

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 ($R-O-S-S-R$) isomerization³⁹ 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

(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.; Magdry, P.; Bass, L.; Arnold, E. V.; Clardy, J. *J. Am. Chem. Soc.* **1980**, 102, 2134.

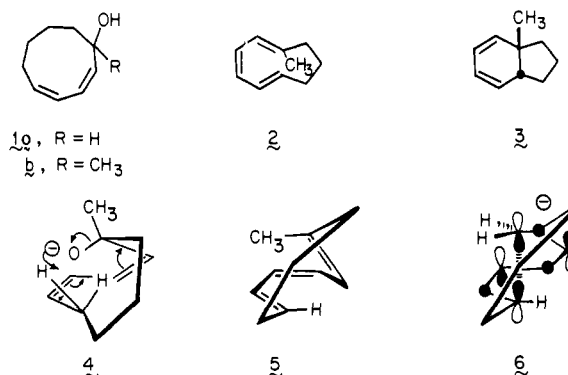
Table I. Product Data^a

compd	yield, %			
	KH, THF, reflux		KH, 18-crown-16, Et ₂ O, 20 °C	
	9	11	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 ₆ H ₅ , R ₂ = H	100	0 ^c	100	0 ^c
7e, R ₁ , R ₂ = CH ₂ CH 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.

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.

In contrast to the behavior of the potassium alkoxide of **1a** which delivers 3-cyclononone 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 dehydration³ to deliver **2** and subsequent disrotatory cyclization⁴ 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

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

(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.

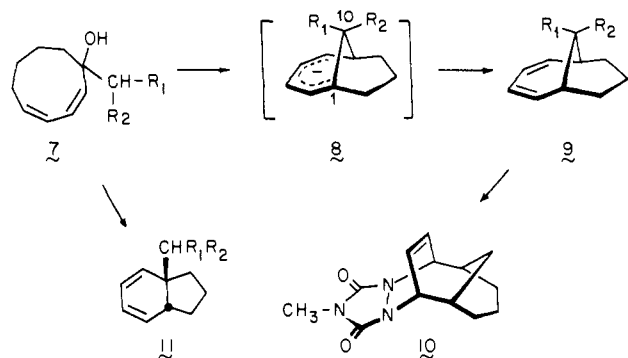
(3) Usually, the dehydration of alcohols with base is effected at elevated temperatures. For example, see: (a) Bamberger, E.; Lodter, W. *Chem. Ber.* **1890**, 23, 197. (b) Strauss, F.; Lemmel, L. *Ibid.* **1913**, 46, 232. (c) Sabetay, S. *Bull. Soc. Chim. Fr.* **1929**, 45, 69; **1930**, 47, 614. (d) 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.

(4) (a) Wathney, J. W. H.; Winstein, S. *J. Am. Chem. Soc.* **1963**, 85, 3715. (b) Vogel, E.; Grimme, W.; Dinné, E. *Tetrahedron Lett.* **1965**, 391. (c) Dauben, W. G.; Kellogg, M. S. *J. Am. Chem. Soc.* **1971**, 93, 3805; **1980**, 102, 4456.

(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.

the environment local to the methyl group should exert an acidifying effect on its protons and facilitate conversion to the coiled 8π -7C anion.⁶ A particularly notable aspect of this anion is its HOMO which, because of the inward-folded, coiled conformation, is characterized by sterically compressed synphasic⁷ terminal lobes as shown in **6**. There should consequently be little impedance to C-C bond formation at these terminal positions since the requirement of antarafaciality is clearly met. Indeed, 2,4-cyclononadienols (**7**) can be efficiently converted to bicyclo[4.3.1]nona-2,4-dienes (**9**), although the choice of conditions is critical.

Heating **7a** with KH in anhydrous tetrahydrofuran for 3 h as before² induces smooth dehydration and formation of a 60:40 mixture of **11a**² and **9a** (Table I). Upon addition of 1.2 equiv of 18-crown-6, remarkably lower temperatures (ether, 20 °C, 2 h) are required, and bicyclic diene **9a** is now generated exclusively. Evidently, the presence of the crown ether causes more efficient deprotonation of initially formed cyclononatriene **5**. While **5** can cyclize to **11a** (=3), its conjugate base does not have this option. Rather, electrocyclization delivers the bicyclic anion **8a** which ultimately experiences protonation at its trigonal bridgehead carbon.



