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Application of Iron(III) Complexes, Tris(2,2′-bipyridyl)iron(III) Perchlorate and Some Iron(III) Solvates, for Oxidative Aryl–Aryl Coupling Reactions

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Oxidative aryl–aryl coupling reactions of phenols and phenol-ethers utilizing tris(2,2′-bipyridyl)iron(III) perchlorate, $Fe(bpy)_3(ClO_4)_3 \cdot 3H_2O$, and some iron(III) solvates, $Fe(ClO_4)_3 \cdot 9H_2O$ in acetonitrile (AN), $Fe(AN)_3(ClO_4)_3$, $FeCl_3$ in AN, $Fe(ClO_4)_3$ in Ac_2O, and $FeCl_3$ in Ac_2O, were explored. The structures of the solvates of $FeCl_3$ in AN and Ac_2O were clarified to be $Fe(AN)_6(FeCl_4)_3$ and $Fe(Ac_2O)_3(FeCl_4)_3$, respectively.

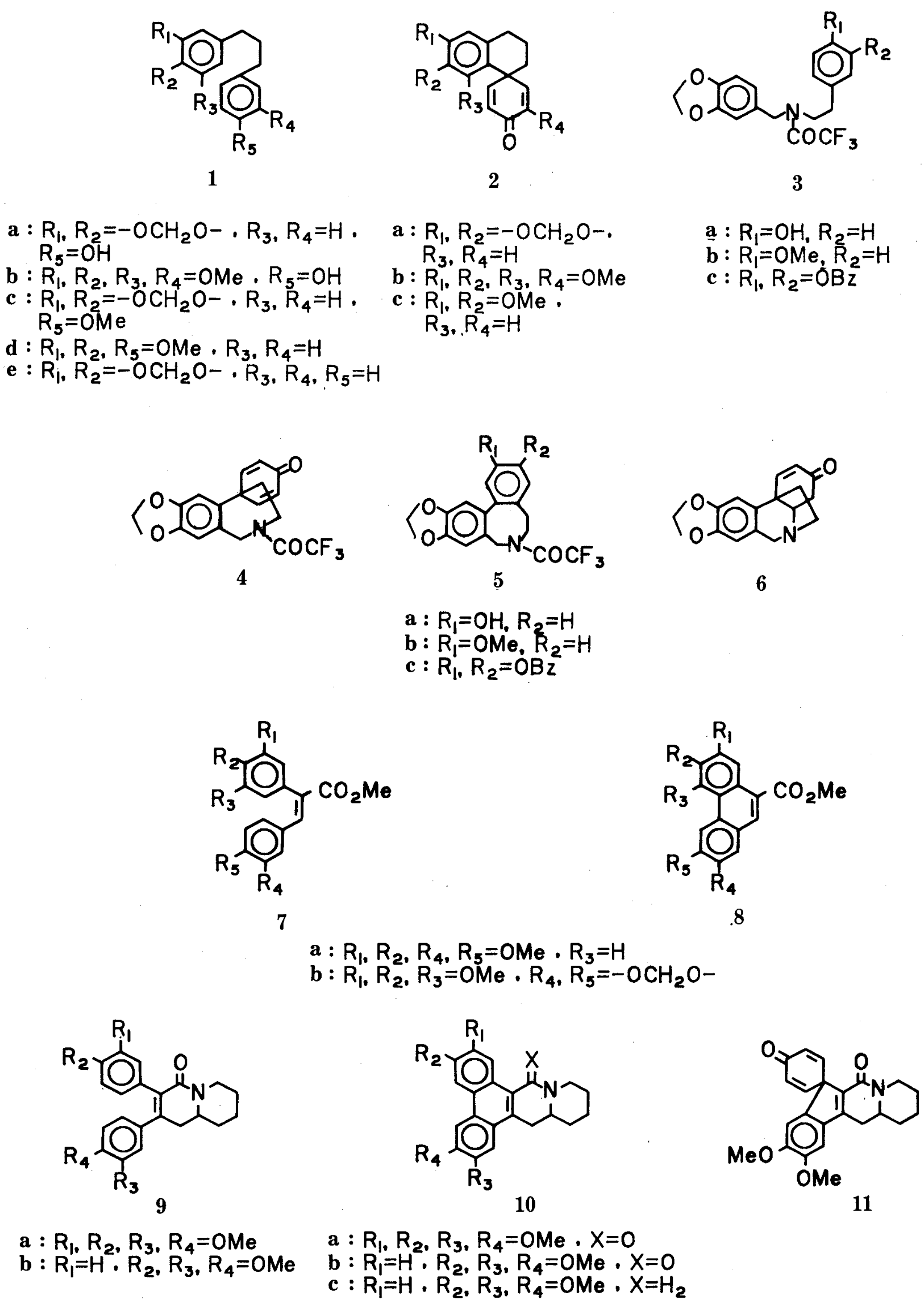
Keywords——aryl–aryl coupling; phenol; phenol-ether; oxidation; tris(2,2′-bipyridyl)iron(III) perchlorate; iron(III) solvate

