on observed NOEs to the imino protons of T3 and T19 within the T3·*A12·T19 triple (supplementary Figure 1). These results establish that the duocarmycin–triplex complex under study corresponds to site-specific covalent modification of the N^3 of A12 in the triplex.

The observation of hydrogen-bonded amino protons of protonated cytidines from the pyrimidine third strand between 9.75 and 10.25 ppm (designated by arrows) in both the unmodified triplex (Figure 1A) and the duocarmycin–triplex complex (Figure 1B) establishes that the covalently bound duocarmycin A in the minor groove does not expel the pyrimidine third strand from the major groove of the triplex at low temperature and acidic pH.

However, the covalently bound duocarmycin A in the minor groove affects the pH-dependent triplex–duplex equilibrium which reflects protonation of the third strand cytidines involved in C^+·GC triple formation.[16] The transition midpoint for this equilibrium for the unmodified triplex has a pK_a of 6.8,[17] while the value drops to a pK_a of 5.0 for the duocarmycin–triplex complex[18] (supplementary Figure 2). This result establishes that the covalently bound duocarmycin A in the minor groove lowers the pK_a for protonation of third strand cytidines in the major groove by 1.8 pH units in the complex.

The narrow imino protons in the 10.5–15.5 ppm region for both the triplex and the complex have been assigned following analysis of NOESY data sets using procedures reported previously.[11,12] These assignments are listed over the spectra and establish large upfield shifts at the imino protons of T3 ($\Delta\delta$ = 2.04 ppm) and T19 ($\Delta\delta$ = 2.31 ppm) on complex formation. This suggests weakening of the hydrogen bonds involving these imino protons at the modified T3·*A12·T19 triple induced by the covalently bound duocarmycin A.

The directionality of the duocarmycin A covalently linked to the N^3 atom of A12 in the minor groove of the triplex has been determined by monitoring intermolecular NOEs in the duocarmycin–triplex complex. We observe NOEs between the duocarmycin A indole OCH_3-6′ protons and the imino protons of T5 and T6 in the triplex (supplementary Figure 1), establishing that the duocarmycin A indole ring is directed toward the central T·A·T triple rich segment of the triplex. Consistent with this conclusion are the complexation shifts observed at the thymine imino protons of the T4-A11-T18 triple which flanks the T3·*A12·T19 triple modification site (Figure 1). Further characterization of the intermolecular contacts in the duocarmycin–triplex complex must await analysis of nonexchangeable proton data.

Our research complements the contributions of Park and Breslauer[5] who reported on the temperature-dependent optical and calorimetric measurements of the binding of netropsin to the poly(dT·dA·dT) triplex. They established that noncovalent netropsin binding in the minor groove of the triplex occurs without disruption of the third strand in the major groove and profoundly influences the melting energetics and cooperativity of the triplex–duplex transition.[5]

Acknowledgment. This research was supported by NIH Grants GM-34504 and CA-46778 to D.J.P. We thank Dr. Hiromitsu Saito of the Kyowa Hakko Kogyo Co. for a generous supply of duocarmycin A and Dr. Hiroshimi Suziyama of Kyoto University for advice and encouragement.

Supplementary Material Available: A NOESY plot of the duocarmycin–triplex complex and plots of pH dependence of the triplex–duplex equilibrium for the unmodified 31-mer triplex and the complex (4 pages). Ordering information is given on any current masthead page.

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(17) The imino protons of the duplex and triplex are in slow exchange in the unmodified 31-mer, and the pH-dependent transition midpoint can be monitored by changes in the area of the assigned imino protons in both states during the transition.

(18) The imino protons of the duplex and triplex are in intermediate exchange in the complex, and the pH-dependent transition midpoint can be monitored by the average chemical shift changes during the transition.

Highly Efficient Oxidation of Alkanes and Alkyl Alcohols with Heteroaromatic *N*-Oxides Catalyzed by Ruthenium Porphyrins

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Many transition metal-catalyzed oxidation systems for alkenes or other relatively unreactive compounds have been developed,[1,2] however, it still remains, intellectually and practically, a challenging objective to oxidize such compounds efficiently by using chemically stable and tractable oxidants. We studied the reactivity of ruthenium porphyrin complexes as oxidation catalysts because of their relation to cytochrome P-450[3] and have reported the unique reactivity of these complexes to catalyze the efficient epoxidation of olefins by heteroaromatic *N*-oxides.[4] These *N*-oxides, represented by pyridine *N*-oxide, are highly stable and have never been used as effective oxidants for the catalytic oxidation of olefins or alkanes except in our work.[5,6] We have now found that the catalytic ability of ruthenium porphyrins is enhanced by the presence of a small amount of HCl or HBr and that, in the presence of these acids, the oxidation of alkanes or alkyl alcohols with pyridine *N*-oxides is also catalyzed by ruthenium porphyrins with high efficiency.

