Table II. ^{13}C NMR Data for New Cryptands and Bis(aza-crowns)

compd	1	2	3	4	5	6	7	8
$N\mathit{C}H_2CH_2O$	55.0, 55.3	55.2	55.0	54.99	54.44	55.72, 56.16	55.37	55.3
$N\mathit{C}H_2CH_2CH_2O$		51.8	51.6	51.98	51.94		53.92	54.0
$NCH_2\mathit{C}H_2CH_2$		28.1	28.2	27.97	27.90		27.63	27.8

to δ 53.9 ± 0.1 for bis(aza-crowns) **7** and **8** (see Table II). Similar but much smaller shifts were observed for the peaks attributable to the carbons of the ethylene moieties next to the bridgehead nitrogen.

An interesting method to distinguish the two products is provided by silica gel TLC analysis (methanol/30% aqueous ammonium hydroxide = 5/1) after purification by alumina chromatography. The cryptand TLC spot has the unusual property of considerable fronting while the TLC spot for the bis(aza-crown) has the usual tailing (see Figure 1). The unusual TLC spot was also observed for commercially available cryptands [2.2.1], [2.2.2], and benzo[2.2.2] as shown in Figure 1. It is important to note that these unusual TLC properties are mainly observed where methanol/30% aqueous ammonium hydroxide is used as the eluant. It is likely that the cryptands are leaching trace metal ions from the silica gel and the resulting complex moves at a faster rate to produce fronting. Indeed, sodium and potassium complexes of the cryptands move faster on silica gel TLC under these conditions (R_f = 0.95 for the complex vs 0.1 for the cryptand).

Conclusion

This new synthetic method allows an inexpensive one-step synthesis of a variety of cryptands from commercially available α,ω-diamine and α,ω-diiodide starting materials. Bis(aza-12-crown-4) compounds, formed by a cyclization reaction on each primary amine group of the diamine starting material, are the major byproducts. These two products can be distinguished by their ^{13}C NMR spectra and by their TLC spots using silica gel TLC with methanol/30% aqueous ammonium hydroxide as the eluant.

Experimental Section

Proton and carbon NMR spectra were obtained at 200 MHz in deuteriochloroform. Molecular weights were determined by electron-impact HRMS. Starting amines were used as received from Fluka, Aldrich, or Tokkyo-Kassei Chemical Cos. 1,11-Diiodo-3,6,9-trioxaundecane was prepared from the corresponding dichloride.[25] Silica gel 60_{F254} and alumina 69_{F254} (neutral, Type E) plates (Merck) were used for TLC. Similar material without the fluorescence indicator was used for column chromatography. Compound detection on the TLC plates was obtained by iodine vapor or 5% phosphomolybdic acid in ethanol followed by drying.

General Procedure for the Preparation and Separation of Cryptands and Bis(aza-crowns). The diiodocompound (10.5 mmol) was slowly added to a stirred mixture of 10 mmol of the appropriate diamine and 20 g of anhydrous metal carbonate (see Table I for the metal ion) in 300–350 mL of CH_3CN. The stirred mixture was refluxed for 24–36 h. The mixture was cooled, filtered, and evaporated, and the residue was dissolved in 20 mL of water. The aqueous phase was extracted three times with 20-mL portions of spectrograde CH_2Cl_2. The aqueous layer was saturated with NaCl before the third extraction. The combined CH_2Cl_2 solutions were evaporated and the resulting mixture was titurated three times with dry CH_2Cl_2. The combined CH_2Cl_2 solutions were filtered and evaporated and the solid residue was chromatographed on alumina (THF followed by THF/ethanol = 100/1) to give the products. When the products were not clearly separated or contained other impurities, they were chromatographed a second time in silica gel (CH_3OH/30% NH_4OH = 20/1). The products and yields are listed in Table I. Selected carbon NMR data are given in Table II. Proton NMR spectral data and analyses for all products are as follows.

