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Preparation and Reactivities of Hexakisacetonitrile Iron(III) Perchlorate and Related Complexes as Strong Oxidizing Reagents

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The iron(III) complexes $Fe(S)_6(ClO_4)_3$, S=solvent, were prepared from $Fe(H_2O)_6(ClO_4)_3$ in the donor solvents. Reactions of alkylbenzenes with $Fe(AN)_6(ClO_4)_3$ (AN=acetonitrile) were explored because the AN complex has the highest formal redox potential, $E^\circ = 1.73$ V *vs.* SCE, among these complexes. Oxidation of the primary alkylbenzenes by the iron(III) AN complex gave the corresponding acetamides (Table II). Oxidation of the secondary alkylbenzenes, namely, cumene, 2-phenylbutane, and 2-*exo*-phenylnorbornane, afforded the corresponding acetates and acetamides (Charts 2 and 3), consuming over 4 mol eq of reagent. Reactions of *p*-xylene and hexamethylbenzene with $Fe(CH_2=CHCN)_6(ClO_4)_3$ also yielded the amides **31a** and **31b**. These results demonstrate the applicability of the iron(III) AN complex as a powerful reagent to oxidize organic substrates which have onset potentials of anodic current of *ca.* 2.0 V *vs.* SCE.

Keywords——oxidation; primary alkylbenzene; secondary alkylbenzene; oxidizing reagent; iron(III) perchlorate solvate; hexakisacetonitrile iron(III) perchlorate; hexakisacrylonitrile iron(III) perchlorate

There is considerable interest in iron complexes which are effective oxidizing agents for organic compounds from the viewpoints of safety and the involvement in the reactions of enzymes such as iron porphyrin oxidases.[1] Although a few iron (III) complexes which have moderately high redox potentials, namely, $Fe(phen)_3(ClO_4)_3 \cdot H_2O$ ($E^\circ = 1.12$ V), $Fe(5\text{-}NO_2\text{-}phen)_3(ClO_4)_3$ ($E^\circ = 1.25$ V), and $Fe(bpy)_3(ClO_4)_3 \cdot 3H_2O$ ($E^\circ = 1.10$ V), *etc.* (E°: formal redox potential, V *vs.* SCE) are known, iron(III) complexes which have higher redox potentials are required. The present paper is concerned with the preparation of iron(III) complexes which have high redox potentials, hexakisacetonitrile iron(III) perchlorate, $Fe(AN)_6(ClO_4)_3$,[2] (AN: acetonitrile), $E^\circ = 1.73$ V,[3] and related iron(III) complexes, and some reactions of these complexes with organic substrates.

Preparation of the Iron(III) Complexes, $Fe(S)_6(ClO_4)_3$

Recently, considerable attention has been focussed on solvent effects in the reactions of metals and metal ions with the aim of activating organic substrates[4] and forming complexes with donor solvents leading to changes in redox potentials.[5] We were interested in ferric solvates in order to prepare new complexes which have high redox potentials, and thus we synthesized the complexes $Fe(S)_6(ClO_4)_3$, S=solvent, from $Fe(H_2O)_6(ClO_4)_3$ in donor solvents. The complexes $Fe(S)_6(ClO_4)_3$, in which the donor number (*DN*)[5] of the solvent is larger than that of water except for some ethers which have small dielectric constants,[6] were prepared by simple dissolution of $Fe(H_2O)_6(ClO_4)_3$ in the solvents.[7] On the other hand, when *DN* of the solvent is smaller than that of water, the complexes $Fe(S)_6(ClO_4)_3$ cannot be synthesized by the above method. Therefore, these complexes were synthesized from $Fe(AcOH)_6(ClO_4)_3$,[8] which was prepared from $Fe(H_2O)_6(ClO_4)_3$ by the addition of 6 mol of

acetic anhydride.[9] These reactions are represented by the following equations.

$DN(S) > DN(H_2O)$

$$Fe(H_2O)_6(ClO_4)_3 + 6S \rightarrow Fe(S)_6(ClO_4)_3 + 6H_2O$$

$DN(S) < DN(H_2O)$

$$Fe(H_2O)_6(ClO_4)_3 + 6Ac_2O \rightarrow Fe(AcOH)_6(ClO_4)_3 + 6AcOH$$

$$Fe(AcOH)_6(ClO_4)_3 + 6S \rightarrow Fe(S)_6(ClO_4)_3 + 6AcOH$$

Solvation of the metal ion depends mainly upon electrostatic forces, though the covalent contribution should not be neglected. It was reported by Gutmann[5] that an almost linear relationship is observed between the solvation energy and donicity (donor number) of ligands, and the electrostatic contribution in solvation is also strongly influenced by the dielectric constant of the solvents as might be expected from the Born equation.[10] Although the donicity of acetic acid ($pK_a = -6.1$) is unknown, it may be similar to that of ethyl acetate ($pK_a = -6.5$; $DN = 17.1$) from the pK_a values, being larger than those of nitromethane, acetic anhydride, AN, sulfolane, and propylene carbonate, as shown in Table I. On the other hand, the dielectric constant of acetic acid is very small ($\varepsilon = 6$) compared with that of the above solvents. Therefore, acetic acid as ligand can be replaced by solvents which have larger dielectric constants than that of acetic acid in spite of their smaller donicity. Among these complexes, in particular, the structure of $Fe(AN)_6(ClO_4)_3$ which has the highest E°, was supported by the fact that the cyclic voltammogram of this iron(III) complex in AN (Fig. 1) shows the same reversible wave as that of $Fe(AN)_6(ClO_4)_2$ prepared by the known method.[2]

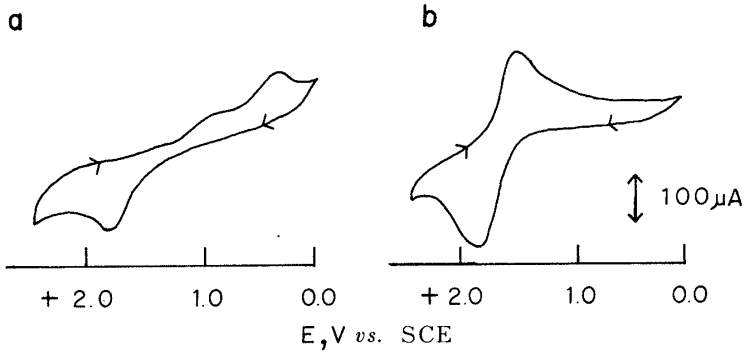


Fig. 1. Cyclic Voltammograms of (a) 0.01 M $Fe(H_2O)_6(ClO_4)_3$ and (b) 0.01 M $Fe(AN)_6(ClO_4)_3$ in CH_3CN

Supporting electrolyte, 0.1 M Et_4NClO_4; working electrode, glassy carbon; sweep rate, 100 mV s^{-1}.

The formal redox potentials (E°) of these complexes are listed in Table I.[11] The linear relationship between E° and DN such as is found in the redox solvates $Sm(solv)^{3+/2+}$, $Eu(solv)^{3+/2+}$ and $Yb(solv)^{3+/2+}$ [5] was not observed in this case, and the AN complex showed the highest value.

