Iron(III) Picolinate-Catalyzed Oxidative Demethylation of *N,N*-Dimethylaniline with Hydrogen Peroxide in the Presence of Acetic Anhydride

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Received June 12, 1997; accepted August 11, 1997

Oxidation of *N,N*-dimethylaniline (1) utilizing the $Fe(PA)_3/H_2O_2/MeCN$ system and the $Fe(ClO_4)_3 \cdot 9H_2O/PAH\text{-}Py/H_2O_2/MeCN$ system, simple model systems for mono-oxygenases, in the presence of acetic anhydride (Ac_2O) afforded predominantly the *N*-acetylative demethylation product, *N*-methylacetanilide (4), along with a few other compounds.

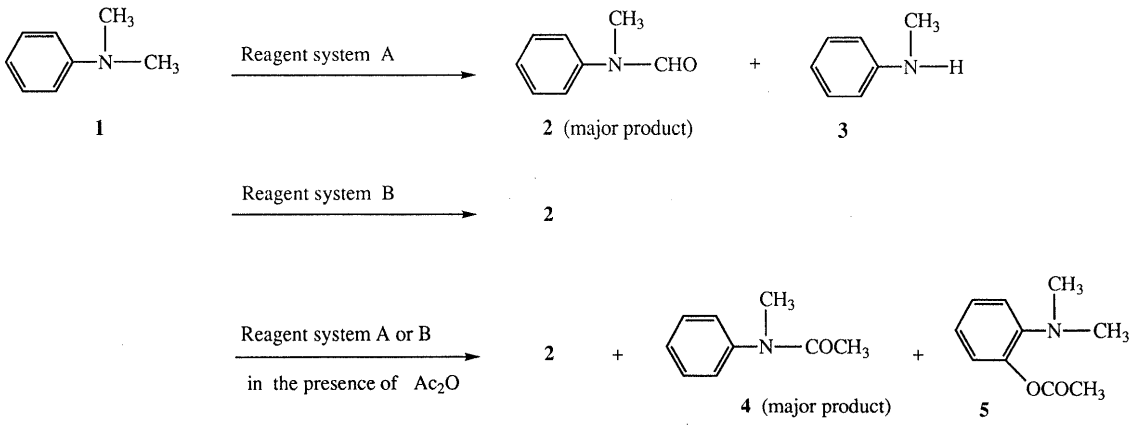
Key words oxidative demethylation; *N*-acylative dealkylation; *N,N*-dimethylaniline; iron(III) picolinate; acetic anhydride; hydrogen peroxide

The oxidation of amines by a number of different enzymes including the cytochrome P-450s is a reaction of central importance in the biotransformation of a great many organic compounds, both endogenous and xenobiotic.[1,2]

Model reactions of oxidation of a tertiary amine, *N,N*-dimethylaniline, by means of chemical,[3] electrolytic,[4] and photochemical[5] methods have been studied extensively. Among the various reagent systems studied, several employing transition metalcatalysts, *e.g.*, Fe^{III}TPPCl (*meso*-tetra-phenylporphinato iron(III) chloride),[3a,d,f,g,i] Co^{II}(bpy; bipyridyl)$_2(ClO_4)_2$,[3b] and $RuCl_2(PPh_3)_2$[3c,h] with various oxygen sources have been used as models for cytochrome P-450 to elucidate its biotransformation mechanisms. We have been searching[6] for a catalytic reagent system which involves the generation of a high-valent oxoiron species (abbreviated as $Fe^V=O$) as the active species. Recently, we reported that the modified system Fe(PA; picolinate)$_3/H_2O_2/MeCN$, as an alternative to the Gif model system for mono-oxygenase, is effective in stereoselective 7α-hydroxylation of 3β-acetoxy-Δ^5 steroids.[6e] During further investigations to characterize this reagent system containing iron(III)picolinate [$Fe(PA)_3$] with hydrogen peroxide (H_2O_2), we found that oxidation of *N,N*-dimethylaniline (**1**) utilizing the $Fe(PA)_3/H_2O_2$/MeCN system (reagent system A) and the $Fe(ClO_4)_3 \cdot 9H_2O$/picolinic acid(PAH)–pyridine(Py)/H_2O_2/MeCN system (reagent system B) in the presence of acetic anhydride (Ac_2O) predominantly provided *N*-methylacetanilide (**4**), along with a few other compounds. We report herein *N*-acetylative demethylation of *N,N*-dimethylaniline by various reagent systems.

