An attractive explanation for the divergent influence of arenediazonium ion substituents on the rates for oxidation of hemoglobin is that electron transfer occurs in the heme pocket for those diazonium salts that would undergo electron transfer slowly, if at all, outside of this cavity. Once inside the hydrophobic pocket, electron transfer produces a neutral aryldiazo radical that is more likely to expel dinitrogen and combine with iron(III) than to reenter the hydrophilic region outside of the heme pocket where hydrogen abstraction is the product-forming process.[20]

The rate for electron transfer is dependent on the distance between the reaction centers.[21] In the case of diazonium salts, crossover from the hydrophilic region outside of the heme pocket to the hydrophobic region inside the heme pocket reduces the distance for approach of the diazonium salt to hemeiron(II) so that the rate for oxidation becomes a function of the kinetic barrier for entrance of the diazonium ion to the heme cavity. If this kinetic barrier reflects the hydrophilic to hydrophobic crossover, correlation with hydrophobic parameters should be evident. Accordingly, the semilog plot of second-order rate constants for those diazonium salts that produced σ-aryliron(III) complexes against π[22] gave a reasonable correlation (slope = 0.67, corr. coef. 0.90) whereas, as is evident from Figure 2, no correlation exists with σ_p or other electronic parameters. Furthermore, if there is a kinetic barrier to crossover, increasing the hydrophilicity of the diazonium salt should reduce the relative rate for reduction by hemoglobin and cause electron transfer to occur outside of the heme pocket. Indeed, reduction of the diazonium salt derived from (*p*-aminophenyl) acetic acid by deoxyhemoglobin at pH 7.0, which occurs with a second-order rate constant (k_2 = 31 M^{-1} s^{-1}) that is nearly one-quater that for reduction of *p*-toluenediazonium tetrafluoroborate (k_2 = 113 M^{-1} s^{-1}), produces only phenylacetic acid (90% yield). The near identity of second-order rate constants for ferrocyanide reduction of this diazonium salt (k_2 = 2.4 M^{-1} s^{-1}) and *p*-toluenediazonium tetrafluoroborate (k_2 = 2.1 M^{-1} s^{-1}) demonstrates the electronic similarity of the acetate and methyl substituents for electron transfer to the diazonium functional group.

Acknowledgment. We are grateful to the National Institute of Environmental Health Sciences for their support of this research (ES01673 and ES03609). We thank Kathlene Bassett and Amy Scamman for their preliminary results.

(18) Saito, S.; Itano, H. A. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5508.
(19) For example, the Soret band of the *p*-tolyl σ-iron(III) complex exhibited a maximum at 410 nm, and an additional distinct absorption was observed at 562 nm with a shoulder at 530 nm.[6] The Soret band for the zinc(II) complex of *N*-tolylprotoporphyrin IX dimethyl ester was at 442 nm, and characteristic absorptions at 550 and 608 nm with a shoulder at 648 nm were evident. Substituent effects on absorption maxima for these complexes varied by <5 nm from those reported for the *p*-tolyl complexes.
(20) Rüchardt, C.; Merz, E.; Freudenberg, B.; Opgenorth, H.-J.; Tan, C. C.; Werner, R. *Spec. Publ.—Chem. Soc.* **1970**, *No. 24*, 51.
(21) Margalit, R.; Pecht, I.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 301.
(22) Hansch, C.; Leo, A.; Unger, S. H.; Kim, K. H.; Nikaitani, D.; Lien, E. J. *J. Med. Chem.* **1973**, *16*, 1207.

Stereoselective, Chemodirected Formal S_N2' Addition of Organometallic Reagents to β'-Amino Cyclopentenyl Sulfone Derivatives[1]

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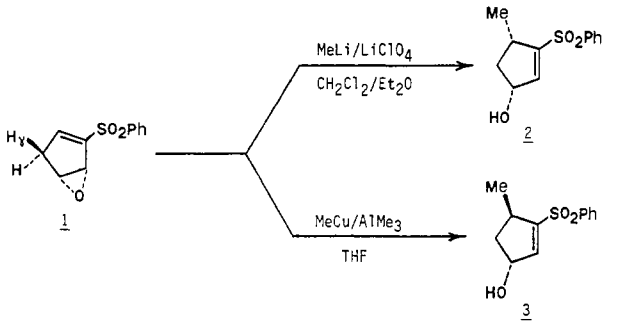
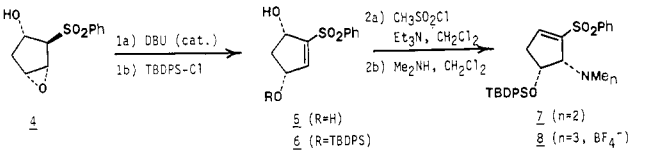
Several years ago we reported a stereoselective method to effect the nucleophilic S_N2' methylation of chiral epoxyvinyl sulfone **1**.[2]

