and

$$1/T_2 = \tfrac{1}{90}\gamma^2 H_0^2(\sigma_\parallel - \sigma_\perp)^2 \left\{ \frac{6\tau_R}{1 + \omega^2\tau_R^2} + 8\tau_R \right\} \quad (2)$$

where the symbols have their usual meanings.[8] For the planar heme moiety, the chemical shift tensor is likely to be axially symmetric, as indicated in eq 1 and 2.

There are thus two unknowns, $|\sigma_\parallel - \sigma_\perp|$ and τ_R, but also two observables, T_1 and T_2. Thus, both $|\sigma_\parallel - \sigma_\perp|$ and τ_R can be determined, at least if we assume T_2 can be obtained from the line width. Alternatively, we can use the known τ_R for MbCO under these conditions (τ_R = 20 ns, ref 4) to obtain $|\sigma_\parallel - \sigma_\perp|$ from eq 1 and then *predict* the CSA contribution to the line width from eq 2.

For τ_R = 20 ns, eq 1 yields $|\sigma_\parallel - \sigma_\perp|$ = 3600 ppm, and eq 2 predicts a line width, W, of 48.6 Hz, which is close to the observed line width of 55 ± 5 Hz (Figure 1B). Alternatively, we can use the observed T_1 (17 ms) and line width (55 Hz) and eq 1 and 2, as shown in Figure 2, to predict $|\sigma_\parallel - \sigma_\perp|$ = 3680 ppm and τ_R = 22 ns. Iron-hydrogen dipolar contributions to the iron-57 relaxation are minimal since the nearest hydrogens are at least ~3 Å away (on the proximal histidine residue) and yield T_1^{-1} and T_2^{-1} contributions of 0.003 and 0.009 s^{-1}, respectively.

A second source of relaxation could be via ^{57}Fe–^{14}N scalar coupling of the second kind, to the four heme nitrogens directly coordinated to iron. On the basis of the ^{14}N quadrupole coupling constants for pyrrole and a series of metal-coordinated pyridines[9-11] we estimate τ_s for ^{14}N to be $\sim 2 \times 10^{-5}$ s (assuming τ_R = 20 ns). Since $^1J_{Fe-N} \sim 6$ Hz,[2,12] we compute scalar contributions of $T_1^s = 2 \times 10^8$ s and T_2^s = 50 s, which are both quite negligible. Thus, as observed experimentally, there is no resolvable Fe–N J coupling, and the ~50-Hz line widths predicted from the T_1 and τ_R data are in excellent agreement with observation.

We now consider the prognosis for iron-57 NMR studies of proteins. The results of Figure 2 show, at least for the case $|\sigma_\parallel - \sigma_\perp|$ = 3600 ppm, that for small proteins characterized by τ_R ~20 ns (such as cytochrome c and myoglobin, ref 4), T_1 values will be at or close to the minimum value possible (15.8 ms at τ_R = 14 ns), favorable circumstance for rapid data acquisition. In future studies using optimum recycle/pulse width combinations, it is clear from the results of Figures 1B (inset, 27 400 scans) and 2 that acceptable signal-to-noise ratio spectra should be achievable in $\sim 27\,400 \times 2T_1 \approx 15$ min of data acquisition.

For larger species, the results of Figure 2 indicate longer T_1 values and broader line widths. For hemoglobin (τ_R ~44 ns, ref 4, corrected for r_{CH} = 1.10 Å), we predict T_1 ~28 ms and a line width of ~92 Hz—not greatly different from the results with MbCO. For much larger proteins (M_r ~200 000, τ_R ~0.1 μs), T_1 values will be ~60 ms and line widths ~200 Hz, and again such species should be accessible, although of course the inherent dilution expected will increase data acquisition periods considerably.

Note for a system the size of hemoglobin, or larger, eq 1 reduces to

$$1/T_1 = 2(\sigma_\parallel - \sigma_\perp)^2/15\tau_R \quad (3)$$

so that T_1 values are independent of magnetic field strength (and the gyromagnetic ratio of the nucleus in question). However, the full sensitivity gains expected from high-field operation will be partially offset by the quadratic increases in line width. Indeed, we find for MbCO at 11.7 T T_1 = 15 ms and W = 110 Hz, which compares favorably with the predicted values of 14.6 ms and 98 Hz, respectively.