We investigated the non-enzymic oxidation of **1** with various systems using iron(III) picolinate as shown in Table 1. First, oxidation of **1** was carried out with reagent system A according to the following procedure. A 30% aqueous H_2O_2 solution (30 mmol) was added dropwise to a stirred solution of **1** (10 mmol) and $Fe^{III}(PA)_3$ (1 mmol) in MeCN (50 ml) under a nitrogen atmosphere at 0 °C and the reaction mixture was stirred for 1 h. The above reaction afforded the *N*-formylation product, *N*-methylformanilide (**2**) in 43.1% yield along with the *N*-demethylation product, *N*-methylaniline (**3**) in 15.7% yield (run 1). Similar reaction of **1** using reagent system B gave only **2** in good yield (run 2).

The character of reagent system B is considered to be similar to that of reagent system A, though the iron(III) picolinate was used as a solution of components in place



Reagent system A ; $Fe(PA)_3/H_2O_2/MeCN$, Reagent system B; $Fe(ClO_4)_3 \cdot 9H_2O/PAH\text{-}py/H_2O_2/MeCN$

Chart 1

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Table 1. Oxidation of *N*,*N*-Dimethylaniline (**1**) with Various Reagent Systems in the Presence or Absence of Acetic Anhydride (Ac_2O)

Run	Reagent system	Product (yield, %)				Recovery (%)
1	$Fe(PA)_3/H_2O_2/MeCN$ (A)[a]	**2** (43.1)	**3** (15.7)			**1** (21.1)
2	$Fe(ClO_4)_3 \cdot 9H_2O/PAH\text{-}py/H_2O_2/MeCN$ (B)[b]	**2** (89.1)				—
3	Reagent system (A)+Ac_2O[a]	**2** (5.5)	**4** (40.0)	**5** (6.8)		**1** (25.0)
4	Reagent system (B)+Ac_2O[b]	**2** (13.7)	**4** (73.1)	**5** (12.5)		—
5	$Mn(PA)_3(H_2O)/H_2O_2/MeCN$ (C)+Ac_2O[b]	**2** (15.9)	**4** (51.7)	**5** (8.9)		—
6	$H_2O_2/MeCN+Ac_2O$[b]	**2** (2.9)	**3** (1.5)	**4** (16.0)	**5** (67.5)	**1** (8.4)
7	Reagent system (A)+AcOH[b]	**2** (92.0)				**1** (2.4)
8	$Fe(PA)_3/AcOOH/MeCN$ (D)[b]	**2** (71.9)	**3** (16.5)	**4** (3.4)		**1** (5.3)

a) Isolated yields after silica gel column chromatography. *b*) Yields were determined by GLC analysis.

