For a series of complexes having a common bridging group but different ligands in the trans position, the stronger the crystal-field influence of the trans ligand the farther away it must be moved to lower the energy of the e_g acceptor orbital the necessary extent.[11] The ligand-field strengths of the groups trans to the bridged chloride in the complexes of Table II are en ~ NH_3 $\gg H_2O >$ R–S–R.[12,13] The observed general trend in increased rate of reduction parallels the decrease in field strength of the donor ligand positioned trans to the bridging atom.[14]

Table II. The Reduction of Several Cobalt(III) Complexes by Iron(II) (25°, $\Sigma ClO_4^- = 1.0\ M$)

Complex	k, M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
$Co(NH_3)_5Cl^{2+}$	0.00135	+12.5	−30
cis-$Co(en)_2Cl_2^+$	0.0016		
trans-$Co(en)_2ClH_2O^{2+}$	0.24		
cis-$Co(eee)Cl_2^+$	1.35	+9.25	−36.6

A comparison of the rate constants for reduction of a series of related complex ions is presented in Table II. The $Co(eee)Cl_2^+$–Fe^{2+} reaction proceeds at a rate which is extremely rapid compared to the corresponding reduction of *trans*-$Co(en)_2ClH_2O^{2+}$, the most reactive member of that class of oxidants. Arguments using molecular models, entropy considerations relative to solvation, and/or successive chelation tend to indicate that steric effects cannot account for the observed rate enhancement.

A similar rate enhancement factor of 10^3 for reduction of $Co(eee)Br_2^+$ and $Co(eee)C_2O_4^+$ compared to the reduction of ethylenediamine analogs by iron(II) has been observed.[15] This suggests that the contributions of these bridging and nonbridging functions to $\Delta G^{\ddagger}$ may be partitioned separately.[16] Three possibilities for the free energies of precursor complex formation are consistent with this: (a) they contribute rather negligibly, (b) they are unaffected by this particular nonbridging ligand variation,[17] and (c) they are affected similarly, which, admittedly, seems unlikely.

A most important feature of the present investigation has been the demonstration that dramatic rate enhancement is observed when two mutually cis thioether functions are positioned *trans* to a bridging atom. The scope, versatility, and stereochemical factors influencing the reduction process for this new class of compounds is currently being investigated in detail.

Acknowledgment. We wish to acknowledge financial support for this work from a Research Corporation, Frederic Gardner Cottrell Project Grant and National Science Foundation Undergraduate Research Participation Program No. GY-7621. The referees' comments and suggestions have been very helpful and are gratefully acknowledged.

W. K. Wilmarth, *Inorg. Chem.*, **6**, 611 (1967); (d) D. R. Stranks and J. K. Yandell, *ibid.*, **9**, 751 (1970).

(11) A. E. Ogard and H. Taube, *J. Amer. Chem. Soc.*, **80**, 1084 (1958).

(12) J. H. Worrell and D. H. Busch, *Inorg. Chem.*, **8**, 1572 (1969).

(13) R. A. D. Wentworth and T. S. Piper, *ibid.*, **4**, 709 (1965).

(14) P. Benson and A. Haim, *J. Amer. Chem. Soc.*, **87**, 3826 (1965).

(15) The general range of reactivity observed for other *s-cis*-Co(eee)-X_2^{n+} complexes reduced by iron(II) at conditions similar to those reported here gives $k_t \approx$ 1-3 M^{-1} sec^{-1}.

(16) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," Ronald Press, New York, N. Y., 1966, p 74.

(17) For an example where this is not observed, see M. P. Liteplo and J. F. Endicott, *J. Amer. Chem. Soc.*, **91**, 3982 (1969).

(18) NSF-URP participant, summer 1970.

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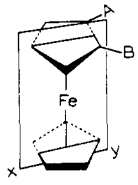
Pseudochirality in Ferrocenes

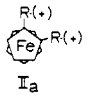
Sir:

Optical activity in recent years has been demonstrated for a number of 1,2-disubstituted ferrocenes, corresponding to the generalized representation I.[1] These molecules do not possess a chirality center or a chirality axis. They do, however, possess a chirality plane (XY), and an interesting situation, which has heretofore gone unnoticed, develops when the different achiral substituents (A and B) are replaced by two constitutionally identical, but chiral, groups.

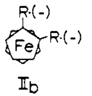


I

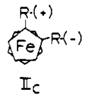
When the two identical groups are also of the same chirality, the plane (XY) is still chiral, and two enantiomers, IIa and IIb, are generated. On the other hand, the substituents may also be of opposite chirality. In this situation, two *achiral diastereomers*, IIc and IId, are generated, and the XY plane, which is no longer an element of chirality, may be cited as a plane of pseudochirality or pseudoasymmetry.[2] The two optically inactive forms may be designated as pseudochiral or pseudoasymmetric isomers.



