orientation of the hydroxy group is especially instructive. In **3** and **5** this group is slightly bent away from the gegenion and the HO bond is directed in such a way as to allow for the best lone pair orientation. Cation-dependent differences are seen in **4** and **6**. In **4** the OH group is moved toward the Li⁺, much like H_a, allowing for a maximum orientation of the pseudo-π-density toward the cation as well as an optimum cation-induced polarization of the O lone pairs. In **6**, however, the OH group is bent toward the opposite face of the ligand, away from Na⁺. Due to the larger size of sodium it necessarily needs to assume a position in closer proximity to the N lone pair, as compared to **4**, and the orientation of this lone pair becomes dominant.

The 6-31+G*/3-21+G SPE is 2.6 kcal mol⁻¹ for the isolated anions. Ion pair formation increases the SPE to 3.2 kcal mol⁻¹ for Li⁺ and 7.0 kcal mol⁻¹ for Na⁺. These results suggest that bases with larger cations may achieve increased regioselectivity.

Extensions of the present work to ketoximes and studies of solvation and aggregation effects at the ab initio level are in progress. Preliminary results for the ketoximes show no major differences from the aldoxime results presented here. Preliminary results for lithioacetaldoxime show that the incorporation of one molecule of water solvating lithium is not accompanied by large changes in structure and that significant conclusions will not be changed.

Supplementary Material Available: Tables of bond lengths and angles and energies for **1–6** and contour map of the electrostatic potential of **2** (5 pages). Ordering information is given on any current masthead page.

Stereospecific Oxygenation of 3-Adamantylidenetricyclo[3.2.1.0²,⁴]octane: Singlet Oxygen vs. Electron-Transfer Oxygenations[1]

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Much attention has been drawn to singlet oxygen (¹O₂) and electron-transfer oxygenations of electron-rich olefins.[2] Electron-transfer reactions (i.e., Foote-type[3-5] and Barton-type[6-9]

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(5) (a) Santamaria, J. *Tetrahedron Lett.* **1981,** *22,* 4511. (b) Manring, L. E.; Gu, C.-L.; Foote, C. S. *J. Phys. Chem.* **1983,** *87,* 40. (c) Dobrowolski, D. C.; Ogilby, P. R.; Foote, C. S. *Ibid.* **1983,** *87,* 2261. (d) Araki, Y.; Dobrowolski, D. C.; Goyne, T. E.; Hanson, D. C.; Jiang, Z. Q.; Lee, K. J.; Foote, C. S. *J. Am. Chem. Soc.* **1984,** *106,* 4570.

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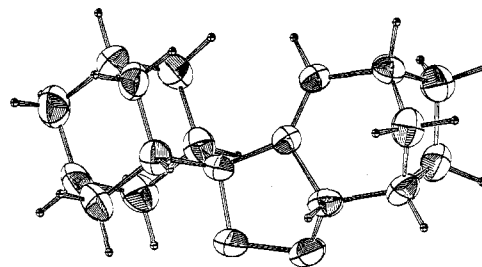
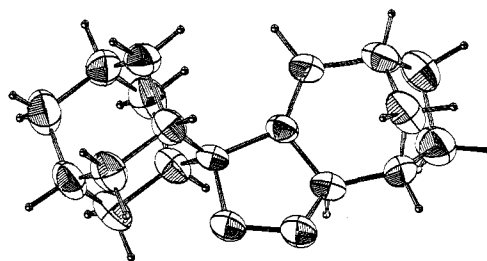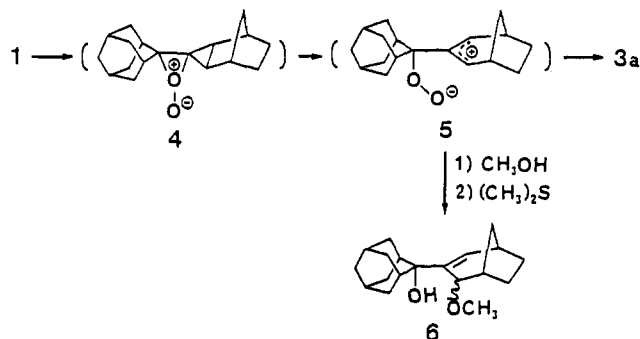**Figure 1.** ORTEP drawing of **3a**.