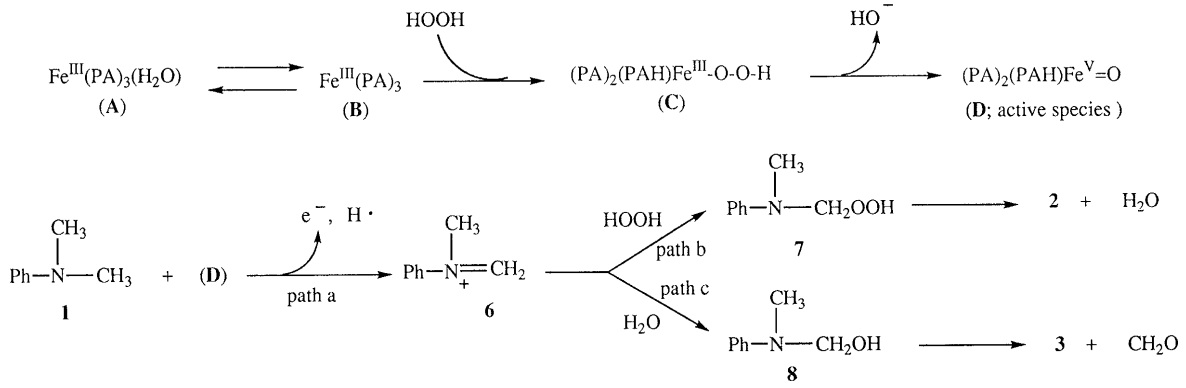

Chart 2. Proposed Mechanism for the Reaction of **1** Using Systems A and B in the Absence of Acetic Anhydride

of the complex itself in reagent system A. This was supported by the following facts: (i) crystals of $Fe(PA)_3$ could be isolated from reagent system B in the presence of Ac_2O without 30% H_2O_2 and (ii) the cyclic voltammogram of a solution of $Fe(PA)_3$ (1 mmol) in MeCN (5 ml) shows almost the same reversible wave as that of a solution of $Fe(ClO_4)_3 \cdot 9H_2O$ (1 mmol), picolinic acid (3 mmol), and pyridine (5 mmol) in MeCN (5 ml).[7]

We found that the major product changed drastically in the presence of Ac_2O in reagent systems A and B. In the reaction of **1** with reagent system A in the presence of Ac_2O, the *N*-acetylative demethylation product, *N*-methylacetanilide (**4**) (40.0%) was predominantly produced, together with **2** (5.5%) and 2-acetoxy-*N*,*N*-dimethylaniline (**5**) (6.8%) (run 3). Similar reaction of **1** using reagent system B in the presence of Ac_2O gave **4** (73.1%) as major product, along with **2** (13.7%) and **5** (12.5%) (run 4).

Next, we investigated the reaction of **1** with another reagent system, $Mn(PA)_3(H_2O)/H_2O_2/MeCN$ (reagent system C) in the presence of Ac_2O for comparison with the reaction using reagent system A in the presence of Ac_2O. The reaction afforded the same oxidation product in a similar yield (run 5).

To throw light on the formation mechanism of **4** in reagent system A or B in the presence of Ac_2O, the following reactions were carried out. In the absence of iron-metal complex $Fe(PA)_3$, the Polonovski-type reaction[8] of **1** with $H_2O_2/MeCN$ in the presence of Ac_2O gave mainly **5** in 67.5% yield (run 6). This result suggests that the major pathway for the formation of **4** was not the Polonovski reaction process. In addition, the reaction with reagent system A in the presence of AcOH instead of Ac_2O gave **2** in 92% yield without the formation of **4** (run 7). This result indicated that AcOH is not involved in the formation of **4**.

Although various reaction mechanisms for oxidation of tertiary amine by P-450 enzymes[9,10] and by model systems[3] have been proposed, three major mechanisms are currently considered plausible: (i) an electron/proton transfer mechanism (*via* the formation of aminium cation radicals), (ii) a hydrogen atom abstraction mechanism (*via* the formation of α-primary carbon radicals), and (iii) an electron/hydrogen atom transfer mechanism (*via* the formation of iminium cations).

A probable mechanism for the reaction of *N*,*N*-dimethylaniline (**1**) using reagent systems A and B in the presence of Ac_2O is illustrated in Chart 3. It is analogous to that proposed for the reaction with the reagent systems A and B without Ac_2O, as shown in Chart 2, until the iminium cation **6** is formed. The reaction of the iron complex, $Fe^{III}(PA)_3$ (B), with peracetic acid (AcOOH) prepared from the reaction between Ac_2O and H_2O_2 gives the acylperoxy complex (E) which undergoes O–O bond cleavage to generate the $Fe^V=O$ complex (D) (iron may be in the form of $Fe^V=O$, a hypothetical active species[6e]). Subsequently, the dimethylaniline **1** would undergo electron transfer with the $Fe^V=O$ complex (D) followed by α-hydrogen atom abstraction to give the iminium cation **6**, in which the Fe^{III} complex (B) completes the catalytic cycle (path a). Compound **6** reacts with Ac_2O to give the acetanilide **4** and formaldehyde *via* the formation of **9** (path d). This formation process of **4** is similar to that of the previously reported reaction of **1** with $Pb(OAc)_4$,[11a,b,c] $Mn(OAc)_3$,[11d] etc. in $CHCl_3$–Ac_2O. On the other hand, the formanilide **2** is generated by

