possesses only a single conformation, which is ideally organized for octahedral binding. Diminished spherand $(CH_3C_6H_2OCH_3)_4(C_6H_4)_2$ (**5**), with only four oxygens, also gave $-\Delta G° < 6$ kcal mol^{-1}. Standard crown Nap(OEOEO)$_2$E (**10**) and hemispherand $(CH_3C_6H_2OCH_3)_3(CH_2OCH_2)_3$ (**11**) with values of ~6 and 7.2 kcal mol^{-1}, respectively, lack conformations that provide direct cooperative binding by more than three or four oxygens of ions as small as Li^+. Diminished spherand $(CH_3C_6H_2OCH_3)_5(C_6H_4)$ (**4**) as a molecular model possesses an enforced cavity lined with five oxygens and one aryl hydrogen. Spheres of diameters of 1.3–1.5 Å can be inserted and fit snugly into this cavity without apparent increase in strain. The aryl hydrogen must adapt to larger spheres with strain-inducing molecular deformations. The $-\Delta G°$ value for **4** is 10.4 kcal mol^{-1}, >11 kcal mol^{-1} less than that of the ideally organized spherand $(CH_3C_6H_2OCH_3)_6$ (**1**). Although the cavity of augmented spherand $(CH_3C_6H_2O)_6(CH_3)_2(EOE)_2$ (**3**) provides seven oxygens that contact Li^+ in structure **3a**, the binding energy of only 15.9 kcal mol^{-1} indicates that the organization of O's in the free host is far from ideal. Shaved molecular models of **3** provide an elongated cavity into which only spheres of 1.7–2.0 Å can be inserted snugly. To bind seven O's simultaneously, Li^+ may have to decrease the near oxygen–oxygen distances. The increase in compression energy is paid for by a decrease in binding energy. Cryptand N(EOE)$_2$(EOEOE)N (**12**) gives $-\Delta G° = 16.6$, and bridged spherand $(CH_3C_6H_2O)_6(CH_3)_2(CH_2CH_2CH_2)_2$ (**2**), gives $-\Delta G° = 16.8$ kcal mol^{-1} for binding Li^+. Host **12** is the strongest Li^+ binder among the simple cryptands and contains six heteroatom binding sites. In the crystal structure of **12**·LiI, all unshared electron pairs are turned inward,[22] but in CPK models of **12** itself, one or two methylenes can turn inward and nearby oxygens can turn outward to provide strain-free conformations, as in the crystal structure of the [2.2.2]cryptand analogue.[23] These conformations must be frozen out during capsular complexation. Shaved models of $(CH_3C_6H_2O)_6(CH_3)_2(CH_2CH_2CH_2)_2$ (**2**) and the crystal structure **2a** both indicate that only five oxygens can simultaneously contact an inserted sphere of the ~1.3-Å diameter of Li^+. Interestingly, the five binding oxygens of **2** provide a slightly higher $-\Delta G°$ value than the seven binding oxygens of **3**. Shaved models of **2** suggest a cavity diameter more complementary to the diameter of Li^+ than do models of **3**. The binding free energy of >22 kcal mol^{-1} that $(CH_3C_6H_2OCH_3)_6$ (**1**) shows toward Li^+ correlates with the nearly ideal organization of the six binding sites prior to complexation.

