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.

Acknowledgment. We thank the National Institute of General Medical Sciences and the Humphrey Chemical Company for grants in support of this research. Professor Martin Saunders kindly made available his interactive graphics input routine for the MM2 calculations, Professor S. L. Schreiber called our attention to the work cited in ref 12b and c, and Professor V. Schurig provided helpful advice.

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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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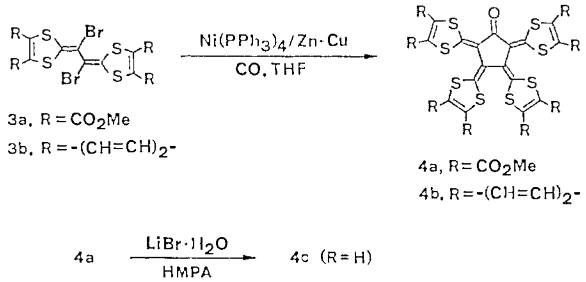
Received August 12, 1987

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 $LiBr{\cdot}H_2O$ in HMPA



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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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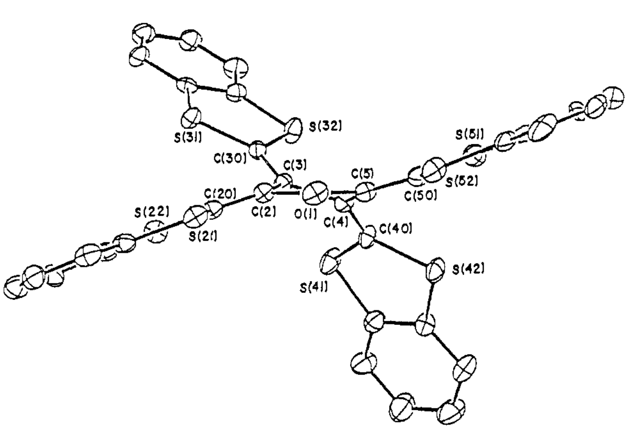

Figure 1. Molecular structure of **4b** by an ORTEP drawing with thermal ellipsoid at 20% probability level for the non-hydrogen atoms. The hydrogen atoms were omitted for clarity.

at 95–155 °C gave the unsubstituted compound **4c** in 88% yield.[5] The molecular structure of **4b** was determined by X-ray diffraction method.[6] Figure 1 shows the molecular structure projected along the O(1)–C(1) bond of the CO group. The molecule takes half-chair conformation with an approximate twofold symmetry passing through O(1)–C(1) bond. The torsional angles included in the central five-membered ring are smallest around the C(1)–C(2) (7.8°) and C(1)–C(5) (11.1°) bonds and are largest around the C(3)–C(4) (29.9°) bond, while those around the C(2)–C(3) (23.5°) and the C(4)–C(5) (25.7°) bonds take the intermediate values. The two 1,3-dithiole rings at the 3- and 4-positions show a relatively large dihedral angle (61.8°), while those at the 2- and 5-positions are coplanar. The C═O bond distance is 1.22 Å, and the mean values of the endocyclic C–C bond and the exocyclic C═C bond distances are 1.47 and 1.35 Å, respectively.

The redox behavior was investigated by using cyclic voltammetry (solvent, PhCN; room temperature). In all cases two pairs of waves were observed, and the two redox potentials were as follows: **4a**, +0.64 and +1.35 V vs. Ag/AgCl; **4b**, +0.38 and +1.22 V; **4c**, +0.17 and +1.14 V. From the fact that the two peak currents in the oxidation side are almost equal and the dication[7] shows the cyclic voltammogram corresponding to the pair of waves in the lower voltage, it is evident that both pairs of waves are due to two sequential redox processes accompanying a two-electron migration simultaneously.[8] In comparison of these potentials with those of already known compounds containing 1,3-dithiole moieties, the first potentials of **4**'s are lower by 0.05–0.1 V than those of corresponding **1** and **2**. In particular, **4c** has the lowest first potential as compared with TTF (+0.42 V),[9] 2,2′-(ethanediylidene)bis(1,3-dithiole) (+0.23),[10] 2,2′-(2-cyclohexene-1,4-diylidene)bis(1,3-dithiole) (+0.23),[11] and an unsubstituted **1** (+0.23).[1] This is quite unusual, if it is taken into consideration that a strong electron-withdrawing CO group is involved in the central five-membered ring.[12] Furthermore, **4** constructs the same four-electron redox system with **1**, in which the first two electrons migrate simultaneously. A marked difference between both systems is seen in the migration behavior of the two remaining electrons. Thus, **1** involves two one-electron processes, whose energy difference (ΔE) is large (0.43–0.50 V), while in **4** the processes overlap, indicating almost zero ΔE. Considering these results together with the fact that the antiaromatic cyclobutadiene and cyclopentadienone structures participate in the respective tetracation states ($\mathbf{1}^{4+}$ and $\mathbf{4}^{4+}$), it can be deduced that cyclopentadienone is less antiaromatic than cyclobutadiene.[13]

