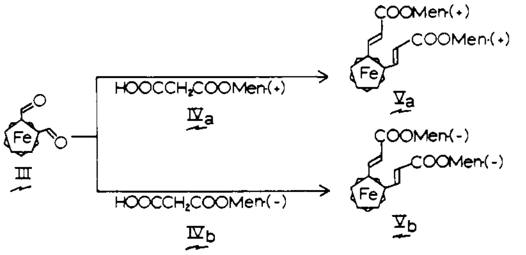
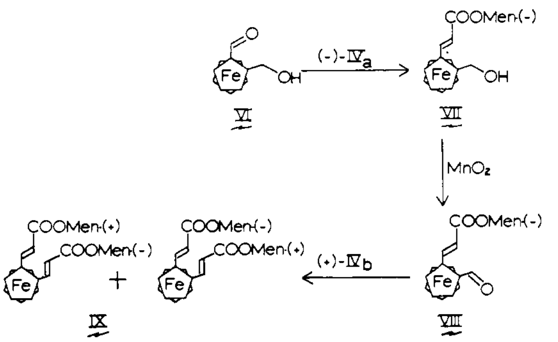
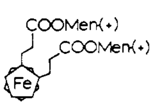


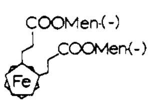
proceeded from (±)-1-formyl-2-hydroxymethylferrocene[3] (VI and mirror image) with initial condensation of 1 equiv of (−)-IVa to yield 1-hydroxymethyl-2-(2-carbomenthoxy-*trans*-ethyl)ferrocene[5] (VII). Oxidation with activated manganese dioxide gave the corresponding formyl compound[5] VIII, which, 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 $[\alpha]^{20}\text{D}$ 0° (*c* 0.250, ethanol). The more soluble isomer[5] was obtained as deep red plates with mp 146–148° and $[\alpha]^{20}\text{D}$ 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.



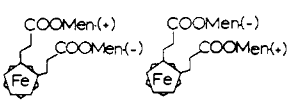
The members of a second set of isomers were obtained through individual catalytic hydrogenation of each isomer of the first set. Thus, (−)-Va and (+)-Vb each gave their saturated analog, (−)-Xa[5] (viscous yellow oil, $[\alpha]^{22}\text{D}$ −54.2 ± 0.9° (*c* 0.500, ethanol)) and (+)-Xb[5] (viscous yellow oil, $[\alpha]^{22}\text{D}$ 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°, $[\alpha]^{22}\text{D}$ 0° (*c* 0.500, ethanol), and viscous yellow oil, $[\alpha]^{22}\text{D}$ 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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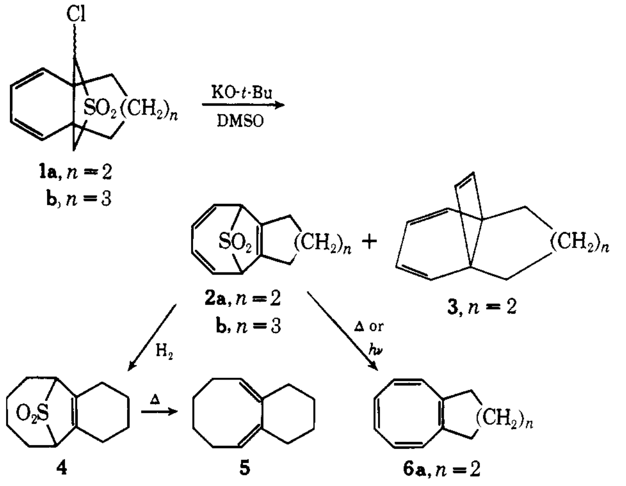
Novel Structural Rearrangements Attending the Dehydrohalogenation of Unsaturated Cyclic α-Halo Sulfones. The Synthesis of 9-Thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-Dioxides[1]

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 [$\lambda_{\max}^{C_2H_5OH}$ 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.

