303.97 (18.20), 271.91 (19.62), 120.98 (18.07), 55.94 (12.99). In preliminary experiments biferrocene was formed in small quantities; however, upon varying the rate of addition of the sulfide, biferrocene production was eliminated.

Acknowledgment

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