In general, the standard redox potentials (E°) of metal ion solvate systems $M(solv)^{3+/2+}$ are obtainable by calculation of the free energy change in the following equation based on the Born–Haber cycle.

$$M(solv)^{3+} + 1/2H_2(gas) \rightleftarrows M(solv)^{2+} + H(aq)^+ (\Delta G^\circ)$$

$$E^\circ(V \text{ vs. SHE}) = -\Delta G^\circ/nF = IP + \Delta G^\circ(M^{3+}) - \Delta G^\circ(M^{2+}) - \Delta G^\circ(H)$$

IP: Ionization potential from $M(gas)^{2+}$ to $M(gas)^{3+}$,

$\Delta G°(M^{3+})$: Solvation energy of M^{3+},

$\Delta G°(M^{2+})$: Solvation energy of M^{2+},

$\Delta G°(H)$: Free energy change of the following reaction.

$1/2H_2(gas) \rightarrow H(aq)^+ + e^-$ $(\Delta G°(H) = 5.10\,eV)$

TABLE I. Formal Redox Potentials ($E°$) of $Fe(S)_6^{3+/2+}$ in Donor Solvents (S)

Solvent (S)	DN_{SbCl_5}	$E°$, V *vs.* SCE[a]
Nitromethane	2.7	1.30
Acetic anhydride	10.5	1.32
Acetonitrile	14.1	1.73
Sulfolane	14.8	1.39
Propylene dicarbonate	15.1	1.28
Acetone	17.0	1.28
Ethyl acetate	17.1	1.24
Acetic acid	—	0.83
Water	18.0	0.48
Methanol	19.0	0.70
Trimethylphosphate	23.0	0.70
Dimethylformamide	26.6	0.38
Dimethylsulfoxide	29.8	0.22

a) 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 electrode potentials for equimolar mixture solutions of 0.01 M ferric and ferrous solvates by potentiometry. The voltage scan rate in cyclic voltammetry was 100 mV s^{-1}.

$E°$ values of $M(solv)^{3+/2+}$ depend only on the differences of solvation energies between $M(gas)^{3+}$ and $M(gas)^{2+}$, since the ionization potentials and $\Delta G°(H)$ are constant. The smaller difference of solvation energies is the higher redox potential becomes.[12]

In metal ion-ligand interaction, electrostatic contribution is an important factor, but covalent contribution based on overlap of orbitals is not negligible. Though it can be considered that the donicity of the ligand is almost proportional to the overlap between *d*-orbitals of the metal ion and occupied σ- and π-orbitals of the ligand, it is also necessary to consider the π-electron accepting ability of the ligand when there is interaction between *d*-orbitals of the metal ion and vacant π-orbitals of the ligand, so called back-donation.[13]

The reason for the very high redox potential in the case of $Fe(AN)_6^{3+/2+}$ may be the large π-electron accepting ability of AN in spite of its small σ-donicity, as indicated by the large crystal-field splitting energy for $Fe(AN)_6^{2+}$ measured by Hathaway and Holah.[14] The solvation energy for Fe^{2+} in $Fe(AN)_6^{2+}$ is increased by the back-donation from Fe^{2+} to AN, while backdonation from Fe^{3+} to AN can be excluded in $Fe(AN)_6^{3+}$.[3,9]

Thus, the difference of solvation energy between $Fe(gas)^{3+}$ and $Fe(gas)^{2+}$ against AN may be the smallest among these complexes, and so the redox potential of the AN complex is the highest.

Reactions of the Alkylbenzenes with $Fe(AN)_6(ClO_4)_3$

Reactions of primary and secondary alkylbenzenes with the iron(III) complex $Fe(AN)_6(ClO_4)_3$ were explored in view of the fact that this complex has the highest redox potential ($E° = 1.73$ V) among these solvates. The half-life of this complex is *ca.* 30 h as measured by potentiometric titration using $Fe(bpy)_3(ClO_4)_2$. Therefore, this complex should be prepared just before use.

Reactions of the primary alkylbenzenes **1** with 2 eq mol of the complex at room temperature for 15 min gave the corresponding acetamides **2** as shown in Table II. These results show this complex can efficiently oxidize compounds which have *ca.* 2 V *vs.* SCE onset potential of anodic current (E_a). These reactions can be presented as shown in Chart 1, in which the postulated acetates **3** (because this reagent contains a small amount of AcOH) were not isolated. Presumably, once generated, the acetates **3** may be transformed to the stable acetamides **2** by the Ritter type reaction[15] because this complex acts as a Lewis acid.

TABLE II. Reactions of Alkylbenzenes **1** with $Fe(AN)_6(ClO_4)_3$

	Alkylbenzene **1**			Product **2**
	R	R′	E_a, V *vs.* SCE[a]	Yield (%)[b]
a	H	H	1.90	11
b	H	*p*-Me	1.80	43
c	H	*m*-Me	1.85	52
d	H	*o*-Me	1.85	31
e	H	3,5-DiMe	1.80	49
f	H	Penta-Me	1.45	56
g	Me	H	1.95	20
h	*n*-Propyl	H	2.05	33
i	Isopropyl	H	2.05	17
j	*n*-Pentyl	H	2.05	57

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) Yield are isolated yields. The residue was almost entirely unchanged starting material.

