Selected Paper

Nitrous Oxide Oxidation Catalyzed by Ruthenium Porphyrin Complex

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Dinitrogen oxide was employed as a clean oxidant for various oxidations in the presence of a catalytic amount of dioxoruthenium tetramesitylporphyrin complex ($Ru(tmp)(O)_2$). A variety of olefins, secondary alcohols, and benzyl alcohols were smoothly oxidized to the corresponding epoxides, ketones, and aldehydes in high yields. In the oxidation of 9,10-dihydroanthracene derivatives, the competitive reactions affording anthraquinones and anthracenes could be regulated by the reaction conditions. At a high temperature (200 °C), anthraquinones were selectively produced, while the anthracenes were selectively produced by the addition of sulfuric acid.

Much attention has been recently drawn to various oxides of nitrogen, NO_x such as NO,[1] NO_2, and N_2O,[2] because enormous amounts of nitrogen monoxide (NO) or nitrogen dioxide (NO_2) have been emitted in the exhaust gas from internal-combustion engines and industries causing serious air pollution. Dinitrogen oxide (nitrous oxide, N_2O) has been used in the medical field as an anesthetic gas for a long time, whereas it is recently regarded as one of the most influential greenhouse gases.[3] Nitrogen dioxide (NO_2) in organic chemistry has been produced industrially and is indispensable for nitration reaction.[4] On the other hand, nitrogen monoxide (NO)[5] or dinitrogen oxide (N_2O) has rarely been used in organic synthesis. Although dinitrogen oxide is expected to work as a clean oxidant, releasing only nitrogen gas as a by-product during the oxidation reaction, it has seldom been employed as an oxidant because of the high activation energy required for its decomposition to a nitrogen molecule and an oxygen atom.[6] In order for obstacles to its synthetic application to be overcome, drastic reaction conditions, such as high temperature, high pressure, or a super-critical phase, were generally required.[7] In the manufacturing process of 6,6-nylon, one of the practical methods successfully introduced was as follows: dinitrogen oxide emitted during the HNO_3 oxidation of cyclohexane/cyclohexanol to adipic acid was reused for the oxidation of benzene to phenol, which was then transformed into cyclohexanone/cyclohexanol by partial hydrogenation.[8] Although the recycling system for dinitrogen oxide is excellent, low energy efficiency and/or limited applicability of the functionalized organic compounds have remained. Therefore, milder activation of dinitrogen oxides has been desired,[9] and transition-metal complex catalysis is expected to be one of the most reliable methods to decrease the activation energy. Because of its strong affinity for electrons,[10] dinitrogen oxide could be captured and reacted with the complexes with low valency metals. Indeed, some stoichiometric reactions of dinitrogen oxide oxidation with transition-metal complexes were reported.[11] In the course of the studies on the reactivity of N_2O, it was found that dinitrogen oxide oxidation of phosphine to phosphine oxide was catalyzed by a zero-valent nickel complex.[12] Although the catalytic oxidation of phosphines proceeded even at −40 °C, the system could not be applied to the oxidation of organic compounds. Hence, screening of various transition-metal complexes revealed that ruthenium porphyrin complexes showed catalytic activity for dinitrogen oxide oxidation. It was reported by Groves that a dioxorutheniumporphyrin complex, prepared by dinitrogen oxide oxidation from a ruthenium(II) complex, could epoxidize 1-phenylpropene derivatives.[13] A few stoichiometric examples were reported, though the catalytic system was not established.[14] In this article, the catalytic dinitrogen oxide oxidation in the presence of a catalytic amount of the ruthenium complex for organic substrates is fully described; e.g., epoxidation of olefins, oxidation of alcohols, and dehydrogenative aromatization of anthracenes proceeded using dinitrogen oxide as an oxidant.

Results and Discussion

Ruthenium Porphyrin Complex Catalysis for Dinitrogen Oxide Epoxidation. It is expected that transition-metal complexes can capture and activate dinitrogen oxide to generate the corresponding metal-oxo species while releasing nitrogen and that the resulting metal-oxo complexes can oxidize organic substrates as shown in Fig. 1. On the basis of this concept, the dinitrogen oxide oxidation of phosphine to phosphine oxide was developed using a low valency nickel–dppp complex catalyst,[12] though this catalysis system could not be applied to the oxidation of olefins or alcohols at all. Various kinds of metal complexes were screened again after adopting the ep-

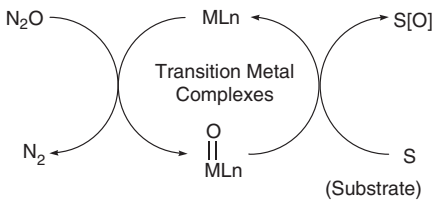

Fig. 1. Catalytic cycle of N_2O oxidation.

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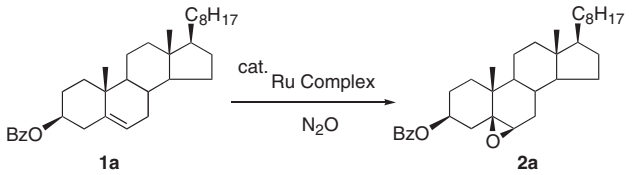
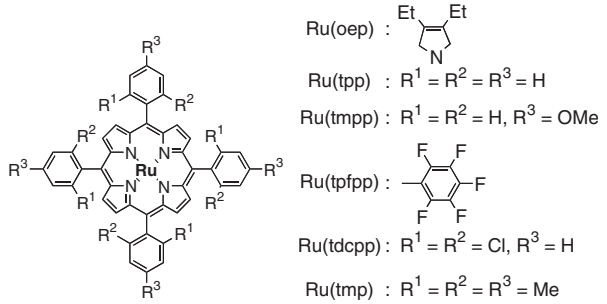
Table 1. Dioxoruthenium Porphyrin Complexes for N_2O Oxidation



1a **2a**

Entry[a)]	Ru porphyrin complex		Yield/%	β-Selectivity/%
1	$Ru(oep)(O)_2$	**3a**	0	—
2	$Ru(tpp)(O)_2$	**3b**	1	—
3	$Ru(tmpp)(O)_2$	**3c**	0	—
4	$Ru(tpfpp)(O)_2$	**3d**	6	>99
5	$Ru(tdcpp)(O)_2$	**3e**	53	>99
6	$Ru(tmp)(O)_2$	**3f**	61	>99