These same hosts provide a somewhat different increasing order of $-\Delta G°$ values (kcal mol^{-1}) for binding NaPic: $H(CH_3C_6H_2OCH_3)_6H$ (**9**), <6; $(CH_3C_6H_2OCH_3)_4(C_6H_4)_2$ (**5**), <6; $(CH_3C_6H_2OCH_3)_5(C_6H_4)$ (**4**), 6.6; Nap(OEOEO)$_2$E (**10**), 8; $(CH_3C_6H_2OCH_3)_3(CH_2OCH_2)_3$ (**11**), 12.5; $(CH_3C_6H_2O)_6(CH_3)_2(CH_2CH_2CH_2)_2$ (**2**), 13.6; N(EOE)(EOEOE)$_2$N (**13**), 16.3; $(CH_3C_6H_2O)_6(CH_3)_2(EOE)_2$ (**3**), 18.7; $(CH_3C_6H_2OCH_3)_6$ (**1**), 19.2. The scale covers a range of values >13 kcal mol^{-1} (>10^9 in K_a) with $H(CH_3C_6H_2OCH_3)_6H$ (**9**) at the bottom and $(CH_3C_6H_2OCH_3)_6$ at the top. The larger diameter for Na^+ as compared to Li^+ has the following effects. Diminished spherand $(CH_3C_6H_2OCH_3)_5(C_6H_4)$ (**4**), bridged spherand $(CH_3C_6H_2O)_6(CH_3)_2(CH_2CH_2CH_2)_2$ (**2**), and parent spherand $(CH_3C_6H_2OCH_3)_6$ exhibit $-\Delta G°$ values for Na^+ at least 3.2 kcal mol^{-1} less than for Li^+, but their order remains the same. Conversely, crowns Nap(OEOEO)$_2$E (**10**), hemispherand $(CH_3C_6H_2OCH_3)_3(CH_2OCH_2)_3$ (**11**), and augmented spherand $(CH_3C_6H_2O)_6(CH_3)_2(EOE)_2$ (**3**) bind Na^+ better than Li^+ by 2–5.3 kcal mol^{-1}; the binding order is the same. The best of the simple cryptands for binding Na^+, N(EOE)(EOEOE)$_2$N (**13**), gave a $-\Delta G°$ value of 16.3 kcal mol^{-1}, 2.9 kcal mol^{-1} less than the value for $(CH_3C_6H_2OCH_3)_6$ (**1**) and 2.4 kcal mol^{-1} less than that for $(CH_3C_6H_2O)_6(CH_3)_2(EOE)_2$ (**3**). The results show that when the host–guest relationships are the most complementary in any given host class, the order for binding LiPic and NaPic in $CDCl_3$ saturated with D_2O at 25 °C is spherands > cryptands > hemispherands > crowns > open-chain polyethers.

.The striking generalization that correlates host structure with binding power is *the larger the number of host ligating sites organized for binding during synthesis rather than during complexation, the greater the standard free energy change that accompanies complex formation.* Although the spherands owe their superior binding power mainly to preorganization, compensation for electron–electron repulsion by inserting a positive charge into their enforced cavities also probably contributes in some systems. The severe compression of the oxygens in bridged spherands **2** and **3** in particular may involve the latter effect.

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[21] This compound is constitutionally like ended. It contains 5 potentially chiral elements associated with Ar–Ar rotations and 6 associated with CH_3–Ar rotations, 11 in all. The number of stereoisomers (conformers in this case) for a constitutionally like-ended system containing an odd number of potentially chiral elements is 2^{n-1} [Mislow, K. "Introduction to Stereochemistry"; W. H. Benjamin: New York, 1965; p 88].

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α-Disulfoxide and Sulfinic Anhydride in the Peroxy Acid Oxidation of 2-Methyl-2-propyl 2-Methyl-2-propanethiosulfinate

