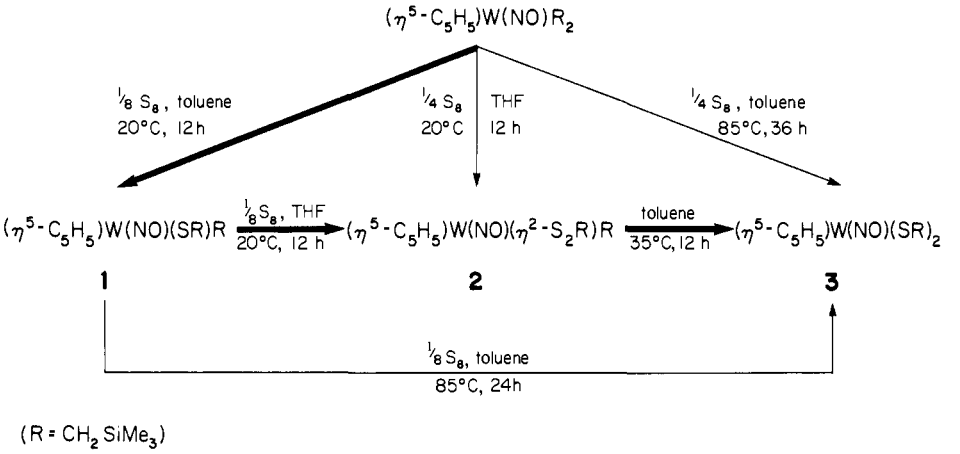
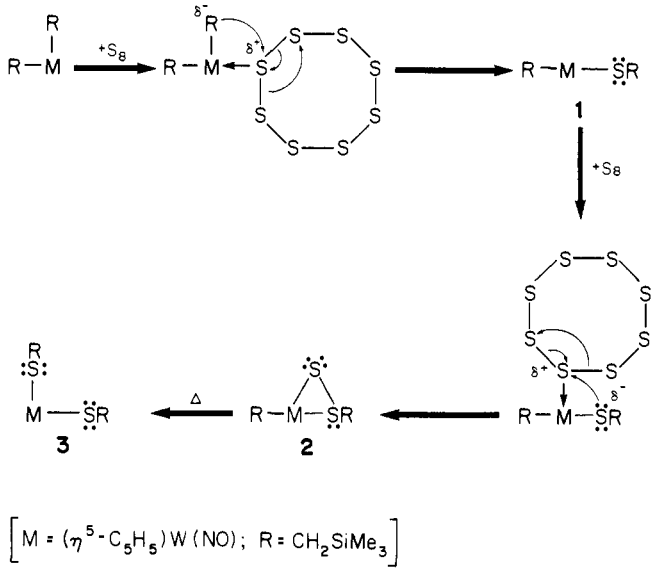
Scheme I



Scheme II



with this view is the fact that the dialkyl reactants which undergo the net conversion

(2)

(M = transition metal, R = alkyl, E = O[9] or Se[10]) are also 16-electron complexes. However, it is possible that in the case of O_2 the alkylperoxo complex similar to **2** in Scheme II is formed in a concerted rather than in a stepwise fashion.[11] In any event, the mechanistic proposals presented for the sulfur complexes in Scheme II suggest other experiments to substantiate their validity. Such experiments are presently in progress.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L., and L.S. acknowledges the Spanish Ministry of Education for the award of a postdoctoral fellowship. We also thank Jeffrey T. Martin for technical assistance and a referee for insightful comments.

Supplementary Material Available: Elemental analysis and spectroscopic (IR, ^1H and $^{13}C\{^1H\}$ NMR, mass spectral) data for **1-3** (1 page). Ordering information is given on any current masthead page.

(9) Lubben, T. V.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1985**, *107*, 701 and references therein.

(10) Gautheron, B.; Tainturier, G.; Meunier, P. *J. Organomet. Chem.* **1981**, *209*, C49 and references therein.

(11) The solid-state structure of a vanadium complex containing an η^2-O_2(*t*-Bu) ligand has been determined: Mimoun, H.; Chaumette, P.; Mignard, M.; Saussine, L.; Fischer, J.; Weiss, R. *Nouv. J. Chim.* **1983**, *7*, 467.