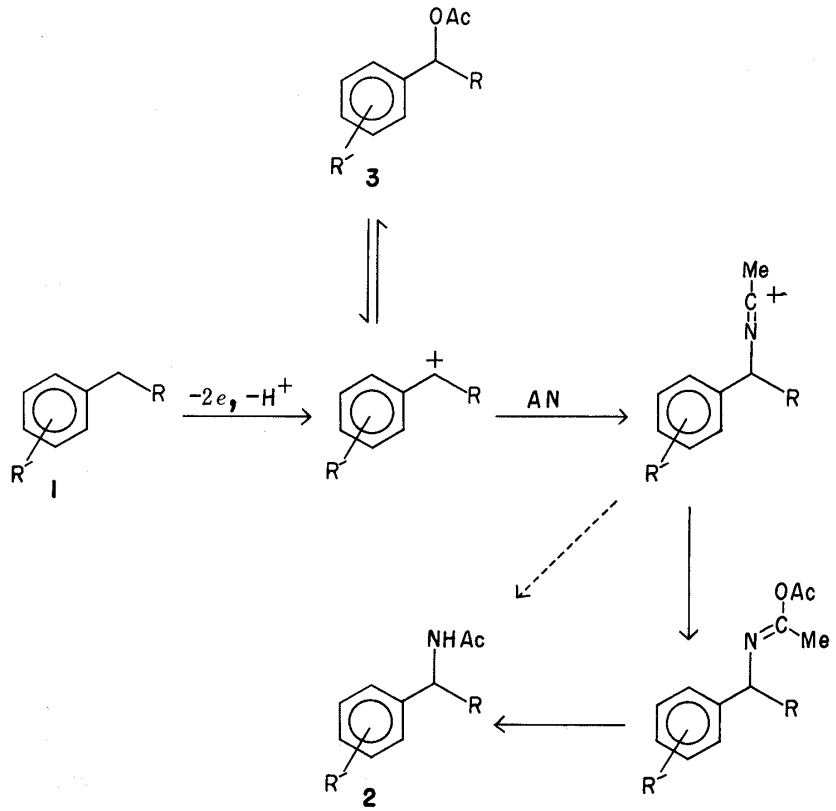


Chart 1

In the case of oxidations of secondary alkylbenzenes with this complex, the reactions proceeded with consumption of 4 or more mol eq of the reagent. Oxidation of cumene with 4 eq of the reagent at room temperature for 20 min gave the products **4**, mp 81—82 °C, **5a**, oil, and **6**, mp 80—81 °C (along with recovered cumene), in yields of 6.9, 6.6%, and trace, respectively. The same reaction for 90 min afforded the products **4**, **5a**, and **6** in yields of 16.1%, trace, and 0.7%, respectively. This result suggests that **4** may be the secondary product formed from **5a** by the Ritter type reaction.

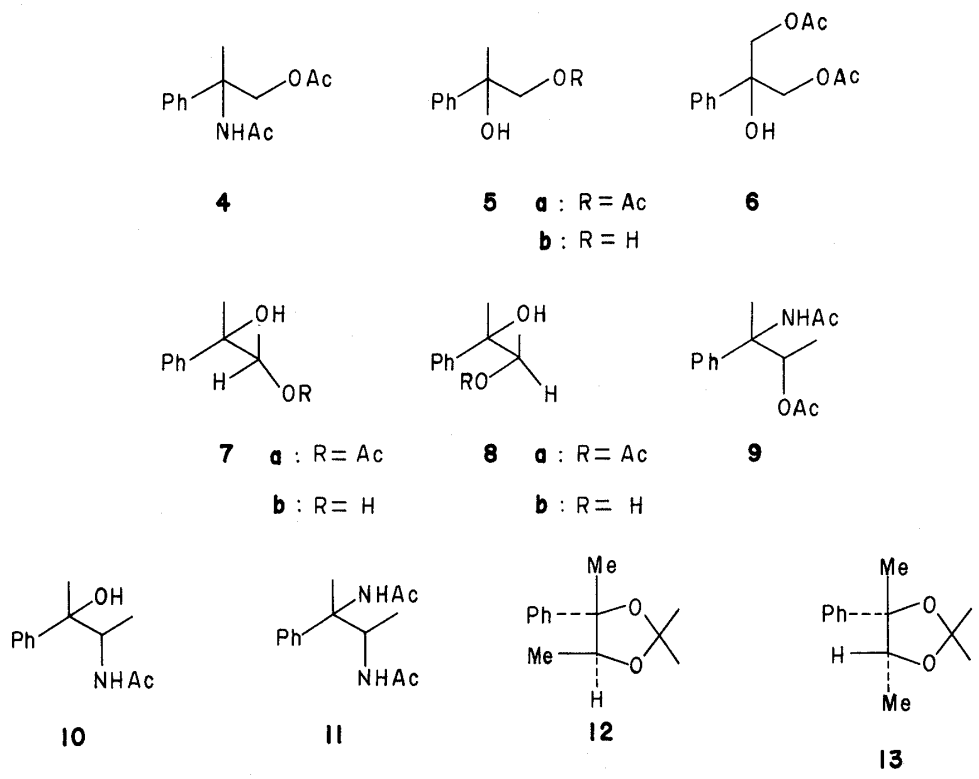


Chart 2

Oxidation of 2-phenylbutane with this complex at room temperature for 90 min yielded the products **7a**, oil, **8a**, mp 55—57 °C, **9**, oil, **10**, oil, and **11**, mp 163—165 °C (along with recovered starting material), in yields of 11.4, 7.4, 1.5, 1.6, and 0.6%, respectively. The structures of **7a** and **8a** were assigned by comparison of the nuclear magnetic resonance (NMR) spectra with those of **12** and **13**, which were synthesized by $LiAlH_4$ reduction of **7a** and **8a** to yield **7b** and **8b**, followed by acetonization. Namely, the signal of C(5)–Me of **12**, centered at δ 1.32 (d, J = 6.3 Hz), is observed at lower field than the signal of **13**, centered at δ 0.86 (d, J = 6.3 Hz), owing to the shielding effect of the phenyl group. The stereochemical features of **9**, **10**, and **11** were not investigated further.

Oxidation of 2-*exo*-phenylnorbornane[16] **14** with the same complex at room temperature for 90 min afforded the products **15a**, mp 105 °C, **16**, mp 44—45 °C, **15b**, mp 55—56 °C, and the $HClO_4$ salt of **17a** or **17b** (exact identity not determined), mp 198—200 °C, in yields of 4.7, 31.4, 2.8, and 4.4%, respectively. The structures of **15** and **16** were assigned by considering the following chemical *trans*-formations and by analyses of the NMR spectra, (i) **15b**, mp 55—56 °C, gave the acetonide **19**, mp 86—86.5 °C, (ii) the OH and OAc may be *exo* in view of the proton signals of C(3)–*endo*-H centered at δ 5.72 (J = 1.7 Hz) in **15** and δ 5.20 (J = 1.7 Hz) in **16** coupled with C(7)–*anti*-H in the NMR. A brief treatment of the $HClO_4$ salt of **17** with 2% Na_2CO_3 in MeOH–H_2O gave the free base **17**, mp 115—116 °C, and further treatment of **17**