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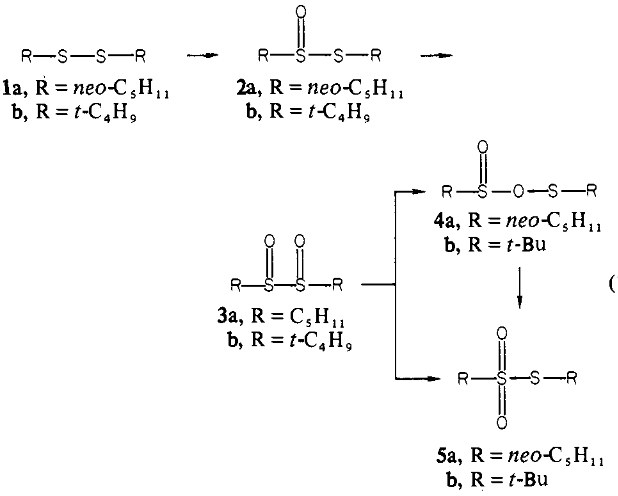
α-Disulfoxides **3** and sulfenyl sulfinates **4** have been postulated as intermediates in the peroxy acid oxidation of disulfides **1** or thiosulfinates **2** to thiosulfonates **5**. However, neither **3** nor **4** has been observed or isolated.[1-9]



1a, R = *neo*-C_5H_{11}
b, R = *t*-C_4H_9

2a, R = *neo*-C_5H_{11}
b, R = *t*-C_4H_9

3a, R = C_5H_{11}
b, R = *t*-C_4H_9

4a, R = *neo*-C_5H_{11}
b, R = *t*-Bu

5a, R = *neo*-C_5H_{11}
b, R = *t*-Bu

(1)

Although it is generally accepted that disulfides **1** and thiosulfinates **2** are oxidized by peracids to thiosulfonates **5**, we have observed[2] that thiosulfonate **5a** is only a minor product in the low temperature *m*-chloroperoxybenzoic acid (MCPBA) oxidation of 2,2-dimethylpropyl 2,2-dimethylpropanethiosulfinate (**2a**). Although it has been reported that 2-methyl-2-propyl disulfide (**1b**) is oxidized to 2-methyl-2-propyl 2-methyl-2-propanethiosulfinate (**2b**, 93%) with peracetic acid,[10,11] other reports claim that **1b** is

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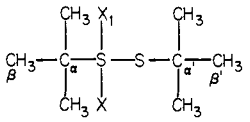
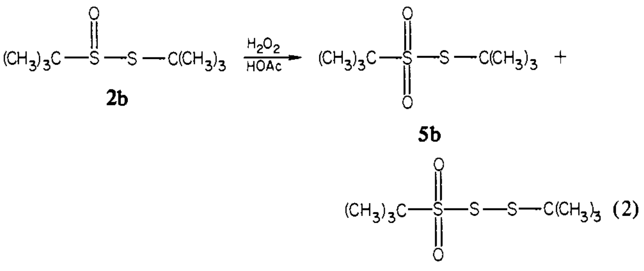
Table I. ^1H NMR and ^{13}C NMR Chemical Shifts of 2-Methyl-2-propyl-Substituted Organosulfur Compounds[a]



	C(CH3)3					
	^1H NMR, δ_H		^{13}C NMR, δ_C			
organosulfur compd	β	β'	α	α'	β	β'
$(CH_3)_3CSSC(CH_3)_3$ (**1b**)[c,d]	1.36		45.63		30.51	
$(CH_3)_3CS(O)SC(CH_3)_3$ (**2b**)[d,e]	1.53[f]	1.32[f]	58.31	47.93	24.01	32.20
$(CH_3)_3CSO_2SC(CH_3)_3$ (**5b**)[c,d]	1.62	1.47	68.02	56.29	23.74	31.52
$(CH_3)_3CSO_2SSC(CH_3)_3$ (**6**)[d]	1.50	1.42				
$(CH_3)_3CSOH$ (**7**)[g]	1.31[h,i]					
$(CH_3)_3CSO_2H$ (**8**)[e]	1.20[h]		56.59[h]		21.35[h]	
$(CH_3)_3CSO_3H$ (**9**)[e]			55.91[j,h]		24.97	
$(CH_3)_3CS(O)OS(O)C(CH_3)_3$ (**10**)[k]	1.27					