Cryptand[2.3.3] (1): ^1H NMR δ 2.85 (t, 12 H), 3.65 (m, 32 H). Anal. Calcd for $C_{22}H_{44}N_2O_8$: C, 56.91; H, 9.54. Found: C, 56.56; H, 9.62; MS m/e 464.

Cryptand[2.2.2Pr$_2$] (2):[24] mp 55–56 °C (isopropyl ether or acetonitrile/hexane); ^1H NMR δ 1.75 (m, 4 H), 2.65 (m, 12 H), 3.75 (m, 24 H); MS *m/e* 404.

Cryptand[2Pr$_2$.3.3] (3): ^1H NMR δ 1.75 (m, 4 H), 2.7 (m, 12 H), 3.6 (m, 32 H); MS *m/e* 492. Anal. Calcd for $C_{24}H_{48}N_2O_8$: C, 58.51; H, 9.82. Found: C, 58.36; H, 9.67.

Cryptand[2.2.3Pr$_2$] (4): ^1H NMR δ 1.7 (m, 4 H), 2.6 (t, 4 H), 2.7 (m, 8 H), 3.6 (m, 28 H); MS *m/e* 448. Anal. Calcd for $C_{22}H_{44}N_2O_7$: C, 58.90; H, 9.89. Found: C, 58.51; H, 9.64.

Cryptand[3.3.3Pr$_2$] (5): ^1H NMR δ 1.7 (m, 4 H), 1.9 (b, 2 H), 2.7 (m, 12 H), 3.6 (m, 36 H); MS *m/e* 536. Anal. Calcd for $C_{26}H_{52}N_2O_9 \cdot H_2O$: C, 56.30; H, 9.81. Found: C, 56.45, H, 9.56.

Bis-crown 6: ^1H NMR δ 2.8 (m, 12 H), 3.65 (m, 32 H); MS *m/e* 464. Anal. Calcd for $C_{22}H_{44}N_2O_8$: C, 56.91; H, 9.54. Found: C, 56.74; H, 9.63.

Bis-crown 7: ^1H NMR δ 1.8 (m, 4 H), 2.6 (t, 4 H), 2.7 (m, 8 H), 3.6 (m, 32 H); MS *m/e* 492. Anal. Calcd for $C_{24}H_{48}N_2O_8$: C, 58.51; H, 9.82. Found: C, 58.40; H, 9.64.

Bis-crown 8: ^1H NMR δ 1.75 (m, 4 H), 2.55 (t, 4 H), 2.7 (t, 8 H), 3.6 (m, 36 H); MS *m/e* 536. Anal. Calcd for $C_{26}H_{52}N_2O_9$: C, 58.18; H, 9.76. Found: C, 57.95; H, 9.55.

Preparation of 1,13-Bis(*N*-monoaza-12-crown-4)-4,7,10-trioxatridecane (8). Diethylene glycol ditosylate (0.9 g, 2.1 mmol) was added to a stirred mixture of 1.16 g (5 mmol) of *N*-1-(3-hydroxypropyl)monoaza-12-crown-4,[26] 10 mL of t-C_4H_9OH, 1 g (8.9 mmol) of KO-t-C_4H_9, and 8 mL of dioxane. The mixture was stirred at 70 °C for 16 h and evaporated and the residue mixed with 2 g of alumina. The mixed alumina was added to the top of a column of alumina, and the products were eluted with THF/C_2H_5OH (50/1) to give 0.4 g (34%) of **8** which had identical spectral properties as reported previously for **8**.

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Ozone Epoxidation of Olefins Catalyzed by Highly Robust Manganese and Iron Porphyrin Complexes

Sandro Campestrini, A. Robert, and B. Meunier*

Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse cedex, France

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Introduction

During the last decade, many different oxygen atom donors (iodosylbenzene, hypochlorite, organic or inorganic peroxides) have been investigated for their ability to generate high-valent oxometalloporphyrin complexes, leading to various catalytic oxidation reactions.[1,2] This