We used 2,6-dichloropyridine *N*-oxide as the oxidant and $RuTMP(O)_2$[7,8] as the catalyst for the oxidation of alkanes or alkyl alcohols, because they were the reagents of choice for the epoxidation reported in a previous paper.[4a] To a mixture of adamantane (1.0 mmol), 2,6-dichloropyridine *N*-oxide (1.3 mmol), 4A molecular sieves (5.0 g)[9], and benzene (5.0 mL) were added 2–3 drops of concentrated aqueous HCl (0.1–0.2 mL, 1–2 mmol) and $RuTMP(O)_2$ (5 μmol). The mixture was stirred under Ar for 24 h at room temperature; almost all of the adamantane was consumed to afford adamantan-1-ol, adamantane-1,3-diol, and adamantan-2-one in yields of 68%, 25%, and 1% based on adamantane, respectively (run 1).

The results for the oxidation of adamantane under several conditions are summarized in Table I. Adamantane was also efficiently oxidized in the presence of HBr[10] instead of HCl (run 2). In contrast, without the addition of these acids, only a 4% yield of oxidation products was obtained and most of the adamantane remained intact after the reaction for 24 h (run 3). RuTMP(CO)[7] was also an effective catalyst (run 5). The reaction

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(6) Heteroaromatic *N*-oxides are less reactive as oxidants than aliphatic amine *N*-oxides. Only photochemical oxygen atom transfer reactions from heteroaromatic *N*-oxides to olefins or alkanes have been reported. However, these reactions did not proceed efficiently and selectively [Tsuchiya, T.; Arai, H.; Igeta, H. *Tetrahedron Lett.* **1969**, 2747].

(7) TPP: tetraphenylporphyrinato. TMP: tetramesitylporphyrinato. TDCPP: tetrakis(2,6-dichlorophenyl)porphyrinato.

(8) Groves, J. T.; Quinn, R. *Inorg. Chem.* **1984**, *23*, 2844. $RuTDCPP(O)_2$ was also prepared according to the method of this report.

(9) The reaction did not proceed efficiently without the addition of molecular sieves. Water may inhibit the reaction. As shown in Figure 1b, anhydrous acids are effective in the absence of these sieves.

(10) 1-Bromoadamantane was not detected under this condition.

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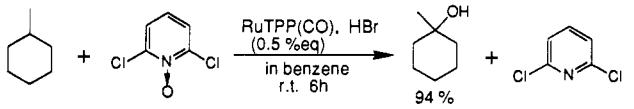
Table I

run	substrate	precatalyst	additive	time, h	products, % yield[a,b] adamantan-1-ol	adamantane-1,3-diol	adamantan-2-one[n]
1[c]	adamantane	$RuTMP(O)_2$	HCl	24	68	25	1
2[c]	adamantane	$RuTMP(O)_2$	HBr	24	63	15	2
3[c]	adamantane	$RuTMP(O)_2$		24	4	nd[j]	trace[k]
4[c]	adamantane		HCl	24	1	nd	nd
5[c]	adamantane	RuTMP(CO)	HBr	24	64	20	2
6[c]	adamantane	RuTPP(CO)	HBr	6	66	27	trace
7[d,i]	adamantane	$RuTMP(O)_2$	HBr	24	62 (12500)[l]	11 (4500)	2 (800)
8[d,i]	adamantane	$RuTDCPP(O)_2$	HBr	6	61 (12300)	13 (5100)	4 (1400)
					1-methylcyclohexanol	methylcyclohexanone (2-, 3-, 4-)[o]	
9[e,i]	methylcyclohexane	$RuTMP(O)_2$	HBr	9	77	6 (3, 2, 1)	
10[f]	methylcyclohexane	RuTPP(CO)	HBr	6	94	trace	
11[g]	ethylbenzene	$RuTMP(O)_2$	HCl	24	acetophenone[p] 88		
12[h]	adamantan-2-ol	$RuTMP(O)_2$	HBr	24	adamantan-2-one 84[m]		
13[h]	cyclohexanol	$RuTMP(O)_2$	HCl	24	cyclohexanone 88		

[a] These reactions were carried out in benzene under Ar at room temperature. The reaction, mixtures contained substrate (200 mM), 2,6-dichloropyridine *N*-oxide, catalyst (1.0 mM), 36% aqueous HCl (20–40 mL/L = 200–410 mM) or 48% aqueous HBr (20–40 mL/L, 120–240 mM), and 4A molecular sieves (100 g/L). Yields were based on starting substrates (%). [b] Determined by GLC. [c] [*N*-oxide] = 260 mM. [d] [*N*-oxide] = [adamantane] = 1.0 M, [catalyst] = 50 μM. [e] [*N*-oxide] = 300 mM. [f] [*N*-oxide] = 400 mM. [g] [*N*-oxide] = 440 mM. [h] [*N*-oxide] = 220 mM. [i] Carried out at 40 °C. [j] Not detected. [k] <0.5%. [l] The turnover number per catalyst (turns). [m] Isolated yield. [n] Adamantan-2-ol was not detected. [o] 2-, 3-, or 4-methylcyclohexanol was not detected. [p] 1-Phenethyl alcohol was not detected.

with $RuTPP(CO)$[7] was faster, being completed within 6 h[11] (run 6).