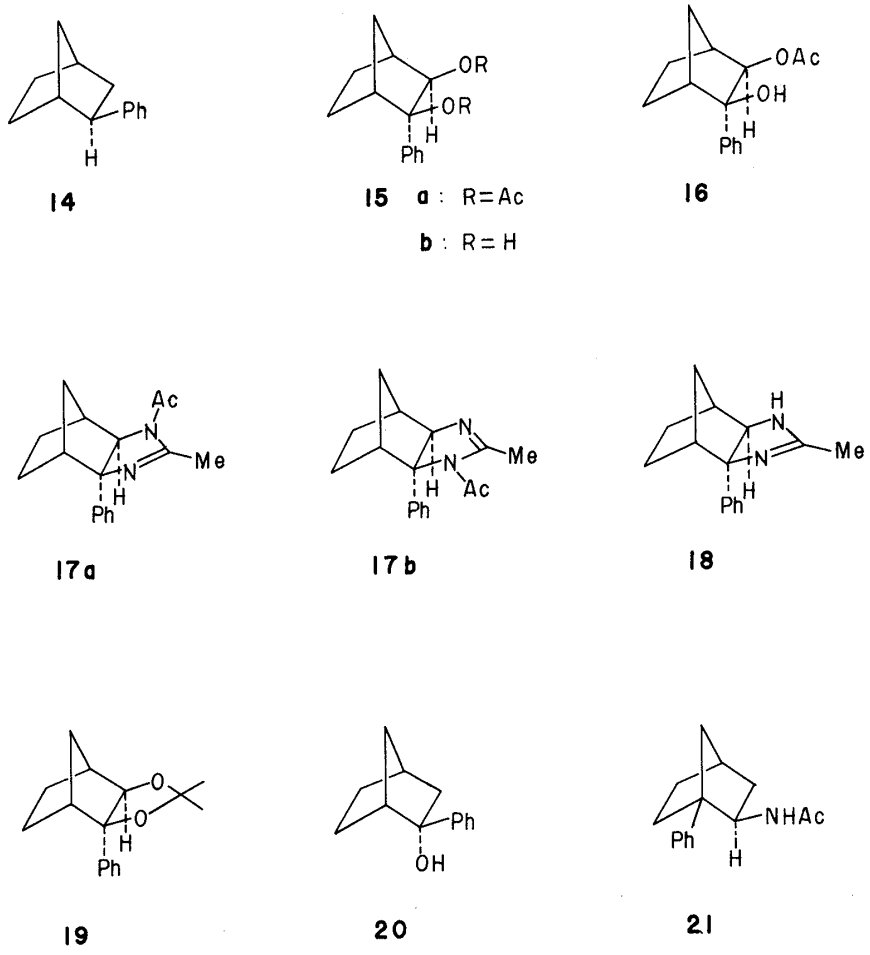


Chart 3

with 5% KOH in EtOH–H_2O afforded the imidazoline **18**, mp 78—81 °C. In the NMR spectrum of **18**, long-range coupling between C(7a)–*endo*-H and C(8)–*anti*-H ($J=0.8$ Hz) was observed.

The routes of formation of **15a**, **15b**, **16**, and **17a** or **17b** by the reaction of **14** with the iron(III) complex can be postulated to be as shown in Chart 4. Two electron oxidation of **14** gives a stable carbonium ion **22** followed by 1,2-hydride shift to yeild **24**, and subsequent reactions with AcOH and AN afford **25** and **28**. Further two-electron oxidations of **25** and **28** lead to the carbonium ions **26** and **29** followed by reactions with AcOH and AN to afford **15a**, **15b**, and **16** through the intermediate **27** as well as **17** through the intermediate **30**.

The hydroxyacetate **16** was also obtained by the reaction of 2-*exo*-phenyl-norborneol[16] **20** with the same complex in a yield of 33.2%. This reaction is considered to proceed through the carbonium ion **22** which is formed by the action as a Lewis acid of the iron complex on **16** and follows the same route as shown in Chart 4. On the other hand, the Ritter reaction of **20** with H_2SO_4–Ac_2O–AN gave only a rearranged product **21**. It is noteworthy that the substituents in all these oxidation products of the phenylnorbornanes possess *exo* configuration.

Synthesis and Reactions of $Fe(RCN)_6(ClO_4)_3$

The complexes $Fe(RCN)_6(ClO_4)_3$ can be prepared in the same way as the AN complex with ferric perchlorate in RCN instead of AN. The measured redox potentials of $Fe(RCN)_6(ClO_4)_3$ are shown in Table III, and these results show that some complexes should have the ability to oxidize the alkylbenzenes described above.

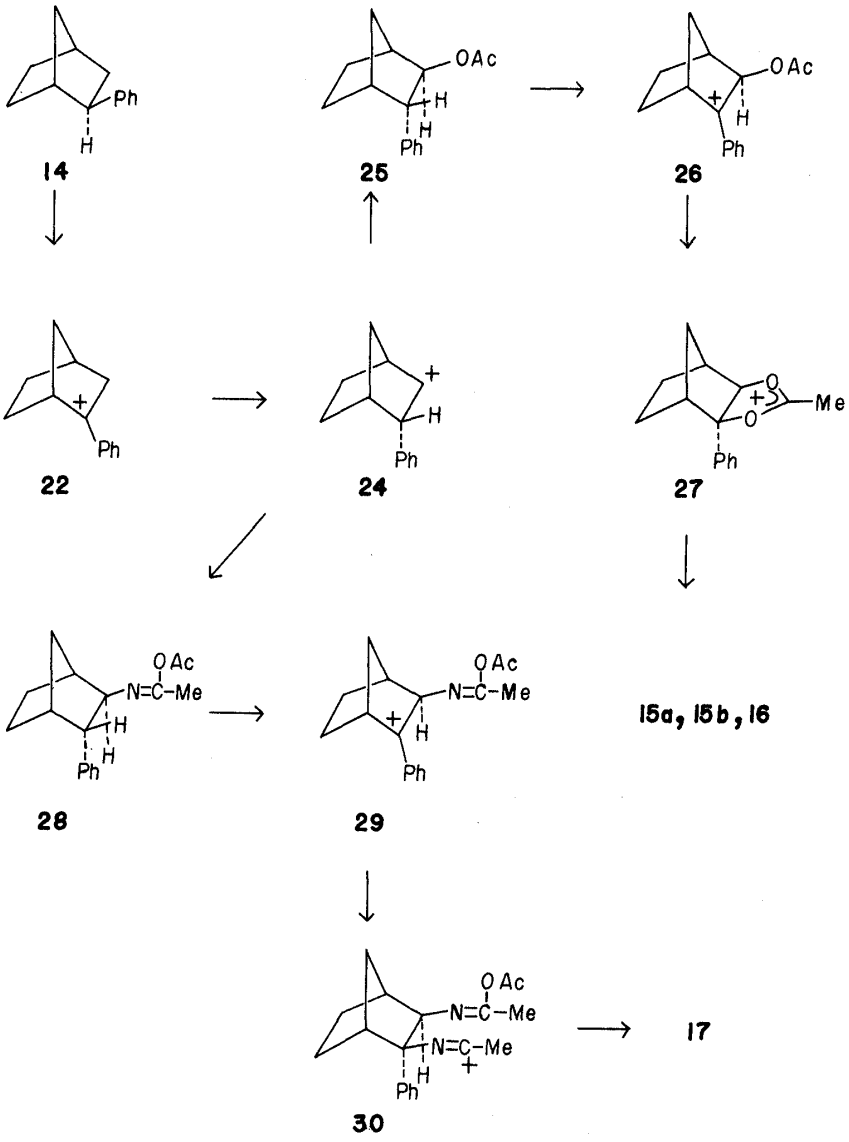
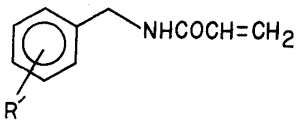


Chart 4

TABLE III. Formal Redox Potentials ($E°$) of $Fe(RCN)_6^{3+/2+}$ in RCN

Nitrile	$E°$, V *vs.* SCE[a]	Nitrile	$E°$, V *vs.* SCE[a]
CH_3CN	1.73	$CH_2=CHCN$	1.50
$NC(CH_2)_4CN$	1.66	$CH_2=CHCH_2CN$	1.48
$CH_3OCH_2CH_2CN$	1.63	$NCCH_2CO_2Et$	1.45
$CH_3CH_2CH_2CN$	1.58	PhCN	1.45
$CH_3CH=CHCN$	1.56	$(CH_3)_2CHCN$	1.30
$PhCH_2CN$	1.52	CCl_3CN	1.17

a) The formal redox potentials ($E°$) were measured by the same method as noted in Table I.