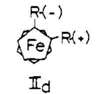
IIa



IIb



IIc



IId

We wish to report the synthesis of each member of two such stereoisomeric sets, the properties of which provide clear experimental demonstration of the stereorelationships discussed above.

The two chiral members (enantiomers) of one set were individually prepared *via* modified Knoevenagel condensations of 1,2-diformylferrocene (III)[3] and (−)-carbomenthoxyacetic acid[4] (IVa) ([α]^{20}D −69.6 ± 0.8° (c 2.5, ethanol)) to give (−)-1,2-bis(2-carbomenthoxy-*trans*-ethenyl)ferrocene[5] (Va) (mp 144–146°, [α]^{22}D −72.3 ± 2.0° (c 0.250, ethanol)), and with (+)-carbomenthoxyacetic acid[4] (IVb) ([α]D 68.5 ± 1.0° (c 2.5, ethanol)) to give the dextrorotatory enantiomer (Vb)[5] (mp 144–146°, undepressed when melted in admixture with (−)-Va, [α]^{22}D 70.0 ± 1.2° (c 2.50, ethanol)).

Synthesis of the achiral, pseudoasymmetric isomers

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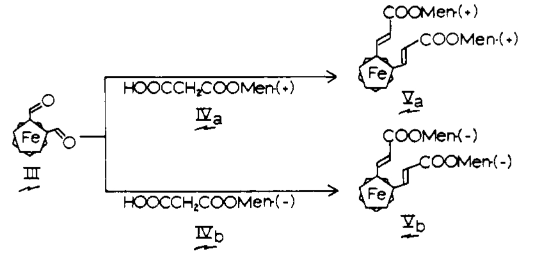
(1) For an account of much of this work, see: K. Schlögl, *Top. Stereochem.*, 1, 39 (1967).

(2) For a fuller account of these relationships, see: V. Prelog, *Proc. Kon. Ned. Akad. Wetensch., Ser. B*, 71, 108 (1968).

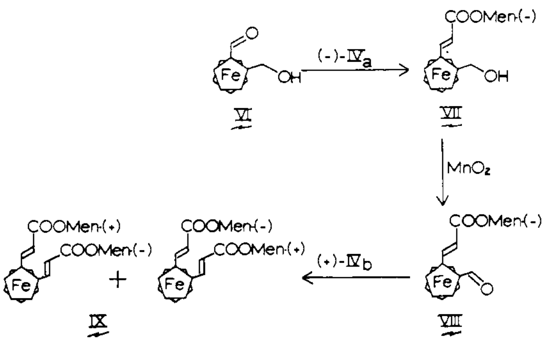
(3) G. Marr, B. W. Rockett, and A. Rushworth, *J. Organometal. Chem.*, 16, 141 (1969).

(4) E. B. Abbot, E. W. Christie, and A. McKenzie, *Chem. Ber.*, 71, 9 (1938).

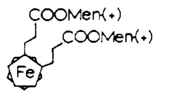
(5) Combustion and analyses and the usual set of spectral data were satisfactory and consistent with the assigned structure.



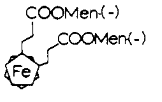
proceeded from (±)-1-formyl-2-hydroxymethylferrocene[3] (VI and mirror image) with initial condensation of 1 equiv of (−)-IVa to yield 1-hydroxymethyl-2-(2-carbomenthoxy-*trans*-ethyl)ferrocene[5] (VII). Oxidation with activated manganese dioxide gave the corresponding formyl compound[5] VIII, which, after treatment with 1 equiv of (+)-IVa, gave a mixture of the pseudoasymmetric isomers, IX. Careful and extended fractional recrystallizations of the mixture from pentane resulted in its separation. The less soluble isomer,[5] fluffy orange crystals, had mp 173.5–174.5° and $[\alpha]^{20}\mathrm{D}$ 0° (c 0.250, ethanol). The more soluble isomer[5] was obtained as deep red plates with mp 146–148° and $[\alpha]^{20}\mathrm{D}$ 0° (c 0.250, ethanol). Melting of these isomers in admixture with each other and in admixture with each of the chiral isomers produced significant melting point depressions in each instance.