Oxidative aryl–aryl coupling is an important reaction for the synthesis of natural products which are considered to be formed by the corresponding reaction in nature. Among various methods, the reactions catalyzed by transition metal salts or complexes have been used predominantly method to date.[1] Although several reagents for this purpose have been developed,[2] a universal reagent for all organic substrates may not exist, because this reaction is initiated by one-electron abstraction from the organic substrate by a metal which has a suitable value of oxidation potential to oxidize the substrate; in other words, the oxidation potentials between reagent and organic substrate should generally be appropriate if a good result is to be obtained. Thus, various reagents are required to extend the applicability of this reaction. Recently, we reported that iron(III) solvates which have various values of redox potential can be prepared conveniently from ferric perchlorate in the corresponding solvents.[3] This paper deals with an application of these iron(III) solvates including some other iron(III) solvates and a ferric bipyridyl complex, $Fe(bpy)_3 (ClO_4)_3 \cdot 3H_2O$, as versatile reagents for oxidative aryl–aryl coupling reactions.

Aryl–Aryl Coupling Reactions with $Fe(bpy)_3 (ClO_4)_3 \cdot 3H_2O$

Tris(2,2′-bipyridyl)iron(III) perchlorate, $Fe(bpy)_3(ClO_4)_3 \cdot 3H_2O$, is a well known redox indicator and has a medium value of redox potential, $E° = 1.10$ V *vs.* saturated calomel electrode (SCE).[4,5] This value suggests that this complex can be used as an oxidative coupling reagent for certain phenols and phenol-ethers. In fact, oxidations of some phenols and phenol-ethers with this complex in acetonitrile (AN) in the presence or absence of 42% HBF_4 aq. gave intramolecular oxidative coupling products in good yields, as shown in Table I.

As described in the experimental section, this reaction is very fast and is completed within a few min. The progress of the reaction can be monitored in terms of the color change from blue to red, which is due to the change from the ferric to the ferrous complex. The results shown in Table I suggest that the phenol-ethers **1e** (onset potential of anodic current, $E_a = 1.25$ V *vs.* SCE) and **3b** ($E_a = 1.36$ V) could not be oxidized by this complex because of their high oxidation potentials. The spirodienone **4**, an oxidation product from a derivative of



1

a : R_1, R_2=−OCH_2O−, R_3, R_4=H, R_5=OH
b : R_1, R_2, R_3, R_4=OMe, R_5=OH
c : R_1, R_2=−OCH_2O−, R_3, R_4=H, R_5=OMe
d : R_1, R_2, R_5=OMe, R_3, R_4=H
e : R_1, R_2=−OCH_2O−, R_3, R_4, R_5=H

2

a : R_1, R_2=−OCH_2O−, R_3, R_4=H
b : R_1, R_2, R_3, R_4=OMe
c : R_1, R_2=OMe, R_3, R_4=H

3

a : R_1=OH, R_2=H
b : R_1=OMe, R_2=H
c : R_1, R_2=OBz

4

5

6

a : R_1=OH, R_2=H
b : R_1=OMe, R_2=H
c : R_1, R_2=OBz

7

8

a : R_1, R_2, R_4, R_5=OMe, R_3=H
b : R_1, R_2, R_3=OMe, R_4, R_5=−OCH_2O−

9

a : R_1, R_2, R_3, R_4=OMe
b : R_1=H, R_2, R_3, R_4=OMe

10

a : R_1, R_2, R_3, R_4=OMe, X=O
b : R_1=H, R_2, R_3, R_4=OMe, X=O
c : R_1=H, R_2, R_3, R_4=OMe, X=H_2

11

Chart 1

norbelladine **3a**, can be transformed easily to crininone (**6**), a precursor of an Amaryllidaceae alkaloid crinine, by treatment with Na_2CO_3.[1e,6] Further, formation of the phenanthroquinolizidinone **10b** and the spirodienone **11** from **9b** provides a new and facile method for the synthesis of the vesicant alkaloids, (±)-cryptopleurine (**10c**) and related compounds. That is, transformations of the spirodienone **11** to the quinolizidinone **10b** by dienone–phenol rearrangement with H_2SO_4–Ac_2O followed by hydrolysis of the acetate and methylation with