Figure 2. ORTEP drawing of **3b**.

Scheme I

oxygenations) giving products once thought to be characteristic of singlet oxygen[2,10,11] are topics of great current interest. We already reported that a stereochemical oxidation of di-*tert*-butylbi(bicyclo[3.3.1])non-9-ylidenes can act as a useful tool for distinction between ¹O₂ and Barton-type oxygenations of hindered olefins.[12] Accordingly, a reliable molecule that may serve as a diagnostic test for distinguishing between ¹O₂ and electron-transfer (both Foote-type and Barton-type) oxygenations is clearly desirable for mechanistic studies of oxygenation reactions. This report describes stereospecific oxygenation of 3-adamantylidene-tricyclo[3.2.1.0²,⁴]octane (**1**),[13] which constitutes a superior mechanistic probe for distinguishing between ¹O₂ and electron-transfer oxygenations, and the results obtained from dye-sensitized photooxygenation of **1**.

Oxidation of **1**[14] with 1,4-dimethylnaphthalene endoperoxide[15]

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(13) Sasaki, T.; Eguchi, S.; Tanida, M.; Nakata, F.; Esaki, T. *J. Org. Chem.* **1983,** *48,* 1579.

(14) Photosensitized oxygenations of unsubstituted adamantylidenecyclopropane (van de Heuvel, C. J. M.; Steinberg, H.; de Boer, Th. J. *Recl. Trav. Chim. Pays-Bas* **1985,** *104,* 145) and 2-adamantylidenebicyclo[4.1.0]heptane (Akasaka, T.; Ando, W. *Tetrahedron Lett.* **1987,** *28,* 217) afforded the corresponding rearranged products such as cyclic ketones and lactones via carbonyl oxide intermediates.

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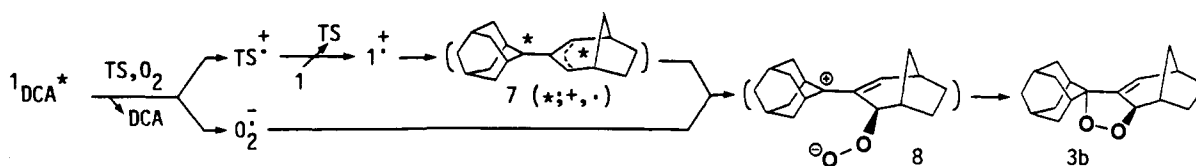
Scheme II

Table I. Dye-Sensitized Photooxygenation of 1

| 1,[a] mmol	sensitizer,[b] mmol	solvent, ϵ[c]	time, h	products and yields, $\%$[d,e,f]		
				recovered 1	3	3a/3b[g]
0.2	MB (0.004)	CH$_2$Cl$_2$ (9)	3	30	63 (90)	88/12
0.2	MB (0.1)	CH$_2$Cl$_2$	3	59	36 (88)	86/14
0.2	TPP (0.003)	CH$_2$Cl$_2$	4	17	80 (96)	100/0
0.2	TPP (0.003)	THF (7)	4	56	39 (89)	100/0
0.1	RB (0.002)	THF	1	78	20 (91)	85/15
0.5	RB (0.02)	THF	4	46	38 (70)	68/32
0.5	RB (0.1)	THF	10	0	90	30/70
0.2	Eosin-Y (0.04)	THF	5	83	13 (78)	100/0
0.2	Ⓟ-RB	CHCl$_3$ (5)	4	61	35 (87)	100/0
0.2	RB (0.015)	CH$_3$COCH$_3$ (21)	4	33	59 (90)	100/0
0.2	RB (0.04)	CH$_3$COCH$_3$	4	19	50 (61)	100/0
0.2	RB (0.04)	CH$_3$CN (38)	4	19	69 (85)	100/0

[a] The solution of **1** (1 × 10^{-2} M) was irradiated with 500-W halogen lamps under bubbling oxygen in a water-cooled Pyrex tube. [b] MB, methylene blue; TPP, tetraphenylporphine; RB, rose bengal; Ⓟ-RB, polymer-bound rose bengal (Schaap, A. P.; Thayer, A. L.; Blossey, E. C.; Neckers, D. C. *J. Am. Chem. Soc.* **1975**, *97*, 3741). [c] Dielectric constant. [d] Isolated yields. [e] Conversion yields are shown in parentheses. [f] Traces of adamantanone were observed. [g] The ratios were determined by means of their NMR spectra.