Note Added in Proof. The ^{57}Fe chemical shift of the isopropyl isocyanide adduct of (^{57}Fe)Mb is at 9256 ppm, over 1000 ppm from the carbonmonoxy species.

(8) Farrar, T. C.; Becker, E. D. "Pulse and Fourier Transform NMR"; Academic Press: New York, 1971.
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Asymmetric Synthesis via Chiral Sulfinylallyl Anion. Total Synthesis of (+)-Hirsutene: Facile Ring Closure Involving Enol Thioether and Enol Acetate Moieties

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Asymmetric induction reactions involving sulfoxides possessing chiral sulfur have received increasing attention in the past decade. The reactions of chiral α-sulfinyl anions with a variety of electrophiles often proceed with substantial asymmetric inductions at the newly formed chiral centers.[1] However, asymmetric induction in reactions involving anions of allylic sulfoxides has only been observed with benzaldehydes.[2] Generally, facile racemization at the sulfur atom occurs via a reversible [2,3] sigmatropic process.[3,4] We now report the regio- and stereochemical aspects of reactions of chiral sulfinylallyl anions with various cyclic enones[5] and the utilization of these reactions in the asymmetric synthesis of (+)-hirsutene (**1**), one of a variety of sesquiterpenoids isolated from the extract of *Coriolus consors*[6] and presumed to be the biogenetic precursor of coriolin,[7] hirsutic acid,[8] and complicatic acid.[9]

Treatment of (+)-(*R*)-allyl *p*-tolyl sulfoxide (**2**)[3] with lithium diisopropylamide (LDA) in THF at −78 °C for 1 h followed by 1 equiv of HMPA and 1 equiv of 2-cyclopentenone at −78 °C for 5 min provided the 1,4-adduct **3**[10] in 90% yield with 96% ee

(1) (a) Tsuchihashi, G.; Iriuchijima, S.; Ishibashi, M. *Tetrahedron Lett.* **1972**, 4605-4608. (b) Tsuchihashi, G.; Iriuchijima, S.; Maniwa, K. *Tetrahedron Lett.* **1973**, 3389-3392. (c) Johnson, C. R.; Schroeck, C. W.; Shanklin, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 7424-7431. (d) Kunieda, N.; Nokami, J.; Kinoshita, M. *Tetrahedron Lett.* **1974**, 3997-4000. (e) Biellmann, J. F.; Vicens, J. J. *Tetrahedron Lett.* **1974**, 2915-2918. (f) Tsuchihashi, G.; Mitamura, S.; Ogura, K. *Tetrahedron Lett.* **1976**, 855-858. (g) Nishihata, K.; Nishio, M. *Tetrahedron Lett.* **1976**, 1695-1698. (h) Mioskowski, C.; Solladie, G. *Chem. Commun.* **1977**, 162-163. (i) Chassaing, G.; Lett, R.; Marquet, A. *Tetrahedron Lett.* **1978**, 471-474. (j) Mioskowski, C.; Solladie, G. *Tetrahedron* **1980**, *36*, 227-236. (k) Posner, G. H.; Malame, J. P.; Miura, K. *J. Am. Chem. Soc.* **1981**, *103*, 3886-3888. (l) Corey, E. J.; Weigel, L. O.; Chamberlin, A. R.; Cho, H.; Hua, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 6613-6615. (m) Solladie, G. *Synthesis* **1981**, 185-196.
(2) Ridley, D. D.; Smal, M. A. *Aust. J. Chem.* **1983**, *36*, 1049-1055 and ref 1 cited therein.
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(5) The regioselectivity of addition to α-enones has been reviewed: Lefour, M. M.; Loupy, A. *Tetrahedron* **1978**, *34*, 2597-2605.
(6) (a) Nozoe, S.; Furukawa, J.; Sankawa, U.; Shibata, S. *Tetrahedron Lett.* **1976**, 195-198. (b) Feline, T. C.; Mellows, G.; Jones, R. B.; Phillips, L. *Chem. Commun.* **1974**, 63-64.
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(9) Mellows, G.; Mantle, P. B.; Feline, T. C.; Williams, D. J. *Phytochemistry* **1973**, *12*, 2717-2720.
(10) Binns, M. R.; Hayne, R. K.; Houston, T. L. *Aust. J. Chem.* **1981**, *34*, 2465-2467. All enantiomers are being depicted with absolute stereochemistry as indicated. All new compounds displayed satisfactory ^1H NMR (400 MHz), ^{13}C NMR (100 MHz), UV, IR, and low-resolution mass spectra and satisfactory elemental analysis or chemical ionization MS.