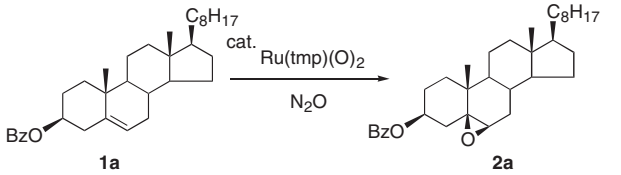
a) All the reactions were carried out with 0.10 mmol cholesteryl benzoate and 0.05 molar amount ruthenium complex in 3 mL fluorobenzene at 100 °C under 1.0×10^3 kPa (10 atm) N_2O for 3 h.



oxidation reaction of cholesteryl benzoate (**1a**) as a model probe, because it was reported that cholesteryl esters were preferentially epoxidized on their α-face using peroxy acid as an oxidant, while their β-epoxides were selectively obtained by the transition-metal oxo species.[15] Because the dioxoruthenium porphyrin complexes were preliminarily found to work as a catalyst, various ruthenium porphyrin complexes were first examined (Table 1). Using dioxoruthenium 2,3,7,8,12,13,17,18-octaethylporphyrin ($Ru(oep)(O)_2$, **3a**), 5,10,15,20-tetraphenylporphyrin ($Ru(tpp)(O)_2$, **3b**), or 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin ($Ru(tmpp)(O)_2$, **3c**), the reaction did not proceed (Entries 1–3), although traces of the epoxide were obtained in the presence of 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin ($Ru(tpfpp)(O)_2$, **3d**) (Entry 4). In the presence of 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin ($Ru(tdcpp)(O)_2$, **3e**) or 5,10,15,20-tetramesitylporphyrin ($Ru(tmp)(O)_2$, **3f**), effective catalysts for aerobic oxidation,[13b] the yield of the epoxides was greatly improved to 53–61% yields with complete β-selectivity (Entries 5 and 6).[16] As mentioned above, the β-selectivity in the present oxidation system suggested that the dioxoruthenium complex was generated as an intermediate for the epoxidation of the carbon–carbon double bond of cholesteryl benzoate **1a**.

Optimization of the Reaction Conditions for Epoxidation of Cholesteryl Benzoate Catalyzed by $Ru(tmp)(O)_2$ Complex. Various solvents were examined for N_2O epoxidation of cholesteryl benzoate (**1a**) in the presence of a 0.05 molar amount $Ru(tmp)(O)_2$ (**3f**). The yields and stereoselectivities

Table 2. Solvent Effect for N_2O Oxidation of Cholesteryl Benzoate



1a **2a**

Entry[a)]	Solvent	Concentration/mM	Yield/%	β/α[b)]
1	THF	33	—	—
2	EtOH	33	—	—
3	CH_3CN	33	—	—
4	PhMe	33	30	>99
5	PhH	33	60	>99
6	PhF	33	61	>99
7	PhF	14[c)]	99	>99
8[d)]	PhCl	14[c)]	94	>99

a) Reaction conditions: 0.10 mmol of cholesteryl benzoate and 0.05 molar amount of $Ru(tmp)(O)_2$ in solvent (3.0 mL) at 100 °C under 1.0×10^3 kPa (10 atm) N_2O for 3 h. b) Determined by ^1H NMR analysis. c) Reaction conditions: 0.20 mmol of cholesteryl benzoate and 0.05 molar amount of $Ru(tmp)(O)_2$ in 14 mL solvent. d) Reaction was performed at 140 °C.

are shown in Table 2. Coordinating solvents, such as THF, EtOH, and CH_3CN, were not suitable for this reaction because of their coordination with the ruthenium complex (Entries 1–3). Aromatic solvents such as toluene and benzene gave better yields (Entries 4 and 5), and fluorobenzene was found to be a suitable solvent for this reaction (Entry 6).[17] The concentration in this reaction had a crucial effect on the yield. When the reaction was performed at a lower concentration, the yield was improved to 99% (Entry 7). It is assumed that a greater amount of dinitrogen oxide dissolved in the solution would accelerate the regeneration of the dioxoruthenium complex in the catalytic cycle. Under vigorous conditions in a chlorobenzene solvent at 140 °C, the product was obtained in a similar yield. The latter reaction conditions were more useful for less reactive substrates than the conditions in Entry 7; therefore, they were adopted as the standard for N_2O epoxidation.

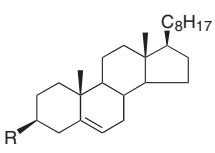
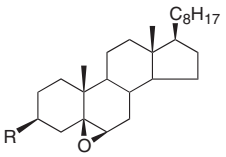
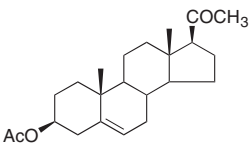
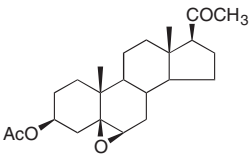
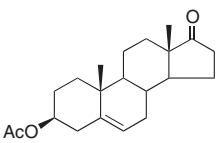
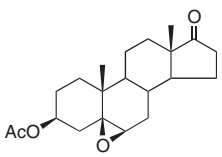
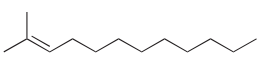
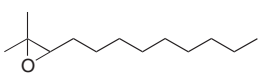
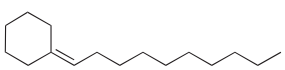
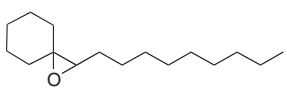
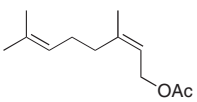
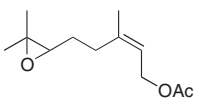
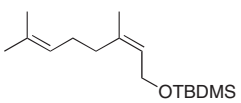
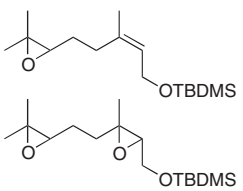
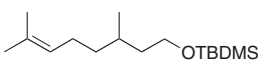
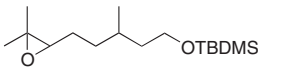
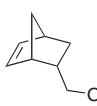
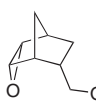
It was confirmed that the reaction did not proceed without $Ru(tmp)(O)_2$ (**3f**) or dinitrogen oxide. When substrate **1a** was treated under an argon atmosphere in the presence of 0.05 molar amount of **3f**, the corresponding oxidized product was obtained in only 9% yield. The oxygen atom of the epoxide was considered to be stoichiometrically transferred from the dioxoruthenium complex. Because dinitrogen oxide of 99.999% purity was employed throughout the present work, oxygen contamination was guaranteed to be less than 1.0 ppm, so that oxidation by contaminated oxygen was negligible. For further confirmation, the evolution of nitrogen was monitored by GC analysis as follows.