(**2**) which generates $^1O_2$ in methylene chloride gave *endo*-bicyclo[3.2.1]octene **3a**[16] stereospecifically (eq 1). None of the exo

(1)

2(50eq)/CH$_2$Cl$_2$ **3a** ; 90%
2(25eq)/THF   94%
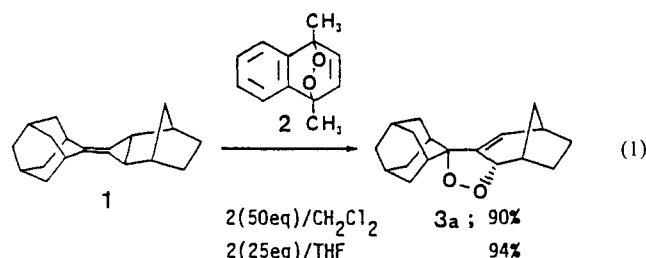
derivative **3b** was produced. The stereochemistry of **3a** was assigned by means of X-ray crystal analysis.[17] Electrophilic attack by $^1O_2$ on **1** would take place stereospecifically at the less hindered endo face of the molecule to give the perepoxide **4** and the zwitterionic peroxide **5** followed by cyclization to **3a**. When **1** was oxidized in the presence of methanol and then treated with dimethyl sulfide,[18] the alcohol **6**[19] was isolated in substantial yield. The formation of **6** is significant as it constitutes evidence for the existence of intermediary zwitterionic peroxide **5**, which is intercepted by alcohol.[2] When **1** (0.08 M) was photooxygenated with 9,10-dicyanoanthracene (DCA) in acetonitrile–methylene chloride (1:1) containing 0.4 M *trans*-stilbene (TS),[7d] **3b**[17,20] was

Scheme III
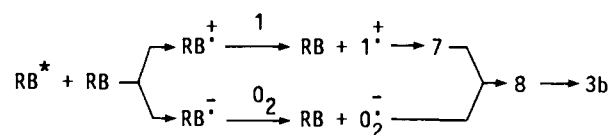
isolated in 93% yield stereospecifically. Since TS is present in high concentrations, the photooxygenation of **1** proceeds via initial formation of TS$^{\cdot+}$ followed by electron transfer from **1** to TS$^{\cdot+}$ to give **1**$^{\cdot+}$ [7d,21] which opens to cation radical **7**. In subsequent recombination of the pair of ion radicals once formed (Foote-type[7]), attack by superoxide anion radical (O$_2^{\cdot-}$) on **7** may take place stereospecifically at the less hindered exo face of the molecule[22] to give the zwitterionic peroxide **8** followed by cyclization to **3b** (Scheme II). Electronic factors[23] which favor exo face attack may also be important in making **3b** the only product. However, the cation radical produced by the electrolysis[24] of **1** and the reaction with tris(*p*-bromophenyl)amine cation radical[11] was not oxidized by $^3O_2$ (Barton-type[10]).[25-27]

In some cases, dye-sensitized photooxygenations may involve $^1O_2$ and an electron-transfer process, but no chemical differentiation between $^1O_2$ and electron-transfer oxygenations has been done.[28,29] It might be worthwhile to use **1** as a mechanistic probe

(16) **3a**: mp 96–97 °C; IR (KBr) 3050, 2940, 2900, 2850, 1445 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.0 (d, 1 H, J = 5.4 Hz), 4.87 (d, 1 H, J = 3.4 Hz), 2.40–2.80 (m, 2 H), 1.36–2.40 (m, 20 H); ^{13}C NMR (CDCl$_3$) δ 144.3 (s), 125.2 (d) 86.4 (s), 85.7 (d), 37.7, 36.0, 35.8, 35.5, 35.2, 34.9, 34.6, 33.7, 33.2, 26.8, 20.7; MS, *m/e* 272 (M$^+$). Anal. Calcd for C$_{18}$H$_{24}$O$_2$: C, 79.37; H, 8.88. Found: C, 79.34; H, 8.88.