Judging from the first low oxidation potentials, **4b** and **4c** are expected as new electron donors for organic metals. In accord with this expectation, with a 2,3,5,6-tetrafluoro-TCNQ electron acceptor they formed the 1:2 CT complexes,[14] but their room temperature electrical conductivities on compressed pellets were not so high (10^{-8}–10^{-5} s/cm). However, the radical cation salts ($\mathbf{4b}\cdot I_3$ and $(\mathbf{4c})_2\cdot(I_3)_3$), obtained by electrolysis of **4b** and **4c** in CH_2Cl_2 containing $(n\text{-}Bu)_4NI_3$, showed fairly high electrical conductivities of ca. 10^{-2} s/cm at room temperature on compressed pellets.[15]

Supplementary Material Available: Molecular structure of **4b** with full atomic numberings and tables of fractional atomic coordinates and interatomic bond distances in **4b** (3 pages). Ordering information is given on any current masthead page.

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(6) Crystal data of **4b**: $C_{33}H_{16}OS_8$, fw = 685.0, monoclinic, space group $P2_1/c$, $a = 18.596$ (3) Å, $b = 8.358$ (2) Å, $c = 25.488$ (6) Å, $\beta = 114.38$ (1)°, $U = 3608.5$ (1.3) Å^3, $D_x = 1.260$ g cm^{-3}, $Z = 4$. X-ray diffraction data were measured on a Rigaku four-circle diffractometer by using graphite-monochromatized Mo Kα radiation. A total of 6338 reflections were collected up to $2\theta = 50°$ by the θ–2θ scan technique. The crystal structure was solved by the direct method (MULTAN-78) (Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. *MULTAN-78: A System Computer Program for the Automatic Solution of Crystal Structures from X-ray Diffractometer Data*; University of York: England, and Louvain, Belgium, 1978) and refined by the full-matrix least-squares method (XRAY-76) (Stewart, J. M. *XRAY-76*; University of Maryland, 1976; report TR-446) by using the 3853 observed reflections $[|F_o| > 3\sigma(F_o)]$ of the R index of 0.133 with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were not located. The difficulty of the interpretation of diffused electron densities, which resulted presumably from the crystal solvent, limited the accuracy of the refinement.

(7) The chemical oxidation of **4c** with 1.2 equiv of Br_2 in CH_2Cl at 0 °C gave the dibromide salt of dication ($\mathbf{4c}^{2+}\cdot 2Br^-$) as a greenish blue solid (mp 280 °C dec) quantitatively.

(8) The first process was electrochemically reversible for **4b** and **4c** but quasireversible for **4a**. On the other hand, the second process was irreversible in all cases.

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(12) Presumably, this unusual observation should be related to the markedly increasing change of the central five-membered ring to the planar configuration in one- and two-electron oxidations of **4** to its radical cation and dication.

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(14) **4c** formed no CT complex with TCNQ.

(15) Their perchlorate salts were also obtained, but the electrical conductivities were very low (ca. 10^{-8} s/cm). The detailed electrical properties of $\mathbf{4b}\cdot I_3$ and $(\mathbf{4c})_2\cdot(I_3)_3$ in single crystals are under investigation.

Homogeneous Asymmetric Hydrogenation of Functionalized Ketones

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Received October 1, 1987

Homogeneous asymmetric hydrogenation of ketones has remained far less fruitful than the catalysis of olefinic substrates.[2] However, now with the BINAP–Ru(II) complexes[3,4] effecting

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(2) Reviews: Kagan, H. B. In *Asymmetric Synthesis*: Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, Chapter 1. Halpern, J. In *Asymmetric Synthesis*; Vol. 5, Chapter 2. Koenig, K. E. In *Asymmetric Synthesis*; Vol. 5, Chapter 3. *Asymmetric Catalysis*; Bosnich, B., Ed.; Martinus Nijhoff Publishers: Dordrecht, 1986. Brown, J. M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 190.

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