Table I. Oxidative Aryl–Aryl Coupling Reactions of Phenols and Phenol-ethers with $Fe(bpy)_3(ClO_4)_3 \cdot 3H_2O$

Phenol and phenol-ether	E_a[a]	Product (%)[b]	Reference for product
1a	1.10	**2a** (95)[c]	1*c*, 1*e*, 6
1b	0.95	**2b** (77)	8
1c	1.20	**2a** (56)	1*c*, 1*e*, 6
1d	1.17	**2c** (85)	2*a*, 6
1e	1.25	[d]	
3a	1.30	**4** (50)	1*e*, 6
3b	1.36	[d]	
3c	1.22	[d]	
7a	1.10	**8a** (95)[e]	7, 9
7b	1.15	**8b** (82)[e]	7, 9
9a	0.95	**10a** (95)[c]	7
9b	1.10	**10b** (60), **11** (20)[c]	7

a) The onset potentials of anodic current (E_a) were obtained by cyclic voltammetry of 1 mM solutions of the substrates in AN containing 0.1 M Et_4NClO_4 as a supporting electrolyte. *b*) Yields are isolated yield. *c*) Almost no reaction in the absence of HBF_4 aq. *d*) Recovered starting material. *e*) It was not necessary to add HBF_4 aq.

diazomethane, and **10b** to (±)-cryptopleurine (**10c**) by reduction with $LiAlH_4$, have already been achieved in good yields.[7]

Oxidative Aryl–Aryl Coupling Reactions with Some Iron(III) Solvates

It is known that solvates of ferric perchlorate show various values of redox potentials depending on the solvent (see Table II and Fig. 1); for example, the acetic anhydride solvate (reagent E), $Fe(Ac_2O)_3(ClO_4)_3$,[10] ($E° = 1.32$ V), and AN solvate (reagent C), $Fe(AN)_6(ClO_4)_3$, ($E° = 1.73$ V).[3] These values are higher than that of the ferric bipyridyl complex, and suggest the utility of these compounds as reagents for oxidative aryl–aryl coupling reactions. Other related solvates of ferric perchlorate or ferric chloride, for example, $Fe(AN)_x(H_2O)_y(ClO_4)_3$ ($E° = 1.30$ V),[11] (reagent B), can be prepared by simple addition of $Fe(ClO_4)_3 \cdot 9H_2O$ to AN, and $Fe(AN)_6(FeCl_4)_3$ ($E° = 1.38$ V) (reagent D) or $Fe(Ac_2O)_3(FeCl_4)_3$ ($E° = 1.18$ V) (reagent F) can be prepared by simple addition of anhydrous ferric chloride to AN or Ac_2O.

Although the structures of $FeCl_3$ solvates in AN and Ac_2O are not clearly elucidated, but have been tentatively shown as $FeCl_2(AN)_4(FeCl_4)$ and $FeCl_2(Ac_2O)_2$ $(FeCl_4)$,[12,13] the structures of the iron complexes in reagents D and F were clarified to be $Fe(AN)_6(FeCl_4)_3$ and $Fe(Ac_2O)_3(FeCl_4)_3$, respectively. For the structure of the iron complex in reagent D, the following three structures are possible, as shown in Eqs. 1—3.

$$2\ FeCl_3 + 4\ AN \longrightarrow FeCl_2(AN)_4\ (FeCl_4) \tag{1}$$

$$3\ FeCl_3 + 5\ AN \longrightarrow FeCl(AN)_5\ (FeCl_4)_2 \tag{2}$$

$$4\ FeCl_3 + 6\ AN \longrightarrow Fe(AN)_6\ (FeCl_4)_3 \tag{3}$$

The structure of the iron complex in reagent D was confirmed by the following evidence. (a) The cyclic voltammograms (CV) of $FeCl_3$ (Figs. 1 and 3) in AN and $Fe(AN)_6(ClO_4)_3$ in $AN + 3Et_4NCl$ (Fig. 2) (Eq. 4) were the same. Further, the formation of $FeCl_4^-$ was observed in a solution of $Fe(AN)_6(ClO_4)_3$ in AN + one mol of Et_4NCl (Fig. 2b). Therefore, the reaction shown in Eq. 5 can be excluded. (b) The CV of reagent D shows a wave similar to that of $Fe(AN)_6(FeCl_4)_2$ prepared by the known method from iron wire and Cl_2[14] (Fig. 3). Thus, four mol of $FeCl_3$ may have only one mol equivalent of oxidation power in reagent D, because $FeCl_4^-$ has no oxidizing ability. The structure of the iron complex in reagent F was elucidated in a similar manner.

