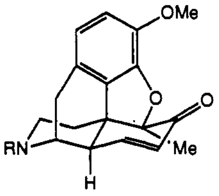
(80%); **1b** was stable to extended irradiation in benzene solution at 366 nm.

Reduction of **2a** with lithium aluminum hydride gave the highly crystalline saturated keto amine **3** in 90% isolated yield. An X-ray diffraction study of **3** provided the molecular structure shown in Figure 1. It is noteworthy that the solvolytic photorearrangement of **1b** results in cleavage of the dihydrofuran ring with overall 1,2-migration of the aryl nucleus.

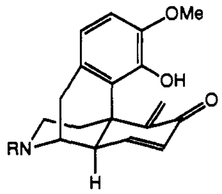
A plausible mechanism for photorearrangement of **1b** to **2a** and **2b** involves benzodihydrofuran rearrangement[4,8] of **1b** to an intermediate cyclopropanespiro-2,4-cyclohexadien-1-one, **4b**. Abnormal Claisen rearrangement[9] of **4b** (C–O migration of H$_a$) does not occur presumably because the resulting bridgehead olefin (not shown) would have excessive ring strain. Instead, **4b** reverts to **1b**. In methanol, solvolytic opening of the cyclopropane ring in **4b** gives the methyl ether **2a**; in the presence of water, **4b** gives the alcohol **2b**.

It was suspected that the failure to observe photorearrangement of codeinone (**1a**) was a result of competing electron transfer processes involving the tertiary amine group in **1a**.[10] To test this supposition, the C(5)-methyl-substituted codeinone analogues **5a** and **5b** were prepared from thebaine.[11]

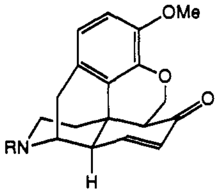
Irradiation of **5a** in methanol solution at 366 nm gave benzopyran **7a** in quantitative yield. This product presumably is formed by photorearrangement of **5a** to cyclopropanespiro-2,4-cyclohexadien-1-one **4c**, from which abnormal Claisen rearrangement involving the C(5) methyl substituent gives the intermediate phenolic dienone **6a** (not observed). An intramolecular Michael addition would convert **6a** to benzopyran **7a**.



5a, R = Me
b, R = CO$_2$Me



6a, R = Me
b, R = CO$_2$Me



7a, R = Me
b, R = CO$_2$Me

Irradiation of **5b** in benzene solution gave the dienone **6b** as the exclusive reaction product. In methanol, **5b** gave a mixture of **6b** (44%) and pyran **7b** (54%), which was separated by flash chromatography on silica gel. Thus, solvolytic rearrangement of **4d** in methanol is not competitive with the thermal abnormal Claisen rearrangement to give **6b**. Dienone **6b** was converted to pyran **7b** in quantitative yield by treatment with diethylamine in CH_2Cl_2.

These data suggest that the apparent absence of photoreactivity of **1a** in benzene or methanol and **1b** in benzene is a result of reversible photorearrangements of **1** to **4**. The reaction **4a** → **1a** might be initiated by photoexcitation of **4a** followed by electron transfer from the amine group to the cyclopropane-coupled enone and dienone chromophores.[12] Such electron transfer is less probable in carbamate **4b**, although **4b** might revert to **1b** by another, less efficient photochemical or thermal pathway.[4b,8] In both **4c** and **4d**, back reactions to **5a** and **5b** are not competitive with the apparently efficient abnormal Claisen rearrangements.

Alternatively, there may be reversible photoinitiated electron transfer in **1a**, but with **5a** photorearrangement to **4c** may be faster than the electron-transfer process. We reserve further discussion of mechanistic questions until more detailed studies of **1a**, **1b**, **5a**, and **5b** have been completed. The receptor binding and photoaffinity properties of these and related opiate derivatives will be reported in due course.

Acknowledgment. This work was supported by the National Institute of General Medical Science (Grant GM 33061) to A.G.S. Inquiries regarding the X-ray crystallographic analysis should be directed to F.S.T.

Supplementary Material Available: Tables of crystal structure data, atomic coordinates, bond lengths, bond angles, anisotropic parameters, and hydrogen atom coordinates for **3** (6 pages). Ordering information is given on any current masthead page.

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[8] Flash photolysis studies of spiro[benzofuran-2(3*H*),1′-cyclohexane]-2-carboxylic acid methyl ester[4] and a tetradeuterio derivative provided spectroscopic evidence for the 2,4-cyclohexadien-1-one chromophore in the photogenerated intermediate as well as activation parameters and a deuterium isotope effect for the thermal abnormal Claisen rearrangement to α-(1-cyclohexenyl)-2-hydroxybenzeneacetic acid methyl ester; see: Wisniewski, K. Ph.D. Thesis, Rensselaer Polytechnic Institute, 1985.