[a] Chemical shifts of samples in deuteriochloroform ($CDCl_3$) solutions with Me_4Si as internal standard. [b] $X = X_1$ = lone pair electrons (disulfide); X = pair electrons, X_1 = oxygen atom (thiosulfinate); $X = X_1$ = oxygen atoms (thiosulfonate). [c] Reference 17. [d] Reference 19. [e] This work. [f] Reference 15. [g] Reference 23. [h] C_α is the carbon atom attached to the sulfenyl, sulfinyl, or sulfonyl sulfur atom. [i] In CCl_4. [j] Spectrum obtained in 20–80% CD_3OD–$CDCl_3$ solution. [k] Reference 26.

not oxidized by peracetic acid[12–15] or superoxide anion (KO_2 and 18-crown-6-ether in pyridine).[16] In another report,[17] oxidation of **1b** with peracetic acid in the presence of anhydrous tungsten(VI) oxide gave 2-methyl-2-propanesulfenic 2-methyl-2-propanesulfonic thioanhydride (**6**)[18,19] and other colorless products. The peracetic acid oxidation of **2b** gives a mixture of 2-methyl-2-propyl 2-methyl-2-propanethiosulfonate (**5b**) and **6**.[6,10,19]



$$(CH_3)_3C-S(=O)-S-C(CH_3)_3 \xrightarrow[HOAc]{H_2O_2} (CH_3)_3C-S(=O)_2-S-C(CH_3)_3 + (CH_3)_3C-S(=O)_2-S-S-C(CH_3)_3 \quad (2)$$

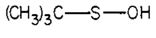
2b **5b** **6**

Table II. Variation of the Composition of the Product Mixture Obtained by Oxidation of **2b** Using MCPBA in $CDCl_3$ with Temperature

time	temp, °C	observations
0	−45	filtration completed
17 min	−40	^{13}C NMR and ^1H NMR spectra obtained
1 h 25 min	−40	continuous scanning shows that the composition of the reaction mixture remains unchanged
1 h 25 min–1 h 27 min	−40 → −30	temperature raised to −30 °C
1 h 38–1 h 53 min	−30	^{13}C NMR spectrum obtained, shows slow decrease of **3b** (Figure 1)
1 h 54 min–1 h 55 min	−30 → −20	temperature raised to −20 °C
2 h 10 min	−20	^1H NMR and ^{13}C NMR spectra obtained
2 h 39 min–2 h 40 min	−20 → 0	temperature raised to 0 °C
2 h 40 min–3 h 33 min	0	continuous scanning shows that the composition of the reaction mixture remains the same
3 h 33 min–3 h 34 min	0 → 25	temperature raised to 25 °C
3 h 56 min		^1H NMR and ^{13}C NMR spectra obtained

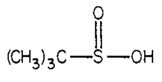
In order to elucidate the influence of steric factors and the nature of reaction intermediates (**3b**, **4b**), we have investigated the low-temperature (−40 °C) MCPBA oxidation of **2b** in a dry inert atmosphere via ^1H NMR and ^{13}C NMR spectroscopy.[17,19–22]

The ^1H NMR and ^{13}C NMR of reference 2-methyl-2-propyl substituted organosulfur compounds, including **1b**, **2b**, **5b**, **6**, 2-methyl-2-propanesulfenic acid (**7**),[23] 2-methyl-2-propanesulfinic acid (**8**),[24] 2-methyl-2-propanesulfonic acid (**9**),[25] and 2-methyl-2-propanesulfinic anhydride (**10**),[26] are shown in Table I.



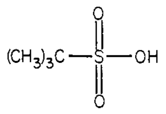
$(CH_3)_3C-S-OH$

7



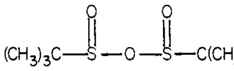
$(CH_3)_3C-S(=O)-OH$

8



$(CH_3)_3C-S(=O)_2-OH$

9



$(CH_3)_3C-S(=O)-O-S(=O)-C(CH_3)_3$

10a, *R,R*
b, *R,S*

Thiosulfinate **2b** was oxidized with 1 equiv of MCPBA in $CDCl_3$ at −40 °C in a dry nitrogen atmosphere for 1 h and filtered under nitrogen in order to remove *m*-chlorobenzoic acid (MCBA).

