J. Am. Chem. Soc. 1982, 104, 291-292

°C afford the corresponding fluoridates 3 (80–90%) (reaction 1).

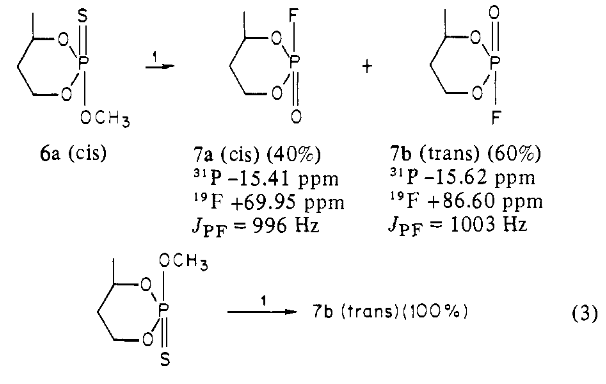
$$\underset{\mathbf{2}}{\mathrm{RR'P(S)OR''}} + \underset{\mathbf{1}}{\mathrm{SO_2FCl}} \rightarrow \underset{\mathbf{3}}{\mathrm{RR'P(O)F}} + \mathrm{SO_2} + \mathrm{R''Cl} + {}^1/_x\mathrm{S}_x \quad (1)$$

The phosphine sulfides **4** are distinctly less reactive but on prolonged warming at 20 °C were pressure with **1** yield the difluorophosphoranes **5** in satisfactory yields (reaction 2).

$$\underset{\mathbf{4}}{\mathrm{R_3P{=}S}} + 2\mathbf{1} \rightarrow \underset{\mathbf{5}}{\mathrm{R_3PF_2}} + 2\mathrm{SO_2} + \mathrm{SCl_2} \quad (2)$$

A single distillation or crystallization gave the pure fluorinated organophosphorus compounds (**3** and **5**),[7] which were characterized by ^{31}P and ^{19}F NMR spectroscopy, elemental analysis, and spectral comparisons with literature data.

Diastereoisomeric *cis*- (**6a**) and *trans*-2-methoxy-2-thioxo-4-methyl-1,3,2-dioxaphosphorinan (**6b**) are fluorinated stereoselectively by **1** (reaction 3).[5]



6a (cis)

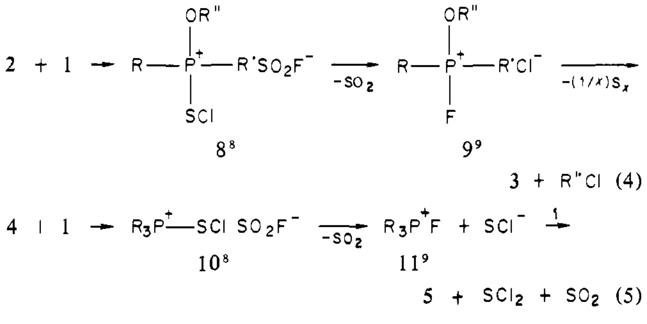
7a (cis) (40%)
^{31}P -15.41 ppm
^{19}F +69.95 ppm
J_{PF} = 996 Hz

7b (trans) (60%)
^{31}P -15.62 ppm
^{19}F +86.60 ppm
J_{PF} = 1003 Hz

6b (trans)

The selenoesters **2** (R,R′ = alkyl or alkoxy, X = Se) with sulfuryl chloride fluoride, under similar conditions as described for **2** (X = S), also give the corresponding fluorinated organophosphorus compounds **3** in excellent yields. The selenides **4** (X = Se) are distinctly more reactive than the corresponding sulfides and react vigorously below 0 °C. This provides, in our opinion, the simplest known synthesis of difluorophosphoranes **5** in 75–90% yields.[6]

The above experimental results, together with our previous studies on the chlorination of **2** (X = S),[3] indicated th mechanisms of reactions 4 and 5. The key step in each case is displacement of an SCl ligand by a strongly P-nucleophilic fluoride anion.