Measurement of Nitrogen Gas Released during Dinitrogen Oxide Oxidation. During the dinitrogen oxide oxidation, an equimolar amount of nitrogen gas based on the product should be released. The amount of the evolved nitrogen gas was measured in the epoxidation of cholesteryl benzoate (**1a**). The analysis of the gas phase in the reaction vessel

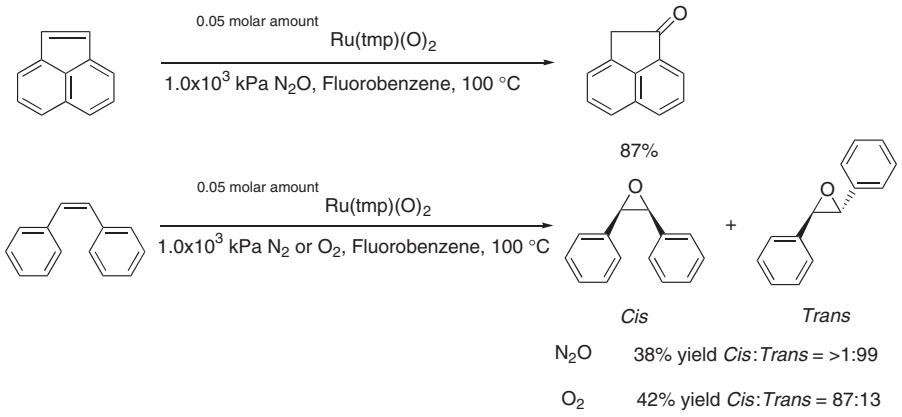
was done as follows: the gas in the autoclave after the reaction was collected in a flask and a small amount of carbon dioxide was added as an internal standard. The thus obtained sample was analyzed by GC attached to a TCD detector and a Porapak Type Q column. As a result, about equimolar amount of nitrogen vs the substrate was detected in the N_2O oxidation. It was confirmed that dinitrogen oxide was employed as the oxidant.

N_2O Epoxidation of Various Olefinic Compounds. The dinitrogen oxide epoxidation catalyzed by the ruthenium complex was successfully applied to various olefins (Table 3). Cholesteryl esters, such as cholesteryl acetate (**1b**), decanoate (**1c**), formate (**1d**), and ethyl carbonate (**1e**) were smoothly epoxidized in high yield (Entries 1–4). The reaction of cholesteryl bromide (**1f**) proceeded in 66% yield along with a small amount of the debrominated product (Entry 5). Other substrates containing a steroidal framework were also epoxidized to give β-epoxides in high yields (Entries 6 and 7). Trisubstituted unfunctionalized olefins (**1i**–**1j**) could be smoothly epoxidized in 86–90% yield (Etnries 8 and 9). The isolated carbon–carbon double bond in neryl acetate (**1k**) was selectively epoxidized to afford the mono-epoxide **2k** in good yield (Entry 10). Although the diepoxide **4l** was observed in the epoxida-

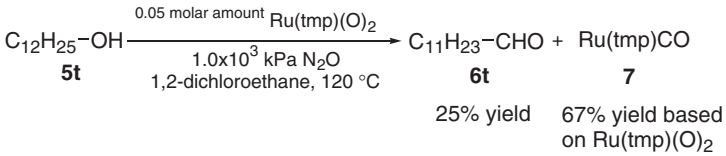
Table 3. N_2O Oxidation of Various Olefinic Compounds

Entry[a]	Substrate		Product		Yield/%
1		R = AcO– **1b**		**2b**	99
2		R = $C_9H_{19}CO_2$– **1c**		**2c**	91
3		R = HCO_2– **1d**		**2d**	87
4		R = $EtOCO_2$– **1e**		**2e**	90
5		R = Br– **1f**		**2f**	66
6		**1g**		**2g**	99
7		**1h**		**2h**	97
8		**1i**		**2i**	86
9		**1j**		**2j**	90
10[b]		**1k**		**2k**	64
11		**1l**		**2l** 44 **4l** 28	72 (total)
12		**1m**		**2m**	94
13		**1n**		**2n**	94

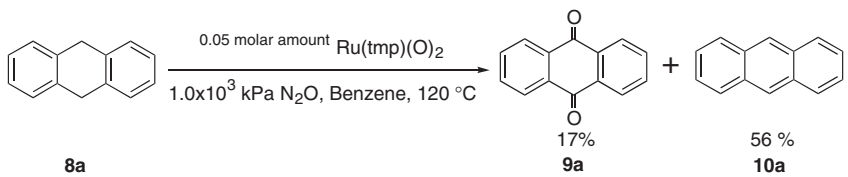
a) Reaction conditions: 0.2 mmol of olefins and 0.05 molar amount of $Ru(tmp)(O)_2$ in 14 mL chlorobenzene at 140 °C under 1.0×10^3 kPa (10 atm) N_2O. b) 0.085 molar amount catalyst was employed.



Scheme 1.



Scheme 2.

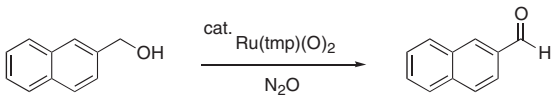


Scheme 3.

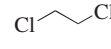
tion of the *t*-butyldimethylsilyl (TBDMS) ether of nerol (**1l**), the isolated carbon–carbon double bond was preferentially oxidized (Entry 11). The TBDMS ether of citronelol (**1m**) was converted to the corresponding epoxide in high yield (Entry 12). The reaction could be applied to a reactive disubstituted olefin (**1n**) (Entry 13). Although the yields of most of the di- and monosubstituted olefins were low, the oxidation of acenaphthylene and *cis*-stilbene gave acenaphthenone, a rearranged product from the epoxide, and *trans*-stilbene oxide in 87% and 38% yield, respectively (Scheme 1). When molecular oxygen was used instead of dinitrogen oxide for epoxidation of *cis*-stilbene under the same conditions, *cis*-stilbene oxide was preferentially obtained (*cis*/*trans* = 87/13). The results indicated that the lifetime of the Ru(II) porphyrin complex was longer in dinitrogen oxide than in an oxygen atmosphere; hence, the rearrangement and isomerization caused by the Ru(II) or Ru(IV) porphyrin complex occurred more easily.[18]

Optimization of the Reaction Conditions for N_2O Oxidation of Alcohols. The present system was next subjected to the oxidation of alcohols, using 2-naphthalenemethanol (**5a**) as a model substrate. Because the solvents have a crucial effect on the N_2O epoxidation, various solvents were reexamined for optimization (Table 4). In aromatic solvents, which were suitable for epoxidation, **5a** was converted to the corresponding aldehyde **6a** in 39–62% yield (Entries 1–3). Although the yields were moderate in dichloromethane and chloroform (Entries 4 and 5), they were greatly improved in 1,2-dichloroethane (Entry 6). The aldehyde was obtained in a quantitative yield when the reaction was carried out at 120 °C for 9 h in 1,2-dichloroethane (Entry 7). In all cases, no carboxylic acid was observed.