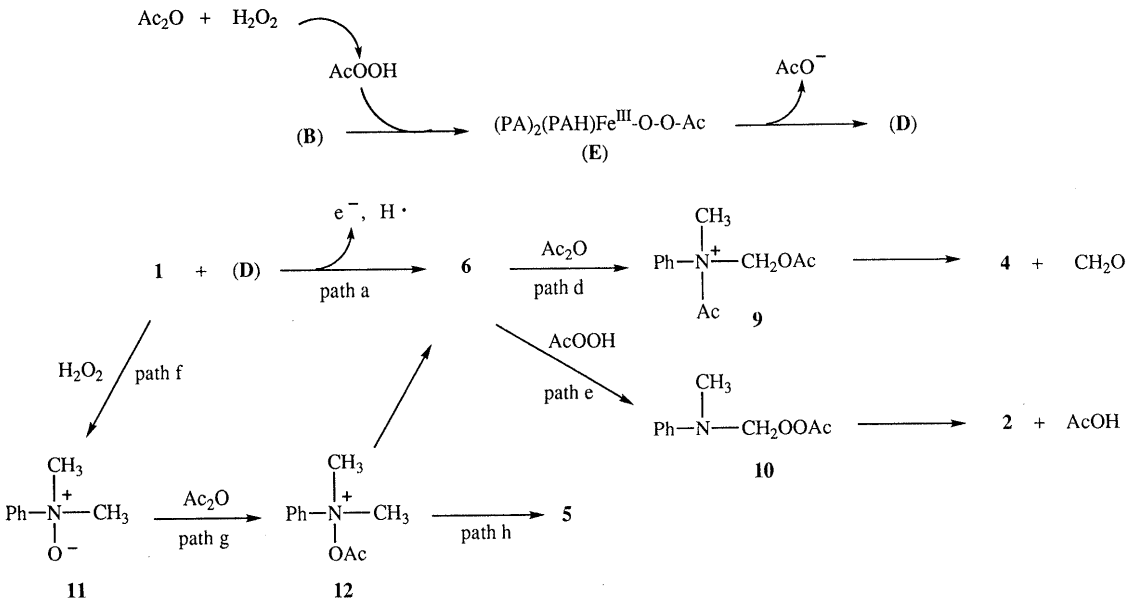

Chart 3. Proposed Mechanism for the Reaction of **1** Using Systems A and B in the Presence of Acetic Anhydride

nucleophilic attack[3c,e,4,12] of AcOOH on the iminium cation **6** followed by loss of AcOH (path e).

This speculation is also supported by the result of the reaction with reagent system (D) using AcOOH as an oxidant in place of H_2O_2 (run 8). The acetoxy compound **5** is formed through a minor pathway, that is, the oxidation of **1** by H_2O_2 contained in these systems followed by the Polonovski reaction process from **11** (path f→path g→path h).

The preferential formation of **4** in comparison with **2** in the reactions with reagent systems A and B in the presence of Ac_2O may be due to the existence of sufficient Ac_2O in these systems in the presence of Ac_2O although the details are not clear. Accordingly, **6** reacts more rapidly with Ac_2O in preference to AcOOH to give **4**.

On the other hand, the preferential formation of **4** in comparison with **2** in the reactions with reagent systems A and B in the absence of Ac_2O may be due to the high nucleophilicity of H_2O_2 (the so-called "α effect"[13]) relative to H_2O in the nucleophilic attack on the iminium cation **6**.