(17) The X-ray analyses were performed by Drs. T. Sakurai and K. Kobayashi, of the Institute of Physical and Chemical Research.

(18) The MB-sensitized photooxygenation of **1** was carried out in methylene chloride and methanol (1:1).

(19) **6**: 40% yield; IR (KBr) 3440, 2940, 2910, 2850, 1445, 1260 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.16 (d, 1 H, J = 7.6 Hz), 4.10 (s, 1 H, D$_2$O exchangeable), 3.96 (d, 1 H, J = 3.0 Hz), 3.08 (s, 3 H), 1.11–2.77 (m, 22 H); ^{13}C NMR (CDCl$_3$) δ 137.0 (d), 129.8 (s), 81.6 (s), 72.2 (d), 47.0 (q), 39.7, 37.4, 35.4, 34.9, 34.5, 34.2, 32.6, 32.1, 31.4, 30.9, 28.2, 27.5, 26.8, 24.9; MS, *m/e* 288 (M$^+$); exact mass calcd for C$_{19}$H$_{28}$O$_2$ 288.2087, found 288.2076.

(20) **3b**: mp 131–132 °C; IR (KBr) 3050, 2930, 2900, 2845, 1445, 1045 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.49 (dd, 1 H, J = 1.2,7.6 Hz), 4.22 (s, 1 H), 2.42–2.71 (m, 2 H), 0.72–2.28 (m, 20 H); ^{13}C NMR δ (CDCl$_3$) 143.8 (s), 131.0 (d), 86.4 (s), 84.1 (d), 37.4, 36.1, 35.9, 35.2, 34.8, 34.5, 34.4, 32.5, 31.4, 28.1, 26.8; MS, *m/e* 272 (M$^+$). Anal. Calcd for C$_{18}$H$_{24}$O$_2$: C, 79.37; H, 8.88. Found: C, 79.24; H, 8.92.

(21) Oxidation potential (Ep vs. SCE) of **1** is 1.44 V. Ando, W.; Sato, R.; Yamashita, M.; Akasaka, T.; Miyazaki, H. *J. Org. Chem.* **1983**, *48*, 542.

(22) The highly stereoselective nucleophilic attack of acetate anion on bicyclo[3.2.1]oct-3-en-2-yl carbonium ion takes place at the exo face of the molecule. Goering, H. L.; Towns, D. L. *J. Am. Chem. Soc.* **1963**, *85*, 2295.

(23) Nelsen, S. F.; Kapp, D. L. *J. Am. Chem. Soc.* **1986**, *108*, 1265.

(24) Constant-potential electrolysis (1.7 V vs. SCE) was carried out at a carbon electrode.[9]

(25) None of the products, **3a** and **3b**, was obtained, but a complex mixture of the products was afforded.

(26) An important paper has just come to our attention in which the cation radical stabilized by allylic conjugation derived from biadamantylideneethene does not react with $^3O_2$. Nelsen, S. F.; Teasley, M. F.; Kapp, D. L. *J. Am. Chem. Soc.* **1986**, *108*, 5503.

(27) The cation radical of arylmethylenecyclopropanes reacts with $^3O_2$ to give the 4-methylene-1,2-dioxolanes. Takahashi, Y.; Miyashi, T.; Mukai, T. *J. Am. Chem. Soc.* **1983**, *105*, 6511.

(28) Koizumi, M.; Kato, S.; Mataga, N.; Matsuura, T.; Usui, Y. *Photosensitized Reactions*; Kagakudojin Publishing: Kyoto, Japan, 1978; Chapter 12, pp 366–394.