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work represents the first report of ozone[3] as an oxygen atom donor in an olefin epoxidation reaction catalyzed by metalloporphyrins. High-valent oxometalloporphyrin species might be generated by O_3 according to the following equation:

$$O_3 + (\text{Por})M^{III} \rightarrow (\text{Por})M^{V}{=}O \text{ [or } (\text{Por}^{\bullet+})M^{IV}{=}O] + O_2$$

Ozone is produced in a stream of molecular oxygen. But the presence of dioxygen (at least when diluted in nitrogen, in the absence of a reducing agent and at ambient temperature) is not supposed to have an influence on oxygenation reactions catalyzed by metalloporphyrins. The main question concerns the ability to create metal–oxo species from ozone, a very (not oxidant able to react with a large variety of organic molecules[4] (not only olefins, but also saturated hydrocarbons) and a "clean oxidant" widely used in the treatment of drinking water.

Results and Discussion

Typical experiments were performed at room temperature as follows: 150 μmol of olefin, 150 μmol of the appropriate internal standard (see the following text), 1.5 μmol of metalloporphyrin, and 50 μmol of an axial ligand (pyridine or 4-*tert*-butylpyridine) were used in 1 mL of dichloromethane.[5] A 0.2–0.6-L portion of O_3/O_2 (260–780 μmol of ozone) was bubbled through the solution for 15–40 min in order to have a complete conversion of the starting olefin, and then 100 mL of argon was bubbled through the reaction mixture before GC analysis. We have checked that no reaction occurred when ozone is replaced by a stream of oxygen.

In the absence of catalyst, but in the presence of ozone, full olefin conversions were observed in 15–40 min. The reaction products observed in these noncatalyzed ozonizations were identified as the aldehydes and carboxylic acids resulting from the olefin bond cleavage. *But it must be noted that the corresponding epoxide was never observed. We have checked that epoxide derivatives are stable under these reaction conditions.* The internal standards (chlorobenzene, 1,2-dichlorobenzene, 1,4-dibromobenzene, or 1,3,5-tribromobenzene) are also stable under the same conditions.

The manganese complex of the β-octabrominated tetramesitylporphyrin, $Mn(Br_8TMP)Cl$,[6,7] is quickly oxidized by ozone. A new Soret band is observed at 456 nm. The same band can be generated by potassium monopersulfate and is attributed to a high-valent manganese–oxo species. In the same conditions, the two other "robust" catalysts, Mn(TMP)Cl and Mn(TDCPP)Cl, are quickly bleached by ozone (the Soret band disappears within a few minutes). The highly reduced bleaching observed with $Mn(Br_8TMP)Cl$, a metalloporphyrin containing bromine atoms at all β-pyrrole positions, suggests that the degradation of the complex might occur *via* the ozonolysis of the carbon–carbon double bond at the β-positions of the pyrrole units. Ozone is an electrophilic agent and, therefore, reacts more rapidly with electron-rich double bonds. The substitution of hydrogen by bromine atoms, makes double bonds much more resistant toward ozonolysis.[8] In addition, if an intermediate ozonide was involved in a porphyrin modification, it should give rise to an isoporphyrin derivative without complete porphyrin destruction as reported by Bruice et al.[9]

Table I. Olefin Epoxidation by O_3 Catalyzed by $Mn(Br_8TMP)Cl$ in the Presence of Pyridine or 4-*tert*-Butylpyridine[a]

olefin	mol % catalyst	[axial ligand]/[cat.][b]	epoxide yield (%)	turnover no.
cyclooctene	1.0	0	4.8	5
	0.33	52	12	37
	1.1	33	29	28
	3.1	49	38	12
trans-stilbene	0.8	36	11	13
	3.0	52	14	5
cis-stilbene	1.1	34	34 (cis) + 7.8 (trans)	39
styrene	1.1	31	26	24
1-octene	1.0	35	7	7
trans-2-hexene	1.0	35	6.4	7
cis-2-hexene	1.0	35	21 (cis) + 3 (trans)	25
cis-3-heptene	1.1	32	24	21

[a] In all cases, the olefin conversion was above 94–98%. Reaction time, 15–40 min at room temperature. For more experimental details, see text. Yields are based on the starting olefin. [b] Pyridine was used as axial ligand in the case of cyclooctene, stilbene, styrene, and 4-*tert*-butylpyridine for 1-octene, 3-heptene, and 2-hexene.