The oxidation of *N*,*N*-dimethylaniline (**1**) with reagent systems A and B thus proceeds through two pathways depending on the presence or absence of Ac_2O. In the absence of Ac_2O, the *N*-formylation product **2** was predominantly obtained, while with Ac_2O the *N*-acetylative demethylation product **4** was mainly produced. The added Ac_2O is considered to act as a trapping reagent for the iminium cation **6**, including a function as an indirect effector[14] in acceleration of the O–O bond cleavage for generation of the high-valent oxoiron species (D).

Further investigations on the reaction mechanism of **1** in these reagent systems are in progress.

Experimental

All melting points are uncorrected. Infrared (IR) spectra were recorded with a JASCO IR-700 spectrometer, and ^1H- and ^{13}C-NMR spectra with JEOL JNM-EX90, JNM-GX270 and JNM-GSX500 spectrometers, with tetramethylsilane as an internal standard ($CDCl_3$ solution). Mass spectra were recorded on a JEOL JMS-D300 spectrometer. Elemental analyses were done using a Yanaco CHN-MT-3 apparatus. Wako silica gel C-200 (200 mesh) and Merck Kieselgel 60 F_{254} were used for column chromatography and thin-layer chromatography (TLC), respectively. Each organic extract was dried over Na_2SO_4. Preparative HPLC (high-performance liquid chromatography) was carried out with a JASCO HPLC system (pump, JASCO 880; RI-detector, JASCO 830) using a silica-3301-N (Senshu Pac, 8f × 300 mm i.d.) column. GLC-MS data were obtained with a Shimazu QP-5000 spectrometer. GLC analysis was carried out with a Shimazu GC-380 gas chromatograph.

N,*N*-Dimethylaniline (**1**), *N*-methylformanilide (**2**), *N*-methylaniline (**3**), *N*-methylacetanilide (**4**), and 2-acetoxy-*N*,*N*-dimethylaniline (**5**) were commercial products (Tokyo Kasei Co.). $Mn(PA)_3(H_2O)$ was prepared by the method reported previously.[15]

Preparation of Iron(III) Picolinate, $Fe(PA)_3$ A solution of $Fe(ClO_4)_3 \cdot 9H_2O$ (25.8 g, 50 mmol) in H_2O (100 ml) was added in one portion with stirring to a mixture of picolinic acid (18.5 g, 150 mmol) and NaOH (6 g, 150 mmol) in H_2O (200 ml), and the whole was stirred for 5 min. The resulting pale yellow precipitate was collected by filtration, and washed with water and acetone to give the crude product $Fe(PA)_3 \cdot H_2O$. The crude product was recrystallized from MeOH to yield 19.0 g (90%) of the iron complex $Fe(PA)_3$ as pale yellow-green crystals, mp 285—287 °C. *Anal.* Calcd for $C_{18}H_{12}O_6N_3Fe$: C, 51.21; H, 2.87; N, 9.95. Found: C, 50.97; H, 3.09; N, 9.72.

Isolation of $Fe(PA)_3$ from Reagent System B in the Presence of Ac_2O without 30% H_2O_2 A solution of picolinic acid (370 mg, 3 mmol) and pyridine (400 mg, 5 mmol) in MeCN (10 ml) was added with stirring to a mixture of $Fe(ClO_4)_3 \cdot 9H_2O$ (516 mg, 1 mmol) and Ac_2O (2 ml, 21.2 mmol), and the whole was stirred for 5 min. The solvent was evaporated off *in vacuo*, and anhydrous benzene was added to the residue. The resulting precipitates were collected by filtration, and washed with anhydrous benzene to give the crude product, which was recrystallized from MeOH to yield 367 mg (87%) of the iron complex $Fe(PA)_3$ as pale yellow-green crystals. The structure of the resulting $Fe(PA)_3$ was identified by comparison of the physical data with those of $Fe(PA)_3$ prepared by the reaction of $Fe(ClO_4)_3 \cdot 9H_2O$ in H_2O, picolinic acid, and NaOH in H_2O as described above.