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Table III. ^1H NMR and ^{13}C NMR Chemical Shifts of the Products from the MCPBA Oxidation of **2b** in $CDCl_3$

organosulfur compd	^{13}C NMR, δ_C		relative integral,[b] %	^1H NMR, δ_H	^{13}C NMR, δ_C		relative integral,[b] %	^{13}C NMR, δ_C		relative integral,[b,e] %
	−40 °C, 17 min[c]			−40 °C, 15 min[c,d]	−20 °C, 2 h 10 min[c]			25 °C, 3 h 56 min[c]		
$(CH_3)_3CS(O)SC(\mathbf{CH_3})_3$ (**2b**)	32.06	48.88	23	1.38	32.15	48.79	30	32.26	48.91	32
$(\mathbf{CH_3})_3CS(O)SC(CH_3)_3$ (**2b**)	24.00	59.44	24	1.58	24.06	59.44	31	24.23	59.65	34
$(CH_3)_3CS(O)S(O)C(CH_3)_3$ (**3b**)	23.06	57.20	28	1.41						
$(CH_3)_3CS(O)\text{-}O\text{-}S(O)C(CH_3)_3$ (**10a**)	21.41	60.18	15	1.30	21.47	60.18	23	21.62	60.23	28
$(CH_3)_3CS(O)\text{-}O\text{-}S(O)C(CH_3)_3$ (**10b**)	21.59	60.70	10	1.32	21.65	60.62	17	21.76	60.59	2.0

[a] Me_4Si is used as internal standard, spectrometer frequency is 62.89 MHz (^{13}C) and 250 MHz (^1H). ^{13}C NMR spectra required 200 scans in 15 min with broadband decoupling. [b] Relative integrals of quaternary carbon atoms are tabulated. Calibration experiments show that the relative integral of the α carbon atom of simple acyclic thiosulfinates, thiosulfonates, and sulfinic acids corresponds to their respective relative molar concentrations (within 10%) when the alkyl group is the same. [c] See Table II for time scale. [d] A satisfactory integral could not be obtained owing to overlapping peaks. [e] Small peaks at δ_C 56.68, 57.44, and 68.03, which are probably due to the presence of **5b** and **8**, account for approximately 5% of the relative integral.

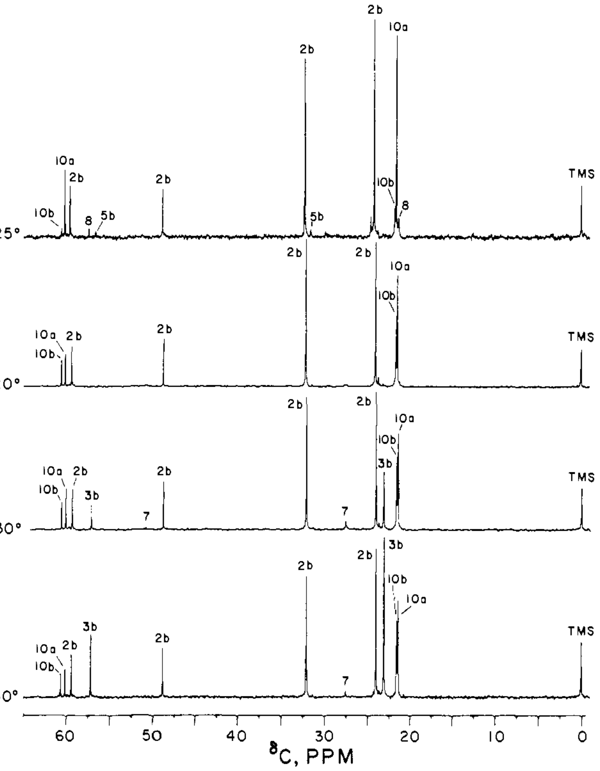
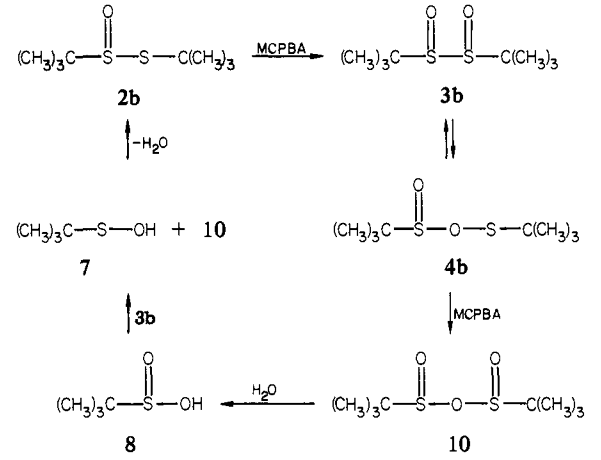