Table 4. Optimization of the Reaction Conditions for N_2O Oxidation of Alcohols



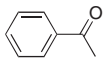
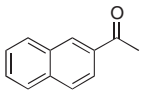
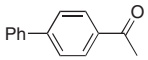
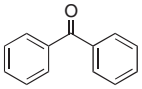
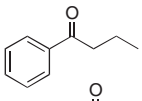
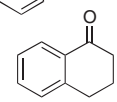
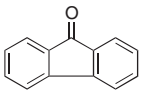
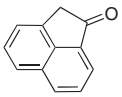
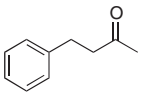
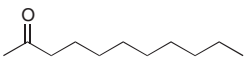
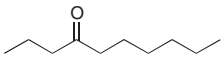
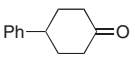
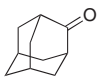
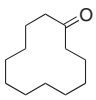
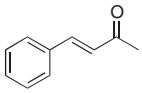
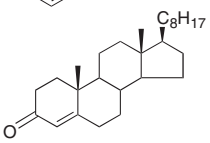
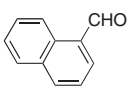
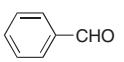
5a 6a

Entry[a)]	Solvent	Temp/°C	Conv/%	Yield/%
1	PhH	100	41	41
2	PhF	100	62	62
3	PhCl	100	41	39
4	CH_2Cl_2	100	23	22
5	$CHCl_3$	100	33	32
6		100	71	71
7[b)]		120	100	quant

a) Reaction conditions: 0.30 mmol of 2-naphthalenemethanol and 0.05 molar amount of $Ru(tmp)(O)_2$ in solvent (14.0 mL) under 1.0×10^3 kPa (10 atm) of N_2O for 6 h. b) For 9 h.

Scope and Limitation of N_2O Oxidation of Various Alcohols. A variety of alcohols was successfully oxidized in this system (Table 5). Secondary benzyl alcohols **5b–5i**

Table 5. N_2O Oxidation of Various Alcohols

Entry[a]	Product		Yield/%
1		**6b**	92[c]
2		**6c**	94
3		**6d**	quant
4		**6e**	96
5[b]		**6f**	quant
6		**6g**	99
7		**6h**	99
8		**6i**	95
9[b]		**6j**	98
10[b]		**6k**	97
11[b]		**6l**	89
12[b]		**6m**	97
13[b]		**6n**	86
14[b]		**6o**	97
15		**6p**	89
16		**6q**	quant
17		**6r**	92
18		**6s**	95[c]

a) Reaction conditions: 0.3 mmol of alcohols and 0.05 molar amount of $Ru(tmp)(O)_2$ in 14 mL 1,2-dichloroethane at 120 °C under 1.0×10^3 kPa (10 atm) N_2O. b) At 150 °C. c) GC yield.

were smoothly converted to the corresponding ketones **6b–6i** in excellent yields in the presence of 0.05 molar amounts of $Ru(tmp)(O)_2$ (**3f**) (Entries 1–8). Various secondary alkanols **5j–5o** were also oxidized at 150 °C to give the corresponding alkyl ketones **6j–6o** in high yields (Entries 9–14). Interestingly, an α,β-unsaturated ketone **6p**, **6q** was selectively obtained from 4-phenyl-3-buten-2-ol (**5p**) or cholest-4-en-3-ol (**5q**) without any epoxidation of the carbon–carbon double bond (Entries 15 and 16). Like 2-naphthalenemethanol (**5a**), other benzylic primary alcohols such as 1-naphthalenemethanol (**5r**) and benzyl alcohol (**5s**) were selectively oxidized to the corresponding aldehydes **6r** and **6s** (Entries 17 and 18).

The oxidation of 1-dodecanol (**5t**) as a primary alkanol was then attempted under the reaction conditions, but dodecanal (**6t**) was obtained in only 25% yield, and the ruthenium complex was recovered as the tetramesitylporphyrin carbonyl complex (Ru(tmp)(CO)) (**7**) (Scheme 2). The low reactivity for primary alkanols could be similarly ascribed to the low yield in the epoxidation of a terminal olefin with molecular oxygen;[19] e.g., the reaction of an aldehyde and the Ru(II) porphyrin complex produced an inactive Ru(II)CO porphyrin complex. Indeed, 67% of **7** was recovered after the reaction of 1-dodecanol.

N_2O Oxidation of 9,10-Dihydroanthracene. Next, 9,10-dihydroanthracene (**8a**) was subjected to dinitrogen oxide oxidation for examination of C–H oxidation. When the reaction was carried out in the presence of a 0.05 molar amount $Ru(tmp)(O)_2$ (**3f**) in benzene at 120 °C under 10 atm of dinitrogen oxide atmosphere, a mixture of anthraquinone (**9a**) and anthracene (**10a**) was obtained in moderate yield (Scheme 3). In order to achieve the respective selectivities for anthraquinone (**9a**) and anthracene (**10a**), a reaction pathway was assumed (Fig. 2). Anthracene was first oxidized at the C–H bond to generate benzyl alcohol **11a**,[20] and then dehydration from alcohol **11a** gave anthracene (**10a**). On the other hand, the consecutive oxidation of alcohol **11a** via **14a** would afford the quinone **9a**. Based on this hypothesis, vigorous conditions might accelerate the formation of quinone because many oxidation steps were required for the production of quinone. According to the results of the examination of various solvents and temperature (Table 6), it was found that the solvents had a great influence on the ratio of anthraquinone (**9a**) vs anthracene (**10a**). For example, almost equal amounts of **9a** and **10a** were obtained in hydrocarbon solvents such as cyclohexane or decaline (Entries 1 and 2), while anthracene was preferentially obtained in halogenated solvents (Entries 3–5). Anthraquinone was preferentially obtained in aromatic solvents such as chlorobenzene or benzene (Entries 6 and 7). The reaction temperature was then examined for the benzene solvent. It was found that the higher the temperature was, the more anthraquinone was produced. Finally, anthraquinone was obtained in 90% yield in benzene at 200 °C (Conditions A).