Synthesis and Thermal Rearrangement of Homopentafulvalenes

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Thermal rearrangements of cyclopropanes belong to the most thoroughly investigated fields of organic chemistry due to their low activation energies.[1] In the course of our work on the preparations of cyclopenta[*a*]pentalenes,[2] we have synthesized dispiro[4.0.4.1]undeca-1,3,7,9-tetraene (homopentafulvalene) (**2**) and its di-*tert*-butyl derivatives and found them to undergo stereoselective cyclopropane ring opening reactions already at room temperature.

The unsubstituted homopentafulvalene (**2**)[3] is easily prepared in 24% yield by oxidation of the dianion **1**[4] with copper(II) chloride in tetrahydrofuran at −70 °C. When a 10^{-3} M solution of **2** in pentane is refluxed for 10 h, rearrangement to *trans*-3a,3b-dihydro-7*H*-cyclopenta[*a*]pentalene (**3**)[3] occurs. Due to its great

(1) (a) Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981; pp 27-39. (b) Berson, J. A. "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; pp 324-387.

(2) Hafner, K.; Thiele, G. F. *Tetrahedron Lett.* **1984**, *25*, 1445-1448.

(3) Physical data of compounds **2**, **3**, **5**, and **6**. **2**: mp 47 °C; UV (*n*-hexane) λ_{max} (log ϵ) 234 nm (4.07); ^1H NMR ($CDCl_3$) δ 2.64 (s, 2 H, CH_2), 6.32, 6.42 (AA'BB', 8 H, $J_{1,2}$ = 5.3, $J_{1,3}$ = 1.4, $J_{1,4}$ = $J_{2,3}$ = 2.1 Hz). Anal. ($C_{11}H_{10}$) C, H. **3**: oil; UV (*n*-hexane) λ_{max} 260 nm; ^1H NMR ($CDCl_3$) δ 2.57 (s, 2 H, CH_2), 3.31 (br s, 2 H, $H_{3a,3b}$), 6.18 (m, 2 H, $H_{1,6}$), 6.45 (m, 2 H, $H_{3,4}$), 6.57 (dd, 2 H, $H_{2,5}$, $J_{1,2}$ = 1.8, $J_{2,3}$ = 5.2 Hz). Anal. ($C_{11}H_{10}$) C, H. **5**: oil; UV (*n*-hexane) λ_{max} 236 nm; ^1H NMR (benzene-d_6), **5a**, δ 1.09 (s, 18 H, *t*-Bu), 2.26 (s, 2 H, CH_2), 5.86 (dd, 2 H, $H_{1,7}$), 6.25 (dd, 2 H, $H_{4,10}$), 6.45 (dd, 2 H, $H_{3,9}$) ($J_{1,3}$ = 1.7, $J_{1,4}$ = 2.1, $J_{3,4}$ = 5.4 Hz), **5b**, δ 1.09 (s, 18 H, *t*-Bu), 2.21, 2.26 (AB, 2 H, CH_2, J = 4.0 Hz), 5.90 (dd, 2 H, $H_{1,7}$), 6.23 (dd, 2 H, $H_{4,10}$), 6.45 (dd, 2 H, $H_{3,9}$) ($J_{1,3}$ = 1.7, $J_{1,4}$ = 2.1, $J_{3,4}$ = 5.4 Hz). **6a**: mp 101 °C; UV (*n*-hexane) λ_{max} (log ϵ) 239 (3.53) 260 nm (3.56); ^1H NMR (benzene-d_6) δ 1.19 (s, 18 H, *t*-Bu), 2.69 (s, 2 H, H_7), 3.23 (s, 2 H, $H_{3a,3b}$), 6.09 (s, 2 H, $H_{3,4}$), 6.19 (s, 2 H, $H_{1,6}$). Anal. ($C_{19}H_{26}$) C, H. **6b**: ^1H NMR (benzene-d_6) δ 1.19 (s, 9 H, *t*-Bu_2), 1.24 (s, 9 H, *t*-Bu_4), 2.72, 2.82 (AB, 2 H, H_7, J = 11 Hz), 3.20 (s, 2 H, $H_{3a,3b}$), 6.00 (m, 1 H, H_5), 6.17 (m, 2 H, $H_{1,6}$), 6.26 (s, 1 H, H_3).