Figure 1. ^{13}C NMR spectra at several temperatures of the product mixture from the MCPBA oxidation of **2b**.

The filtrate was analyzed via ^1H NMR and ^{13}C NMR spectroscopy at low temperatures (Figure 1, Tables II and III). The low temperature (−40 °C) NMR spectra show the presence of an intermediate α-disulfoxide (**3b**, δ_H 1.41; δ_C 57.2)[27] and diastereomeric sulfinic anhydrides (**10**, δ_H 1.30, δ_C 60.18 and δ_H 1.32, δ_C 60.70).[26,28] α-Disulfoxide **3b** apparently is converted to **2b** and **10** on warming the product mixture from −40 to −30 to −20 °C. The conversion of **3b** to **2b** and **10** is relatively slow at −30 °C. The ^{13}C NMR spectrum of the product mixture showed a small amount of another intermediate (δ_C 28.45, 50.99), which disappeared on warming to −20 °C. These resonances are tentatively assigned to 2-methyl-2-propanesulfenic acid (**7**).[4,20,21,29-31]

Scheme I



The IR spectrum ($CDCl_3$), which was obtained as soon as the product mixture was warmed to 25 °C (<3 min), showed a strong band at 1140 cm^{-1} owing to the presence of **10**[26] and a band at 1050 cm^{-1} due to **2b**.

The resonances at δ_C 21.41, 60.18 (**10a**) and δ_C 21.59, 60.70 (**10b**) are tentatively assigned to the *R,R* and *R,S* diastereomers of **10**.[28] The ^1H NMR spectra at 25 °C show that the concentration of **10b** decreases rapidly (<10 min) relative to the concentration of **10a** (Table III).[32,33] The sulfinic anhydrides (**10**) decompose on standing (>30 min) at 25 °C.

The above results are explicable in terms of an electrophilic attack by MCPBA at the sulfenyl sulfur atom of **2b** to give α-disulfoxide **3b** which can be in equilibrium with sulfenyl sulfinate **4b** at −40 °C (Scheme I). Competing oxidation of **4b** by MCPBA could account for unreacted **2b** and the formation of **10**. However, peaks which can be assigned to **4b** are absent from the low-temperature NMR spectra, and **7** is observed at −30 °C while **3b** is slowly disappearing. A reasonable reaction pathway for conversion of **3b** to **2b** and **10** involves the reaction of **8**, which is produced by reaction of **10** with trace amounts of water, with **3b** to give **7** and **10**. The reaction considered to be most characteristic of sulfenic acids (**7**) is dehydration to thiosulfinates (**2b**), possibly via an intermediate such as **11**.[18,34,35] Intermediate **12**[18] could be involved in the formation of **7** and **10** and intermediate **13** could be involved in the formation of **2b** and **10**.