$$Fe(AN)_6(ClO_4)_3 + 3Et_4NCl \longrightarrow 1/4Fe(AN)_6(FeCl_4)_3 + Et_4NClO_4 \qquad (4)$$

$$Fe(AN)_6(ClO_4)_3 + Et_4NCl \longrightarrow FeCl(AN)_5(ClO_4)_2 + Et_4NClO_4 \qquad (5)$$

Thus, we investigated the reactivities of these iron(III) solvates as reagents for oxidative aryl–aryl coupling reaction utilizing the compounds **3a** ($E_a = 1.30$ V), **3b** ($E_a = 1.36$ V), and **3c**

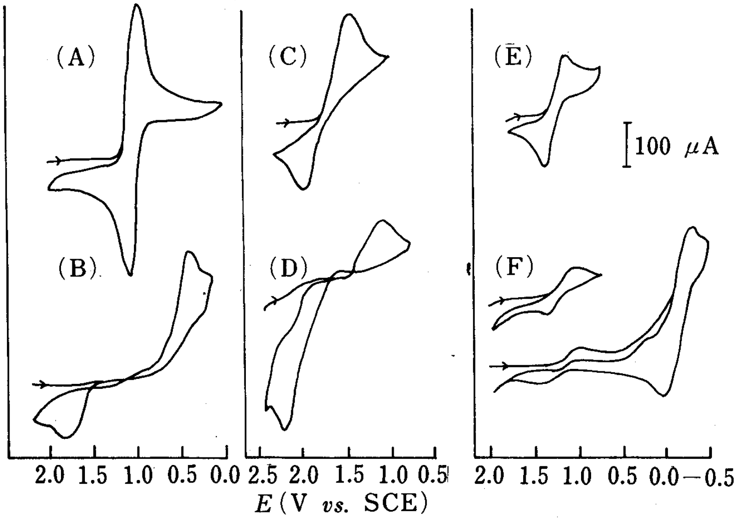


Fig. 1. Cyclic Voltammograms of 0.01 M Iron(III) Complexes

(A) $Fe(bpy)_3(ClO_4)_3 \cdot 3H_2O$ in AN. (B) $Fe(ClO_4)_3 \cdot 9H_2O$ in AN. (C) $Fe(AN)_6(ClO_4)_3$ in AN. (D) $FeCl_3$ in AN or C + $3Et_4NCl$. (E) $Fe(Ac_2O)_3(ClO_4)_3$ in Ac_2O. (F) $FeCl_3$ in Ac_2O or E + $3Et_4NCl$.

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

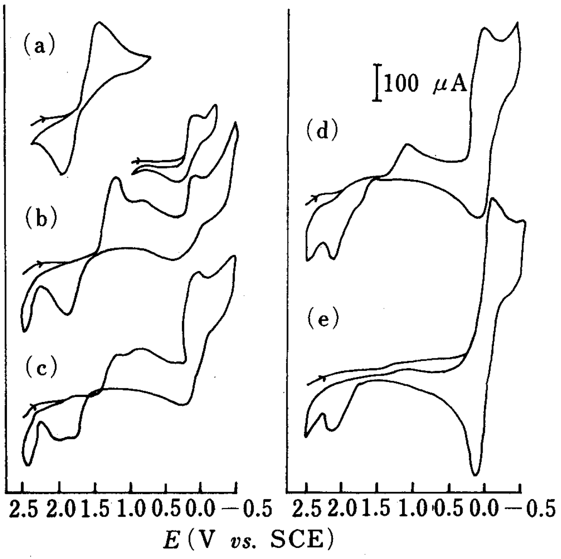


Fig. 2. Cyclic Voltammograms of (a) a Solution of $Fe(AN)_6(ClO_4)_3$ (0.1 mmol) in 10 ml of AN, (b), (c), (d) and (e) after Addition of Et_4NCl (0.1, 0.2, 0.3 and 0.4 mmol, Respectively)