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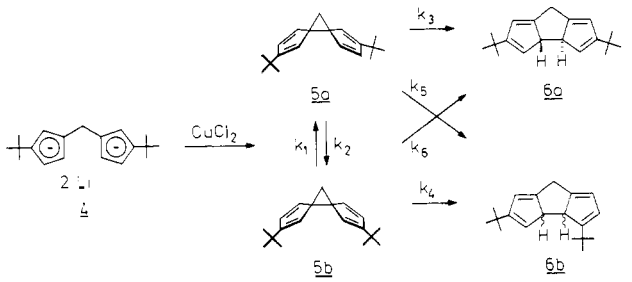
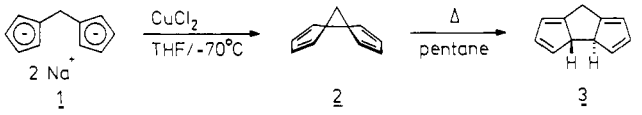
Scheme I[a]



[a] Rate constants at 24.0 ± 0.3 °C in 10^{-5} s^{-1}: $k_1 = 13.6 \pm 1.4$; $k_2 = 10.9 \pm 1.8$; $k_3 = 16.3 \pm 1.2$; $k_4 = 0.8 \pm 0.8$; $k_5 = 0.14 \pm 0.10$; $k_6 = 0$.

tendency to polymerize, monomeric **3** could be isolated in only 90% purity. The assignment of trans stereochemistry is based on the ^{1}H NMR spectrum of **3**, showing a sharp singlet for the methylene protons. No signals were observed that could be assigned to the cis isomer of **3**,[5] thus proving the high stereoselectivity of the rearrangement.



Oxidation of the recently prepared dianion **4**[2] by the procedure described above gives the di-*tert*-butyl derivatives **5**[3] of homopentafulvalene. The cis and trans isomers **5a** and **5b** can be separated by MPLC with pentane on alumina at −30 °C to give samples with isomeric purities of up to 98%. Both isomers rearrange even faster than does **2**. We have measured the rates of these rearrangements for each of the isomers by ^{1}H NMR spectroscopy at 24.0 ± 0.3 °C in benzene-d_6. The observed reactions and the corresponding rate constants are summarized in Scheme I.[6]

The trans stereochemistry of product **6a**[3,5] can be proven unambigiously by the use of the chiral NMR shift reagent Ag-FOD/Eu(hfc)$_3$, which gives separate spectra for both enantiomers of **6a**, thus ruling out the meso-cis structure. However, a similar assignment for **6b**[3,5] was not possible.

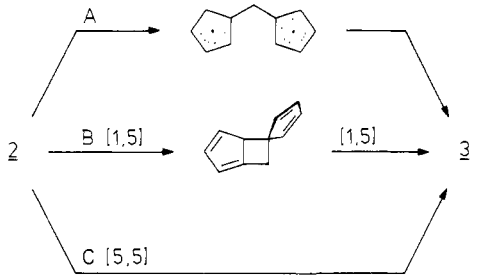
Surprisingly, the homopentafulvalenes **5a** and **5b** are readily interconverted, a reaction that has to follow a diradical path. The ease of C–C bond homolysis is explained by the resonance stabilization of the cyclopentadienyl radical. This effect has already been observed with spiro[2.4]hepta-4,6-dienes.[7]

These findings suggests a diradical mechanism for the rearrangement of **2** to **3**. However, two further alternatives have to be taken into account as depicted in Scheme II. .