The absence of a significant amount of thiosulfonate **5b** from the oxidation of **2b** is consistent with our studies of the MCPBA oxidation of **2a**[2] and different from previous reports of the peracetic acid oxidation of **2b** to **5b** and **6**.[6,10,19,36] It is also surprising that

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(27) In principle, formation of diastereomeric α-disulfoxides **3b** is possible. The α-carbon atom of **3b** is upfield relative to that of **2b** possibly due to an increased γ shielding effect of the sulfinyl oxygen atoms.[20]

(28) It is not possible to make definitive configurational assignments at this time.

(29) The quaternary carbon atom of 2-methyl-2-propanethiol appears at δ_C 41.12. Thus, since the β effect of oxygen is ~10 ppm,[30,31] the assignment of these resonances to **7** is reasonable.

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(32) It may be possible that diastereomer **10b** stereomutates to **10a** as well as decomposes and converts to other products.[33]

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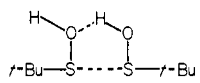

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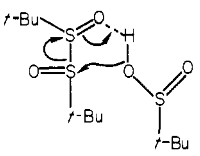

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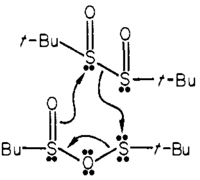

13

unstable **4b**, if formed, does not readily isomerize to **5b**.[2,8,37] It may be possible that **4b** is oxidized to **10** (Scheme I) or reacts with **3b** (cf. **13**) faster than it can isomerize to **5b**. Moreover, although the free energy difference is small, the sulfoxide (>S=O) structure is thermodynamically more stable than the sulfenate (—S—O—) structure.[38] However, the possibility of an equilibrium between **3b** and **4b** is consistent with the thiosulfinate [RS(O)SR]–thiosulfoxylate (R–O–S–S–R) isomerization[39] and the thermodynamics of sulfoxides vs. sulfenates.[38]

Although there are still unanswered questions, the above spectral data represent the first direct evidence for the long-sought α-disulfoxide **3b** intermediate. The results are uncomplicated owing to the presence of only three components in the product mixture. The spectral bands assigned to **3b** are consistent with its structure and are not easily explicable in terms of other known sulfur compounds.

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(36) The experimental conditions used in this study (MCPBA in $CDCl_3$) are different than those of previous workers (AcOOH in AcOH). Moreover, the mechanistic details for the formation of **6** have not been fully elucidated.

(37) It is also possible that α-disulfoxide **3b** could dissociate into two *t*-BuSO which can interact to form **4b**.[2,6,8]

(38) Kice, J. L. *Adv. Phys. Org. Chem.* **1980**, 100.

(39) Baldwin, J. E.; Höfle, G.; Choi, S. C. *J. Am. Chem. Soc.* **1971**, *93*, 2810.

Mild Base-Promoted Conversion of Tertiary *cis,cis*-2,4-Cyclononadienols to Bicyclo[4.3.1]nona-2,4-dienes. Antarafacial Cyclization of Coiled 8π-7C Conjugated Anions

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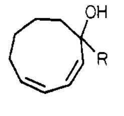
Despite the preeminent position of helical biopolymers and the availability of simpler classes of coiled molecules,[1] ionic species in which the reactive center is an *integral* component of a coiled π network have remained unknown. In our view, the unique structural features which are present within spiraled atomic networks hold promise for unparalleled chemical reactivity and comprise a promising area of new chemical investigation. Here we describe recent observations most cogently reconcilable with the generation and antarafacial cyclization of helical carbanions under extraordinarily mild conditions.