Procedure for Oxidation of *N*,*N*-Dimethylaniline (1) with the $Fe(PA)_3$/H_2O_2/MeCN System (Reagent System A) A 30% H_2O_2 solution (3 ml, 30 mmol) was added dropwise to a solution of $Fe(PA)_3$ (422 mg, 1 mmol), and **1** (1.21 g, 10 mmol) in MeCN (50 ml) at 0 °C with vigorous stirring under a nitrogen atmosphere, and the mixture was stirred at 0 °C for 1 h. It was then poured into ice water and extracted with ether. The organic layer was washed with saturated Na_2SO_3, $NaHCO_3$, and brine. The ethereal solution was dried and concentrated. The residue was purified by column chromatography on silica gel with hexane–AcOEt (20 : 1, v/v). The first fraction contained the recovered

material **1** (255 mg, 21.1%). From the second fraction *N*-methylaniline **3** (168 mg, 15.7%) was obtained. From the third fraction the formanilide **2** (582 mg, 43.1%) was obtained. Analysis by GLC-MS and GLC confirmed the formation of **1**, **3**, and **2**.

With $Fe(ClO_4)_3 \cdot 9H_2O$/PAH-Py/H_2O_2/MeCN (Reagent System B) A 30% H_2O_2 solution (0.3 ml, 3 mmol) was added dropwise to a solution of $Fe(ClO_4)_3 \cdot 9H_2O$ (51.6 mg, 0.1 mmol), picolinic acid (37.0 mg, 0.3 mmol), pyridine (40.0 mg, 0.5 mmol), and **1** (121 mg, 1 mmol) in MeCN (5 ml) at 0 °C with vigorous stirring under a nitrogen atmosphere, and the mixture was stirred at 0 °C for 1 h. The reaction mixture was worked up according to the procedure in the case of system A. Analysis by GLC-MS and GLC confirmed the formation of **2**. The yield is listed in Table 1.

With $Fe(PA)_3$/H_2O_2/MeCN (Reagent System A) in the Presence of Ac_2O A 30% H_2O_2 solution (3 ml, 30 mmol) was added dropwise to a solution of Fe $(PA)_3$ (422 mg, 1 mmol), Ac_2O (10 ml, 106 mmol) and **1** (1.21 g, 10 mmol) in MeCN (50 ml) at 0 °C, with vigorous stirring under a nitrogen atmosphere, and the whole was stirred at 0 °C for 1 h. The reaction mixture was poured into ice water and extracted with ether. The organic layer was washed with saturated Na_2SO_3, $NaHCO_3$, and brine. The ethereal solution was dried and concentrated. The residue was purified by column chromatography on silica gel with hexane–AcOEt (20 : 1, v/v). The first fraction contained the recovered material **1** (303 mg, 25.0%). The second fraction gave the 2-acetoxyaniline **5** (122 mg, 6.8%), and the third fraction, the formanilide **2** (74 mg, 5.5%). From the end fraction the acetanilide **4** (596 mg, 40.0%) was obtained. Analysis by GLC-MS and GLC confirmed the formation of **1**, **5**, **2**, and **4**.

With $Fe(ClO_4)_3 \cdot 9H_2O$/PAH-Py/H_2O_2/MeCN (Reagent System B) in the Presence of Ac_2O A 30% H_2O_2 solution (0.3 ml, 3 mmol) was added dropwise to a solution of $Fe(ClO_4)_3 \cdot 9H_2O$ (51.6 mg, 0.1 mmol), picolinic acid (37 mg, 0.3 mmol), pyridine (40 mg, 0.5 mmol), Ac_2O (1 ml, 10.6 mmol), and **1** (121 mg, 1 mmol) in MeCN (5 ml) at 0 °C, with vigorous stirring under a nitrogen atmosphere, and the whole was stirred at 0 °C for 1 h. The reaction mixture was worked up according to the procedure in the case of system A. Analysis by GLC-MS and GLC confirmed the formation of **5**, **2**, and **4**. The yield is listed in Table 1.