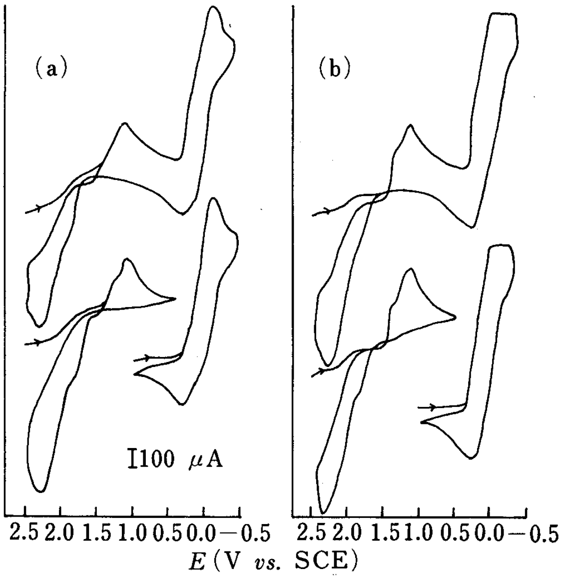


Fig. 3. Cyclic Voltammograms of (a) a Solution of $Fe(AN)_6(FeCl_4)_2$ (0.1 mmol) in 10 ml of AN, and (b) a Solution of Anhydrous $FeCl_3$ (0.4 mmol) in 10 ml of AN

TABLE II. Oxidative Aryl–Aryl Coupling Reactions of Phenols and Phenol-ethers with some Iron(III) Solvates

Reagent[a]	A	B	C	D	E	F
$E°$ V *vs.* SCE[b]	1.10	1.30	1.73	1.38	1.32	1.18
Substrate			Product (%)[c]			
3a	**4** (50)	**4** (48)	**5a** (94)	**5a** (58)		
3b[d]		**4** (66)	**5b** (76)	**5b** (96)	**5b** (37)	**5b** (53)
3c		**5c** (60)	**5c** (73)	**5c** (60)		

a) A: $Fe(bpy)_3(ClO_4)_3 \cdot 3H_2O$. B: $Fe(ClO_4)_3 \cdot 9H_2O$ in AN. C: $Fe(AN)_6(ClO_4)_3$. D: $FeCl_3$ in AN. E: $Fe(ClO_4)_3$ in Ac_2O. F: $FeCl_3$ in Ac_2O. *b*) The formal redox potentials ($E°$) were determined from measurements of both the cyclic voltammograms of 0.01 M ferric solvates in the corresponding solvents containing 0.1 M Et_4NClO_4 and the rest potentials for equimolar mixture solutions of 0.01 M ferric and ferrous solvates by potentiometry. The voltage scan rate in cyclic voltammetry was 100 mVs^{-1}. The $E°$ of $FeCl_3$ in AN was determined from measurement of the rest potential for an equimolar mixture of 0.02 M $FeCl_3$ and $FeCl_2$ in AN solution, which was prepared by adding 2 mol eq. of Et_4NCl to 0.02 M $Fe(AN)_6(ClO_4)_2$ solution. The $E°$ of $FeCl_3$ in Ac_2O was also determined by the same method. *c*) Yields are isolated yields. *d*) The E_a values of **3a** in AN and Ac_2O were almost the same: 1.36 and 1.35 V *vs.* SCE, respectively.

($E_a = 1.22$ V) as organic substrates. The results are shown in Table II in comparison with those obtained using the iron(III) bipyridyl complex (reagent A).

Oxidations of the phenol **3a** with water containing complexes A and B gave the dienone **4**, but anhydrous reagents reagent C and D yielded the phenol **5a**, a rearranged product, after *para–para* aryl–aryl coupling reaction. Though oxidation of **3b** with reagent A did not give any coupling product because of the high oxidation potential of **3b**, oxidation with reagent B afforded the dienone **4** and oxidations with reagents C and D yielded the phenol-ether **5b** similarly to oxidation of **3a**. Oxidations of **3a** and **3c** with reagents E and F gave only complex mixtures. Thus, there seems to be a relationship between the redox potentials ($E°$) of reagents and the onset potentials (E_a) of organic substrates to afford coupling products from the results shown in Table II, except for reagents E and F. These exceptions may be due to the participation of Ac_2O to give acetates.