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The Endocyclic Restriction Test: An Experimental Evaluation of the Geometry at Oxygen in the Transition Structure for Epoxidation of an Alkene by a Peroxy Acid

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The epoxidation of olefins by peroxy acids is a widely used reaction of synthetic value and mechanistic interest.[1] The bimolecularity and stereospecificity of the process have been generally rationalized by the Bartlett "butterfly" transition structure, shown as A, which was suggested over 40 years ago.[2] According to this mechanism, an S_N2-like reaction takes place at the terminal oxygen of the hydroperoxide group with the π HOMO of the olefin approaching the σ^* LUMO of the O–O bond at 180°. An alternative transition structure, which resembles a 1,3-dipolar cycloaddition, has been suggested and is shown as B.[3] In this communication we provide evidence based on the endocyclic restriction test that shows that the geometry at oxygen in this reaction is consistent with the transition-structure geometry expected for A and inconsistent with that shown for B.[4]

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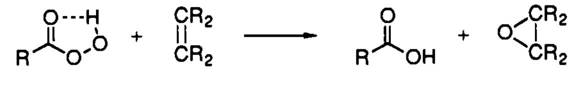
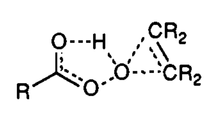
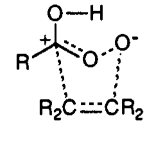


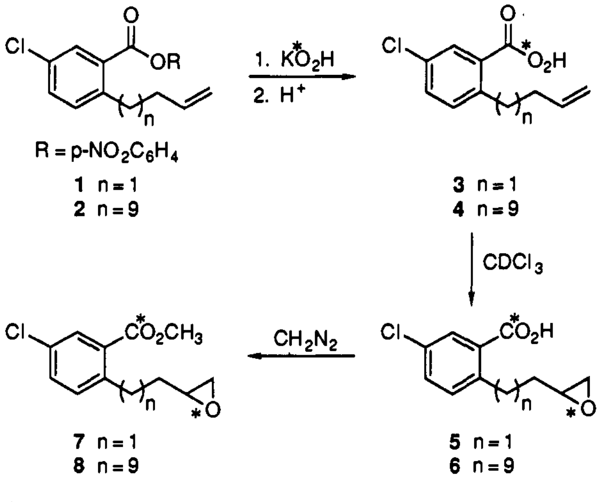


A



B

Our approach to distinguishing between transition structures A and B involves the conversion of the peroxy acid olefins **3** and **4** to the acid epoxides **5** and **6**, respectively.[5] This application of the endocyclic restriction test with different lengths of tethers between the reactive groups allows limits to be placed on the trajectory in the oxygen transfer. The geometry allowed by the short tether of **3** is favorable for an intramolecular reaction through a transition structure corresponding to B.[6] In contrast, the butenyl side chain of **3** is of insufficient length to allow the reaction to occur intramolecularly under the alignment of a transition structure corresponding to A, and the reaction should be intermolecular. The longer tether of **4**, on the other hand, is of adequate length for the double bond to achieve the geometry required by the butterfly mechanism, and the reaction could be expected to be intramolecular under appropriate conditions for either transition structure A or B.



R = p-NO$_2$C$_6$H$_4$
1 n=1
2 n=9

3 n=1
4 n=9

5 n=1
6 n=9

7 n=1
8 n=9

$^{*}O = {}^{16}O$ or ^{18}O

Double-label experiments were carried out to distinguish between intramolecular and intermolecular processes. The *p*-nitrophenyl esters **1** and **2**, respectively, in THF-d_8 were treated with a mixture of KOOH and $K^{18}O^{18}OH$ (ca. 60% ^{16}O–^{16}O/40% ^{18}O–^{18}O) in separate experiments to give the peroxy acid anions of **3** and **4** as a mixture of unlabeled and doubly labeled compounds.[7] The *p*-nitrophenol was removed by extraction and oxygen transfer initiated by acidification and extraction into $CDCl_3$. Conversions of the peroxy acids to the epoxy acids were monitored by observing the disappearance of the peaks due to the olefinic protons in the ^{1}H NMR spectra. After 30 h the crude products were treated with diazomethane, and the resultant mixtures of esters **7** or **8** were isolated and analyzed by mass spectrometry to determine the isotopic distribution. A completely intramolecular reaction would result in the same label distribution in the products as in the reactants whereas an intermolecular reaction would lead to a statistical distribution of the labels in the products.