0002-7863/85/1507-4088$01.50/0

(enantiomeric excess) at C-3. The absolute configuration and optical purity at this C-3 was determined by two methods: (1) Sulfoxide **3** was degraded to the known acid, (+)-(*R*)-3-oxocyclopentaneacetic acid (**4**),[11] $[\alpha]_D^{21}$ + 109° (lit.[11c] −115.5° for *S* configuration), by the sequence (i) reduction of the sulfoxide group with zinc–acetic acid at room temperature to the corresponding sulfide, 95% yield, (ii) protection of the carbonyl group with ethylene glycol–pyridinium tosylate, 96% yield, (iii) ozonolysis of the double bond in CH_2Cl_2 at −78 °C, and (iv) oxidation of the resulting aldehyde group with *n*-Bu_4NMnO_4 in CH_2Cl_2 at room temperature followed by $NaHSO_3$–HCl workup[12] (70% yield in two steps; the HCl workup also effected removal of the ketal protecting group). (2) Ketone **3** was reduced with $NaBH_4$ in MeOH followed by oxidation with MCPBA in CH_2Cl_2 at 0 °C to give a mixture of alcohols **5** and **6** (3:2). The enantimeric composition at C-1 and C-3 of **5** and **6** was determined by ^{19}F and ^1H NMR spectra of the Mosher's derivatives[13] which indicated 96% ee at the C-3 of **3**.

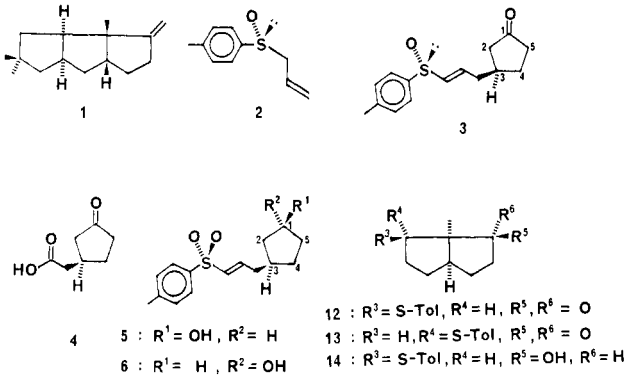


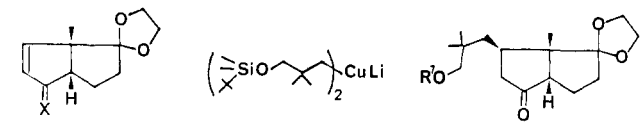
Table I summarizes the results from the reactions of the anion derived from (*R*)-**2** and various cyclic enones. In all cases but one the enantiomeric excess was determined by Mosher's method. In the γ-crotonolactone case (entry 5), the absolute configuration and optical purity at C-3 of the adduct **10** was determined by desulfurization of **10** with Raney nickel (W-2) in refluxing acetone to provide 80% yield of (*S*)-β-propyl-γ-butyrolactone,[14] $[\alpha]_D^{25}$ −7.3° (lit.[14b] +6.7° for *R* configuration, >90% ee).

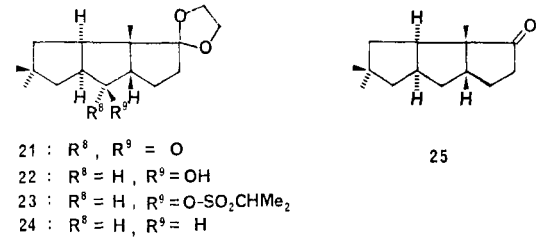
Entry 2 shows an example of kinetic resolution. When 2 equiv of racemic 4-[(1,1′-dimethylbenzyl)oxy]-2-cyclopentenone was allowed to react with the anion derived from (*R*)-**2**, only the *S* enone reacted.