Low-temperature FT ^{31}P NMR spectroscopy confirmed the presence of the intermediate phosphonium salts **8**, and **10** prior to ligand exchange.[8]

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[7] NMR data for **3** (R ≡ R′ ≡ C_2H_5O–): ^{31}P NMR −9.52 ppm, $^1J_{P-F}$ = 964 Hz; ^{19}F NMR 81.46 ppm. **3a** (R ≡ R′ ≡ CH_3O–): ^{31}P NMR −7.9 ppm, $^1J_{P-F}$ = 974,1 Hz; ^{19}F NMR 80.6 ppm. **5** (R ≡ C_6H_5–): ^{31}P NMR −54.14 ppm, $^1J_{P-F}$ = 665.6 Hz; ^{19}F NMR −37.3 ppm.

[8] The ^{31}P spectral data of **8** and **10** are close to those observed in the reaction between **2** and **4** with sulfuryl chloride:[3] range of δ +40–+90.

[9] The structures of **9** and **11** need to be further confirmed by the independent synthesis.

Macrocyclic Effect in Transition-Metal Ion Complexes of a Mixed (Nitrogen, Oxygen) Donor Macrocycle

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Two types of evidence suggest that the macrocyclic effect is small or nonexistent when nitrogen donors are replaced by oxygens in complexes of macrocycles with transition-metal ions.[1] Firstly, the complexes of transition-metal ions such as Ag(I) with ligands such as 18-aneN_2O_4 demonstrate no extra stability compared with the open-chain analogue.[2] Secondly, Lindoy and co-workers[3] have studied the complexing abilities of ligands such as I and found them to be rather weak. Neither type is strong evidence that a normal macrocyclic effect cannot be obtained when nitrogens are replaced by oxygens. Ag(I) is not a typical transition-metal ion with its linear coordination geometry, and the "hole" in a ligand such as 18-aneN_2O_4 is too large for complexation to more typical transition-metal ions. Previous work[4] has shown the importance of inductive effects in stabilizing complexes of N-donor macrocycles so that the electron-withdrawing benzo groups on I are likely to be related to its poor complexing abilities. In order to study a mixed-donor macrocycle with appropriate geometry for coordination to transition-metal ions, and with no electron-withdrawing groups, 9-aneN_2O was synthesized by the route outlined in Figure 1. Ligand 9-aneN_2O may be compared with 9-aneN_3 to see what effect substituting an O for an N has on the complexing ability of the ligand and with HEEN and ODEN (Figure 2), which are its linear analogues. The important features of the macrocyclic effect in N-donor macrocycles are [4] (1) increased stability, (2) greater kinetic inertness, and (3) a more intense ligand field, compared with complexes of the linear analogue.

pK_1 and pK_2 were determined by standard potentiometric techniques[5] to be 9.59 and 5.32 for 9-aneN_2O. Log K values for 9-aneN_2O determined for Cu(II), Ni(II), and Zn(II) are shown in Table I, along with log K for 9-aneN_3, dien, HEEN, and ODEN. In Cu(II) the replacement of an N, which must occupy the unfavorable axial site in the 9-aneN_3 complex, has led to a more favorable macrocyclic effect in 9-aneN_2O, where the O presumably occupies the axial site. In Ni(II), log K_1 for 9-aneN_2O at 8.59 is larger than for any other diamine ligand. However, log K_1(9-aneN_3) − log K_1(dien) is 5.74, while log K_1(9-aneN_2O) − log K_1 (ODEN) is only 2.97 log units, a smaller macrocyclic effect. This could be evidence for the role of solvation[6] in producing the macrocyclic effect. Solvation of oxygen is weaker than nitrogen so that the desolvation that takes place when we cyclize ODEN to form 9-aneN_2O is less than when dien is cyclized to form 9-aneN_3. On the other hand, in Zn(II) the macrocyclic effect for 9-aneN_2O is 2.9 log units, similar to the 2.8 found for 9-aneN_3. This similarity would, as pointed out by a referee, militate against interpretation of the macrocyclic effect for Ni(II) with 9-aneN_2O and 9-aneN_3 in terms of desolvation effects.

