superhyperfine splitting associated with the elongated Mn(2)–N(5) distance ("*z*" for Mn^{III}) relative to those for Mn(2)–N(4) and Mn(2)–N(6) ("*x*, *y*" for Mn^{III}, Figure 1). The EPR spectra of **3** have also been simulated by using the same principles.

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Supplementary Material Available: Tables of positional and thermal parameters for $[Mn_2(bcmp)(\mu\text{-}OAc)_2]\cdot CH_2Cl_2$ (6 pages). Ordering information is given on any current masthead page.

Exclusion of a 1,4-Cyclohexenediyl as a Metastable Intermediate in the [3,3] Sigmatropic Rearrangement of a 1-Hexen-5-yne

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Although semiempirical calculations[1,2] suggest that the much discussed[3,4] 1,4-cyclohexanediyl species **1** (R_1–R_3 = H) is a true intermediate on the reaction coordinate of the thermal Cope ([3,3] sigmatropic) rearrangement of 1,5-hexadienes (Scheme I), ab initio calculations,[5] thermochemical kinetic arguments,[6] and a study[7] of the rearrangement's stereospecificity (when R_1, R_3 = Me, R_2 = Ph) do not bear out this result. As the first stage in an effort to give the hypothetical biradical pathway a chance to manifest itself, we now have examined the mechanism of the eneynic–enallenic [3,3] sigmatropic process which interconverts a 1-hexen-5-yne and a 1,2,5-hexatriene (**3** → **4**, Scheme I).

The biradical corresponding to **1** in this case would be a 1,4-cyclohexenediyl, **2**. By using the 1981[6] (or 1976[8]) values of bond energies, one may estimate that species **2** lies only 3.6 (or 1.2) kcal/mol higher in energy than the transition state (E_a = 32.7 kcal/mol[9]) and hence might be a better candidate than is **1** for the role of a true intermediate.

In a formal sense, the distinction between **2** as an intermediate and **2** as a transition state is that, in the latter case, cleavage of the C_5–C_6 bond must occur at the rate of $\kappa RT/Nh$ (about $1 \times 10^{13}\ \mathrm{s}^{-1}$ at 200 °C). We propose to use a ring conformational change as an internal clock by which to measure the bond cleavage rate. There is good reason to believe that the rate of ring inversion in **2** will be much greater than in **1** (see below), thereby providing a faster clock and again increasing the chance for the intermediate to make its existence known.

The content of stereochemical information of starting material **3** will be transferred intact to product **4** if the rearrangement occurs by a concerted pathway either exclusively "allowed" or exclusively "forbidden" (see Figure 1). The same result is predicted for a biradical mechanism via **2**, but only if bond cleavage (k_1) is much faster than ring inversion (k_2, Scheme II). However, this stereospecificity will be degraded if **2** is an intermediate that lives long on the time scale of its own conformational inversion or if both "allowed" and "forbidden" pathways are followed. Moreover, if this occurs, the reversibility of the sigmatropic rearrangements guarantees that all of the sigmatropically related species ultimately will be racemized.

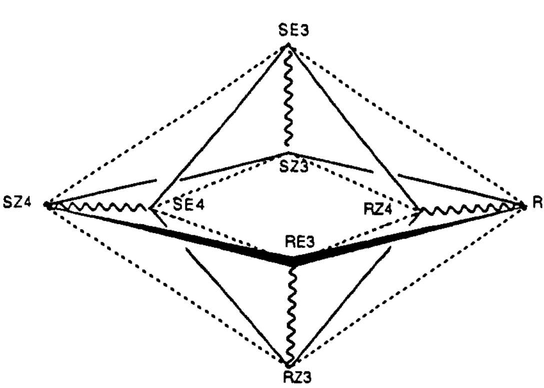
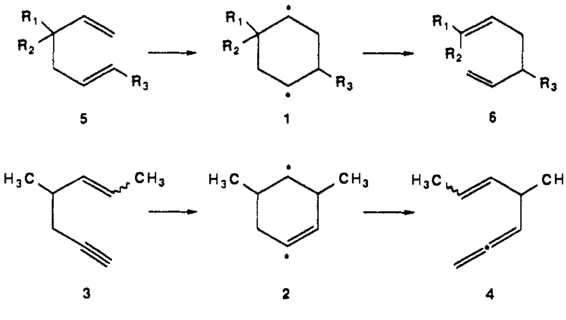
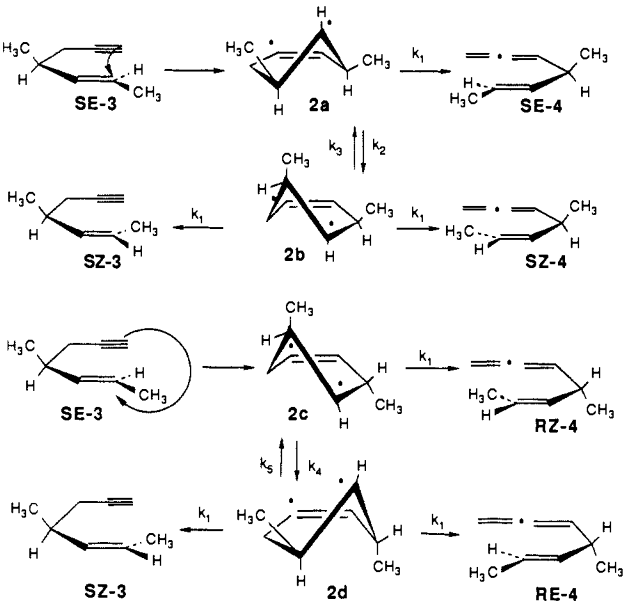