(29) Recently, it has been reported that $^1O_2$ and electron-transfer oxygenations compete in DCA-sensitized photooxygenation of α,α'-dimethylstilbenes. Gollnick, K.; Schnatterer, A. *Photochem. Photobiol.* **1986**, *43*, 365.

for those oxygenations. The results of dye-sensitized photo-oxygenation of **1** are shown in Table I. In MB-sensitized photooxygenation, the ratio **3a/3b** shows that the main oxidation process is $^1O_2$, but about 10% electron-transfer process (Foote-type[7]) is involved.[30] The ratio **3a/3b** is drastically altered by RB-sensitized photooxygenation in THF.[31] The ratio was significantly influenced by the concentration of RB and the addition[32] of both triphenylmethane, a free-radical scavenger,[33] and p-dimethoxybenzene as an electron-transfer quencher.[7c] The thermochemical singlet oxygenation in the dark was, however, not affected by addition of RB.[34] These observations suggest that the RB-sensitized photooxygenation may involve both singlet oxygen and an electron-transfer process (D-D process) which produces $\mathbf{1^{\bullet+}}$ and $O_2^{\bullet-}$.[28] Subsequent recombination of this pair of ion radicals might afford **3b** stereospecifically as shown in Scheme III.[35] The apparent function of THF might facilitate an electron-transfer process and separation of ion radicals.[36]

The further mechanistic studies on oxygenation reactions are in progress.

Supplementary Material Available: Tables of crystal data, atomic parameters, anisotropic temperature factors, and bond distances and angles (13 pages); listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

(30) Manring, L. E.; Eriksen, J.; Foote, C. S. J. Am. Chem. Soc. 1980, 102, 4275 and references cited therein.

(31) Dye bleaching occurred rapidly.

(32) The product ratio **3a/3b** was changed by the additive: 67/33 (none), 81/19 (triphenylmethane), and 75/25 (p-dimethoxybenzene).

(33) Russell, G. A. J. Am. Chem. Soc. 1956, 78, 1047.

(34) **3a** was obtained stereospecifically.

(35) An alternative mechanism pointed out by a referee, in which a radical chain process initiated by reaction of RB with THF is involved, may also be conceivable.

(36) For the solvent-separated ion pair, see: Goodman, J. L.; Peters, K. S. J. Am. Chem. Soc. 1985, 107, 6459. Mizuno, K.; Kamiyama, N.; Ichinose, N.; Otsuji, Y. Tetrahedron 1985, 41, 2207.

Model Complexes for the Cis Ru(VI)-Dioxo System. Novel Chemistry of [Ru^{III}(N$_4$O)(OH$_2$)][ClO$_4$]$_2$ (N$_4$OH = Bis[2-(2-pyridyl)ethyl][2-hydroxy-2-(2-pyridyl)ethyl]-amine)

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High-valent oxo complexes of ruthenium have long been known to be active oxidants for a variety of substrate oxidation reactions.[1-6] However, relatively few examples of high-valent cis Ru(VI)-dioxo complexes have been reported, despite their potential as strong oxidizing agents. Meyer and co-workers recently reported the electrochemical generation of a "cis-[Ru^{VI}-(bpy)$_2$O$_2$]$^{2+}$" species from cis-[Ru^{II}(bpy)$_2$(OH$_2$)$_2$]$^{2+}$ (bpy = 2,2'-bipyridine).[7,8] In this paper, we report the electrochemistry and oxidizing behavior of a high-valent ruthenium-oxo complex prepared from cis-[Ru^{III}(tepa)Cl$_2$]$^+$ (tepa = tris[2-(2-pyridyl)-ethyl]amine, Figure 1a).[9] The tripodal nature of the ligand necessitates its coordination to the ruthenium ion to be in the cis
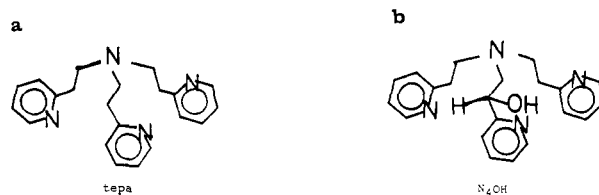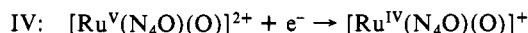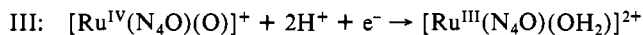

Figure 1. Structure of the ligands.

configuration and possibly provides an ideal precursor for the generation of the cis Ru(VI)-dioxo system.