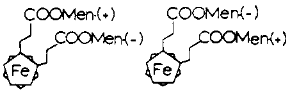
The members of a second set of isomers were obtained through individual catalytic hydrogenation of each isomer of the first set. Thus, (−)-Va and (+)-Vb each gave their saturated analog, (−)-Xa[5] (viscous yellow oil, $[\alpha]^{22}\mathrm{D}$ −54.2 ± 0.9° (c 0.500, ethanol)) and (+)-Xb[5] (viscous yellow oil, $[\alpha]^{22}\mathrm{D}$ 56.3 ± 1.0° (c 0.450, ethanol)), respectively. And, the unsaturated, pseudoasymmetric isomers, higher melting and lower melting, were each hydrogenated to their pseudoasymmetric, saturated analogs,[5] XI, mp 116–118°, $[\alpha]^{22}\mathrm{D}$ 0° (c 0.500, ethanol), and viscous yellow oil, $[\alpha]^{22}\mathrm{D}$ 0° (c 0.500, ethanol), respectively.



Xa



Xb



XI

Experiments directed toward elaboration of the absolute configurations of the pseudochiral isomers are continuing and will be reported in a complete account of this work.

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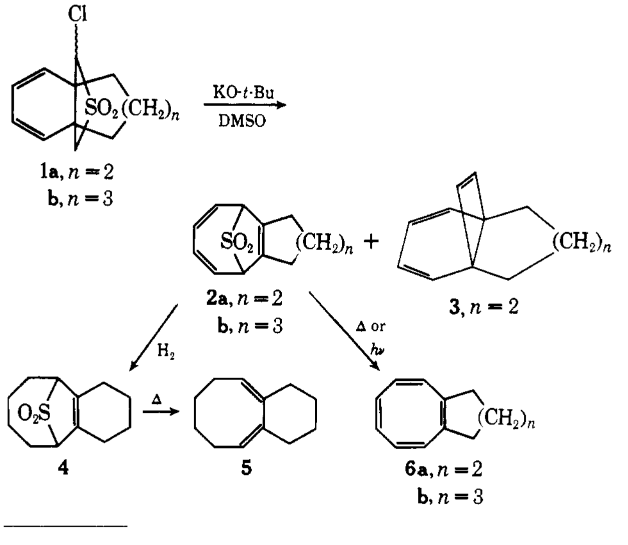
Novel Structural Rearrangements Attending the Dehydrohalogenation of Unsaturated Cyclic α-Halo Sulfones. The Synthesis of 9-Thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-Dioxides[1]

Sir:

Despite the unreactivity of α-halo sulfones in intermolecular nucleophilic displacement processes, their propensity for base-induced 1,3 elimination with ejection of halide ion, loss of sulfur dioxide, and formation of an olefinic linkage (the Ramberg–Bäcklund reaction[2]) is now well recognized.[3] We now report an intriguing variation of the normal reaction pathways usually observed during the elimination of HX from α-halosulfones and, for simplicity, shall refer to these transformations as "bishomoconjugative Ramberg–Bäcklund rearrangements."[4] The overall reaction provides a useful synthetic method for the controlled formation of polyunsaturated bridged sulfones and substituted cyclooctatetraenes.

When chlorosulfone **1a**[5,6] was treated with potassium *tert*-butoxide in dimethyl sulfoxide at room temperature for 20 min, bridged tricyclic sulfone **2a**, mp 167.5–169° dec,[7] was obtained in 56% yield after recrystallization from ether–hexane. Only a trace amount of "normal" Ramberg–Bäcklund product **3**[5a,8] was produced under these conditions. The structure assigned to **2a** rests firmly on spectroscopic and chemical evidence. Thus, the substance was shown to possess extended conjugation by the ultraviolet spectrum [$\lambda_{\max}^{\mathrm{C_2H_5OH}}$ 282 nm (ϵ 2100)] and the presence of the sulfone group was apparent from intense infrared bands at 1310, 1145, 1135, and 1100 cm^{-1}. The nmr spectrum



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[1] α-Halo Sulfones. XX. For the previous paper in this series, see L. A. Paquette and R. W. Houser, *J. Amer. Chem. Soc.*, in press.

[2] L. Ramberg and B. Bäcklund, *Ark. Kemi, Mineral. Geol.*, 13, 27 (1940); *Chem. Abstr.*, 34, 4725 (1940).

[3] (a) L. A. Paquette, *Accounts Chem. Res.*, 1, 209 (1968); (b) F. G. Bordwell, *ibid.*, 3, 281 (1970).

[4] No necessary mechanistic relationship is implied in this phraseology.

[5] (a) L. A. Paquette and J. C. Philips, *Chem. Commun.*, 680 (1969); (b) L. A. Paquette, R. E. Wingard, Jr., J. C. Philips, G. L. Thompson, L. K. Read, and J. Clardy, *J. Amer. Chem. Soc.*, in press.

[6] The rearrangement is equally successful with either of the two pure isomers (which undergo equilibration under the reaction conditions), or the corresponding mixture.

[7] All new compounds cited herein gave acceptable (±0.3%) combustion analysis values.

[8] L. A. Paquette, J. C. Philips, and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, in press.