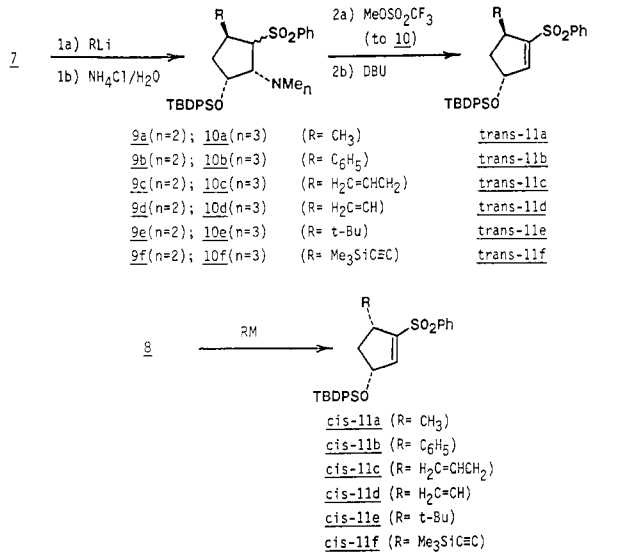
Scheme I



Scheme II



Scheme III



Although the specific procedure worked exceptionally well for the cases required (**1** to **2** and **1** to **3**), our recent attempts to extend this reaction to additional organometallic reagents which encompass tertiary alkyl, alkynyl, aryl, vinyl, and allyl moieties have been most disappointing. The source of the problem seems to be principaly associated with competitive deprotonation of **1** in the γ position, a difficulty that was observed but was correctable in the methyl series[2] (Scheme I).

We now wish to report a *general* and highly efficient solution to this problem. Treatment of β-epoxy sulfone **4**[3] with DBU (to produce the water-soluble vinyl sulfone-diol **5**[3]) followed by in situ silylation with *tert*-butyldiphenylsilyl chloride[4] affords an 86% yield of vinyl sulfone **6**.[5,6] Mesylation[7] of the alcohol moiety

(1) Syntheses via vinyl sulfones 13. For paper 12, see: Hamann, P. R.; Toth, J. E.; Fuchs, P. L. *J. Org. Chem.* **1984**, *49*, 3865.
(2) Saddler, J. C.; Fuchs, P. L. *J. Am. Chem. Soc.* **1981**, *103*, 2112.
(3) Donaldson, R. E.; McKenzie, A.; Byrn, S; Fuchs, P. L. *J. Org. Chem.* **1983**, *48*, 2167.
(4) Hanessian, S.; Lavallee, P. *Can. J.* Chem. **1977**, *55*, 562.
(5) Use of TBDPS-Cl in place of TBDMS-Cl reduces the amount of bis silyl compound[3] produced in this reaction to less than 5%.
(6) All new compounds exhibit satisfactory ^1H NMR, ^{13}C NMR, mass, exact mass, and/or elemental analysis. Yields refer to isolated material of >95% purity.
(7) Crossland, R. K.; Servis, K. E. *J. Org. Chem.* **1970**, *35*, 3195.