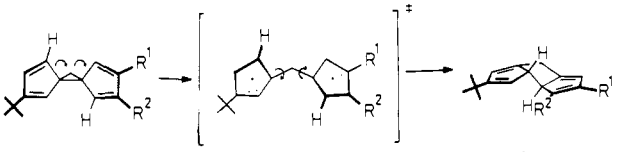
Reaction sequence B consists of two consecutive [1,5] shifts. Since [1,5]-allyl shifts proceed as slow as [1,5]-alkyl shifts,[8] the first step of this sequence should be comparable with the [1.5]-alkyl shift of spiro[2.4]hepta-4,6-diene. The high activation energy of 38 kcal/mol reported for this reaction[7a] suggests that path B does not contribute to the isomerizations of **2** and **5**.

The second alternative is a concerted [5,5]-sigmatropic rearrangement.[9] No predictions can be made on the rate of this reaction yet, since there are scarcely any kinetical data available on [5,5]-sigmatropic reactions.[10]

Scheme II



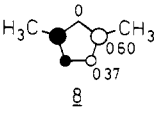
Both mechanisms A and C are also consistent with the rearrangement of **5a,b** to **6a,b**. However, the observed rate constants rule out a common diradical intermediate for all reactions of **5a** and **5b**. The reactions of such a species should be independent of its precursors and hence k_3/k_5 should equal k_6/k_4, which is apparently not the case. A modification of path A, which can account for the observed regio- and stereoselectivities, is conrotatory cyclopropane ring opening of **5a,b** to diradicals **7a,b**, which close to **6a,b** with trans stereochemistry by a least motion pathway.[11]



The large difference between the rate constants k_3 and k_4, which corresponds to $\Delta\Delta G^{\ddagger} = 1.8$ kcal/mol, cannot be explained by different cyclopropane bond strengths in **5a** and **5b**, since these homopentafulvalenes are interconverted at near equal rates. Therefore, the transition states **7a** and **7b** must be differentiated by either steric or electronic effects.

Molecular models of **6a** and **6b** show some steric repulsion between the "inner" *tert*-butyl group and the hydrogens on C-3 and C-3a in **6b**, which is not found with **6a**. If this occurs already in the transition state, the reaction rate k_4 should be lowered as observed.

The electronic substituent effects may be estimated by a qualitative PMO treatment of transition states **7a,b**. If the new bond is already formed to some extent in the transition state, the activation energy will be lcwered by a bonding SOMO–SOMO interaction between the cyclopentadienyl moieties. The SOMO coefficients of the related 1,3-dimethylcyclopentadienyl (**8**)[12] show clearly that this interaction should be much stronger for **7a** than



8

(4) (a) Schaltegger, H.; Neuenschwander, M.; Meuche, D. *Helv. Chim. Acta* **1965**, *48*, 955–961. (b) Katz, T. J.; Acton, N.; Martin, G. *J. Am. Chem. Soc.* **1969**, *91*, 2804–2805.

(5) No other isomers of **3** and **6** arising from possible [1,5-]-hydrogen shifts could be detected.

(6) The ^{1}H NMR spectra were recorded at 300 MHz without removing the samples from the spectrometer between the measurements. The concentrations of **5a,b** were determined from the $H_{1,7}$ signals, those of **6a,b** from the H_7 signals. The rate constants were calculated from two runs with 14 data sets each, using a simplex optimization. Complete experimental data are available as supplementary material.

(7) (a) Krekels, J. M. E.; de Haan, J. W.; Kloosterziel, H. *Tetrahedron Lett.* **1970**, 2751–2754. (b) Gilbert, K. E.; Baldwin, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 1593–1595.

(8) Semmelhack, M. F.; Weller, H. N.; Foos, J. S. *J. Am. Chem. Soc.* **1977**, *99*, 292–294.

(9) Fray, G. I.; Hearn, G. M.; Petts, J. C. *Tetrahedron Lett.* **1984**, *25*, 2923–2924. The authors assumed a [5,5]-sigmatropic rearrangement for the formation of 1,2,3,3a,3b,4,5,6-octachloro-**3** from octachloropentafulvalene and diazomethane via an octachloro derivative of **2**. Octachloro-**2** was not detected, nor was the stereochemistry of octachloro-**3** proven, although the cis stereochemistry was assumed, based upon both mechanistic and strain arguments.

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(11) For a review on stereoselectivity in diradical reactions by least motion pathways, see ref 1a.

