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A Convenient and Mild Dethioacetalization Method Using $Fe(bpy)_3(ClO_4)_3 \cdot 3H_2O$

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Reactions of 1,3-dithianes, 1,3-dithiolanes, and benzenethioacetals with tris(2,2′-bipyridyl)-iron(III) perchlorate, $Fe(bpy)_3(ClO_4)_3 \cdot 3H_2O$, gave the parent carbonyl compounds in high yields, immediately. These reactions may proceed by one-electron abstraction from the sulfur atom of acetals by the iron(III) complex, and they provide a new convenient and mild dethioacetalization method.

Keywords——dethioacetalization; 1,3-dithiane; 1,3-dithiolane; benzenethioacetal; tris(2,2′-bipyridyl)iron(III) perchlorate; one-electron abstraction

Various methods for the transformation of S,S-acetals into the corresponding carbonyl compounds have been developed and can be classified into two categories, namely: (a) the reactions of the soft base sulfur atom of an S,S-acetal with soft acids or oxidants, for example, Hg^{2+}, Ag^{+}, Cd^{2+}, Cu^{2+}, Ce^{4+}, Tl^{3+}, NO^{+}, X^{+} (Cl^{+}), and R^{+} (CH_3^{+}, $C_2H_5^{+}$) *etc.*,[1] (b) one-electron abstraction reaction from a sulfur atom by electrochemical oxidation.[2]

In the preceding paper,[3] we reported that tris(2,2′-bipyridyl)iron(III) perchlorate, $Fe(bpy)_3(ClO_4)_3 \cdot 3H_2O$, is a versatile reagent for oxidative aryl–aryl coupling reactions. During the investigation, we found that the ferric bipyridyl complex is a good reagent for dethioacetalization, giving the parent carbonyl compounds in high yields. The procedure for this reaction is very simple, as follows. Crystals of thioacetals were added to a partially suspended solution of the ferric bipyridyl complex in CH_3CN in the presence of a small amount of 42% HBF_4 aq. with stirring at room temperature.[4] Reaction progress can be monitored by following the color change from ferric blue to ferrous red in the solution. After a few minutes, the resultant solution was worked up in a usual manner to give the deprotected

TABLE I

Type of acetal	Parent carbonyl compound	Yield (%)
1,3-Dithiane	Benzophenone	96
	3,4-Dihydroxybenzaldehyde	85
	3,4,5-Trimethoxybenzaldehyde	95
	trans-Cinnamaldehyde	90
	Cholestanone	96[a]
Benzenethioacetal	Cyclohexanone	85[b]
	3,4-Dimethoxybenzaldehyde	96
1,3-Dithiolane	3-Acetylindole	71

a) Reaction was run in tetrahydrofuran–CH_3CN (1 : 1). *b*) Yield based on the isolated 2,4-dinitrophenylhydrazone.

carbonyl compounds. Some experimental results in CH_3CN are summarized in Table I. Acetone and dimethylformamide as the solvents gave similar results to CH_3CN, but benzene, chloroform, ethyl ether, tetrahydrofuran, methanol, and water were not suitable for this reaction.

In the course of the reactions of 1,3-dithianes derivatives, significant amounts of trimethylene disulfide, mp 71 °C, and a white amorphous polymer $(-S(CH_2)_3S-)_n$[5] were deposited as insoluble materials from the solution. Similarly, in the reactions of the 1,3-dithiolane derivatives, insoluble rubbery polymers[5] were deposited. This facilitates purification of the resultant carbonyl compounds. Reactions of benzenethioacetals and thiols with this complex were as follows: benzenethioacetals gave the corresponding carbonyl compounds and diphenyldisulfide; thiophenol or 2-mercaptobenzothiazole gave diphenyldisulfide or 2,2′-dithiobis[benzothiazole], mp 186 °C, but thioethers such as diphenylsulfide or thioanisole did not give any reaction products. The latter results differ from the results of reactions of thioethers with $Tl(NO_3)_3$ which give the corresponding sulfoxides.[6]

This dethioacetalization reaction is considered to belong to reaction category (b) described above, namely, this reaction may proceed by one-electron transfer through an outer-sphere mechanism without bond formation between the sulfur atom of the acetal and the reagent as shown in Chart 1.