Optimization of the reaction conditions for the selective synthesis of anthracene was next examined. In Table 6, anthracene was preferentially obtained in halogenated solvents. It was assumed that an acid generated by the decomposition of the solvents should enhance the production of anthracene. That is, an acid protonated the hydroxy group of 9,10-dihydroan-

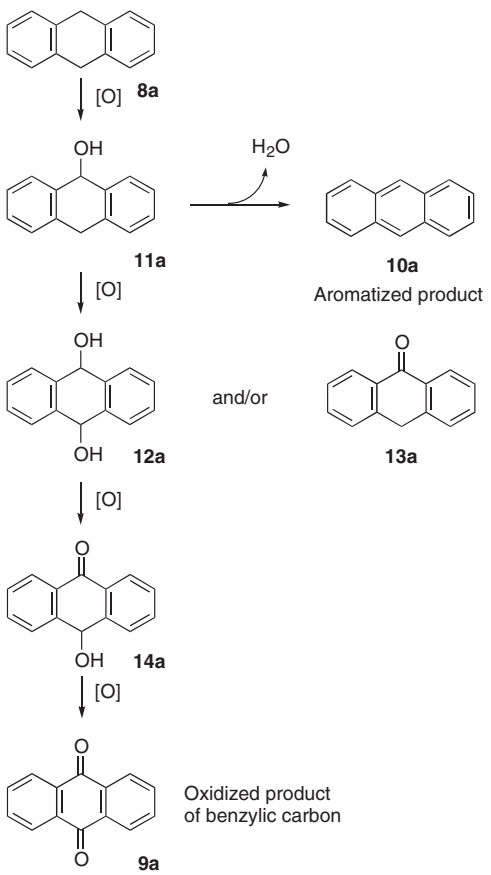
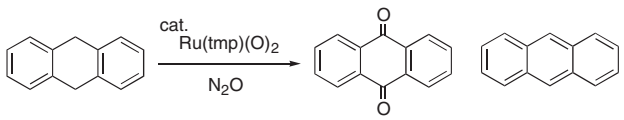


Fig. 2. Reaction pathway from 9,10-dihydroanthracene to anthraquinone and anthracene.

Table 6. Optimization for the Synthesis of Quinone

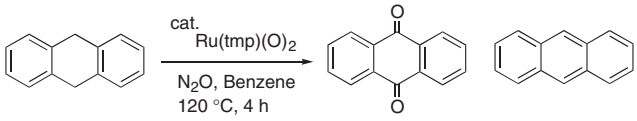


Entry[a]	Solvent	Temp/°C	Time/h	Yield/%	
				9a	**10a**
1	cyclohexane	160	4	27	55
2	decaline	160	4	29	44
3	CH_2Cl_2	160	4	8	41
4	$CHCl_3$	160	4	—	13
5		160	4	34	57
6	chlorobenzene	160	4	62	38
7	benzene	160	4	57	34
8	benzene	120	4	17	56
9[b]	benzene	200	20	90	9

a) Reaction conditions: 0.15 mmol of 9,10-dihydroanthracene and 0.05 molar amount of $Ru(tmp)(O)_2$ in solvent (14.0 mL) under 1.0×10^3 kPa (10 atm) of N_2O. b) 0.10 molar amount of catalyst.

thracen-9-ol (**11a**) intermediate and accelerated the dehydration. Hence, various acids were examined as additives (Table 7). All of the acidic additives suppressed the production

Table 7. Optimization for the Synthesis of Anthracene



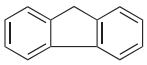
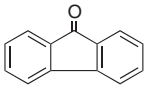
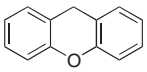
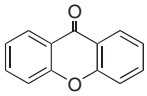
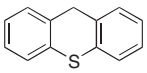
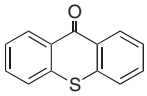
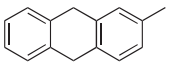
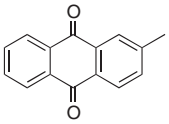
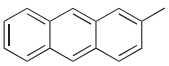
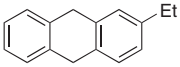
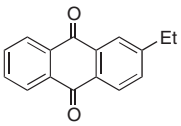
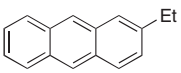
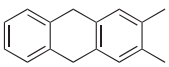
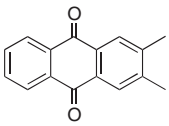
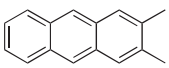
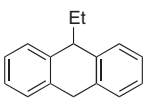
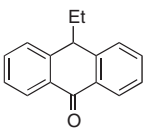
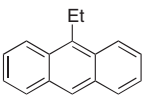
Entry[a]	Additive	Yield/%	
		9a	**10a**
1	TsOH	0	19
2	CH_3CO_2H	0	32
3	CF_3CO_2H	1	16
4	HCl[d]	0	24
5	HBr	2	11
6	H_2SO_4	0	99
7[b]	H_2SO_4	0	9
8[c]	H_2SO_4	0	5
9	$FeSO_4/7H_2O$	16	77
10	$CuSO_4/5H_2O$	23	74
11	$Ce(SO_4)_2/4H_2O$	0	90

a) Reaction conditions: 0.15 mmol of 9,10-dihydroanthracene and 0.05 molar amount of $Ru(tmp)(O)_2$ in solvent (14.0 mL) under 1.0×10^3 kPa (10 atm) of N_2O. b) Under 1.0×10^3 kPa (10 atm) of argon. c) Without catalyst. d) 1.0 mol/L ether solution.

of anthraquinone, although most of the acids also decreased the yield (Entries 1–5). It was assumed that the counter anions of the acids could coordinate with the ruthenium complex and deactivate it. Because of the relatively low coordination ability of sulfonate, sulfuric acid was then examined to afford the anthracene quantitatively (Entry 6, Conditions B). It was confirmed that aromatization did not proceed only with sulfuric acid in the absence of N_2O or the catalyst (Entries 7 and 8). Because sulfonate was found to be as an efficient counter anion, several metal sulfonates were examined as additives. Most of the metal sulfonates varied the ratio of anthracene vs anthraquinone, and cerium sulfonate was the most effective additive for anthracene selectivity among them (Entries 9–11). Many additives, such as 1-methylimidazole,[21] HCl/HBr,[22] or carboxylic acid,[23] were reported for aerobic oxidation using metal porphyrins or related metal complexes; however, the combined use of the ruthenium porphyrin complex with sulfuric acid or some metal sulfonates was novel.