Table I. Isotopic Composition of **7** from **3**[a]

concn, M	label[b]	reactants 3, %	7, % intra-molecular[c]	7, % inter-molecular[c]	7, % exptl
0.01	^{16}O–^{16}O	57 ± 4	57 ± 4	34 ± 3	35 ± 3
	^{16}O–^{18}O	3 ± 1	3 ± 1	48 ± 4	47 ± 4
	^{18}O–^{18}O	40 ± 4	40 ± 4	17 ± 2	17 ± 3

[a] Errors are calculated with the assumption of an error of ±5 in the relative intensities in the mass spectrum (peaks normalized to 100). [b] The ^{16}O–^{18}O in the peroxy acid starting material is a consequence of less than 100% ^{18}O enrichment in the $^{18,18}O_2(g)$ used as the source of the label. [c] Theoretically expected values.

Table II. Isotopic Composition of **8** from **4**[a]

concn, M	label[b]	reactants 4, %	8, % intra-molecular[c]	8, % inter-molecular[c]	8, % exptl
0.02	^{16}O–^{16}O	59 ± 3	59 ± 3	32 ± 3	52 ± 3[d]
	^{16}O–^{18}O	3 ± 1	3 ± 1	48 ± 3	19 ± 3[d]
	^{18}O–^{18}O	38 ± 3	38 ± 3	16 ± 2	30 ± 3[d]
0.005	^{16}O–^{16}O	51 ± 3	51 ± 3	28 ± 2	49 ± 3
	^{16}O–^{18}O	4 ± 1	4 ± 1	50 ± 3	7 ± 3
	^{18}O–^{18}O	45 ± 3	45 ± 3	22 ± 2	43 ± 3

[a] Errors are calculated with the assumption of an error of ±5 in the relative intensities in the mass spectrum (peaks normalized to 100). [b] The ^{16}O–^{18}O in the peroxy acid starting material is a consequence of less than 100% ^{18}O enrichment in the $^{18,18}O_2(g)$ used as the source of the label. [c] Theoretically expected values. [d] The values calculated for 65% intramolecular and 35% intermolecular reaction are 51 ± 2, 19 ± 1, and 30 ± 2, respectively.

The mass spectrometric results for the double-label experiment of **3** at ≤0.01 M are listed in Table I along with the theoretical values calculated for both the completely intramolecular and completely intermolecular processes. The values obtained experimentally are in close agreement with those calculated for the crossover of an intermolecular reaction. Appropriate controls were carried out to ensure that scrambling of the label did not occur in the reactants or the products.

When a double-label experiment was carried out with **4** at a concentration of ≤0.02 M, the results were in accord with ≥65% intramolecular reaction, as shown in Table II. Repetition of the crossover experiment at ≤0.005 M gave an isotopic distribution in agreement with ≥90% intramolecular reaction, as shown in Table II.

Our results show that the conversion of **3** to **5** is an intermolecular reaction and the conversion of **4** to **6** can be an intramolecular reaction under comparable conditions. The possible 8.5-membered transition structure from **3** does not meet the geometric requirements needed for the oxygen to transfer intramolecularly. Oxygen transfer from the peroxy acid with a longer tether, **4**, occurs intramolecularly through a 16.5-membered transition structure to the extent of ≥90%.

These results are consistent with the requirement that approach of the olefin occurs at 180° to the O–O bond according to the butterfly mechanism and transition structure A proposed by Bartlett and supported by calculations.[8] These results are inconsistent with transition structures corresponding to B. In essence, the epoxidation can be categorized as an S_N2 substitution at oxygen with a transition structure in which the oxygen being transferred is at the center of a trigonal bipyramid with the entering and leaving groups in the apical positions, shown as C.[9]

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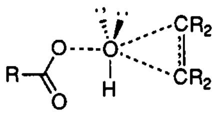
The Bartlett mechanism has been widely used to rationalize the results of olefin epoxidations by peroxides, and this determination of the disposition of the atoms in the transition structure can be reasonably extended to related oxygen-transfer reactions.



C

Acknowledgment. We are grateful to the National Science Foundation and the National Institutes of Health for support of this work.

Supplementary Material Available: Experimental details and spectral data for compounds **1**, **2**, **7**, and **8** and experimental procedures for double-label crossover experments and control studies to rule out label scrambling (6 pages). Ordering information is given on any current masthead page.