Figure 1. Interconversion paths among acetylenes **3** and allenes **4**. The stereochemical descriptors are indicated before the numerals. Solid and dashed lines, respectively, represent "allowed" and "forbidden" sigmatropic rearrangements; wiggly lines represent stereomutation about the olefinic bond by the mechanism of Scheme II. Hypothetically interconverting biradicals (not shown) are to be imagined as connecting adjacent "allowed" and "forbidden" pathways in Figure 1 (see Scheme II).

Scheme I



Scheme II



The compound (−)-(*S*,*E*)-**3** of 62.2 ± 2% ee was obtained in four synthetic steps from the known[10] ethyl (−)-(*S*,*E*)-3-

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methylhex-4-enoate. After pyrolysis of **3** in the gas phase at 200 °C, the reaction mixture contained (*Z*)- and (*E*)-**4**,(*Z*)- and (*E*)-**3**, three slowly formed cyclization products,[9] and dimeric materials. We obtained a refined set of rate constants for the system by computer-assisted simulation with a Runge–Kutta scheme.

After pyrolysis, **3** and **4** were separated by preparative gas chromatography (GC), and each was selectively epoxidized at the isolated double bond and reduced[11] to yield 3-methyl-2-(2-pentyl)oxirane (**7**). The major component (trans) of **7** consisted of two diastereomers, one of which was amenable to analysis by capillary GC on an optically active stationary phase[12] (nickel(II) bis(3-heptafluorobutyryl-1*R*-camphorate), 23 m), which allowed measurement of the retained optical purity.

Acetylene (*E*)-**3** recovered from pyrolysis after 2 and 6 half-lives and converted to trans epoxide **7** had 96 ± 3%[13] and 94 ± 4%, respectively, of the original ee. Similarly, analysis of the epoxide **7** derived from the allene (*E*)-**4** after 2 and 6 half-lives also showed the high stereospecificity of the rearrangement, although a systematic error lowered the values slightly: 90 ± 2 and 90 ± 4%. A better measure of the stereospecificity is obtained by simulation of the concentration versus time profiles of all the species in the mechanism of Figure 1 with a stochastically based computer program.[14] The assignment of a rate constant for a hypothetical minor stereochemical pathway that is 2% of the major one leads to percent racemization values that are barely inside the experimental error limits. With 5% contribution from the minor pathway, the values are well outside ($4s_m$) these limits. The rearrangements thus are shown to proceed with near-perfect preservation of enantiomeric purity, which indicates the exclusive operation of either the "allowed" or "forbidden" pathway of Figure 1. A decision in favor of the "allowed" pathway became clear from the experimental observation that the enantiomeric ratio in the allene-derived epoxide **7** was the *inverse* of that in the acetylene-derived epoxide.