Reaction of K$_2$[RuCl$_5$H$_2$O] with tepa in refluxing ethanol for 1 day gave cis-[Ru^{III}(tepa)Cl$_2$]$^+$ isolated as the ClO$_4^-$ salt. (IR (Nujol) no ν(O-H) stretch in the 3000-3500 cm^{-1} region). Treatment of cis-[Ru(tepa)Cl$_2$]$^+$ with silver toluene-p-sulfonate at 80 °C in the presence or absence of H$_2$O$_2$ yielded [Ru^{III}-(N$_4$O)(OH$_2$)]$^{2+}$ (N$_4$OH = bis(2-(2-pyridyl)ethyl)(2-hydroxy-2-(2-pyridyl)ethyl)amine, Figure 1b) isolated as the ClO$_4^-$ salt (golden brown crystals; IR (Nujol) ν(O-H) 3290 cm^{-1}). Both the magnetic susceptibility (μ_{eff} = 1.79 μ_B, crystalline sample, Guoy method) and conductivity (Λ_M in water = 253.3 Ω^{-1} mol^{-1} dm^3) measurements are in accord with the chemical formulation of [Ru(N$_4$O)(OH$_2$)][ClO$_4$]$_2$ (Ru(III) low-spin (t_{2g})^5, 1:2 electrolyte). The optical spectrum of the Ru(III) complex in water showed no appreciable absorption in the visible region (λ/nm (ϵ): 405 sh (920), 290 (6990), 267 (7930), 228 (7370), 200 (14620), thereby excluding its possible alternative as a Ru(III)-O-Ru(III) species in water.[8,10,11] The structure of [Ru^{III}(N$_4$O)(OH$_2$)][ClO$_4$]$_2$ has been established by X-ray crystallography.[12]

The cyclic voltammograms of [Ru^{III}(N$_4$O)(OH$_2$)]$^{2+}$, obtained with an edge-plane pyrolytic graphite electrode in aqueous medium, are shown in Figure 2. At pH 1 (0.1 M HClO$_4$), two couples, I and II, are observed at 0.33 and 0.98 V vs. SCE. Couple I is a one-electron reduction wave (n = 1 by coulometry; i_{pa}/i_{pc} ≈ 1; ΔE_p ~ 60 mV), corresponding to the reduction of Ru(III) to Ru(II), respectively. However, as the pH is increased, couple II begins to split into two quasi-reversible one-electron couples, III and IV, which appear at 0.74 and 0.96 V vs. SCE (pH 4.2), respectively. We attribute the electrode reactions to be at a pH >3.5.

III: [Ru^{IV}(N$_4$O)(O)]$^+$ + 2H$^+$ + e$^-$ → [Ru^{III}(N$_4$O)(OH$_2$)]$^{2+}$

IV: [Ru^V(N$_4$O)(O)]$^{2+}$ + e$^-$ → [Ru^{IV}(N$_4$O)(O)]$^+$

As expected, the $E_{1/2}$ for couple III shifts 120 mV per pH unit, whereas for couple IV, it is independent of pH (pH 3-7). Rotating-disc voltammetric studies also indicated that the limiting current for couple II was much larger than that for couple I at pH 1.1 (rotating speed, 900 rpm; scan speed, 5 mV s^{-1}; working electrode, glassy carbon), indicating the two-electron nature of couple II, [Ru^{III}(N$_4$O)(OH$_2$)]$^{2+}$ − 2e$^-$ − 2H$^+$ → [Ru^V(N$_4$O)-(O)]$^{2+}$.

The cyclic voltammogram in Figure 2 demonstrates the catalytic

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†Croucher studentship holder (1985-1987).