Experimental

All melting points are uncorrected. Infrared (IR) spectra were recorded with a Hitachi 260-10 spectrometer, proton nuclear magnetic resonance (^{1}H-NMR) spectra with a JEOL JNM-FX 100, JEOL JNM-GX 270 or Varian T-60 spectrometer with tetramethylsilane as an internal standard ($CDCl_3$ or DMSO-*d* soln.) and mass spectra (MS) with a JEOL JMS-d 300 spectrometer. Elementary analyses were done by Mrs. K. Sasaki, Ms. A. Sakamoto, and Ms. M. Takeda, Kissei Pharmaceutical Company, Matsumoto, Japan. Mallinckrodt silica gel (100 mesh) and Merck Kieselgel 60 F254 were used for column chromatography and thin-layer chromatography (TLC), respectively.

Cyclic voltammetric analyses were carried out using a Yanagimoto P8 polarograph. Voltammograms were recorded on a Riken F-35 X-Y recorder. (Details of the measurement have been given in ref. 3.) Rest potentials were taken on a Toa Denpa HM-20E potentiometer or a Hokuto Denko HA-501 potentiostat.

Typical Oxidation Procedure with $Fe(bpy)_3(ClO_4)_3 \cdot 3H_2O$ (Reagent A)——A solution of **1a** (120 mg, *ca.* 0.5 mmol) in AN (2 ml) was added in one portion to a partially suspended solution of $Fe(bpy)_3(ClO_4)_3 \cdot 3H_2O$ (880 mg, 1 mmol) and 42% HBF_4 aq. (1 ml) in AN (10 ml) with stirring at room temperature. At that time, the blue color of the ferric complex changed immediately to red (due to the ferrous complex). After several minutes, sat. NaCl (50 ml) was added to the reaction mixture, and extracted with ether–chloroform (3 : 1, 2 × 50 ml). The combined organic layer was washed with dil. HCl, brine, and sat. $NaHCO_3$, and then dried on Na_2SO_4 and evaporated. The residue was recrystallized from ether–hexane to yield 112 mg (95%) of **2a**[1c,e,6] as colorless crystals, mp 169—171 °C.

Typical Oxidation Procedure with $Fe(AN)_x(H_2O)_y(ClO_4)_3$ (Reagent B)——A solution of **3b** (381 mg, 1 mmol) in dry AN (2 ml) was added in one portion to a red solution of $Fe(AN)_x(H_2O)_y(ClO_4)_3$ [prepared by the addition of $Fe(ClO_4)_3 \cdot 9H_2O$ (2.064 g, 4 mmol) to AN (8 ml) at *ca.* 50 °C], with stirring at *ca.* 30 °C. After 5 min, dil. HCl was added to the reaction mixture, and the whole was extracted with chloroform (2 × 20 ml). The organic layer was washed with sat. $NaHCO_3$ and brine, and then dried on Na_2SO_4 and evaporated to give a brown liquid (324 mg) which gave a single spot on TLC. Silica gel column chromatography using chloroform as a eluent afforded the spirodienone **4**[1e,6] 240 mg (66%), mp 181—182 °C, as colorless crystals (ether–hexane).

6-Trifluoroacetyl-10,11-dibenzyloxy-2,3-methylenedioxy-5,6,7,8-tetrahydrodibenz[*c*,*e*]azocine (5c)——Oxidation of **3c** by the procedure described above gave **5c** in a yield of 60% as colorless crystals, mp 169—171 °C. IR (KBr) cm^{-1}: 1680. NMR ($CDCl_3$) δ: 2.24 (1H, dd, $J=14.7$, 9.5 Hz, C(8)-H), 2.87 (1H, dd, $J=14.2$, 7 Hz, C(7)-H), 3.11 (1H, dd, $J=14.2$, 9.5 Hz, C(7)-H), 3.23 (1H, d, $J=13.7$ Hz, C(5)-H), 4.20 (1H, dd, $J=14.7$, 7.0 Hz, C(8)-H), 5.13 (1H, d, $J=13.7$ Hz, C(5)-H), 5.13, 5.17 (each 2H, s, $-CH_2-Ph$), 5.98 (2H, s, $-OCH_2O-$), 6.67, 6.79, 6.86 (each 1H, s, aromatic-H), and 7.35 (11H, m, aromatic-H). MS *m/e*: Calcd for $C_{32}H_{26}F_3NO_5$ (M^+): 561.1763. Found: 561.1785. *Anal.* Calcd for $C_{32}H_{26}F_3NO_5$: C, 68.44; H, 4.67; N, 2.49. Found: C, 68.39; H, 4.57; N, 2.57.