With this system, ethylbenzene was converted into acetophenone in satisfactory yield (88%) (run 11), and 1-methylcyclohexanol was selectively obtained with high efficiency in the oxidation of methylcyclohexane (94%) (run 10). Alkyl alcohols were also oxidized to afford the corresponding ketones (runs 12, 13).



Ruthenium catalysts were extremely stable under these conditions. Adamantane (2.0 mmol) reacted with 2,6-dichloropyridine *N*-oxide (2.0 mmol) in the presence of $RuTMP(O)_2$ (0.1 μmol) and HBr at 40 °C (substrate:oxidant:catalyst = 20000:20000:1). The oxidant was exhausted in 30 h, at which time the turnover number was 17800 (run 7). Under the same conditions, $RuTDCPP(O)_2$[7,8] worked more efficiently as a catalyst: the reaction with this catalyst was completed in 6 h and the turnover number reached 18800 (run 8). The turnover frequencies for the reactions with $RuTMP(O)_2$ and $RuTDCPP(O)_2$ were 0.16 and 0.87 turn/s, respectively.

$RuTMP(O)_2$ was allowed to react with HCl in benzene at room temperature for 2 h ($RuTMP(O)_2$ = 1 μM, concentrated aqueous HCl = 30 mL/L, 4A molecular sieves = 100 g/L), and the resulting ruthenium porphyrin complex (I) was isolated (82%). The reaction conditions were the same as for the catalytic oxidations described above (run 1) except that the mixture did not contain substrate or oxidant. The IR spectrum of I lacked the band at 821 cm^{-1} due to ruthenium–oxo bonds, and peaks at −54.65 and 12.49 ppm were observed in the 400-MHz ^1H NMR spectrum of I.[12] It was reported that $RuTPP(Cl)_2$ was obtained by the reaction of $(RuTPP)_2$ with HCl and displayed peaks at −57.72 and 11.52 ppm in its ^1H NMR spectrum due to pyrrole proton and meta proton, respectively.[13] Thus, we considered I must be the dichloro complex of ruthenium porphyrin, formulated as $RuTMP(Cl)_2$. The catalytic abilities of a series of complexes, I, $RuTMP(O)_2$, and RuTMP(CO), were compared in the absence of HCl or HBr at 40 °C. As shown in Figure 1a, I was the most efficient catalyst among them, suggesting that ruthenium porphyrins acted as efficient catalysts after conversion into Cl^- or Br^- coordinated complexes or at least into complexes which could be generated more easily from I than from $RuTMP(O)_2$ or RuTMP(CO). However, the oxidation with $RuTMP(O)_2$ in the presence of HCl at 40 °C proceeded far more efficiently than that with I in the absence of acid, and the amount of added HCl affected the efficiency of the oxidations (Figure 1b). All of these results support the hypothesis that HCl or HBr plays two roles in this system. The first is to convert the dioxo or CO complexes of ruthenium porphyrins into the appropriate catalytic complexes, and the second is to accelerate the deoxygenation of *N*-oxide by ruthenium porphyrins or to enhance the reactivity of generated active intermediates. We have not identified the active intermediate in this system, but the candidates are the ruthenium porphyrin oxo complexes $[Ru^V(por)(X)(O)]$ and $[Ru^{VI}(por)(X)(O)]^+$ (X = Cl or Br).[14] We cannot exclude the possibility