Table II. Olefin Epoxidation by O_3 Catalyzed by $Fe(Br_8TMP)OAc$[a]

olefin	mol % catalyst	epoxide yield (%)	turnover no.
cyclooctene	1.0	4.6	4.4
	1.0[b]	4.5	4.1
trans-stilbene	1.1	3.4	3.1
cis-stilbene	1.0	10 (cis) + 2 (trans)	12
	1.1[c]	7.2 (cis) + 1.8 (trans)	8.4
styrene	1.0	3.7	3.8
	1.0[b]	2.1	2.0
1-octene	1.0	0.4	0.4
trans-2-hexene	1.0	2.0	1.8
cis-2-hexene	1.0	2.7 (cis) + 0.8 (trans)	2.3

[a] In all cases, the olefin conversion was above 94–98%. Reaction time, 15–40 min at room temperature. Fore more experimental details, see text. Yields are based on the starting olefin. [b] One equivalent of pyridine with respect to the catalyst was added in the reaction mixture. [c] $Fe(Br_8TMP)Cl$ was the catalyst in this case.

The main results on the epoxidation of various olefins by ozone catalyzed by $Mn(Br_8TMP)Cl$ in the presence of an axial nitrogen ligand are reported in Table I. The most striking feature of these metalloporphyrin-mediated olefin oxidations by ozone is the catalytic formation of epoxide with yields ranging from 5 to 42%, which correspond to catalytic activities from 5 to 39 turnovers. For a reactive olefin like cyclooctene, the catalytic activity reaches 90 cycles/h. As expected for a metalloporphyrin-catalyzed epoxidation, *cis* olefins are more reactive than the corre-

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sponding *trans* isomers. The cis/trans epoxide ratio is 7 in the case of an aliphatic olefin and 4.3 in the case of a conjugated aromatic olefin like *cis*-stilbene. Terminal olefins are slowly epoxidized (7 turnover numbers for 1-octene).

The iron analogue, $Fe(Br_8TMP)OAc$, was also evaluated as a possible catalyst under the same reaction conditions, but without pyridine derivative (Table II). The iron octabromo-TMP derivative is less efficient than the manganese complex. The highest catalytic activities are always in the range of two to four cycles, with a maximum for *cis*-stilbene at 8–12 cycles. Since the binding constant of a second pyridine for iron porphyrin complexes is higher than the binding constant for ligation of the first one,[10] it is not possible to take advantage of the proximal effect of pyridine ligands to enhance the catalytic activity of this iron porphyrin. Yields are the same with or without addition of pyridine in the reaction mixture. In the case of manganese porphyrin complexes, the monopyridine adduct is the major species up to 50–200 equiv of nitrogen base with respect to the porphyrin complex. In the epoxidation of *cis*-stilbene, the isomer epoxide ratio is 4–5 in favor of the cis isomer. The same reactivity is observed with $Fe(Br_8TMP)Cl$, suggesting that the anionic axial ligand does not largely influence the selectivity of the catalytic reaction.

As a general comment on the selectivity of this metalloporphyrin-catalyzed ozone epoxidation, it can be mentioned that the key factor reducing the selectivity is the noncatalyzed direct ozonolysis of the olefin. For example, three products have been detected in the direct ozonolysis of *cis*-stilbene after its complete conversion: benzaldehyde (54% yield), benzoic acid (7%), and a nonidentified compound[11] (34%) (balance material: 95%). In the $Mn(Br_8TMP)Cl$-catalyzed oxidation of the same olefin, the following products have been detected at a conversion of 95%: *cis*-stilbene oxide (34% yield), *trans*-stilbene oxide (8%), benzaldehyde (22%), benzoic acid (12%), and traces of deoxybenzoin (<1%). In this case, the balance material was 76%. So, the epoxide formation is the main pathway of the catalytic reaction, whereas benzaldehyde and benzoic acid are the products of the direct ozonolysis reaction.