As a model for the absolute rate of conformational inversion of biradical **2**, we use the rate recently measured experimentally[15] of the inversion in the closely related 4-cyclohexenyl radical. This corresponds to a rate constant of 3×10^{11} s^{-1} at our reaction temperature of 200 °C. Since methyl substituents have little effect on barriers to conformational inversion in cyclohexenes[16] (or cyclohexanes[17]), we assume the same to be true for the 4-cyclohexenyl radical. Stochastic simulation of the experimental data with the inversion rate constant in **2** based on this value[18] and variable values of the bond-cleavage rate constant shows that the latter, k_1, must be $\geq 10^{13}$ s^{-1}. Therefore, to the extent that the model is reliable, the present experiments permit **2** to be a transition state but not a true intermediate.

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(11) Reduction of **3** could be carried out with H_2/Pt–C, but **4** required diimide reduction to avoid the partial racemization observed in its catalytic hydrogenation.

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(18) In the simulation, the inversion rate constants, k_2 and k_3, were assigned as 2 and 6×10^{11} s^{-1}; k_4 and k_5 were assigned as 4 and 2×10^{11} s^{-1} since MM2 calculations[19] on the corresponding conformers of the model compounds *cis*- and *trans*-2,6-dimethylcyclohex-3-en-1-one suggest a 3:1 preference for the diequatorial form in the former and a 2:1 preference for the equatorial-pseudoaxial form in the latter. All of the cleavage rate constants, k_1, were assumed to be equal and were varied to fit the experimental data.

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Tetrakis(1,3-dithiol-2-ylidene)cyclopentanone: A New Electron Donor with Remarkably Low Oxidation Potential

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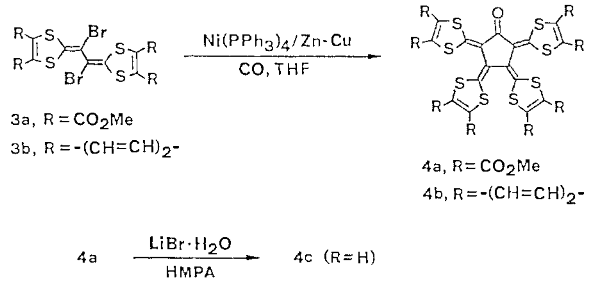
1,3-Dithiol[*n*]radialenes are of much interest in multistep redox behavior and in utilization as a component for the preparation of organic conducting materials because of their expected electron-donating properties. Of those the [4]- and [6]radialenes (**1**[1] and **2**,[2]respectively) were recently synthesized in our laboratory by using Ni(0)-catalyzed reductive cyclooligomerization of 2,2′-(1,2-dibromoethanediylidene)bis(1,3-dithiole) **3**. However, the strategy for the synthesis of the [even number]radialenes cannot be applicable to the synthesis of the [odd number]radialenes. In the course of our study on synthesizing the [odd number]radialenes, in particular [5]radialene, we found that Ni(0)-catalyzed reductive CO inserting cyclooligomerization proceeds very efficiently by conducting the above reaction under a carbon monoxide atmosphere[3] to provide the tetrakis(1,3-dithiol-2-ylidene)cyclopentanone **4**,[4] which has an unexpectedly very low oxidation potential in spite of the presence of a strong electron-withdrawing CO group in the central five-membered ring. In this paper we wish to report the synthesis of **4** and its derivatives, the molecular structure determined by X-ray crystallographic analysis, the novel redox behavior, and the electrical properties of its charge-transfer (CT) and radical cation salts.

When a THF solution of tetracarbomethoxy and dibenzo derivatives of **3** (**3a** and **3b**)[1,2] was allowed to react with 0.2 equiv of $Ni(PPh_3)_4$ in the presence of excess Zn–Cu at 50 °C and 1 atm of carbon monoxide pressure, octacarbomethoxy and tetrabenzo derivatives **4a** and **4b** were obtained in the respective yields of 77 and 84%.[5] Treatment of **4a** with excess LiBr·H_2O in HMPA



3a, R = CO_2Me
3b, R = -(CH=CH)$_2$-

4a, R = CO_2Me
4b, R = -(CH=CH)$_2$-

4a $\xrightarrow[\text{HMPA}]{\text{LiBr·H}_2\text{O}}$ 4c (R = H)

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(4) **4** is expected as a good precursor for the [5]radialene synthesis. Attempts on substitution of the carbonyl group of **4** for the 1,3-dithiole group are now in progress.

(5) **4a**, red crystals (mp 292 °C); **4b**, reddish orange crystals (mp 298 °C); **4c**, reddish purple crystals (mp 250 °C dec). Satisfactory elemental analyses and spectral data were obtained for these compounds.

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