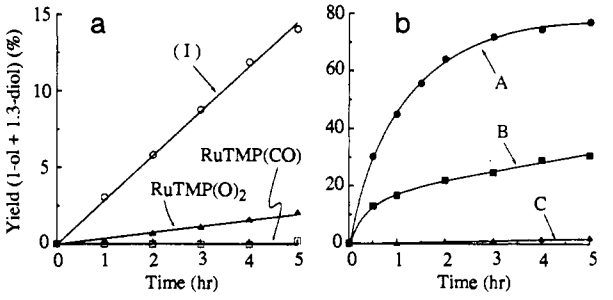


Figure 1. (a) Hydroxylation of adamantane with 2,6-dichloropyridine *N*-oxide catalyzed by $RuTMP(Cl)_2$, $RuTMP(O)_2$, and RuTMP(CO). These reactions were carried out in benzene under Ar at 40 °C ([adamantane] = [2,6-dichloropyridine *N*-oxide] = 100 mM, [catalyst] = 0.4 mM). Neither HCl (or HBr) nor molecular sieves were added to the reaction mixtures. Yields (based on starting adamantane) were determined by GLC. (b) Hydroxylation of adamantane with 2,6-dichloropyridine *N*-oxide catalyzed by $RuTMP(O)_2$ in the presence or the absence of HCl. These reactions were carried out in benzene under Ar at 40 °C ([adamantane] = [2,6-dichloropyridine *N*-oxide] = 100 mM, $[RuTMP(O)_2]$ = 0.4 mM). A saturated HCl solution of benzene was added to these reaction mixtures (A, 10 mL/L, B, 5 mL/L, C, 0 mL/L). Molecular sieves were not added to the mixture, because the added HCl solution was anhydrous. Yields (based on starting adamantane) were determined by GLC.

(11) RuTPP(CO) did not act as an efficient catalyst for the oxidation of ethylbenzene.

(12) I: ^1H NMR (400 MHz) ($CDCl_3$/TMS) δ −54.65 (s, 8 H), 3.84 (s, 12 H), 4.07 (s, 24 H), 12.49 (s, 8 H).

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(14) Oxo–metal species are often regarded as the active intermediates in metal-catalyzed oxidations [Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401].

that other intermediates which do not include Cl^- or Br^- as an axial ligand are generated under the catalytic conditions.[15]

Recently, some efficient alkane oxidation systems have been developed using manganese porphyrins.[16] The systems with transition metal-substituted polyoxometalate catalysts[17] and the Gif systems[18] are also efficient. However, our system seems to be the most efficient metal-catalyzed alkane oxidation system in terms of turnover numbers and yields based on substrates. Moreover, this system offers various practical advantages for use as a synthetic reagent, such as mild conditions, simple handling procedures, and the use of a highly stable and tractable oxidant. Studies to extend the scope of this system and to elucidate the mechanistic details are in progress in our laboratory.

Acknowledgment. This work was supported in part by a Grant-in-Aid from the Ministry of Education, Science, and Culture, Japan.

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A New Method for Controlling the Orientation of Functional Molecules in Langmuir-Blodgett Films

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The Langmuir-Blodgett (LB) method has been widely studied as one of the most versatile techniques to fabricate organic thin films with well-controlled compositions, structures, and thicknesses.[1,2] Due to these features the LB technique has been used to construct prototypes of molecular electronic and bioelectronic devices.[3-12]

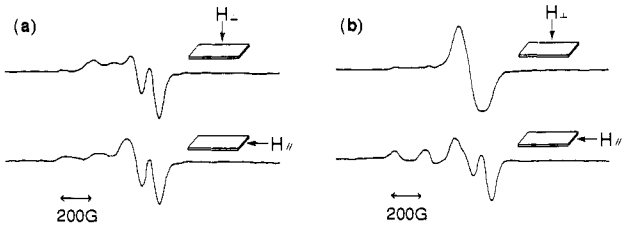

Figure 1. First-derivative ESR spectra of the LB film (40 layers on both sides) at the angles of 0° and 90° between the external magnetic field and the film surface: (a) PM/cadmium icosanoate = 1.5/10; (b) PM/cadmium icosanoate/hexatriacontane = 1.5/10/2.

Typical LB films consist of amphiphilic molecules with long alkyl chains. The alternative is to employ lightly-substituted molecules or molecules without long alkyl chains, which enables dense packing of functional molecules in the films.[13-17] Further, this strategy makes the orientation of the chromophores different from that obtained for the usual LB films of amphiphilic molecules. Such nonamphiphilic molecules have been mixed with film-forming molecules such as fatty acids to obtain good LB films.[18-20]

A great deal of effort has been made to control the orientation of functional molecules in LB films. Chemical modification seems to be very efficient in this respect. The orientation of anthraquinone has been controlled by changing the position of the attached alkyl chains.[21] Physical methods have also been employed for this purpose.[22-24]

In this communication we report that a small amount of long-chain *n*-alkane, when added in the preparation of monolayers, can drastically change the orientation of a dye molecule in the LB films.

[Tetrakis(3,5-di-*tert*-butylphenyl)porphinato]copper(II), PM,[25] was used as a dye molecule. A chloroform solution of molar ratio PM/icosanoic acid/*n*-alkane = $1.5/10/r$ ($0 \le r \le 5$) was spread onto an aqueous subphase of pH 6.0 containing 4.0×10^{-4} M of $CdCl_2$ and 5.0×10^{-5} M of $KHCO_3$ at 17 °C. The monolayers

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