31a: R′=*p*-methyl
31b: R′=pentamethyl

Chart 5

In fact, the reaction of *p*-xylene or hexamethylbenzene with hexakisacrylonitrile iron(III) perchlorate, $Fe(CH_2=CHCN)_6(ClO_4)_3$, in acrylonitrile at room temperature for 30 min gave the corresponding amide **31a**, mp 109—111 °C, or **31b**, mp >300 °C, in a yield of 52 or 66%, respectively.

Further applications of these complexes to organic synthesis are under investigation.

Experimental

All melting points are uncorrected. Infrared (IR) spectra were recorded with a Hitachi 285 grating spectrophotometer, ^{1}H-NMR spectra with a JEOL JNM-FX 100 spectrometer with tetramethylsilane as an internal standard ($CDCl_3$ soln.) and mass spectra (MS) with a JEOL JMS-D 300 spectrometer. Elementary analyses were done by Ms. M. Takeda and Ms. S. Okamura, Kissei Pharmaceutical Company, Matsumoto, Japan. Preparative thin-layer chromatography (TLC) was performed on aluminum oxide F-254 (type E, Merck). Mallinckrodt silica gel (100 mesh) and Merck Kieselgel 60 F254 were used for column chromatography and TLC, respectively.

Cyclic voltammetric analyses were carried out using a Hokuto Denko HA-501 potentiostat. Voltammograms were recorded on a Riken F-35 X-Y recorder. The cyclic voltammetry cell was a *ca.* 10 ml cylindrical glass vessel, 2.2 cm in diameter and 6 cm in height, equipped with inlet and outlet side glass tubes for nitrogen gas. Either a Yanagimoto glassy carbon disk (GC-P2, 3 mmϕ) or a Toa Dempa platinum disk (HP-105, 5 mmϕ), which were both sealed into the end of a glass tube, was used as the working electrode. A platinum wire was used as the counter electrode, with either a saturated calomel electrode (SCE) or a silver–silver chloride electrode, separated by a salt bridge containing 0.1 M Et_4NClO_4 in the non-aqueous solvent, as the reference electrode. The working electrode and the reference electrode were placed parallel to each other in the glass cylinder, and the counter electrode was set into the side gas inlet tube after dry nitrogen gas had been passed for a few min.

Electrode potentials were taken on a Toa Denpa HM-20E potentiometer using the same cell and electrodes as for cyclic voltammetry. All electrochemical measurements were carried out at 25 °C under a nitrogen atmosphere in solvents which had been dried and purified by standard techniques prior to use.

Preparation of $Fe(AN)_6(ClO_4)_3$ Solution——Ac_2O (34 ml, 9×40 mmol) was added slowly over 10 min to a solution of $Fe(ClO_4)_3 \cdot 9H_2O$ (20.64 g, 40 mmol) in freshly distilled AN (220 ml) with stirring under ice-water cooling to give a pale yellow solution.

Measurement of the Half-Life of This Reagent——Potentiometric titration curves were obtained with the potentiometer by the titration of 0.01 M $Fe(AN)_6(ClO_4)_3$ solution (10 ml) with 0.01 M $Fe(bpy)_3(ClO_4)_2$ in AN. The consumed volumes of $Fe(bpy)_3(ClO_4)_2$ solution were *ca.* 10 ml after 6 h and 5 ml after 30 h.

General Procedure for Oxidation of Primary Alkylbenzenes with $Fe(AN)_6(ClO_4)_3$——A primary alkylbenzene (3 mmol) was added to a freshly prepared solution of $Fe(AN)_6(ClO_4)_3$ (6 mmol), and the mixture was stirred for 15 min at *ca.* 25 °C. The reaction mixture was poured into ice-water and extracted with ether–ethyl acetate (2 : 1, 3×20 ml). The combined extracts were washed with brine and dried on Na_2SO_4. The solvent was evaporated off to leave a white solid. Recrystallization of the residue from hexane–ethyl acetate provided the corresponding acetamide. (When the residue was liquid, it was purified by silica gel column chromatography.)

General Procedure for the Oxidation of Secondary Alkylbenzenes with $Fe(AN)_6(ClO_4)_3$——A secondary alkylbenzene (10 mmol) was added to a solution of $Fe(AN)_6(ClO_4)_3$ (40 mmol) with stirring at room temperature. The reaction mixture was stirred vigorously for 90 min and then poured into ice-water and extracted with ether–ethyl acetate (2 : 1, 3×100 ml). The combined extracts were washed with brine, dried on Na_2SO_4, and then evaporated. The residue was purified by column chromatography or preparative TLC.

***N*-(1-Phenylhexyl)acetamide (2j)**——**2j** was obtained as colorless needles from the oxidation of 1-phenylhexane in a yield of 57%, mp 74—75 °C (ethyl acetate–hexane). IR (KBr) cm^{-1}: 3310, 1650, and 1540. NMR ($CDCl_3$) δ: 0.85 (t, J=6.0 Hz, 3H, –Me), 1.25—1.85 (m, 8H, $-CH_2-$), 1.95 (s, 3H, –NHCOMe), 4.95 (td, J=7.0 and 7.3 Hz, 1H, C(1)–H), 6.10 (br, 1H, –NHCO–), and 7.28 (s, 5H, aromatic-H). MS *m/e*: Calcd for $C_{14}H_{21}NO$ (M^+): 219.1622. Found: 219.1622. *Anal.* Calcd for $C_{14}H_{21}NO$: C, 76.66; H, 9.65; N, 6.38. Found: C, 76.79; H, 9.84; N, 6.30.

Oxidation of Cumene——Silica gel column chromatography of the reaction residue gave **5a** and **6** from the eluates with hexane–chloroform (5 : 1) in trace and 0.7% yields, respectively, and **4** from the eluates with chloroform in 16.1% yield.

2-Hydroxy-2-phenylpropyl Acetate (5a)——Colorless oil. IR (neat) cm^{-1}: 3460, 1730, 1240, and 1040. NMR ($CDCl_3$) δ: 1.58 (s, 3H, –Me), 2.05 (s, 3H, –OCOMe), 2.50 (br, 1H, –OH), 4.26 (s, 2H, $-CH_2-$), and 7.30—7.60 (m, 5H, aromatic-H). MS *m/e*: Calcd for $C_{11}H_{14}O_3$ (M^+): 194.0944. Found: 194.0964.

3-Acetyl-2-hydroxy-2-phenylpropyl Acetate (6)——Colorless crystals, mp 80—81 °C (chloroform–hexane). IR (KBr) cm^{-1}: 3460, 1730, 1240, and 1040. NMR ($CDCl_3$) δ: 2.02 (s, 6H, 2×–OCOMe), 2.60 (br, 1H, –OH), 4.36 (s, 4H, $-CH_2-$), and 7.30—7.60 (m, 5H, aromatic-H). MS *m/e*: Calcd for $C_{13}H_{16}O_5$ (M^+): 252.0998. Found: 252.1111.