N_2O Oxidation of 9,10-Dihydroanthracene Derivatives. The oxidation of various substrates was attempted under the optimized reaction conditions A and B (Table 8); Condition A was suitable for the oxidation of benzylic carbon into the corresponding carbonyl group, and condition B was suitable for dehydrogenative aromatization. Fluorene (**8b**) was smoothly oxidized to the corresponding ketone **9b** under condition A (Entry 1). This reaction was not prevented by the presence of ether or the sulfide moiety in substrates. When xantene (**8c**) or thioxantene (**8d**) was used as a substrate, the corresponding ketone **9c** or **9d** was obtained in good-to-high yield (Entries 2 and 3). In Entry 3, C–H oxidation of the carbon atom was more preferable than the oxidation of sulfur, though the oxidized product of the sulfur atom was present in 15% yield. When 2-methyl-9,10-dihydroanthracene (**8e**) was employed, 2-meth-

Table 8. N_2O Oxidation of 9,10-Dihydroanthracene Derivatives

Entry[a)]	Substrate		Conditions[a,b)]	Product		Yield/%
1		**8b**	**A**		**9b**	85
2		**8c**	**A**		**9c**	92
3		**8d**	**A**		**9d**	75
4		**8e**	**A**		**9e**	88
5			**B**		**10e**	98
6		**8f**	**A**		**9f**	98
7			**B**		**10f**	99
8		**8g**	**A**		**9g**	86
9			**B**		**10g**	96
10		**8h**	**A**		**9h**	47[c)]
11			**B**		**10h**	95[d)]

a) Conditions **A**: 0.05 mmol of substrates and 0.10 molar amount of $Ru(tmp)(O)_2$ in 14 mL benzene at 200 °C under 1.0×10^3 kPa (10 atm) N_2O. b) Conditions **B**: 0.15 mmol of substrates and 0.05 molar amount of $Ru(tmp)(O)_2$ in 14 mL benzene with 1.0 molar amount of H_2SO_4 at 120 °C under 1.0×10^3 kPa (10 atm) N_2O. c) 42% of anthraquinone was obtained. d) 0.10 molar amount of catalyst.

ylanthraquinone (**9e**) and 2-methylanthracene (**10e**) were selectively obtained (Entries 4 and 5). Similarly, from various alkyl-group-substituted 9,10-dihydroanthracenes, anthraquinones and anthracenes could be selectively obtained only by the reaction conditions (Entries 6–11).

Conclusion

In summary, it was revealed that the ruthenium porphyrin complex catalyzed dinitrogen oxide oxidation. That is, the epoxidation of olefins, the oxidation of alcohols to the corresponding aldehydes and ketones, and dehydrogenative aromatization smoothly proceeded using dinitrogen oxide as an oxidant.

Experimental

Dinitrogen oxide with 99.999% purity was purchased from Air Liquid Japan Ltd. Cholesteryl benzoate (**1a**), cholesteryl acetate (**1b**), cholesteryl decanoate (**1c**), cholesteryl formate (**1d**), cholesteryl ethyl carbonate (**1e**), cholesteryl bromide (**1f**), pregrenolone acetate (**1g**), androsterone acetate (**1h**), and neryl acetate (**1k**) were purchased from Tokyo Kasei Kogyo (TCI) Co., Ltd. 1-(*tert*-Butyldimethylsiloxy)-3,7-dimethyl-2,6-octadiene (**1l**), 1-(*tert*-butyldimethylsiloxy)-3,7-dimethyl-6-octene (**1m**), and 5-(*tert*-butyldimethylsiloxymethyl)bicyclo[2.2.1]hept-2-ene (**1n**) were prepared by a reported method.[24] 1-Phenylethanol (**5b**), 9-fluorenol (**5h**), 1-acenaphthenol (**5i**), 2-adamantanol (**5n**) were purchased from Tokyo Kasei Kogyo (TCI) Co., Ltd. Benzyl alco-

hol (**5s**) was purchased from Wako Pure Chemical Industries, Ltd. 1-Dodecanol (**5t**) was purchased from Kanto Chemical Co., Inc. 2-Naphthylmethanol (**5a**), 1-(2-naphthyl)ethanol (**5c**), 1-[1,1′-biphenyl]-4-ylethanone (**5d**), diphenylmethanol (**5e**), 1-phenyl-1-butanol (**5f**), 1,2,3,4-tetrahydro-1-naphthol (**5g**), 4-phenyl-2-butanol (**5j**), 2-undecanol (**5k**), 4-decanol (**5l**), 4-phenylcyclohexanol (**5m**), cyclododecanol (**5o**), *trans*-4-phenyl-3-buten-2-ol (**5p**), cholest-4-en-3-ol (**5q**), and 1-naphthylmethanol (**5r**) were prepared by the reduction of the corresponding ketones or aldehydes with sodium borohydride. 9,10-Dihydroanthracene (**8a**) and fluorene (**8b**) were purchased from Tokyo Kasei Kogyo (TCI) Co., Ltd. Xanthene (**8c**) was purchased from Kanto Chemical Co., Inc. Thioxanthene (**8d**) was prepared by the reduction of 9*H*-thioxanthene-9-one. 2-Methyl-9,10-dihydroanthracene (**8e**), 2-ethyl-9,10-dihydroanthracene (**8f**), 2,3-dimethyl-9,10-dihydroanthracene (**8g**), and 9-ethyl-9,10-dihydroanthracene (**8h**) were prepared by a reported method.[25]

Preparation of 2-Methyl-2-dodecene (1i). Bromodecane (36 g, 0.16 mol) and triphenylphosphine (50 g, 0.19 mol) were dissolved in benzene (100 mL) and stirred at 100 °C for 40 h. Benzene was removed in vacuo, and the phosphonium salt was obtained quantitatively. To a suspension of the phosphonium salt in 150 mL of THF, acetone (24 mL, 0.33 mol) and potassium *tert*-butoxide (19.2 g, 0.17 mol) were added and stirred for 20 h at room temperature. The mixture was diluted with 250 mL of hexane; then the white precipitate appeared. The precipitate was removed by filtration, and next the filtrate was concentrated. The residue was distilled to give pure 2-methyl-2-dodecene (17.9 g, 60% yield). b.p. 75–77 °C/467 Pa (3.5 mmHg); ^{1}H NMR (400 MHz) δ 5.09 (1H, m), 1.94 (2H, br), 1.69 (3H, s), 1.60 (3H, s), 1.26 (14H, m), 0.88 (3H, t, $J = 6.62$ Hz); ^{13}C NMR (100 MHz) δ 124.9, 100.5, 32.0, 30.0, 29.72, 29.69, 29.4, 28.3, 28.1, 25.8, 22.8, 17.8, 14.2; IR (NaCl) 2926, 2855, 2360, 2253, 1465, 1378, 911, 740, 651 cm^{-1}; HRMS Calcd for $C_{13}H_{26}$: (M^+), 182.2035. Found: m/z 182.2041.