Ligand 9-aneN_2O reacts with Zn(II) and Cu(II) fairly slowly, equilibrium taking about 20 min while Ni(II) takes several hours; 9-aneN_3 with Ni(II) takes several weeks.[7] Faster reaction makes 9-aneN_2O more convenient to study and may mean that mixed

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[1] Melson, G. A. In "Coordination Chemistry of Macrocyclic Compounds"; Melson, G. A., Ed. Plenum Press: New York, 1979; pp 98–103. Lamb, J. D.; Izatt, R. M.; Christensen, J. J.; Eatough, D. J. *Ibid.*, pp 173–174.

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[5] Hancock, R. D.; Marsicano, F. *J. Chem. Soc., Dalton Trans.* **1978**, 228–234.

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[7] Zompa, L. J. *Inorg. Chem.* **1978**, *17*, 2531–2536.

[8] Smith, R. M.; Martell, A. E. "Critical Stability Constants. Volume 2: Amines"; Plenum Press: New York, 1975.

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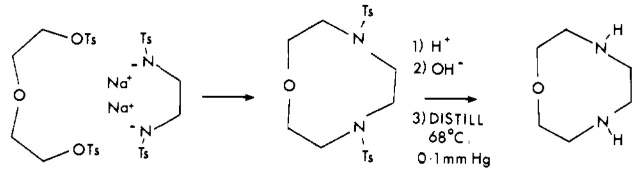

Figure 1. Synthetic route used for synthesis of 9-aneN$_2$O. (Ts = tosyl, i.e., *p*-toluenesulfonyl)

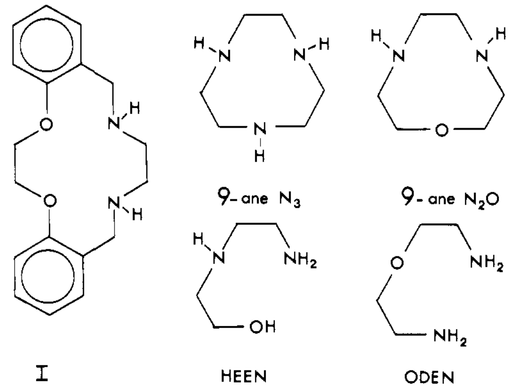

Figure 2. Ligands discussed in this paper.

Table I. Log K for 9-ane Macrocycles and Their Linear Analogues[a]

metal ion		Cu(II)	Ni(II)	Zn(II)
9-aneN$_2$O[b]	log K_1	10.85	8.59	6.32
	log K_2	8.64	7.27	5.07
HEEN[c]	log K_1	10.09	6.82 (6.85)[d]	4.75
	log K_2	7.53	5.62 (5.49)[d]	
ODEN[c]	log K_1	8.70	5.62	(3.5)[e]
	log K_2	4.4	3.39	
9-aneN$_3$[f]	log K_1	15.52	16.24	11.62
dien[c]	log K_1	15.9	10.5	8.8

[a] At 25 °C at ionic strength 0.1. [b] This work, 0.1 M NaNO$_3$. [c] Reference 8. [d] This work, run as a check on potentiometric system. [e] Estimated by comparison with Cu(II) and Ni(II) complexes. [f] Reference 7.

N,O-donor macrocycles have greater potential application than their all-nitrogen analogues.