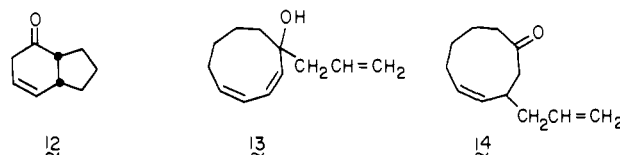
The structural assignment to **9a** follows from (a) its NMR spectra⁸ which show it to be a symmetrical diene, (b) catalytic hydrogenation to bicyclo[4.3.1]nonane, identical with an independently prepared authentic sample,⁹ and (c) Diels-Alder reaction with *N*-methyltriazolinedione to give **10**.¹⁰

The unprecedented behavior of methyl derivative **7a** is paralleled by the ethyl (**7b**) and isopropyl (**7c**) alcohols. The variations in product distributions (Table I) are thought merely to reflect alterations in the basicity of the proton whose abstraction generates the heptadienyl anion. As progression is made from 1 to 3°, a gradual increase is seen in the amount of **11** produced in the absence of 18-crown-6. The relative magnitudes of the competing rate constants are seen to differ most dramatically in the cyclo-

propyl example (**7e**). While both **7b** and **7c** continue to be transformable into **9b**¹¹ and **9c**¹² when the potassium ion is sequestered, **7e** cyclizes exclusively to **11e** under these conditions.

The absence of isomers at C_{10} in **9b** is noteworthy. The syn configuration ($R_1 = \text{CH}_3$, $R_2 = \text{H}$) has been assigned on the basis of the shielded nature of its methyl doublet (δ 0.85, $J = 7$ Hz). The reference point is **9c** where the differently shielded methyl substituents appear as singlets at δ 1.20 and 0.98. The unreactivity of **9b** and **9c** toward *N*-methyltriazolinedione (compare **9a**) provides less direct confirmation of the fact that steric congestion has materialized above the diene surface.

In light of the preceding discussion, the high propensity of benzyl derivative **7d** for conversion to **9d** ($R_1 = \text{C}_6\text{H}_5$, $R_2 = \text{H}$)¹² under either set of conditions is fully expected. Curiously, some side chain fragmentation was noted in this example, ketone **12**¹³ being isolated in 24% yield when the crown ether was omitted.



At present, the general effect of oxyanion substitution on neighboring center chemistry is known to be substantially better for [3,3]-C (10^{10} -fold acceleration at 25 °C)¹⁵ than for [1,5]-H sigmatropy (10^6 -fold rate enhancement at 25 °C). In an effort to rank the present dehydrative process, the tertiary allyl alcohol **13** was treated with KH in dry tetrahydrofuran. Since ketone **14** proved to be the sole detectable product, the kinetic dominance of the anionic oxy-Cope rearrangement remains unchallenged.

Finally, we return to the structural features of the coiled anions of type **6** which are believed to intervene in these cyclizations. In contrast to the more usual electrocyclizations where con- or disrotatory motions are required to achieve phase consistent σ overlap, intraannular bond formation within **6** can be realized without the need for additional p orbital alignment or any disadvantage of antibonding level encroachment. The facility with which the conversion of **6** to **8** occurs is consistent with a low reaction enthalpy and favorable entropy. The driving force arises from the transformation of a π bond into a σ bond (-20 kcal/mol). Importantly, this favorable energy term is not offset by the increased ring strain within **8** and its decreased delocalization energy. Strain differences, while unknown, should not realistically exceed 5 kcal/mol. While the conversion of a heptatrienyl to a penta-dienyl anion can be expected to incur less than a 12 kcal/mol decrease in resonance stabilization, the effects brought on by the torsion about C_1 in **8** are more difficult to assess. Suffice it to point out that the bicyclo[4.3.1]decatetraenyl anion is unquestionably a delocalized Hückeloid species.^{16,17}

(6) Many examples of such polyolefin deprotonations have been reported. For example: (a) (NH_2^-) Kloosterziel, H.; Van Drunen, J. A. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 368. Staley, S. W.; Pearl, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 3437. (b) (K metal) Stapp, P. R.; Kleinschmidt, R. F. *J. Org. Chem.* **1965**, *30*, 3006. (c) (KH) Slauch, L. H. *Ibid.* **1967**, *32*, 108. (d) (KO-*t*-Bu) Eglinton, G.; McCrae, W.; Raphael, R. A.; Zabkiewicz, J. A. *J. Chem. Soc. C* **1969**, 474. (e) (*n*-BuLi) Bates, R. B.; McCombs, D. A. *Tetrahedron Lett.* **1969**, 977. Bates, R. B.; Deines, W. H.; McCombs, D. A.; Potter, D. E. *J. Am. Chem. Soc.* **1969**, *91*, 4608.