Preparation of Decylidenecyclohexane (1j). Olefin (**1j**) was prepared from cyclohexanone and bromodecane under the same conditions as for the synthesis of **1i** (66% yield). b.p. 126 °C/573 Pa (4.3 mmHg); ^{1}H NMR (400 MHz) δ 5.06 (1H, t, $J = 7.3$ Hz), 2.13–1.94 (6H, m), 1.56–1.45 (6H, m), 1.35–1.20 (14H, m), 0.88 (3H, t, $J = 6.8$ Hz); ^{13}C NMR (100 MHz) δ 139.3, 121.5, 37.2, 32.0, 30.3, 29.70, 29.65, 29.4, 29.3, 28.8, 28.7, 27.9, 27.12, 27.05, 22.8, 14.2; IR (NaCl) 2927, 2854, 2253, 1467, 1380, 910, 733, 651 cm^{-1}; HRMS Calcd for $C_{16}H_{30}$: (M^+), 222.2347. Found: m/z 222.2377.

Preparation of Dioxoruthenium Tetramesitylporphyrin Complex (3f). Complex **3f** was prepared by a reported method.[13b]

General Procedure for Epoxidation of Olefins Using Dinitrogen Oxide. To a chlorobenzene solution of Ru(tmp)(O)$_2$ (**3f**, 21 mg, 0.023 mmol) in an autoclave, 2-methyl-2-dodecene (**1i**, 50 mg, 0.27 mmol) was added under a dinitrogen oxide atmosphere. After the solvent amount was fixed at 14 mL, the reaction mixture was heated to 140 °C under 1.0×10^3 kPa (10 atm) of N_2O for 5 h. The desired epoxide (**2i**) was purified by silica gel column chromatography (Hexane:EtOAc 20:1, 86% yield).

Spectral Data. The spectral data of obtained epoxides **2a**, **2b**, **2c**, **2d**, **2e**, **2f**, **2g**, **2h**, and **2k** were in good agreement with literature.

5,6-β-Epoxycholesteryl Benzoate (2a):[26] ^{1}H NMR (400 MHz) δ 8.02 (2H, m), 7.55 (1H, t, $J = 7.3$ Hz), 7.43 (2H, t, $J = 7.3$ Hz), 5.03 (1H, m), 3.12 (1H, s), 2.32–0.65 (43H, m).

5,6-β-Epoxycholesteryl Acetate (2b):[26] ^{1}H NMR (400 MHz) δ 4.70 (1H, m), 3.01 (1H, s), 2.07–1.80 (6H, m), 1.76–1.73 (2H, m), 1.51–0.91 (26H, m), 0.89–0.80 (9H, m), 0.57 (3H, s).

5,6-β-Epoxycholesteryl Decanoate (2c):[26] ^{1}H NMR (400 MHz) δ 4.80 (1H, m), 3.09 (1H, m), 2.21–0.57 (62H, m).

5,6-β-Epoxycholesteryl Formate (2d):[26] ^{1}H NMR (400 MHz) δ 7.95 (1H, s), 4.84 (1H, m), 3.02 (1H, s), 2.13–0.57 (43H, m).

5,6-β-Epoxycholesteryl Ethyl Carbonate (2e):[26] ^{1}H NMR (400 MHz) δ 4.56 (1H, m), 4.11 (2H, m), 3.01 (1H, s), 2.14–0.57 (46H, m).

5,6-β-Epoxycholesteryl Bromide (2f):[27] ^{1}H NMR (400 MHz) δ 3.97 (1H, m), 3.06 (1H, s), 2.53 (1H, m), 2.12–0.85 (39H, m), 0.63 (3H, s).

5,6-β-Epoxypregnanone Acetate (2g):[28] ^{1}H NMR (400 MHz) δ 4.78 (1H, m), 3.09 (1H, d, $J = 2.4$ Hz), 2.49 (1H, t, $J = 9.2$ Hz), 2.18–1.96 (12H, m), 1.83–0.66 (16H, m), 0.59 (3H, s).

5,6-β-Epoxyandrostanone Acetate (2h):[29] ^{1}H NMR (400 MHz) δ 4.71 (1H, m), 3.08 (1H, d, $J = 2.4$ Hz), 2.40 (1H, dd, $J = 19.2$, 8.8 Hz), 2.16–1.10 (20H, m), 0.97 (3H, s), 0.78 (3H, s), 0.62 (1H, m).

2,3-Epoxy-2-methyldodecane (2i): ^{1}H NMR (400 MHz) δ 2.71 (1H, t, $J = 5.9$ Hz), 1.60–1.26 (22H, m), 0.90 (3H, t, $J = 6.6$ Hz); ^{13}C NMR (100 MHz) δ 64.6, 58.2, 32.0, 30.7, 29.58, 29.57, 29.4, 28.9, 26.6, 25.0, 22.8, 18.8, 14.2; IR (NaCl) 2927, 2856, 2252, 1467, 1379, 1250, 1120, 913, 742, 650, 470 cm^{-1}; HRMS Calcd for $C_{13}H_{26}O$: (M^+), 198.1984. Found: m/z 198.1972.

2-Nonyl-1-oxaspiro[2.5]octane (2j): ^{1}H NMR (400 MHz) δ 2.70 (1H, t, $J = 5.9$ Hz), 1.80–1.20 (26H, m), 0.88 (3H, m); ^{13}C NMR (100 MHz) δ 64.5, 62.3, 36.1, 32.2, 30.0, 29.91, 29.89, 29.8, 29.7, 28.6, 27.2, 26.1, 25.5, 25.4, 23.0, 14.4; IR (NaCl) 2929, 2857, 2252, 1457, 1378, 909, 736, 651 cm^{-1}; HRMS Calcd for $C_{16}H_{30}O$: (M^+), 238.2297. Found: m/z 238.2311.

6,7-Epoxy-3,7-dimethyl-2-octenyl Acetate (2k):[30] ^{1}H NMR (400 MHz) δ 5.41 (1H, t, $J = 6.6$ Hz), 4.58 (2H, d, $J = 6.6$ Hz), 2.71 (1H, t, $J = 6.3$ Hz), 2.26 (2H, t, $J = 7.8$ Hz), 2.05 (3H, s), 1.78 (3H, s), 1.63 (2H, dt, $J = 7.8$, 6.3 Hz), 1.31 (3H, s), 1.27 (3H, s).