With $Mn(PA)_3(H_2O)$/H_2O_2/MeCN (Reagent System C) in the Presence of Ac_2O This reaction was carried out according to the procedure used for the oxidation with system A in the presence of Ac_2O. Analysis by GLC-MS and GLC confirmed the formation of **5**, **2**, and **4**. The yield is listed in Table 1.

With H_2O_2/MeCN in the Presence of Ac_2O (the Polonovski-type Reaction) A 30% H_2O_2 solution (0.3 ml, 3 mmol) was added dropwise to a solution of Ac_2O (1 ml, 10.6 mmol), and **1** (121 mg, 1 mmol) in MeCN (5 ml) at room temperature under vigorous stirring, and the whole was stirred at room temperature for 1 h. The reaction mixture was worked up according to the procedure used for oxidation with system A in the presence of Ac_2O. Analysis by GLC-MS and GLC confirmed the formation of **1**, **3**, **5**, **2**, and **4**. The yield is listed in Table 1.

With $Fe(PA)_3$/H_2O_2/AcOH (Reagent System A) in the Presence of AcOH A 30% H_2O_2 solution (0.3 ml, 3 mmol) was added dropwise to a solution of $Fe(PA)_3$ (42.2 mg, 0.1 mmol), AcOH (1.5 ml, 25 mmol), and **1** (121 mg, 1 mmol) in MeCN (5 ml) at 0 °C, with vigorous stirring under a nitrogen atmosphere, and the whole was stirred at 0 °C for 1 h. The reaction mixture was worked up according to the procedure used for oxidation with system A. Analysis by GLC-MS and GLC confirmed the formation of **1** and **2**. The yield is listed in Table 1.

With $Fe(PA)_3$/AcOOH/MeCN (Reagent System D) A 40% AcOOH solution (0.9 ml, 3 mmol) was added dropwise to a solution of $Fe(PA)_3$ (42.2 mg, 0.1 mmol), and **1** (121 mg, 1 mmol) in MeCN (5 ml) at 0 °C, with vigorous stirring under a nitrogen atmosphere, and the whole was stirred at 0 °C for 1 h. The reaction mixture was worked up according to the procedure used for oxidation with system A. Analysis by GLC-MS and GLC confirmed the formation of **3**, **2**, and **4**. The yield is listed in Table 1.