To determine the absolute configuration and optical purity of the adduct from the reaction of the chiral sulfinylallyl anion with 2-methyl-2-cyclopentenone (entry 3), the adduct was transformed into bicyclo[3.3.0]octanol **14** by the following sequence: (i) in situ O-acetylation with AcCl at −78 °C of the enolate ion formed in the reaction of (*R*)-**2** and 2-methyl-2-cyclopentenone, (ii) reduction with Zn–AcOH at room temperature, 95% yield, (iii) intramolecular cyclization of the enol acetate with the vinylic sulfide moiety in the presence of 1 equiv of $TiCl_4$ in AcOH (50 mL/g of the sulfide) and 4 equiv of H_2O at room temperature for 15 min[15] to give hexahydropentalenones **12** and **13** (4:1), 86% yield, and (iv) reduction of isomer **12** with $NaBH_4$ in MeOH at −10 °C for 1 h, 95% yield. The ^{19}F NMR method[13] was applied to **14** to determine its optical purity.

Although several total syntheses of (±)-hirsutene [(±)-**1**] have been reported [6a,16] the absolute configuration of (+)-**1** remains unknown.[6a] The present synthesis of (+)-**1** from the readily available **12** and **13** establishes its absolute configuration.

The enantiomers of **12** and **13** were obtained from (−)-(*S*)-allyl *p*-tolyl sulfoxide (**2a**) and this mixture of enantiomers was transformed to bicyclooctene **15** in 90% yield by the following sequence: (i) oxidation with 1 equiv of MCPBA in CH_2Cl_2 at 0 °C and (ii) desulfenylation of the resulting sulfoxide with 1 equiv of DBN in refluxing toluene. Allylic oxidation of **15** with 15 equiv of CrO_3-(pyridine)$_2$[17] in CH_2Cl_2 (160 mL/g) at room temperature for 24 h provided 85% yield of enone **16**; $[\alpha]_D^{22}$ +160°, *c* 0.2 ($CHCl_3$).





The C ring was constructed from the 1,4-addition reaction of enone **16** with 1.5 equiv of cuprate **17**[18] in ether (77 mL/g) at −30 °C for 1 h. Extractive isolation and chromatography on silica gel furnished ketone **18** in 88% yield. Conversion of **18** to tricyclic ketone **21**[19] was effected in 85% overall yield by the following sequence: (i) desilylation with 2 equiv of *n*-Bu_4NF in THF at room temperature for 15 h, (ii) tosylation with 1.5 equiv of *p*-toluenesulfonyl chloride in pyridine at room temperature for 20 h, and (iii) cyclization with 2 equiv of NaH in refluxing DME (5 mL/10 mg) for 7 h.

Deoxygenation of **21** to the corresponding tricycloundecane **24** succeeded by the following sequence: (i) reduction with 2 equiv of $NaBH_4$ in MeOH at −20 °C for 0.5 h, 95% yield, (ii) sulfonylation with 1.5 equiv of 2-propanesulfonyl chloride[20] and 3 equiv of Et_3N in ether, 93% yield, and (iii) displacement with 4 equiv

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(12) Sala, T.; Sargent, W. V. *Chem. Commun.* **1978**, 253–254.

(13) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543–2549.

(14) (a) Ceder, O.; Nilsson, H. G. *Acta Chem. Scand., Ser. B* **1977**, *B31*, 189–192. (b) Mukaiyama, T.; Fujimoto, K.; Hirose, T.; Takeda, T. *Chem. Lett.* **1980**, 635–638. Optical purity of (*S*)-β-propyl-γ-butyrolactone was measured by using NMR method as described.[14b]

(15) Cyclization involving enol acetate and vinylic sulfide moieties has not been previously reported. However, ring closure involving a vinylic sulfide moiety and aromatic ring has been described. De Waard, E. R.; Reus, H. R.; Huisman, H. O. *Tetrahedron Lett.* **1973**, 4315–4316.

(16) (a) Ohfune, Y.; Shirahama, H.; Matsumoto, T. *Tetrahedron Lett.* **1976**, 2795–27969. (b) Tatsuta, K.; Akimoto, K.; Kinoshita, M. *J. Am. Chem. Soc.* **1979**, *101*, 6116–6118. (c) Greene, A. E. *Tetrahedron Lett.* **1980**, 3059–3060. (d) Hudlicky, T.; Kutchan, T. M.; Wilson, S. R.; Mao, D. T. *J. Am. Chem. Soc.* **1980**, *102*, 6351–6353. (e) Mehta, G.; Reddy, A. V. *Chem. Commun.* **1981**, 756–757. (f) Little, R. D.; Muller, G. W.; Venegas, M. G.; Carroll, G. L.; Bukhari, A.; Patton, L.; Stone, K. *Tetrahedron* **1981**, *37*, 4371–4383. (g) Wender, P. A.; Howbert, J. J. *Tetrahedron Lett.* **1982**, 3983–3986.