We are currently studying how to improve reaction yields of this rare example of ozone epoxidation catalyzed by metalloporphyrin complexes.

Experimental Section

Gas chromatographic analyses were performed as previously described.[5] Chemicals were purchased from Aldrich or Janssen; noncommercially available epoxides were obtained from the corresponding olefins with *m*-chloroperbenzoic acid (85% pure, Merck). Peroxides were removed from olefins by passing them through a short column of Florisil before use. Dichloromethane (99.95%) was used without purification. The porphyrin ligands $TMPH_2$, $TDCPPH_2$, and Br_8TMPH_2 and their corresponding manganese and iron derivatives were prepared using a modified Lindsey method.[6,7] *meso*-Tetramesityl-β-octabromoporphyrin, Br_8TMPH_2, was obtained by NBS bromination of the β-pyrrole positions of $TMPH_2$.[6] Ozone was generated in a stream of oxygen by an ozonizer Labo 76 type from Trailigaz (Garges-les-Gonesse, France) (oxygen stream: 200 L/h; current intensity 1.25 A; ozone concentration was 1.3 mM by iodometric titration).

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Photodimerization of 9-Vinylanthracene: X-ray Crystal Structure of the Dimer

Hemant K. Sinha, Alan J. Lough, and Keith Yates*

Department of Chemistry, Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada M5S 1A1

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Photodimerization of anthracene is one of the oldest known photochemical reactions and a classical example of photoaddition. Several meso-substituted anthracenes have been known to undergo photodimerization via first excited singlet state.[1] However, in 9-vinylanthracene (VA) there could be other photochemical reaction pathways to compete with the photodimerization. For example, it could undergo photopolymerization or photohydration in the excited state, and both the reactions would involve the vinyl moiety as the reaction center. The present paper deals with the complete characterization of the photoproduct of VA.

VA was obtained from Aldrich Chemical Co. and was recrystallized from ethanol. Preparatory scale irradiations were performed in a Rayonet RPR-100 reactor. The wavelength for the irradiation was 254 or 300 nm. The solution was purged with nitrogen or argon for 20 min prior to irradiation.

Irradiation of a solution (either 50:50 (v/v) acetonitrile/water or pure acetonitrile) of VA results in complete disappearance of the anthracene-like absorption band (387, 368, 351 nm). This clearly indicates that photoexcitation directly effects the anthracene skeleton by removing the conjugation. Prolonged irradiation of a saturated solution in acetonitrile resulted in a white precipitate, which was isolated and subjected to spectroscopic analyses. The solid product was found to be a clean dimer by NMR spectroscopy, and no indication of any polymerization product was found to be associated with it. Furthermore, no other primary photoproduct was found to be present in solution in any significant amount. Though similar precipitation was detected by Ebeid et al.,[2] the complete characterization of the product has not been attempted until now. On the basis of the IR spectral analyses, Ebeid et al. proposed it to be a dimeric species.

UV absorption and ^1H and ^{13}C NMR spectra[8] have been presented in our earlier paper.[3] Present X-ray analysis[9] (see Figure 1) confirms this product to be a highly symmetrical dimer of VA. The vinyl groups are in a trans configuration with respect to the anthracene skeleton. No indication of cis isomer has been found. This indicates the photoaddition reaction is highly stereospecific in nature. The lack of reactivity of VA toward photohydration, unlike several other aromatic alkene and alkyne analogues[4], in aqueous acid solution has been explained as due to inefficient charge transfer in the excited singlet state.[4] This could be due to the fact that the vinyl group and the aromatic moiety are not in the same plane in the ground state due to steric reasons.

$C(sp^3)$–$C(sp^3)$ bond lengths, i.e., C1–C4(I) in Figure 1, which connect the two half-molecules, are quite long (1.61 Å). This is similar to that found in the case of the dimer of 9-anthraldehyde.[5] Each half of the molecule is bent

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