2-Acetamido-2-phenylpropyl Acetate (4)——Colorless crystals, mp 81—82 °C (chloroform–petroleum ether). IR

(KBr) cm^{-1}: 3310, 1730, 1650, 1540 and 1230. NMR ($CDCl_3$) δ: 1.76 (s, 3H, –Me), 1.98 (s, 3H, –NHCOMe), 2.06 (s, 3H, –OCOMe), 4.25 (d, J=11.0 Hz, 1H, C(1)–H), 4.44 (d, J=11.0 Hz, 1H, C(1)–H), 6.30 (br, 1H, –NHCO–), and 7.32 (s, 5H, aromatic-H). MS *m/e*: Calcd for $C_{13}H_{17}NO_3$ (M^+): 235.1209. Found: 235.1210. *Anal.* Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.16; H, 7.49; N, 5.60.

2-Phenyl-1,2-propanediol (5b)——A mixture of **5a** (30 mg, 0.15 mmol) and $LiAlH_4$ (30 mg, 0.79 mmol) in dry ether (15 ml) was stirred at room temperaure for 1.5 h. The resulting solution was treated with cooled ammonium chloride solution and extracted with ether (2 × 30 ml). The ether layer was washed with water, dried on Na_2SO_4, and then concentrated. The residue was purified by silica gel column chromatography using chloroform as the eluent to give **5b** as a colorless oil in quantitative yield. IR (neat) cm^{-1}: 3400. NMR ($CDCl_3$) δ: 1.25 (s, 1H, C(1)–OH), 1.52 (s, 3H, C(2)–Me), 2.10 (br, 1H, C(2)–OH), 3.70 (d, J=4.0 Hz, 1H, $-CH_2-$), and 7.30—7.50 (m, 5H, aromatic-H).

Oxidation of 2-Phenylbutane——Silica gel column chromatography of the oxidation products of 2-phenylbutane afforded **8a** and **7a** from the hexane–chloroform (6 : 1) eluate, **9** from the chloroform eluate, and **10** and **11** from the chloroform–ethyl acetate (7 : 1) eluate in yields of 7.4, 11.4, 1.5, 1.6, and 0.6%, respectively.

***threo*-3-Hydroxy-3-phenyl-2-butyl Acetate (8a)**——Colorless crystals, mp 55—57 °C. IR (KBr) cm^{-1}: 3490, 1720, and 1250. NMR ($CDCl_3$) δ: 1.00 (d, J=6.0 Hz, 3H, C(2)–Me), 1.53 (s, 3H, C(3)–Me), 2.09 (s, 3H, –OCOMe), 2.30 (br, 1H, –OH), 5.16 (q, J=6.0 Hz, 1H, C(2)–H), and 7.35—7.50 (m, 5H, aromatic-H). MS *m/e*: Calcd for $C_{12}H_{16}O_3$ (M^+): 208.1100. Found: 208.1106.

***erythro*-3-Hydroxy-3-phenyl-2-butyl Acetate (7a)**——Colorless oil. IR (neat) cm^{-1}: 3480, 1720, and 1250. NMR ($CDCl_3$) δ: 1.18 (d, J=6.0 Hz, 3H, C(2)–Me), 1.51 (s, 3H, C(3)–Me), 1.89 (s, 3H, –OCOMe), 2.62 (br, 1H, –OH), 5.20 (q, J=6.0 Hz, 1H, C(2)–H), and 7.30—7.45 (m, 5H, aromatic-H). MS *m/e*: Calcd for $C_{12}H_{16}O_3$ (M^+): 208.1099. Found: 208.1149.

3-Acetamido-3-phenyl-2-butyl Acetate (9)——Colorless oil (the stereostructure was not determined). IR (neat) cm^{-1}: 3300, 1740, 1660, 1530, and 1250. NMR ($CDCl_3$) δ: 1.02 (d, J=6.0 Hz, 3H, C(2)–Me), 1.84 (s, 3H, C(3)–Me), 1.96 (s, 3H, –NHCOMe), 2.05 (s, 3H, –OCOMe), 5.14 (q, J=6.0 Hz, 1H, C(2)–H), 6.55 (br, 1H, –NHCO–), and 7.30 (s, 5H, aromatic-H). MS *m/e*: Calcd for $C_{14}H_{19}NO_3$ (M^+): 249.1364. Found: 249.1389.

3-Acetamido-2-phenyl-2-butanol (10)——Colorless oil (the stereostructure was not determined). IR (neat) cm^{-1}: 3320, 1640, and 1520. NMR ($CDCl_3$) δ: 1.20 (d, J=6.0 Hz, 3H, C(3)–Me), 1.50 (s, 3H, C(2)–Me), 1.72 (s, 3H, –NHCOMe), 2.11 (br, 1H, –OH), 4.22 (m, 1H, C(3)–H), 6.10 (br, 1H, –NHCO–), and 7.20—7.40 (m, 5H, aromatic-H). MS *m/e*: 207 (M^+).

***N*-(3-Acetamido-2-phenyl-2-butyl)acetamide (11)**——Colorless crystals, mp 163—165 °C (chloroform–hexane) (the stereostructure was not determined). IR (KBr) cm^{-1}: 3260, 1650, and 1540. NMR ($CDCl_3$) δ: 0.95 (d, J=6.0 Hz, 3H, C(3)–Me), 1.58 (s, 3H, C(2)–Me), 1.88 (s, 3H, –NHCOMe), 2.00 (s, 3H, –NHCOMe), 4.40 (m, 1H, C(3)–H), and 7.28 (s, 5H, aromatic-H). MS *m/e*, Calcd for $C_{14}H_{20}N_2O_2$ (M^+): 248.1460. Found: 248.1491.

***threo*-2-Phenyl-2,3-butanediol (8b)**——**8b** was obtained from **8a** by the same procedure as described for **5b** in 73% yield. Colorless oil. IR (neat) cm^{-1}: 3400. NMR ($CDCl_3$) δ: 0.98 (d, J=6.0 Hz, 3H, C(3)–Me), 1.60 (s, 3H, C(2)–Me), 2.20 (br, 2H, 2 × –OH), 3.90 (q, J=6.0 Hz, 1H, C(3)–H), and 7.35 (s, 5H, aromatic-H).

2,2,*r*-4,*t*-5-Tetramethyl-*t*-4-phenyl-1,3-dioxolane (13)——A solution of **8b** (30 mg) and *p*-toluenesulfonic acid (5 mg) in acetone (10 ml) was refluxed for 2.5 h, and then concentrated *in vacuo*. The residue was filtered through a silica gel column using hexane–chloroform (7 : 3) as the eluent to give **13**, colorless oil, in almost quantitative yield. NMR ($CDCl_3$) δ: 0.86 (d, J=6.3 Hz, 3H, C(5)–Me), 1.53 (s, 3H, C(2)–Me), 1.67 (s, 3H, C(2)–Me), 1.69 (s, 3H, C(4)–Me), 4.28 (q, J=6.3 Hz, 1H, C(5)–H), and 7.25—7.33 (m, 5H, aromatic-H).