The cyclic voltammograms (CV) of 1,3-dithianes and 1,3-dithiolanes (Fig. 1c, d) show that the onset potentials of anodic current (E_a) of these compounds are *ca.* 1.0—1.05 V and are lower than the onset potential of cathodic current ($E_c = 1.25$ V *vs.* saturated calomel electrode (SCE)) of the iron(III) bipyridyl complex (Fig. 1a). These CV data indicate that these compounds can be easily oxidized to give the demasked parent carbonyl compounds. Further, the experimental results show that the easily oxidizable phenol moiety (Fig. 1b) was not affected in this reaction. On the other hand, the E_a values of benzenethioacetals and thioanisole (Fig. 1e—g) are *ca.* 1.25—1.35 V and are equal to or higher than the E_c of the iron(III) bipyridyl complex. Dethioacetalization reactions of the benzenethioacetals with the bipyridyl complex took place immediately, but thioanisole was not affected.[6] The reason for this difference of reactivities is not clear. Though the reactions of thioacetals with ferric nitrate and ferric perchlorate in CH_3CN showed similar reactivity for dethioacetalization, experimental results showed that the bipyridyl complex was superior to other iron salts in terms of yield and reaction velocity. It was suggested that these iron salts in CH_3CN have strong

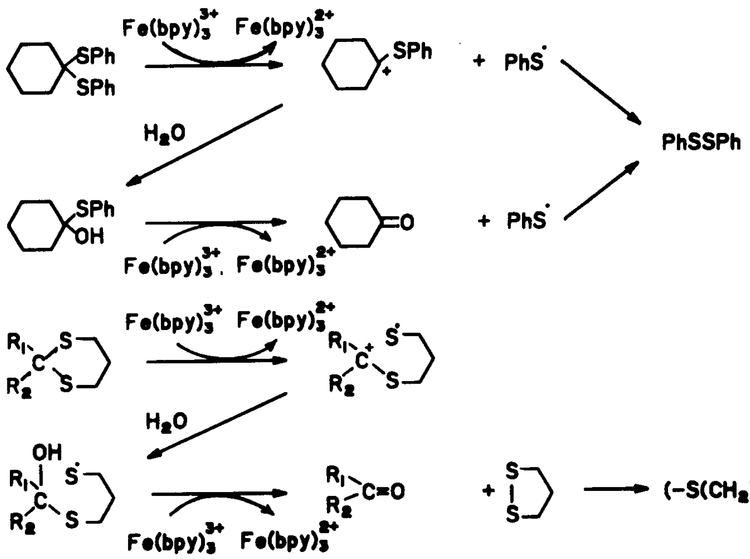

Chart 1

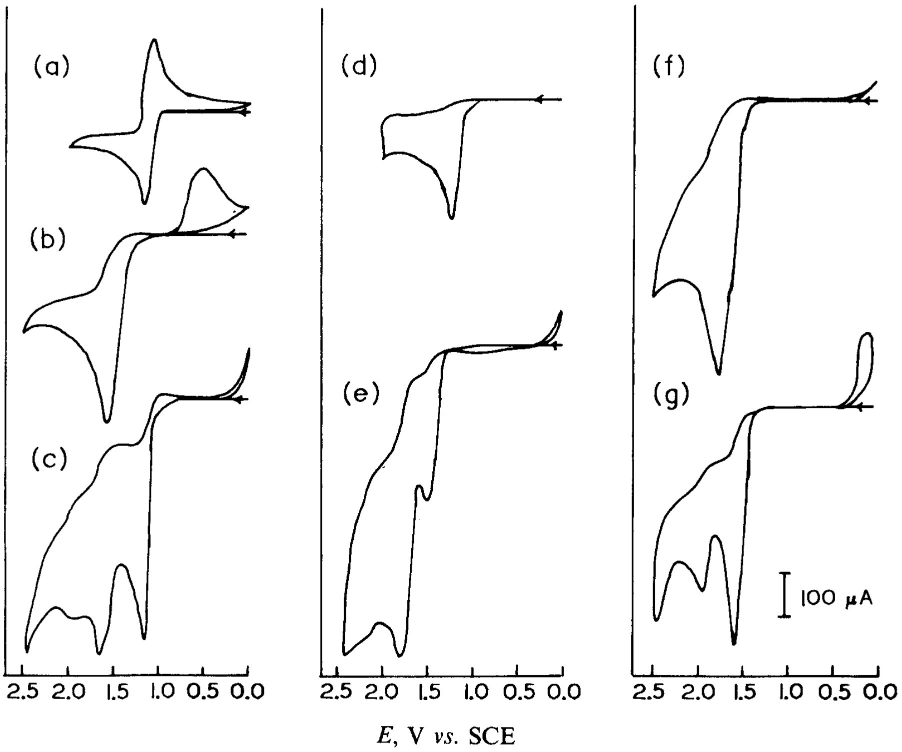

Fig. 1. Cyclic Voltammograms of 5 mM AN Solution of (a) $Fe(bpy)_3(ClO_4)_2$, (b) 3,4-Dihydroxybenzaldehyde, (c) 1,3-Dithiane of (b), (d) 1,3-Dithiolane of 3-Acetylindole, (e) Benzenethioacetal of 3,4-Dimethoxybenzaldehyde, (f) Benzenethioacetal of Cyclohexanone, (g) Thioanisole

Supporting electrolyte, 0.1 M Et_4NClO_4; working electrode, Toa Dempa platinum disk HP-105 5 mmϕ, sweep rate, 100 mV s^{-1}

oxidizing power compared with the oxidation potentials of thioacetals, giving over-oxidation products,[7)] whereas the iron(III)bipyridyl complex has a suitable value of redox potential to oxidize thioacetals.