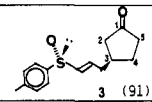
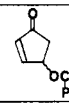
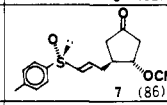
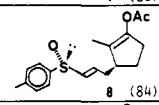
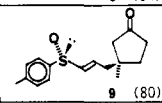
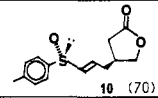
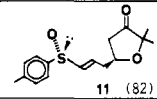
(17) Dauben, W. G.; Lorber, M.; Fullerton, D. S. *J. Org. Chem.* **1969**, *34*, 3587–3592.

(18) Cuprate **17** was prepared by the following sequence: (i) silylation of 3-bromo-2,2-dimethyl-1-propanol[18a] with *t*-$BuMe_2SiCl$–Et_3N–DMAP in CH_2Cl_2 and (ii) metalation with lithium metal in ether at room temperature and followed by the addition of 0.5 equiv of CuI·Me_2S[18b] in Me_2S/ether (1:1) at −10 °C. (a) Searles, S., Jr.; Nickerson, R. G.; Witsiepe, W. K. *J. Org. Chem.* **1960**, *24*, 1839–1844. (b) House, H. O.; Chu, C. Y.; Wilkins, J. M.; Umen, M. J. *J. Org. Chem.* **1975**, *40*, 1460–1469.

(19) The cis,anti,cis pattern of ring fusion of **21** was proven by proton–proton NOE difference spectroscopy and COSY–two-dimensional NMR spectroscopy.

(20) Only with the 2-propanesulfonate were we able to achieve selective replacement of the sulfonate substituent (i.e., C–O cleavage) by hydride. The corresponding mesylate[20a] and tosylate[20b] when treated with $LiEt_3BH$ in THF gave only alcohol **22** (i.e., S–O cleavage). (a) Holder, R. W.; Matturro, M. G. *J. Org. Chem.* **1977**, *42*, 2166–2168. (b) Krishnamurthy, S.; Brown, H. C. *J. Org. Chem.* **1976**, *41*, 3064–3066.

Table I. Yields and Optical Purities from the Reactions of the Anion Derived from (*R*)-Allyl *p*-Tolyl Sulfoxide and Various Enones

Entry	Enones	Product (% yield)	Optical Purity % ee at Carbon 3
1		 3 (91)	96
2		 7 (86)	92
3		 8 (84)	95
4		 9 (80)	90
5		 10 (70)	95
6		 11 (82)	70

[a] The resulting enolate ion was treated with acetyl chloride at −78 °C.

of $LiEt_3BH$[20] in toluene (1 mL/0.12 g) at 90 °C for 18 h, 72% yield.

Deprotection of **24** with 1 equiv of TsOH in THF–MeOH–H_2O (2:3.5:1) at room temperature for 1 h gave 90% yield of the nor ketone **25** ($[\alpha]_D^{22}$ +81°, *c* 0.2 in hexane). Wittig reaction of **25** with 2 equiv of methylenetriphenylphosphorane (derived from $CH_3P^+Ph_3Br^-$ and sodium *tert*-amylate[21]) in refluxing toluene for 2 h afforded (+)-hirsutene (**1**) in 80% yield ($[\alpha]_D^{22}$ +48°, *c* 0.35 in pentane). The spectral data (IR, ^1H and ^{13}C NMRs, and mass) of **25** and **1** were completely identical with those of the authentic materials.[22]

In summary, the asymmetric induction reaction of chiral sulfinylallyl anion with enones provides a facile enantioselective synthesis of substituted cyclic ketones (70–96% ee). The total synthesis of (+)-hirsutene is stereocontrolled and should prove valuable in analogue construction. The cyclization and isopropylsulfonate displacement reactions discovered in the context should be applicable to other important syntheses.[23] Further results on the asymmetric synthesis using substituted chiral sulfinylallyl anions and enones and the application of this method in natural-product synthesis will be discussed in subsequent papers.

