Reduction of Sulfoxides to Sulfides Mediated by Ferrocene and Trifluoroacetic Anhydride

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The reaction of diaryl sulfoxides with trifluoroacetic anhydride in the presence of ferrocene gives the corresponding sulfide. The reduction of sulfoxides composed of the ferrocene-spacer-methylsulfinyl triad system would proceed via a through-bond electron transfer rather than a through-space process.

Much effort has been devoted to the reduction of sulfoxides to sulfides with low-valent metal salts from the viewpoint of synthetic application.[1-3] One-electron electrochemical or chemical reduction of sulfonium salts causes the S-C σ-bond cleavage to provide a sulfide and a carbon radical.[4-7] Ferrocene has been widely used as a redox active probe molecule.[8,9] However, the utility of ferrocene as a reducing agent with respect to sulfoxides and sulfonium salts has not been studied so far. Herein we report the reduction of sulfoxides **1** and **3** to sulfides mediated by ferrocene and trifluoroacetic anhydride (TFAA). We also describe that the reduction of sulfoxides **6**, composed of the ferrocene-spacer-methylsulfinyl triad system, with TFAA would proceed via a through-bond electron transfer.

Treatment of diaryl sulfoxides **1** with ferrocene (1 equiv) and TFAA (1 equiv) in $CHCl_3$ for 24 h gave the corresponding sulfides **2** quantitatively (Table 1). Both ferrocene and TFAA are essential for the reduction of **1**. The reduction of **1a** (X = CH_3) and **1b** (X = H) proceeded at room temperature, while the refluxing temperature was required for **1c** (X = Cl). However, **1d** (X = NO_2) was recovered unchanged. This result suggests that the rate determining step is the formation of trifluoroacetoxysulfonium salt and that one-electron reduction of the resulting sulfonium salt[4-7] with ferrocene causes the S-O σ-bond cleavage to afford **2** and ferrocenium ion.

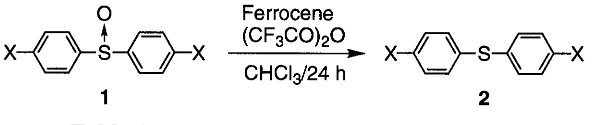


Table 1. Reduction of diaryl sulfoxides **1** mediated by ferrocene and TFAA[a]

Substrate	Temp./°C	Yield/%[b]
1a (X = CH_3)	rt	>95
1b (X = H)	rt	>95
1c (X = Cl)	65	>95
1d (X = NO_2)	65	0

[a] **1**:ferrocene:TFAA = 1:1:1.
[b] Yield was determined by ^1H NMR.

The reaction of dimethyl sulfoxide **3a** and aryl methyl sulfoxides **3b-d** with TFAA (1 equiv) in the presence of ferrocene (1 equiv) in $CHCl_3$ at room temperature quantitatively gave a mixture of sulfide **4a-d** and α-trifluoroacetoxymethyl sulfide **5a-d** (Table 2). The product ratios of **4a-d** to **5a-d** were in the range of 20:80 for **3a** to 34:67 for **3c**. When ruthenocene was used in place of ferrocene, the reaction of **3a** gave **4a** and **5a** in a 11:89 ratio. Thus, the competitive reactions between the reduction and Pummerer rearrangement[10] occur for sulfoxides **3** having α-methyl group.

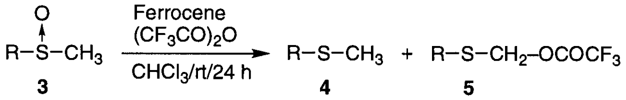


Table 2. Reaction of sulfoxides **3** mediated by ferrocene and TFAA[a]

Substrate	R	Product ratio[b] 4	Product ratio[b] 5	Total yields /%[b]
3a	CH_3	20	80	>95
3b	$C_6H_4CH_3$-*p*	25	75	>95
3c	C_6H_5	34	66	>95
3d	C_6H_4Br-*p*	33	67	>95

[a] **3**:ferrocene:TFAA = 1:1:1.
[b] Product ratio and yield were determined by ^1H NMR.

The electron transfer process of ferrocene-terminated conjugated derivatives, through-bond or through-space interaction, has been intensively studied in the field of electron transfer devices.[11-13] The nature of spacers as a molecular wire affects the electronic communication between donor and acceptor.[14] The present competitive reactions could serve as a probe for the qualitative evaluation of this process. Thus, we have designed the ferrocene-spacer-methylsulfinyl triad molecules **6**. The triad molecules **6** were prepared by the palladium-catalyzed cross-coupling reaction of ferrocenylzinc chloride[15] with *p*-(methylthio)aryl halides followed by the oxidation of the resulting sulfides **7** with *m*-CPBA.

The reaction of **6** with TFAA (1 equiv) in $CHCl_3$ at room temperature for 24 h was carried out (Table 3). The sulfoxides **6a-c** quantitatively afforded only the sulfides **7a-c** as a reduction product. This result is in marked contrast to the reaction of **3** shown in Table 2 and indicates the intramolecular electron transfer of the ferrocene moiety to the sulfonium moiety in **6**. The sulfoxides **6d-e** having biphenyl and diphenylmethane spacers quantitatively gave a mixture of **7d-e** and the Pummerer product **8d-e** in the ratios of **7d**:**8d** = 50:50 and **7e**:**8e** = 33:67, respectively. In both cases, the product ratios of **7d-e** to **8d-e** increased with decreasing the concentration of **6d-e**. It is noted that the ratio of the reduction product **7** to the Pummerer product **8** clearly depends on the nature of spacers such as length and π-conjugation and increases in the following order: diphenylmethane (**6e**) < biphenyl (**6d**) << anthryl (**6c**) ≈ phenyl (**6b**) ≈ none (**6a**). The distance between the ferrocenyl and sulfinyl moieties of **6d** with π-conjugate spacer is ca. 2 Å longer than that of **6e** in which π-conjugation is insulated by the methylene bridge. Nevertheless the reduction is more favorable for **6d** than **6e**. This result strongly suggests that, in the reduction of sulfoxides for the ferrocene-spacer-methylsulfinyl triad system **6**, a through-bond electron transfer of ferrocenyl moiety to sulfonium group is more favorable than a through-space process.

In conclusion, we have demonstrated the reduction of sulfoxides mediated by ferrocene and TFAA. The reduction of the triad molecules **6** could serve as a probe for the qualitative evaluation of the nature of spacers as a molecular wire.

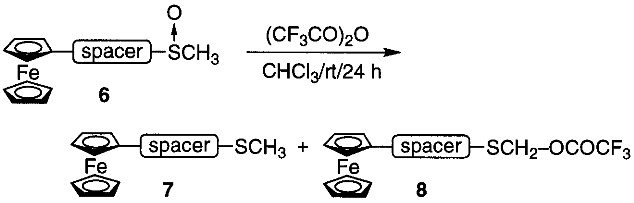
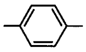
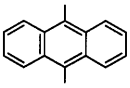
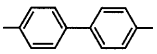
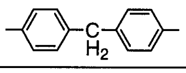


Table 3. Reaction of sulfoxides **6** with TFAA[a]

Substrate	Spacer	Conc. /mM	Product ratio[b]		Total yields/%[b]
			7	8	
6a	none	60	100	0	>95
6b		60	100	0	>95
6c		60	100	0	>95
6d		120	50	50	>95
		3	91	9	>95
6e		120	33	67	>95
		3	60	40	>95

[a] **6**:TFAA = 1:1.
[b] Product ratio and yield were determined by ^{1}H NMR.

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