***erythro*-2-Phenyl-2,3-butanediol (7b)**——**7b** was obtained from **7a** by the same procedure as described for **5b** as a colorless oil in almost quantitative yield. NMR ($CDCl_3$) δ: 1.10 (d, J=6.0 Hz, 3H, C(3)–Me), 1.48 (s, 3H, C(2)–Me), 2.40 (br, 2H, 2 × –OH), 3.94 (q, J=6.0 Hz, 1H, C(3)–H), and 7.30—7.45 (m, 5H, aromatic-H).

2,2,*r*-4,*c*-5-Tetramethyl-*t*-4-phenyl-1,3-dioxolane (12)——**12** was obtained from **7b** by the same procedure as described for **13** in 65% yield as a colorless oil. NMR ($CDCl_3$) δ: 1.32 (d, J=6.3 Hz, 3H, C(5)–Me), 1.46 (s, 6H, C(2)–Me and C(4)–Me), 1.56 (s, 3H, C(2)–Me), 4.07 (q, J=6.3 Hz, 1H, C(5)–H), and 7.25—7.45 (m, 5H, aromatic-H).

Oxidation of 2-*exo*-Phenyl-bicyclo[2.2.1]heptane (14)——Oxidation of **14** was carried out according to the general procedure except for extraction with ethyl acetate–chloroform (4 : 1) instead of ether–ethyl acetate (2 : 1). Silica gel column chromatography of the reaction residue gave **15a** from the hexane eluate, **16** from the hexane–chloroform (1 : 1) eluate, **15b** from the chloroform eluate, and the $HClO_4$ salt of **17** from the chloroform–ethyl acetate (1 : 1) eluate in yields of 4.7, 31.4, 2.8, and 4.4%, respectively.

3-*exo*-Acetoxy-2-*endo*-phenyl-2-*exo*-bicyclo[2.2.1]heptyl Acetate (15a)——Colorless crystals, mp 105—106 °C (hexane–ethanol). IR (KBr) cm^{-1}: 1745, 1240, and 1030. NMR ($CDCl_3$) δ: 0.80—1.60 (m, 4H, C(5)–H and C(6)–H), 1.37 (d, J=1.7 Hz, 1H, C(7)-*anti*-H), 1.97 (s, 3H, –OCOMe), 1.98 (s, 3H, –OCOMe), 2.24 (br, 1H, C(7)-*syn*-H), 2.30 (br, 1H, C(4)–H), 2.60 (br, 1H, C(1)–H), 5.72 (d, J=1.7 Hz, 1H, C(3)-*endo*-H), and 7.30—7.45 (m, 5H, aromatic-H). MS *m/e*: Calcd for $C_{17}H_{20}O_4$ (M^+): 288.1362. Found: 288.1362. *Anal.* Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.78; H, 7.06.

2-*exo*-Hydroxy-2-*endo*-phenyl-3-*exo*-bicyclo[2.2.1]heptyl Acetate (16)——Colorless crystals, mp 44—45 °C (hexane). IR (neat) cm^{-1}: 3460, 1720, 1240, and 1030. NMR ($CDCl_3$) δ: 1.00—1.60 (m, 4H, C(5)–H and C(6)–H), 1.44

(d, J=1.7 Hz, 1H, C(7)–*anti*-H), 2.09 (s, 3H, –OCOMe), 2.25 (br, fine coupling, 1H, C(7)–*syn*-H), 2.33 (br, fine coupling, 1H, C(4)–H), 2.48 (br, fine coupling, C(1)–H), 2.71 (s, 1H, –OH), 5.20 (d, J=1.7 Hz, 1H, C(3)–*endo*-H), and 7.30—7.60 (m, 5H, aromatic-H). MS *m/e*: Calcd for $C_{15}H_{18}O_3$ (M^+): 246.1254. Found: 246.1253. *Anal.* Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.30; H, 7.50.

2-*endo*-Phenyl-2-*exo*,3-*exo*-bicyclo[2.2.1]heptanediol (15b)——Colorless crystals, mp 55—56 °C (ether–hexane). IR (KBr) cm^{-1}: 3450 and 3300. NMR ($CDCl_3$) δ: 1.02—1.50 (m, 4H, C(5)–H and C(6)–H), 1.24 (d, J=1.7 Hz, 1H, C(7)–*anti*-H), 2.10 (br, fine coupling, 1H, C(7)–*syn*-H), 2.18 (br, fine coupling, 1H, C(4)–H), 2.49 (br, fine coupling, 1H, C(1)–H), 2.90 (s, 1H, C(2)–OH), 3.28 (d, J=7.0 Hz, 1H, C(3)–OH), 4.04 (dd, J=1.7 and 7.0 Hz, 1H, C(3)–*endo*-H), and 7.25—7.40 (m, 5H, aromatic-H). MS *m/e*: Calcd for $C_{13}H_{16}O_2$ (M^+): 204.1151. Found: 204.1158.

1-Acetyl-3a,4,5,6,7,7a-hexahydro-2-methyl-3a-*endo*-phenyl-4,7-methanobenzimidazole (17a) or 3-Acetyl-3a,4,5,6,7,7a-hexahydro-2-methyl-3a-*endo*-phenyl-4,7-methanobenzimidazole (17b)——The $HClO_4$ salt of **17a** or **17b**, colorless crystals, mp 198—200 °C (acetone–hexane). IR (KBr) cm^{-1}: 3240, 3150, 3100, 1730, 1620, 1510, and 1130—1110 (ClO_4). MS *m/e*: Calcd for $C_{17}H_{20}N_2O$ (M^+): 268.1585. Found: 268.1590.

The $HClO_4$ salt of **17** was treated with 2% Na_2CO_3 in MeOH–H_2O to give the free base **17** in 90% yield as colorless crystals, mp 115—116 °C (chloroform–hexane). IR (KBr) cm^{-1}: 1670, 1630, and 1380. NMR ($CDCl_3$) δ: 1.20—1.70 (m, 4H, C(5)–H and C(6)–H), 1.43 (d, J=1.2 Hz, 1H, C(8)–*anti*-H), 2.30 (s, 3H, C(2)–Me), 2.36 (s, 3H, –COMe), 2.47 (br, fine coupling, 1H, C(8)–*syn*-H), 2.65 (br, fine coupling, 1H, C(7)–H), 3.56 (br, 1H, C(4)–H), 4.24 (d, J=1.2 Hz, 1H, C(7a)–*endo*-H), and 7.35—7.36 (m, 5H, aromatic-H). MS *m/e*: Calcd for $C_{17}H_{20}N_2O$ (M^+): 268.1574. Found: 268.1548. *Anal.* Calcd for $C_{17}H_{20}N_2O$: C, 76.08; H, 7.51; N, 10.43. Found: C, 76.32; H, 7.80; N, 10.18.