1-(*tert*-Butyldimethylsiloxy)-6,7-epoxy-3,7-dimethyl-2-octene (2l): ^{1}H NMR (400 MHz) δ 5.29 (1H, t, $J = 6.4$ Hz), 4.11 (2H, d, $J = 6.0$ Hz), 2.63 (1H, t, $J = 6.4$ Hz), 2.11 (2H, m), 1.67 (3H, s), 1.55 (2H, m), 1.24 (3H, s), 1.20 (3H, s), 0.83 (9H, s), 0.00 (6H, s); ^{13}C NMR (100 MHz) δ 136.3, 125.7, 63.9, 59.8, 58.4, 28.9, 27.5, 26.1, 24.9, 23.4, 18.8, 18.5, −5.0; IR (NaCl) 2959, 2857, 2253, 1463, 1380, 1255, 1058, 911, 740 cm^{-1}; HRMS Calcd for $C_{16}H_{32}O_2Si$: (M^+), 284.2172. Found: m/z 284.2189.

1-(*tert*-Butyldimethylsiloxy)-2,3:6,7-diepoxy-3,7-dimethyl-2-octane (4l): ^{1}H NMR (400 MHz) δ 3.66 (2H, dd, $J = 5.2$, 4.8 Hz), 2.82 (1H, t, $J = 5.6$ Hz), 2.64 (1H, t, $J = 5.6$ Hz), 1.66–1.51 (4H, m), 1.25 (3H, s), 1.23 (3H, s), 1.19 (3H, s), 0.81 (9H, s), 0.00 (3H, s), −0.01 (3H, s); ^{13}C NMR (100 MHz) δ 64.2, 63.9, 61.8, 60.4, 58.4, 29.8, 25.9, 25.1, 24.9, 22.1, 18.7, 18.3, −5.2; IR (NaCl) 2959, 2930, 2253, 1471, 1382, 1256, 1092, 909, 736 cm^{-1}; HRMS Calcd for $C_{16}H_{32}O_3Si$: (M^+), 300.2121. Found: m/z 300.2112.

1-(*tert*-Butyldimethylsiloxy)-6,7-epoxy-3,7-dimethyloctane (2m): ^{1}H NMR (400 MHz) δ 3.61 (2H, m), 2.65 (1H, t, $J = 6.4$ Hz), 1.57–1.27 (7H, m), 1.26 (3H, s), 1.22 (3H, s), 0.84 (12H, s), 0.00 (6H, s); ^{13}C NMR (100 MHz) δ 64.7, 61.3, 58.3, 39.8, 33.7, 29.4, 26.5, 26.0, 25.0, 19.6, 18.8, 18.4, −5.2; IR (NaCl) 2958, 2929, 2251, 1462, 1379, 1255, 1095, 909, 738 cm^{-1}; HRMS

Calcd for $C_{16}H_{34}O_2Si$: (M^+), 286.2328. Found: m/z 286.2288.

5-(*tert*-Butyldimethylsiloxymethyl)-2,3-epoxybicyclo[2.2.1]-heptane (2n): ^{1}H NMR (400 MHz) δ 3.57–3.45 (2H, m), 3.18 (1H, d, $J = 2.8$ Hz), 3.06 (1H, d, $J = 2.8$ Hz), 2.51 (1H, t, $J = 1.6$ Hz), 2.42 (1H, dd, $J = 3.6$, 1.6 Hz), 2.16–2.08 (1H, m), 1.64–1.57 (1H, m), 1.31 (1H, dd, $J = 9.6$, 2.0 Hz), 0.85 (9H, s), 0.73–0.68 (2H, m), 0.00 (6H, s); ^{13}C NMR (100 MHz) δ 63.7, 51.4, 49,7, 43.7, 38.0, 37.2, 28.1, 27.1, 25.9, 18.3, −5.2; IR (NaCl) 2956, 2858, 2253, 1471, 1387, 1255, 1095, 910, 741 cm^{-1}; HRMS Calcd for $C_{14}H_{26}O_2Si$: (M^+), 254.1702. Found: m/z 254.1702.

General Procedure for Oxidation of Alcohols Using Dinitrogen Oxide. To a 1,2-dichloroethane solution of Ru(tmp)(O)$_2$ (**3f**, 13 mg, 0.015 mmol) in an autoclave, a solution of 1-(2-naphthyl)-ethanol (**5c**, 50 mg, 0.29 mmol) was added under a dinitrogen oxide atmosphere. After the solvent amount was fixed at 14 mL, the reaction mixture was heated to 120 °C under 1.0×10^3 kPa (10 atm) of N_2O for 7.5 h. The desired ketone (**6c**) was purified by silica gel column chromatography (Hexane:Et_2O 10:1, 94% yield).

General Procedure for Oxidation of Benzylic Carbon into Carbonyl Group. To a benzene solution of Ru(tmp)(O)$_2$ (**3f**, 5.5 mg, 0.006 mmol) in an autoclave, a solution of 9,10-dihydroanthracene (**8a**, 10 mg, 0.057 mmol) was added under a dinitrogen oxide atmosphere. After the solvent amount was fixed at 14 mL, the reaction mixture was heated to 200 °C under 10 atm of N_2O for 20 h. The desired anthraquinone (**9a**) was purified by silica gel column chromatography (CH_2Cl_2, 90% yield).

General Procedure for Dehydrogenative Aromatization Using Dinitrogen Oxide. To a benzene solution of Ru(tmp)(O)$_2$ (**3f**, 6.4 mg, 0.007 mmol) in an autoclave, a solution of 9,10-dihydroanthracene (**8a**, 25.1 mg, 0.137 mmol) was added under a dinitrogen oxide atmosphere. After the solvent amount was fixed at 14 mL, sulfuric acid (14.2 mg, 0.137 mmol) was added. The reaction mixture was heated to 120 °C under 10 atm of N_2O for 4 h. The desired anthracene (**10a**) was purified by silica gel column chromatography (Hexane:Et_2O 20:1, 99% yield).

Determination of the Amount of Nitrogen Gas Generated in the N_2O Epoxidation. The quantitative analysis of nitrogen gas was performed with a GC attached to a Porapak Type Q column and a TCD detector. As the internal standard, carbon dioxide was adopted to obtain a calibration curve for N_2 vs CO_2. Into a two-necked 30-mL glass flask evacuated and filled with dinitrogen oxide, 1 mL of dinitrogen oxide and 10 mL of carbon dioxide were injected with a gas-tight syringe. The thus obtained sample was quantitatively analyzed by GC. Various samples containing 1–10 mL nitrogen were similarly prepared and analyzed to obtain the calibration curve. The gas phase from the reaction vessel was introduced to the evacuated two-necked glass flask; 10 mL of carbon dioxide was added as the internal standard, and the gas was then analyzed by GC. Based on the calibration curve, 2.29 mL of nitrogen gas was determined in the 0.102 mmol scale epoxidation (ideal; 2.23 mL at 21 °C).

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