Table I. Product Data[a]

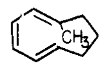
compd	yield, % KH, THF, reflux 9	 11	 KH, 18-crown-16, Et$_2$O, 20 °C 9	 11
7a, $R_1 = R_2 = H$	40	60	100	0
7b, $R_1 = CH_3$, $R_2 = H$	29	71	100	0
7c, $R_1 = R_2 = CH_3$	10	75[b]	68	12
7d, $R_1 = C_6H_5$, $R_2 = H$	100	0[c]	100	0[c]
7e, R_1, $R_2 = CH_2CH_2$	0	100	0	100

[a] Values given are relative percentages determined by VPC analysis; conversions are excellent. Ratios were observed in selected cases to be independent of reaction time. [b] A third product believed to be the 2-isopropyl analogue of 11 was also isolated (15–20%). [c] See text for discussion of accompanying ketone formation.

In contrast to the behavior of the potassium alkoxide of **1a** which delivers 3-cyclononenone via accelerated [1,5]-hydrogen sigmatropy,[2a] treatment of methyl homologue **1b** with KH in tetrahydrofuran at the reflux temperature produces chiefly **3**.[2b] A possible mechanism for the latter reaction involves base-promoted dehydration[3] to deliver **2** and subsequent disrotatory cyclization[4] of this triene. Although the all-cis isomer of **2** could also logically account for the isolation of **3**, Dreiding models of the conjugate base of **1b** suggest that access to **2** is much more kinetically feasible, particularly if the process is intramolecular (see **4**). Although **2** remains unknown, theoretical calculations have shown the demethyl system to be only slightly less thermodynamically stable (ca 3.5 kcal/mol) than its all-cis isomer.[5]



1a, R = H
b, R = CH_3



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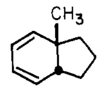

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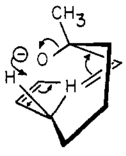

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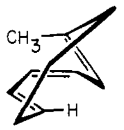

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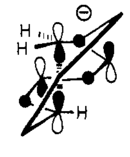

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Because of the coiled geometry of **2** (cf. **5**), its methyl substituent is projected to the interior of the molecule and above the distal double bond. While considering experimental tests which might substantiate this mechanistic scheme, it occurred to us that

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(1) (a) Helicenes: Newman, M. S.; Wise, R. M. *J. Am. Chem. Soc.* **1956**, *78*, 450. Martin, R. H. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 649. (b) Skewed paracyclophanes: Nakazaki, M.; Yamamoto, K.; Miura, Y. *J. Chem. Soc., Chem. Commun.* **1977**, 206. (c) Helical triphenylmethanes: Vögtle, F.; Hohner, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 497. (d) Helixanes: Gange, D.; Magnus, P.; Bass, L.; Arnold, E. V.; Clardy, J. *J. Am. Chem. Soc.* **1980**, *102*, 2134.

(2) (a) Paquette, L. A.; Crouse, G. D.; Sharma, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 3972. (b) Crouse, G. D.; Paquette, L. A. *Tetrahedron Lett.* **1981**, 3167.

(3) Usually, the dehydration of alcohols with base is effected at elevated temperatures. For example, see: (a) Bamberger, E.; Lodter, W. *Chem. Ber.* **1890**, *23*, 197. (b) Strauss, F.; Lemmel, L. *Ibid.* **1913**, *46*, 232. (c) Sabetay, S. *Bull. Soc. Chim. Fr.* **1929**, *45*, 69; **1930**, *47*, 614. (d) Sabetay, S.; Mintsou, T. *Ibid.* **1929**, *45*, 892. (e) Kitchen, L. J. *J. Am. Chem. Soc.* **1951**, *73*, 2368. (f) Ohloff, G.; Schade, G. *Angew. Chem.* **1955**, *67*, 427. (g) Ohloff, G. *Chem. Ber.* **1957**, *90*, 1554. (h) Ohloff, G. *Liebigs Ann. Chem.* **1959**, *627*, 79.

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(5) Buemi, G.; Zuccarello, F.; Grasso, D. *J. Mol. Struct.* **1977**, *42*, 195. Calculations have also been carried out on the isomeric [10]annulenes with similar results: Farnell, L.; Kao, J.; Radom, L.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1981**, *103*, 2147.

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