(12) Davies, A. G.; Lusztyk, E.; Lusztyk, J. *J. Chem. Soc., Perkin Trans. 2* **1982**, 729–736.

for **7b**. Thus **5a** should rearrange faster than **5b**, which is in accord with the experiment.

Since both steric and electronic effects lead to the same result, the obtained kinetics permit no conclusion, whether a [5,5]-sigmatropic shift is contributing to the isomerization of **5a**.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Degussa AG. G.T. thanks the Studienstiftung des Deutschen Volkes for a fellowship. We also thank Prof. W. R. Roth, University of Bochum (FRG), for performing the simplex calculations and Prof. K. N. Houk, University of Pittsburgh, for helpful discussions.

Supplementary Material Available: Experimental procedure and reaction scheme for fomation of **5a,b** and **6a,b** and tables of experimental raw data for and composition of reaction mixture during isomerization of **5a,6** (4 pages). Ordering information is given on any current masthead page.

Sequence-Specific Recognition of B DNA by Bis(EDTA–distamycin)fumaramide

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Received March 18, 1985

One approach for the design of sequence-specific DNA binding molecules that read large sequences of double-helical DNA is to couple DNA binding units of similar or diverse base pair specificities.[1–6] The base-specific recognition elements of each unit and the linkers connecting them must be compatible with the same groove (e.g., major or minor in B DNA) and conformational state of the DNA (e.g., B, A, Z). We have shown that oligo-*N*-methylpyrrolecarboxamides containing 4–7 amide NHs bind sites of A·T rich DNA consisting of 5–8 contiguous base pair in size.[3–6] The general rule of n amide NHs affording binding site sizes of $n + 1$ base pairs is consistent with the oligopeptide binding in the minor groove of right-handed B DNA with the amide NH groups

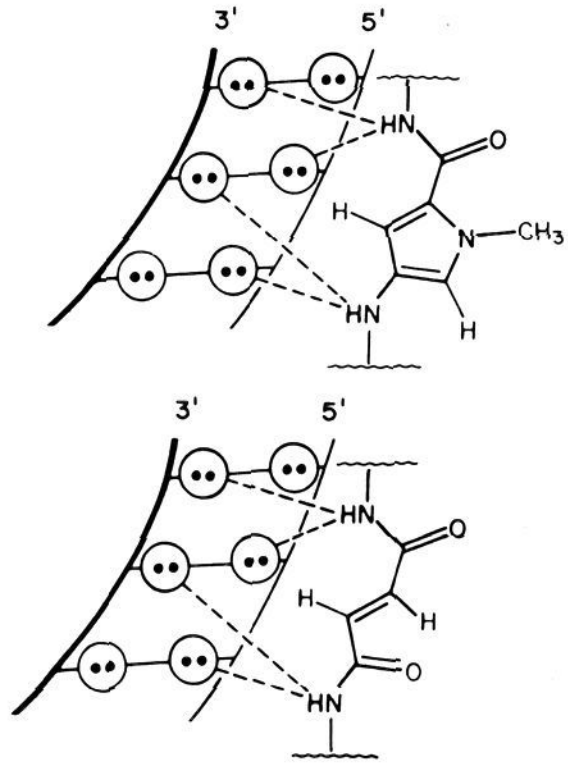

Figure 1. Circles with two dots represent lone pairs of electrons on N3 of adenine (A) and O2 of thymine (T) at the edges of the base pairs on the floor of the minor groove of the right-handed B DNA helix. Dotted lines are bridged hydrogen bonds to the amide NHs.[7] (Top) Model of *N*-methylpyrrolecarboxamide binding in the minor groove of A·T rich DNA.[7] (Bottom) Model of fumaramide binding in the minor groove of A·T rich DNA.