3a,4,5,6,7,7a-Hexahydro-2-methyl-3a-*endo*-phenyl-4,7-methanobenzimidazole (18)——A solution of **17** (130 mg, 0.35 mmol) and 5% KOH in EtOH–H_2O (9 : 1) (20 ml) was refluxed for 20 min. The reaction mixture was poured into ice-water and extracted with ethyl acetate (2 × 30 ml). The combined organic layer was washed with brine, dried on Na_2SO_4, and concentrated. Purification by preparative TLC with aluminium oxide using $CHCl_3$–MeOH (10 : 1) as the developing solvent gave **18** in 90% yield as colorless crystals, mp 78—81 °C (chloroform–hexane). IR (KBr) cm^{-1}: 3150 and 1610. NMR ($CDCl_3$) δ: 1.07—1.53 (m, 4H, C(5)–H and C(6)–H), 1.38 (d, J=0.8 Hz, 1H, C(8)–*anti*-H), 1.83 (s, 3H, C(2)–Me), 2.27 (br, fine coupling, 1H, C(7)–H), 2.58 (br, fine coupling, 1H, C(4)–H), 4.04 (d, J=0.8 Hz, 1H, C(7a)–*endo*-H), and 7.33—7.36 (m, 5H, aromatic-H). MS *m/e*: Calcd for $C_{15}H_{18}N_2$ (M^+): 226.1468. Found: 226.1468.

3a,4,5,6,7,7a-Hexahydro-2,2-dimethyl-3a-*endo*-phenyl-4,7-methano-1,3-benzodioxole (19)——**15b** was obtained from **16** by the same procedure as described for **5b** in almost quantitative yield. Further treatment of **15b** by the same procedure as described for **13** gave **19** as colorless crystals, mp 86—86.5 °C (hexane), in almost quantitative yield. NMR ($CDCl_3$) δ: 0.95 (s, 3H, C(2)–Me), 1.08—1.65 (m, 4H, C(5)–H and C(6)–H), 1.31 (d, J=1.5 Hz, 1H, C(8)–*anti*-H), 1.49 (s, 3H, C(2)–Me), 2.11 (br, fine coupling, 1H, C(7)–H), 2.29 (br, fine coupling, 1H, C(4)–H), 2.39 (br, fine coupling, 1H, C(8)–*syn*-H), 4.42 (d, J=1.5 Hz, 1H, C(7a)–*endo*-H), and 7.25—7.30 (m, 5H, aromatic-H). MS *m/e*: Calcd for $C_{16}H_{20}O_2$ (M^+): 244.1461. Found: 244.1459.

Oxidation of 2-*exo*-Phenyl-2-*endo*-bicyclo[2.2.1]heptanol (20)——Oxidation of **20** was carried out by the procedure described for the oxidation of **14** to give **16** as a major product in 33.2% yield

***N*-(1-Phenyl-2-*exo*-bicyclo[2.2.1]heptyl)acetamide (21)**——Conc. H_2SO_4 (10 ml) was added with stirring to an ice-cooled solution of **20** (0.2 g, 1 mmol) in AN–Ac_2O (3 : 1, 16 ml) under ice-water cooling, and the mixture was allowed to stand at room temperature for 3 h. The resulting solution was worked up in the usual manner to give **21**, mp 106—107 °C (hexane–ethyl acetate), as colorless crystals in 60% yield. IR (KBr) cm^{-1}: 3280, 1650, and 1550. NMR ($CDCl_3$) δ: 1.40—1.91 (m, 7H, C(3)–*exo*-H, C(5)–H, C(6)–H, and C(7)–H), 2.17 (ddd, J=1.8, 7.6, and 14.0 Hz, 1H, C(3)–*endo*-H), 2.34 (br, fine coupling, 1H, C(4)–H), 4.18 (dddd, J=0.5, 3.4, 7.6, and 13.0 Hz, 1H, C(2)–*endo*-H), 5.15 (br, 1H, –NHCO–), and 7.27 (s, 5H, aromatic-H). MS *m/e*: Cacld for $C_{17}H_{19}NO$ (M^+): 229.1465. Found: 229.1460. *Anal.* Calcd for $C_{17}H_{19}NO$: C, 78.56; H, 8.35; N, 6.10. Found: C, 78.60; H, 8.47; N, 6.04.

Oxidation of Primary Alkylbenzenes with Hexakisacrylonitrile Iron(III) Perchlorate——Ac_2O (6.3 ml) was added to an ice-cooled solution of $Fe(ClO_4)_3 \cdot 9H_2O$ (3.1 g, 6.0 mmol) in acrylonitrile (25 ml) with stirring. To this solution, *p*-xylene (0.32 g, 3.0 mmol) or hexamethylbenzene (0.486 g, 3.0 mmol) was added and the mixture was stirred at room temperature for 30 min. The reaction mixture was poured into ice-water and extracted with ether–ethyl acetate (2 : 1, 2 × 50 ml). The organic layer was washed with brine, dried on Na_2SO_4, and evaporated to dryness to afford 0.274 g (52% yield) of **31a** or 0.457 g (66% yield) of **31b** as colorless crystals.

***N*-(4-Methylphenylmethyl)propenamide (31a)**——Colorless crystals, mp 109—110 °C (chloroform–hexane). IR (KBr) cm^{-1}: 3280, 1660, 1620, and 1540. NMR ($CDCl_3$) δ: 2.34 (s, 3H, –Me), 4.43 (d, J=5.6 Hz, 2H, $-CH_2-$), 5.61 (dd, J=2.9 and 9.0 Hz, 1H, $=CH_2$), 6.07 (dd, J=9.0 and 16.85 Hz, 1H, –COCH=), 6.18 (br, 1H, –NHCO–), 6.31 (dd, J=2.9 and 16.85 Hz, 1H, $=CH_2$), and 7.14 (s, 4H, aromatic-H). MS *m/e*: Calcd for $C_{11}H_{13}NO$ (M^+): 175.0997. Found: 175.0977.

***N*-(2,3,4,5,6-Pentamethylphenylmethyl)propenamide (31b)**——mp >300 °C (acetone–EtOH). IR (KBr) cm^{-1}: 3260, 1650, 1620, and 1520. NMR (DMSO d_6) δ: 2.17 (s, 15H, 5 × –Me), 4.34 (br, fine coupling, 2H, $-CH_2-$), 5.54 (dd, J=3.5 and 9.0 Hz, 1H, $=CH_2$), 6.07 (dd, J=3.5 and 16.85 Hz, 1H, $=CH_2$), 6.30 (dd, J=9.0 and 16.85 Hz, 1H,

–COCH=), and 8.00 (br, 1H, –CONH–). MS *m/e*: Calcd for $C_{15}H_{21}NO$ (M^+): 231.1622. Found: 231.1617.

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References and Notes

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9) It was reported that the anhydrous complex, $Fe(AN)_6(ClO_4)_3$, is not present in the solution of $Fe(H_2O)_6(ClO_4)_3$ in AN. See R. Schmeri, V. N. Sapunov, and V. Gutmann, *Inorg. Chim. Acta*, **24**, 25 (1977); *idem, Ber. Bunsenges. Physik. Chem.*, **80**, 456 (1976); and ref. 3).
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