Acknowledgment. We thank the NSF and Kansas State University for a grant for the purchase of the Bruker WM-400 NMR spectrometer. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Research Corp. for generous financial support. We are indebted to Professors Tomas Hudlicky and Kuniaki Tatsuta for providing the spectral data and Professor Albert W. Burgstahler of University of Kansas for obtaining the ORD and CD spectra.

Supplementary Material Available: ^1H and ^{13}C NMR data for compounds **1** and **12–25** (27 pages). Ordering information is given on any current masthead page.

(21) Short R. P.; Ravol, J. M.; Ranu, B. C.; Hudlicky, T. *J. Org. Chem.* **1983**, *48*, 4453-4461.

(22) The IR, NMR (^1H, ^{13}C), and mass spectra of **25** and **1** were provided by Professor Tomas Hudlicky of Virginia Polytechnic Institute and State Univesity and Professor Kuniaki Tatsuta of Keio University.

(23) Experimental procedures will be provided in a full paper to be published at a later date.

Electronic and Structural Requirements for Ring Opening of Azacyclopentadiene Carbenes

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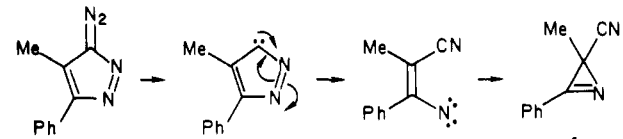
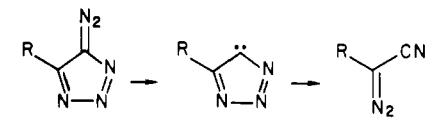
The chemistry of substituted azolylidenes, derivatives of cyclopentadienylidene containing one or more ring nitrogen atoms,[1] have been extensively studied by Shechter and co-workers.[1] These studies have revealed that these carbene species undergo addition, insertion, and substitution reactions, and, perhaps the most interesting, ring opening to form a nitrene. For example, the thermolysis of the 4,5-disubstituted 3-diazopyrazole **1** results in the formation of **4**.[2] The mechanism for formation of **4** has been

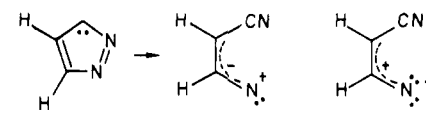


proposed to proceed via ring opening of **2** (as shown by the arrows) to form the intermediate nitrene **3** which closes to **4**.[2] In an apparently related type of reaction the thermolysis of **5** produces an intermediate represented as **6** which undergoes ring opening to the substituted cyanodiazomethane **7**, which in turn undergoes



further reaction under the reaction conditions.[1] In a theoretical study of the structure and reactivity of azacyclopentadienyl reactive intermediates (cations, free radicals, anions, and carbenes),[3] we have discovered that the ring opening occurs spontaneously from only one of the many possible electronic states of the azolylidenes *and* when there are at least two nitrogen atoms present in the 2- and 3-positions.[4]

There are several singlet and triplet, closed- and open-shell electronic configurations possible for each azolylidene. Preliminary calculations on the closed-shell, six-π-electron singlet state of **8** indicated that a cyclic structure did not represent a local energy minimum on the potential energy surface.[5] Geometry optimization calculations at the 3-21G basis level[6] resulted in a continual lengthening of the N2–N3 bond and the shortening of the C1–N2 bond, ultimately resulting in the six-π-electron structure **9**.[7] The



geometry optimized structural parameters of **9** are given in Figure 1. The alternative four-π-electron structure **10** (Figure 1) is

(1) Hui, H. K.-W.; Shechter, H. *Tetrahedron Lett.* **1982**, *49*, 5115 and references cited therein.

(2) Magee, W. L.; Shechter, H. *J. Am. Chem. Soc.* **1977**, *99*, 633.

(3) Pasto, D. J.; Freeman, J. P.; Fettes, M. K., investigation in progress.

(4) It is conceivable that other electronic states may undergo similar ring openings; however, the present studies have focused only on defining minimum-energy structures and not energy surfaces for reactions.

(5) A number of starting geometries were selected on the basis of optimized structures of other six-π-electron structures which were calculated to be energy minima.

(6) Calculations were carried out by using the GAUSSIAN80 package of programs.

(7) The six π-electrons include the four of the aza-allyl anion and nitrile function and not the in-plane π-electrons of the nitrile function.

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