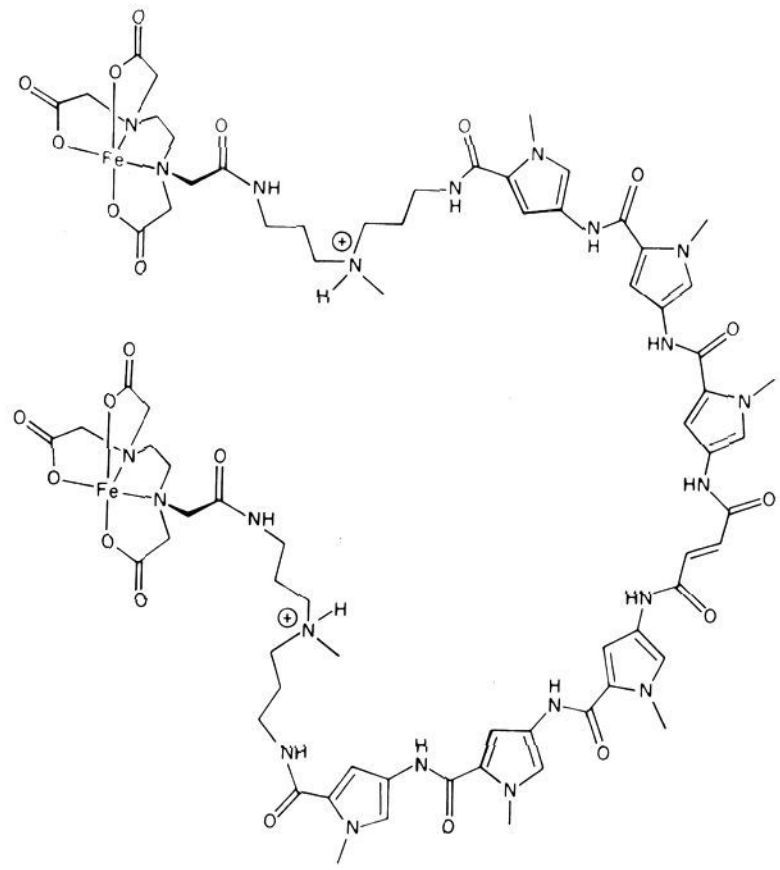

Figure 2. Bis(Fe^{II}·EDTA–distamycin)fumaramide (BEDF·Fe^{II}).

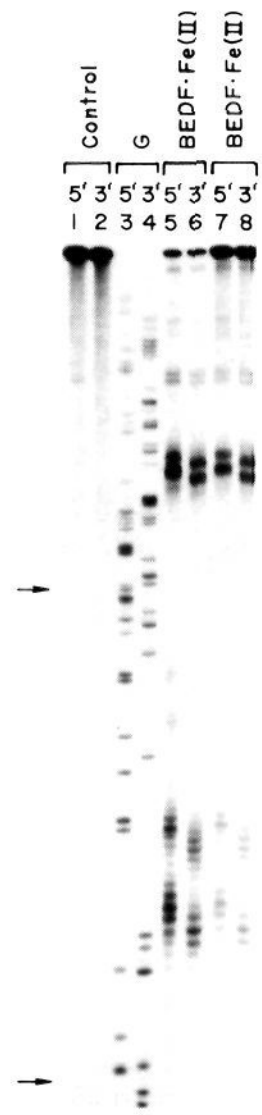

Figure 3. Autoradiogram of 5′ (odd-numbered lanes) and 3′ (even-numbered lanes) ^{32}P end-labeled 517 bp DNA restriction fragment (*Eco RI/Rsa I*) from plasmid pBR322 on a high-resolution denaturing gel.[9] Lanes 1 and 2, intact DNA; lanes 3 and 4, Maxam-Gilbert chemical sequencing G reaction;[10] lanes 5 and 6, BEDF·Fe^{II} at 1.5 μM concentrations; lanes 7 and 8, BEDF·Fe^{II} at 0.5 μM concentrations. Bottom to arrow at the middle of the autoradiogram is the sequence left to right in Figure 4.

(1) Schultz, P. G.; Taylor, J. S.; Dervan, P. B. *J. Am. Chem. Soc.* **1982**, *104*, 6861–6863.
(2) Schultz, P. G.; Dervan, P. B. *J. Am. Chem. Soc.* **1983**, *105*, 7748–7750.
(3) Schultz, P. G.; Dervan, P. B. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 6834–6837.

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