Typical Oxidation Procedure with $Fe(AN)_6(ClO_4)_3$ (Reagent C)——A solution of $Fe(AN)_6(ClO_4)_3$ [prepared by adding Ac_2O (0.8 ml, *ca.* 9 mmol) to a solution of $Fe(ClO_4)_3 \cdot 9H_2O$ (516 mg, 1 mmol) in AN (6 ml)] was added in one portion to a solution of **3a** (180 mg, *ca.* 0.5 mmol) in AN (1 ml) with stirring at room temperature. After 3 min, sat. NaCl aq. (*ca.* 50 ml) and dil. HCl (*ca.* 5 ml) were added to the reaction mixture, and the whole was extracted with CH_2Cl_2. The organic layer was washed with sat. $NaHCO_3$ and brine, and then dried on Na_2SO_4 and evaporated. The white crystalline residue was recrystallized from ether–hexane to yield 170 mg (94%) of 6-trifluoroacetyl-11-hydroxy-2,3-methylenedioxy-5,6,7,8-tetrahydrodibenz[*c*,*e*]azocine (**5a**) as colorless crystals, mp 261—263 °C. IR (Nujol) cm^{-1}: 3400, 1670. NMR (DMSO-*d*) δ: 2.10 (1H, dd, $J=14.5$, 10.8 Hz, C(8)-H), 3.04 (1H, dd, $J=14.5$, 6 Hz, C(8)-H), 3.24 (1H, dd, $J=13.7$, 10.8 Hz, C(7)-H), 3.26 (1H, d, $J=13.8$ Hz, C(5)-H), 4.08 (1H, dd, $J=13.7$, 6 Hz, C(7)-H), 4.98 (1H, d, $J=13.8$ Hz, C(5)-H), 6.07 (2H, d, $J=9.5$ Hz, $-OCH_2O-$), 6.64 (1H, d, $J=2.4$ Hz, C(12)-H), 6.80 (1H, dd, $J=8.4$, 2.4 Hz, C(10)-H), 6.84 (1H, s, C(1)-H), 7.16 (1H, d, $J=8.4$ Hz, C(9)-H), 7.17 (1H, s, C(4)-H), and 9.36 (1H, s, –OH). MS *m/e*: Calcd for $C_{18}H_{14}F_3NO_4$ (M^+): 365.0875. Found: 365.0887.

Typical Oxidation Procedure with $Fe(AN)_6(FeCl_4)_3$ (Reagent D)——A solution of anhydrous $FeCl_3$ (648 mg, 4 mmol) in dry AN (6 ml) was added in one portion to a solution of **3b** (190 mg, 0.5 mmol) in AN (1 ml) with stirring at room temperature. After 3 min, sat. NaCl aq. (*ca.* 50 ml) and dil. HCl (*ca.* 5 ml) were added, and the whole was extracted with CH_2Cl_2 (2 × 50 ml). The combined organic layer was washed with sat. $NaHCO_3$ and brine, and then dried on Na_2SO_4 and evaporated. The white crystalline residue was recrystallized from CH_2Cl_2–ether to yield 182 mg (96%) of 6-trifluoroacetyl-11-methoxy-2,3-methylenedioxy-5,6,7,8-tetrahydrodibenz[*c*,*e*]azocine (**5b**) as colorless crystals, mp 240—241 °C. IR (Nujol) cm^{-1}: 1690. NMR ($CDCl_3$) δ: 2.41 (1H, dd, $J=14.7$, 10 Hz, C(8)-H), 2.97 (1H, dd, $J=14.7$, 6 Hz, C(8)-H), 3.18 (1H, dd, $J=14.2$, 10 Hz, C(7)-H), 3.27 (1H, d, $J=13.8$ Hz, C(5)-H), 3.83 (3H, s, –OMe), 4.22 (1H, dd, $J=14.2$, 6 Hz, C(7)-H), 5.17 (1H, d, $J=13.8$ Hz, C(5)-H), 6.01 (2H, dd, $J=6.23$, 1.35 Hz, $-OCH_2O-$), 6.79 (1H, s, C(1)-H), 6.81 (1H, d, $J=2.8$ Hz, C(12)-H), 6.92 (1H, dd, $J=8.5$, 2.8 Hz, C(10)-H), 7.16 (1H, d, $J=8.5$ Hz, C(9)-H), and 7.37 (1H, s, C(4)-H). *Anal.* Calcd for $C_{19}H_{16}F_3NO_4$: C, 60.16; H, 4.25; N, 3.69. Found: C, 60.34; H, 4.35; N, 3.91.