References and Notes

1) Silverman R. B., "Advances in Electron Transfer Chemistry," Vol. 2, Mariano P. S., ed. JAL Press, Greenwich, CT, 1992, p. 177.
2) Miwa G. T., Walsh J. S., Kedderis G. L., Hollenberg P. F., *J. Biol. Chem.*, **258**, 14445—14449 (1983).
3) *a*) Shannon P., Bruice T., *J. Am. Chem. Soc.*, **103**, 4580—4582 (1981); *b*) Sobkowiak A., Sawyer D. T., *ibid.*, **113**, 9520—9523 (1991); *c*) Murahashi S., Naota T., Yonemura K., *ibid.*, **110**, 8256—8258 (1988); *d*) Murata S., Miura M., Nomura M., *J. Chem. Soc., Chem. Commun.*, **1989**, 116—118; *e*) Murahashi S., Naota T., Miyaguchi N., Nakato T., *Tetrahedron Lett.*, **33**, 6991—6994 (1992); *f*) Miyata N., Kiuchi H., Hirobe M., *Chem. Pharm. Bull.*, **29**, 1489—1492 (1981); *g*) Mori T., Santa T., Higuchi T., Mashino T., Hirobe M., *ibid.*, **41**, 292—295 (1993); *h*) Murata S., Suzuki K., Tamatani A., Miura M., Nomura M., *J. Chem. Soc. Perkin Trans. 1*, **1992**, 1387—1392; *i*) Fujimori K., Fujiwara S., Takata T., Oae S., *Tetrahedron Lett.*, **27**, 581—584 (1986); *j*) Dasgupta G., Mahanti M. K., *Bull. Soc. Chim. Fra.*, 492—496 (1986).
4) Shono T., Matsumura Y., Inoue K., Ohmizu H., Kashimura S., *J. Am. Chem. Soc.*, **104**, 5753—5755 (1982).
5) *a*) Gan H., Zhao Whitten D. G., *J. Am. Chem. Soc.*, **113**, 9409—9411 (1991); *b*) Santamaria J., Ouchabane R., Rigaudy J., *Tetrahedron Lett.*, **30**, 3977—3980 (1989).
6) *a*) Kotani E., Kobayashi S., Ishii Y., Tobinaga S., *Chem. Pharm. Bull.*, **33**, 4671—4679 (1985); *b*) Kotani E., Midorikawa A., Tanaka A., Tobinaga S., *ibid.*, **35**, 916—919 (1987); *c*) Monden R., Manaka A., Kasama T., Kotani E., Tobinaga S., *ibid.*, **36**, 1926—1929 (1988); *d*) Kotani E., Takeya T., Yoshiike M., Watanabe A., Tobinaga S., *ibid.*, **45**, 981—986 (1997); *e*) Kotani E., Takeya T., Egawa H., Tobinaga S., *ibid.*, **45**, 750—752 (1997).
7) Unpublished data.
8) *a*) Grierson D., *Org. React.*, **39**, 85—295 (1990) and references cited therein; *b*) Oae S., Kitao T., Kitaoka Y., *J. Am. Chem. Soc.*, **84**, 3366—3369 (1962); *c*) Oae S., Asai N., Fujimori K., *Bull. Chem. Soc. Jpn.*, **52**, 2409—2412 (1979); *d*) Huisgen R., Bayerlein F., Heydkamp W., *Chem, Ber.*, **92**, 3223—3241 (1959).
9) *a*) Dinnocenzo J. P., Karki S. B., Jones J. P., *J. Am. Chem. Soc.*, **115**, 7111—7116 (1993) and references cited therein; *b*) Karki S. B., Dinnocenzo J. P., Jones J. P., Korzekwa K. R., *ibid.*, **117**, 3657—3664 (1995).
10) Guengerich F. P., Yun C.-H., Macdonald T. L., *J. Biol. Chem.*, **271**, 27321—27329 (1996) and references cited therein.
11) *a*) Galliani G., Rindone B., *J. Chem. Soc. Perkin Trans. 2*, **1976**, 1803—1805; *b*) Galliani G., Rindone B., Scolastico C., *Tetrahedron Lett.*, **1975**, 1285—1288; *c*) Horner L., Winkelmann E., Knapp K., Ludwig W., *Chem. Ber.*, **92**, 288—292 (1959); *d*) Rindone B., Scolastico C., *Tetrahedron Lett.*, **1974**, 3379—3382.
12) Shono T., Matsumura Y., Inoue K., Ohmizu H., Kashimura S., *J. Am. Chem. Soc.*, **104**, 5753—5757 (1982).
13) *a*) Jencks W. P., Carriuolo J., *J. Am. Chem. Soc.*, **82**, 1778—1786 (1960); *b*) Edward J. O., Peason R. G., *ibid.*, **84**, 16—24 (1962); *c*) Gregory M. J., Bruice T. C., *ibid.*, **89**, 2327—2330 (1967).
14) *a*) Creager S. E., Raybuck S. A., Murray R. W., *J. Am. Chem. Soc.*, **108**, 4225—4227 (1986); *b*) Ojima F., Kobayashi N., Osa T., *Bull. Chem. Soc. Jpn.*, **63**, 1374—1380 (1990); *c*) Nagano T., Yoshikawa K., Hirobe M., *Tetrahedron Lett.*, **1980**, 297—301; *d*) Karasevich E. I., Khenkin A. M., Shilov A. E., *J. Chem. Soc., Chem. Commun.*, **1987**, 731—732.
15) Figgis N. B., Raston C. L., Sharma R. P., White A. H., *Aust. J. Chem.*, **31**, 2545—2548 (1978).