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Expanded Heterohelicenes: Molecular Coils That Form Chiral Complexes

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Helical structures are ubiquitous in nature and are essential to life itself (e.g., polypeptides and nucleic acids). In recent years chemists have discovered several metal–ligand combinations that lead to spontaneous assembly of multicomponent helical and double-helical structures.[1] In this communication, we report the first examples of a new class of preorganized, monohelical polypyridine ligands. These "molecular coils" composed of fused six-membered rings wrap around guest ions, forming helical 1:1 complexes. Helicenes[2] such as [6]helicene (**2**) consist only of angularly fused rings; their ideal, planar analogue is coronene (**1**). Combination of angular with linear fusion of benzene rings leads to planar cycloarenes[3] (e.g., kekulene, **3**) and conceptually to unknown, "expanded" carbocyclic helicenes, such as **4**. Replacement of internal C–H groups in cycloarenes with heteroatoms gives torands,[4] such as **5**,[4b–e,5] which tightly bind alkali metals.[4c]

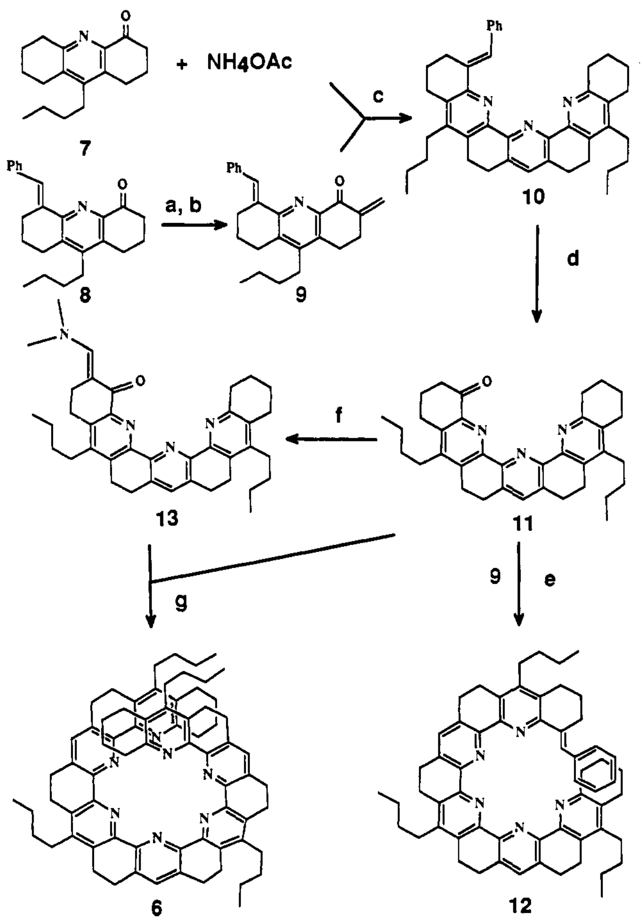

Figure 1. Syntheses of expanded heterohelicenes: (a) Me_2NCH_2Cl, CH_3CN (95%); (b) NaOH, H_2O, $CH_2Cl_2/CH_3I/Et_3N$, CH_2Cl_2 (78%); (c) DMSO (55%); (d) O_3, CH_2Cl_2, CH_3OH/Me_2S (92%); (e) NH_4OAc, DMSO, 95 °C (22%); (f) $t\text{-BuOCH(NMe}_2)_2$, 80 °C (82%); (g) NH_4BF_4, DMF, 150 °C.

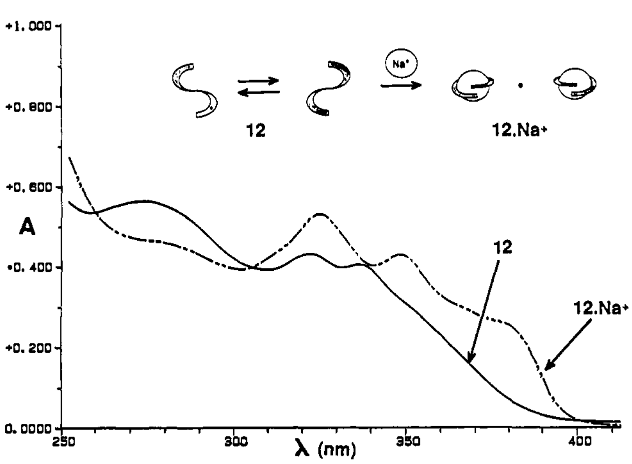

Figure 2. UV-visible absorption spectra of **12** and **12**·Na^+.

Both of the new "expanded" heterohelicenes (**6** and **12**) were synthesized from 9-*n*-butyl-2,3,5,6,7,8-hexahydro-4(1*H*)-acridinone (**7**) and 5-benzylidene-9-*n*-butyl-2,3,5,6,7,8-hexa-

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