Typical Oxidation Procedure with $Fe(Ac_2O)_3(ClO_4)_3$ (Reagent E)——A solution of $Fe(Ac_2O)_3(ClO_4)_3$ [prepared from $Fe(ClO_4)_3 \cdot 9H_2O$ (516 mg, 1 mmol) and Ac_2O (4 ml)] was added in one portion to a solution of **3b** (190 mg, 0.5 mmol) in Ac_2O (1 ml) with stirring at room temperature. After 3 min, the reaction mixture was poured into ice water, then dil. HCl (*ca.* 5 ml) was added and the whole was stirred for several minutes to decompose Ac_2O. The resulted solution was extracted with CH_2Cl_2. The organic layer was washed with sat. $NaHCO_3$ and brine, dried on Na_2SO_4, and then evaporated. The residue was purified on silica gel column chromatography using chloroform as an eluent to give **5b** in 37% yield.

Typical Oxidation Procedure with $Fe(Ac_2O)_3(FeCl_4)_3$ (Reagent F)——A solution of $FeCl_3$ (680 mg, 4 mmol) in Ac_2O (4 ml) was added in one portion to a solution of **3b** (190 mg, 0.5 mmol) in Ac_2O (1 ml) with stirring at room temperature. After 3 min, the reaction mixture was worked up and purified as in the procedure for reagent E.

References and Notes

1) The following metal salts and complexes have been used for oxidative phenolic coupling reactions during the past decade. $Mn(CH_3COCHCOCH_3)_3$: *a*) M. J. S. Dewar and T. Nakaya, *J. Am. Chem. Soc.*, **90**, 7134 (1968); $VOCl_3$: *b*) M. A. Schwartz, R. A. Holton, and S. W. Scott, *ibid.*, **91**, 2800 (1969); *c*) M. A. Schwartz, B. F. Rose, R. A. Holton, S. W. Scott, and B. Vishnuvajjala, *ibid.*, **99**, 2571 (1977); $FeCl_2(DMF)_3FeCl_4$: *d*) S. Tobinaga and E. Kotani, *ibid.*, **94**, 309 (1972); $Tl(OCOCF_3)_3$: *e*) M. A. Schwartz, B. F. Rose, and B. Vishnuvajjala, *ibid.*, **95**, 612 (1973); *f*) M. A. Schwartz and I. S. Mami, *ibid.*, **97**, 1239 (1975); VOF_3: *g*) S. M. Kupchan and A. J. Liepa, *ibid.*, **95**, 4062 (1973); *h*) S. M. Kupchan, A. J. Liepa, V. Kameswaran, and R. F. Bryan, *ibid.*, **95**, 6861 (1973); O_2–Cu_2Cl_2–pyridine: *i*) T. Kametani, M. Ihara, M. Takemura, Y. Satoh, H. Terasawa, Y. Ohta, K. Fukumoto, and K. Takahashi, *ibid.*, **99**, 3805 (1977); $MoOCl_4$: *j*) F. S. El-Feraly, Y. M. Chan, M. A. El-Sohly, and C. E. Turner, *Experientia*, **35**, 1131 (1979).

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$FeCl_3$–SiO_2: *d*) T. C. Jempty, L. L. Miller, and Y. Mazur, *ibid.*, **45**, 749 (1980).
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4) F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, **1952**, 3570.
5) A related iron complex, tris(1,10-phenanthroline)iron(III) perchlorate, Fe(*o*-phen)$_3$(ClO$_4$)$_3$·H_2O, $E^\circ = 1.12$ V, is known. Oxidations of **3a**, **3b**, and **7a** with this complex gave almost the same results as in the case of the bipyridyl complex.
6) E. Kotani, N. Takeuchi, and S. Tobinaga, *J. Chem. Soc., Chem. Commun.*, **1973**, 550.
7) *a*) R. B. Herbert and C. J. Moody, *J. Chem. Soc., Chem. Commun.*, **1970**, 121; *b*) E. Kotani, M. Kitazawa, and S. Tobinaga, *Tetrahedron*, **30**, 3027 (1974) and refs. cited therein.
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