(7) This term is intended to convey the notion that the π orbitals in question enjoy a phase-consistent relationship which may lead to bond formation without any disadvantage of antibonding level encroachment.

(8) ¹H NMR (CDCl_3 , δ) 5.8 (m, 4 H), 2.7 (m, 2 H), and 2.0–1.4 (series of m, 8 H); ¹³C NMR (CDCl_3 , ppm) 138.6, 125.4, 36.0, 32.4, 29.6, and 18.1.

(9) Mp 79–80 °C. A saturated hydrocarbon of the same melting point was obtained upon catalytic hydrogenation of bicyclo[4.3.1]deca-2,4,6,8-tetraene [Rajan Babu, T. V.; Shechter, H. *J. Am. Chem. Soc.* **1976**, *98*, 8261]. The superimposable ¹H NMR spectra [δ 2.2–1.7 (m, 2 H) and 1.7–1 (m, 16 H)] also proved identical with that provided by Dr. Pietra [Del Cima, F.; Pietra, F. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1710], although we have not been able to reconcile the melting point difference (their reported mp is 94–97 °C).

(10) Mp 125.5–126.5 °C; ¹H NMR (CDCl_3 , δ) 6.3 (dd, $J = 6$ and 4 Hz, 2 H), 4.9 (m, 2 H), 3.05 (s, 3 H), 2.4 (m, 2 H), and 2.4–1.3 (series of m, 8 H).

(11) Mp 48.5–50.5 °C; ¹H NMR (CDCl_3 , δ) 5.9–5.4 (m, 4 H), 2.4 (m, 2 H), 2.1–1.0 (series of m, 7 H), and 0.85 (d, $J = 7$ Hz, 3 H); ¹³C NMR (CDCl_3 , ppm) 135.5, 126.2, 42.5, 33.6, 33.5, 10.0, and 17.0.

(12) Mp 94–96 °C; ¹H NMR (CDCl_3 , δ) 6.0–5.5 (m, 4 H), 2.3–2.1 (m, 2 H), 2.1–1.7 (m, 2 H), 1.5–1.3 (m, 4 H), 1.20 (s, 3 H), and 0.98 (s, 3 H); ¹³C NMR (CDCl_3 , ppm) 135.6, 125.5, 46.6, 31.5, 28.3, 27.9, 27.7, and 16.5.

(13) Oil; ¹H NMR (CDCl_3 , δ) 7.45–7.0 (m, 5 H), 5.8 (m, 4 H), 3.3–2.8 (m, 3 H), 2.0–1.65 (m, 3 H), and 1.65–1.3 (m, 3 H); ¹³C NMR (CDCl_3 , ppm) 136.1, 128.1, 127.6, 127.0 (2C), 125.7, 44.2, 40.6, 33.9, and 17.6.

(14) Oil; ¹H NMR (CDCl_3 , δ) 5.7 (m, 2 H), 3.2–2.6 (m, 4 H), and 2.3–1.3 (series of m, 6 H). The identical substance was produced by successive treatment of 1,4-cyclononadiene monoepoxide with lithium diisopropylamide and pyridinium chlorochromate.

(15) (a) Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765; (b) Evans, D. A.; Nelson, J. V. *Ibid.* **1980**, *102*, 774 and pertinent references cited therein.

(16) (a) Radlick, P.; Rosen, W. *J. Am. Chem. Soc.* **1966**, *88*, 3461; **1967**, *89*, 5308. (b) Grimme, W.; Kauffhold, M.; Dettmeier, Y.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 604. (c) Murata, I.; Nakasuji, K.; Morita, T. *J. Chem. Lett.* **1974**, 743. (d) Takahashi, K.; Takase, K.; Kagawa, T. *J. Am. Chem. Soc.* **1981**, *103*, 1186. *J. Chem. Soc., Chem. Commun.* **1979**, 863.

(17) We are grateful to the National Institutes of Health (Grant AI-11490) for financial support and Professor H. Shechter for a sample of bicyclo[4.3.1]deca-2,4,6,8-tetraene.