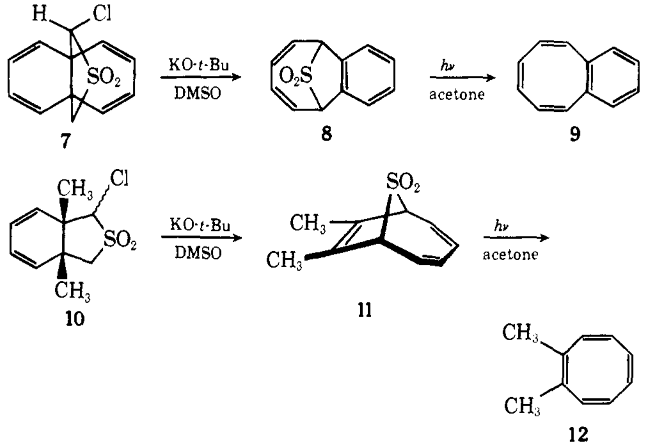
[6] The rearrangement is equally successful with either of the two pure isomers (which undergo equilibration under the reaction conditions), or the corresponding mixture.

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

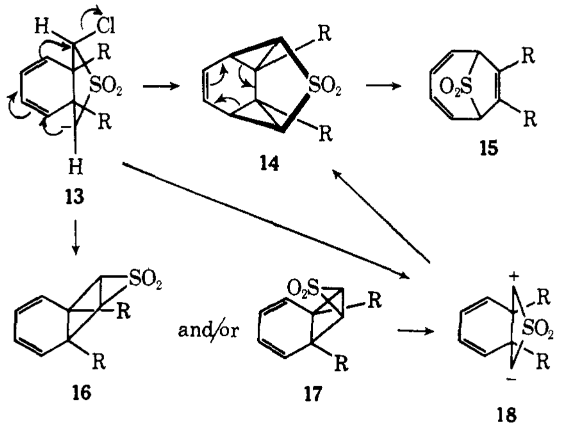
[8] L. A. Paquette, J. C. Philips, and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, in press.

(CDCl$_3$) was characterized by broadened multiplets centered at δ 5.95 (4, vinyl), 3.68 (2, bridgehead), 2.13 (4, allylic), and 1.74 (4, methylene). Catalytic hydrogenation of **2a** over 10% Pd/C in ethyl acetate solution at atmospheric pressure resulted in the rapid uptake of 2 equiv of hydrogen to yield tetrahydrosulfone **4**: mp 138–139°;[7] $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 3.55 (br s, 2, bridgehead) and 1.6–2.4 (m, 16, methylene). Gas-phase pyrolysis of **4** at 500° and 10 mm (contact time ~1 sec) produced diene **5**[9] which when hydrogenated afforded a mixture of *cis*- and *trans*-bicyclo[6.4.0]dodecanes in a 5:1 ratio. This mixture was also obtained by catalytic reduction (5% Rh/Al$_2$O$_3$ in HOAc, 60°, 50 psig) of benzocyclooctene. The gas-phase pyrolysis of **2a** (400°, 10 mm) likewise resulted in sulfur dioxide expulsion with concomitant formation of fused cyclooctatetraene **6a**:[7] $\lambda_{max}^{\text{isooctane}}$ 280 nm (ε 290); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.50–5.97 (m, 6) and 1.5–2.5 (br m, 8).

Compelling evidence for the generality of the title rearrangement was derived from the analogous behavior of chlorosulfones **1b**, **7**, and **10**. Specifically, brief exposure of **1b**[5b] to potassium *tert*-butoxide in dry dimethyl sulfoxide at 25° gave in 56% yield sulfone **2b**: mp 149.5–150.5°;[7] $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.90–6.10 (m, 4), 3.73–3.97 (m, 2), 2.22–2.58 (m, 4), and 1.35–1.95 (m, 6). Photolysis of **2b** (450-W source, acetone solution, Corex filter, 60 min) gave **6b**:[7] $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.53–5.90 (m, 6), 2.0–2.5 (m, 4), and 1.57 (br s, 6). Like treatment of 11-chloro-12-thia[4.4.3]propella-2,4,7,9-tetraene 12,12-dioxide (**7**)[5b,10] conveniently gave rise in 68% yield to **8**: mp 269–271° dec;[7] $\lambda_{max}^{\mathrm{C_2H_5OH}}$ 267 sh (ε 2280), 273 (2470), and 278 sh nm (2280); $\delta_{\mathrm{TMS}}^{\mathrm{DMSO}\text{-}d_6}$ 7.43 (s, 4), 5.93 (br s, 4), and 4.90–5.07 (m, 2). Photolysis of **8** in acetone solution (Hanovia 200-W source, Vycor) led rapidly to benzocyclooctatetraene (**9**),[11] thereby confirming the gross structure of this sulfone. Finally, the bicyclochlorosulfone **10**[7] led with equal facility to **11**, mp 201.5° dec,[7] which displays nmr absorptions (CDCl$_3$) at 5.83–6.08 (m, 4), 3.62–3.95 (m, 2), and 1.88 (s, 6). Photolysis of **11** in acetone solution afforded 1,2-dimethylcyclooctatetraene (**12**), identical with an authentic sample.[12]