The complex [Ni(9-aneN$_2$O)$_2$]$^{2+}$ gives a purple solution, as compared with [Ni(HEEN)$_2$]$^{2+}$, which is the blue color typical of Ni(II) with four aliphatic nitrogen and two oxygen donors. The electronic spectrum shows bands at 11 600, 12 500 (shoulder), 18 800, and 28 250 cm^{-1}. This gives $10Dq$ (Dq = ligand field parameter) 11 600 and B (Racah parameter) = 820 cm^{-1}, assuming octahedral symmetry, whereas $10Dq$ and B for [Ni(HEEN)$_2$]$^{2+}$ are only 10 950 and 870 cm^{-1}. It is remarkable that $10Dq$ in the bis(9-aneN$_2$O) complex is larger than for complexes such as [Ni(en)$_3$]$^{2+}$ (11 200 cm^{-1}) with six nitrogen donor atoms. The increase in $10Dq$ of 650 cm^{-1} on cyclization to form 9-aneN$_2$O may be compared with 1000 cm^{-1} for 9-aneN$_3$ ($10Dq$ for the bis complex[7] of Ni(II) with 9-aneN$_3$ is 12 500 cm^{-1} and for dien $10Dq$ = 11 500 cm^{-1}). Increases in $10Dq$ on cyclization are thought[4] to be due to the formation of more basic secondary from primary nitrogens, without the usual increase in strain. The smaller increase of 650 cm^{-1} for the 9-aneN$_2$O complex must arise because cyclization of the linear analogue HEEN is occurring across an OH and an NH$_2$, and O donors do not appear to benefit as much electronically in changing from primary (alcoholic) to secondary (ethereal). We are at present determining the structure of [Ni(9-aneN$_2$O)$_2$](ClO$_4$)$_2$ in order to see whether trigonal distortion contributes to the high Dq of this complex, as suggested[7] for the 9-aneN$_3$ complex.

In conclusion, the complexes of the mixed nitrogen–oxygen donor 9-aneN$_2$O show all three characteristics of a strong macrocyclic effect, namely, increased stability, kinetic inertness, and ligand field strength, compared with the linear analogues. A study of the chemistry of such ligands with a wider range of metal ions may reveal much about the macrocyclic effect, which we are now investigating with the synthesis of ligands such as 13-aneN$_2$O$_2$, 9-aneNO$_2$, and 13-aneN$_3$O.

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Photochemistry of *syn*- and *anti*-9,10-Epoxy-1,4-dihydro-1,4-dipropyl-1,4-ethanonaphthalene-2,3-dione

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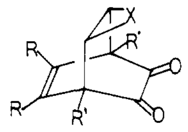
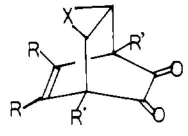
Recently we have found the effect of number and nature of unsaturation on the photochemical behavior of bicyclic α-diketones.[1] It would be very interesting to examine the photochemistry of the compounds in which a double bond of bicyclo[2.2.2]octadienedione is replaced by a three-membered ring such as **1** and **2**.[2] We report herein the photochemistry of the title compounds **3** and **4** which demonstrates the stereoelectronic effect of the epoxy ring on the photochemical behavior of unsaturated β,β'-epoxy-α-diketones.



1



2

X = O, NR″, CR″$_2$

The syn-isomer **3** was synthesized by direct epoxidation of compound **5**[3] with *m*-chloroperbenzoic acid (MCPBA) while the anti-isomer **4** was prepared by epoxidation of **6**[3] with MCPBA followed by alkaline hydrolysis. It is interesting to note that the former method gave only a syn isomer (**3**) (72%); however, the latter procedure afforded both **3** (5%) and **4** (69%). The stereoselective formations of **3** and **4** are presumably due to hydrogen

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(1) (a) Ueng, Y. S. M.Sc. thesis, National Tsing Hua University, Hsinchu, Taiwan 300, 1980. (b) Lin, H. S. Ph.D. dissertation, National Tsing Hua University, Hsinchu, Taiwan 300, 1981.

(2) M. B. Rubin has recently studied the photochemistry of tricyclo[3.2.2.0^{2,4}]non-6-ene-8,9-dione. We thank Professor Rubin for a preprint.

(3) Compounds **5** and **6** have been characterized by elementary analysis and spectroscopic data (IR, ^{1}H NMR, and mass spectra). The detailed procedure for their synthesis will be published in a full paper.

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