Experimental

All melting points are uncorrected. Cyclic voltammetric analyses were carried out using a Hokuto Denko HA-501 potentiostat. Voltammograms were recorded on a Riken F-35 X-Y recorder. Mallinckrodt silica gel (100 mesh) and Merck Kieselgel 60 F_{254} were used for column chromatography and thin layer chromatography (TLC), respectively.

Typical Procedures for Oxidative Dethioacetalization——Reaction of a 1,3-Dithiane Derivative: A solution of the 1,3-dithiane of benzophenone (136 mg, 0.5 mmol) in CH_3CN (AN) (5 ml) was added in one portion to a partially suspended solution of $Fe(bpy)_3(ClO_4)_3 \cdot 3H_2O$ (960 mg, 1.1 mmol) and 42% HBF_4 aq. (1 ml) in AN (10 ml) with stirring at room temperature. The blue color of the ferric complex changed immediately to red (ferrous complex). After 5 min, water was added to the reaction mixture, and the whole was extracted with ether. The organic layer was washed with brine, and then dried on Na_2SO_4 and evaporated. Petroleum ether was added to the residue and the insoluble precipitate was filtered off. The filtrate was concentrated and then purified by silica gel column chromatography using chloroform–hexane (1 : 1) as an eluent to yield 88 mg (96%) of benzophenone as colorless crystals.

Reaction of a 1,3-Dithiolane Derivative: A solution of the 1,3-dithiolane of 3-acetylindole (117.5 mg, 0.5 mmol) in AN (5 ml) was added in one portion to a partially suspended solution of $Fe(bpy)_3(ClO_4)_3 \cdot 3H_2O$ (960 mg, 1.1 mmol) and 42% HBF_4 aq. (1 ml) in AN (10 ml) with stirring at room temperature. The blue color of the ferric complex changed immediately to red (ferrous complex), and a white amorphous precipitate appeared. After 5 min, the precipitate was filtered off, then water was added to the filtrate and the whole was extracted with ethyl acetate. The organic layer was washed with brine, then dried on Na_2SO_4 and evaporated to give a crystalline residue. The residue was purified by silica gel column chromatography using chloroform–ethyl acetate (2 : 0.5) as an eluent to yield

56 mg (71.3%) of 3-acetylindole as colorless crystals (benzene), mp 190—191 °C.

Reaction of a Benzenethioacetal Derivative: Crystals of benzenethioacetal of cyclohexanone (50 mg, 0.17 mmol) were added to a partially suspended solution of $Fe(bpy)_3(ClO_4)_3 \cdot 3H_2O$ (1 g, 1.15 mmol) and 42% HBF_4 aq. (0.2 ml) in AN (3 ml) with stirring at room temperature. After 5 min, a red precipitate appeared. Ether (10 ml) was added to the solution, and then the insoluble materials were filtered off. The filtrate was evaporated under reduced pressure, and then diluted with EtOH, and 2,4-dinitrophenylhydrazine was added to give crystals. Recrystallization from EtOH afforded the 2,4-dinitrophenylhydrazone of cyclohexanone, 118 mg (85%), mp 160—162 °C, as orange crystals.

Reaction of the Benzenethioacetal of 3,4-Dimethoxybenzaldehyde: Dethioacetalization of the benzenethioacetal of 3,4-dimethoxybenzaldehyde (184 mg, 0.5 mmol) with the ferric bipyridyl complex (960 mg, 1.1 mmol) was carried out according to the above procedure. The reaction residue was purified by silica gel column chromatography using chloroform–hexane (1 : 1) as an eluent to give 50 mg of diphenyldisulfide as colorless crystals (EtOH), mp 60—62 °C (subl.), and 80 mg (96%) of 3,4-dimethoxybenzaldehyde as colorless crystals (EtOH), mp 57—58 °C.

Reaction of a Thiol Derivative: 2-Mercaptobenzothiazole (167 mg, 1 mmol) in AN (8 ml) was added to a partially suspended solution of $Fe(bpy)_3(ClO_4)_3 \cdot 3H_2O$ (880 mg, *ca.* 1 mmol) and 42% HBF_4 aq. (1 ml) in AN (8 ml) with stirring at room temperature. After 5 min, water was added to the reaction mixture, and the crystalline precipitate was filtered off. Recrystallization of the precipitate from benzene afforded 160 mg (96%) of 2,2′-dithiobis-[benzothiazole] as colorless crystals, mp 185—187 °C.

References and Notes

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