A plausible mechanistic pathway available for the conversion of these α-chlorosulfones to derivatives of 9-thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-dioxide involves initial conversion to the derived carbanion **13** with subsequent or concomitant bishomoconjugative 1,8 displacement of chloride ion to afford annelated dicyclopropylsulfones such as **14**. Such intermediates, not unexpectedly,[13] are subject to [$_\sigma 2_s + {}_\sigma 2_s + {}_\pi 2_s$] bond reorganization for reasons of steric strain relief, this operation providing direct access to **15**. Accordingly, on this basis, the proximity of the diene functionality to both the developing α-sulfonyl carbanion center and the site of ultimate nucleophilic displacement is seen to offer a kinetically favorable alternative to the competing 1,3-elimination process customarily exhibited by these systems.[5,8,10]



Alternatively, it is likely that episulfones such as **16** and **17** may intervene, but in a polar aprotic medium like DMSO they suffer carbon–carbon bond cleavage of the three-membered ring[14] more rapidly than SO$_2$ expulsion. In this eventuality, intramolecular trapping of zwitterion **18** by the proximate diene unit is required to be appreciably more efficient than loss of SO$_2$.[15] A final possibility is that by using DMSO as solvent, formation of zwitterion **18** may be favored equally well by subsequent ionization of **13**.[16]

We hope to report on the generality of related "bishomoconjugative rearrangements" and on the chemistry of 9-thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-dioxides at a future date.

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(9) D. J. Cram and N. L. Allinger, *J. Amer. Chem. Soc.*, **78**, 2518 (1956).

(10) L. A. Paquette and J. C. Philips, *ibid.*, **91**, 3973 (1969).

(11) L. Friedman and D. F. Lindow, *ibid.*, **90**, 2329 (1968). A direct comparison of samples from the two routes was made.

(12) A. C. Cope and H. C. Campbell, *ibid.*, **73**, 3536 (1951).

(13) For somewhat analogous skeletal rearrangements, consult: (a) W. von E. Doering and J. Rosenthal, *ibid.*, **88**, 2078 (1966); (b) W. Grimme, H. J. Riebel, and E. Vogel, *Angew. Chem., Int. Ed. Engl.*, 7, 823 (1968); (c) M. Jones, Jr., and B. Fairless, *Tetrahedron Lett.*, 4881 (1968); (d) L. A. Paquette, G. R. Krow, and J. R. Malpass, *J. Amer. Chem. Soc.*, **91**, 5522 (1969); (e) R. T. Seidner, N. Nakatsuka, and S. Masamune, *Can. J. Chem.*, **48**, 187 (1970); (f) W. von Philipsborn, J. Altman, E. Babad, J. J. Bloomfield, D. Ginsburg, and M. B. Rubin, *Helv. Chim. Acta*, **53**, 725 (1970), and additional references cited in these papers.

(14) Examples of such processes in closely related three-membered heterocyclic molecules are widespread. For summaries of references, see W. C. Agosta and A. B. Smith, III, *Chem. Commun.*, 685 (1970); J. W. Lown and K. Matsumoto, *ibid.*, 692 (1970).

(15) In the case of **16**, it is possible that the conversion to **14** could be a concerted [$_\sigma 2_s + {}_\pi 2_s + {}_\pi 2_s$] reaction.

(16) When *tert*-BuOK in ether is employed, the diene unit does not intercept the loss of SO$_2$.[5a]

(17) National Institutes of Health Predoctoral Fellow, 1969–1971.