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Table I

substr	RM	conditions	product	yield	stereoselectivity[e]
7	CH_3Li	Et_2O, −10 °C, 10 min	*trans*-**11a**	87%, 99%[c]	1:>99
7	C_6H_5Li	Et_2O, −10 °C, 10 min	*trans*-**11b**	77%, 91%[c]	<5:>95[d]
7	$H_2C{=}CHCH_2Li$[a]	Et_2O, −10 °C, 10 min	*trans*-**11c**	81%, 63%[c]	4.9:95.1
7	$H_2C{=}CHLi$[b]	Et_2O, −10 °C, 10 min	*trans*-**11d**	86%, 88%[c]	1:>99
7	*t*-BuLi	Et_2O, −10 °C, 10 min	*trans*-**11e**	46%, 85%[c]	3.6:96.4
7	$(CH_3)_3SiC{\equiv}CLi$	THF, 0 °C, 30 min	*trans*-**11f**	67%, 65%[c]	1:>99
8	$(CH_3)_2CuLi$	Et_2O or THF, −78 °C, 20 min	*cis*-**11a**	99%	98.7:1.3
8	CH_3Li	THF, −78 °C, 10 min	*cis*-**11a**	33%	72.8:27.2
8	CH_3CeCl_2	THF, −78 °C, 25 min	*cis*-**11a**	95%	97.4:2.6
8	$(C_6H_5)_2CuLi$	THF, −78 °C, 20 min	*cis*-**11b**	91%	>95:5[d]
8	$(CH_2{=}CHCH_2)_2CuLi$[a]	THF, −78 °C, 20 min	*cis*-**11c**	91%	>99:1
8	$(CH_2{=}CH)_2CuLi$[b]	THF, −78 °C, 20 min	*cis*-**11d**	78%	>99:1
8	$(t\text{-Bu})_2CuLi$	THF, −78 °C, 30 min	*cis*-**11e**	25%	96.1:3.9
8	$(CH_3)_3SiC{\equiv}CLi$	THF, −40 °C, 10 min	*cis*-**11f**	85%	>99:1

[a] Via transmetalation from tetraallyltin. [b] Via transmetalation from vinyltri-*n*-butyltin. [c] The first yield reported corresponds to the conjugate-addition reaction with **7**, the second yield represents the overall yield for the alkylation/elimination reaction. [d] *trans*-**11b** and *cis*-**11b** could not be separated by HPLC; the figures given represent a minimum ratio derived from 470-MHz ^1H NMR. [e] See ref 10 for HPLC conditions.

followed by immediate treatment with dimethylamine produces amino vinyl sulfone **7**[6] via a "Lawton" reaction[8] in 87% yield. Reaction of **7** with methyl trifluoromethanesulfonate followed by counterion exchange with sodium tetrafluoroborate produces quaternary ammonium salt **8**[6,9] as a stable crystalline material, mp 157–62 °C (92% yield) (Scheme II).

Treatment of amino vinyl sulfone **7** with methyl, phenyl, allyl, vinyl, *tert*-butyl, and (trimethylsilyl)ethynyllithium affords monoadducts **9a–f**[6] in excellent yield. Reaction of these amines with methyl trifluormethanesulfonate produces the corresponding trimethylammonium sulfonates **10a–f** which were not fully characterized but subsequently treated with DBU to afford the trans isomers **11a–f**[6] respectively (Scheme III). Alternatively, direct reaction of allylammonium salt **8** in THF at −78 °C with the corresponding homo cuprate reagents instantaneously affords the cis adducts **11a–f**[6] in excellent yield. Comparison of each of these reaction products by analytical HPLC[10] establishes the stereoselectivity *of all of these reactions to be in excess of 95%* (Table I).

The stereoselectivity observed in each of these reactions is worthy of comment. The trans additions to amino vinyl sulfone **7** are apparently occurring under steric control; it is interesting to note that coordination of the amine moiety to the lithium reagents is apparently not occurring since this could have afforded the cis adducts, although such a directed addition would have required a 6-endo-trig[11,12] transition state. The complete reversal of stereochemistry seen in the cuprate additions to allylammonium salt **8** is quite striking. Reaction of allylammonium salts with organocuprates has been previously observed in simple systems,[13] but this example provides the first opportunity to observe the stereochemistry of the process in a system biased toward the S_N2' Lawton[8] reaction. Although it is tempting to invoke an "ammonium cuprate" ion pair as the control element for additions to **8**, the observation that methylcerium dichloride[14] and dimethylamine[3] also proceed via a syn addition pathway suggests that further research will be required to elaborate the intimate details of these reactions.[15-17]

Acknowledgment. We thank the NIH (GM 32963) for support of this research. We thank the Purdue University Biological Magnetic Resonance Laboratory (NIH RR01077) for access to the 470-MHz ^1H NMR spectrometer and Tamim Braish for spectral assistance.

(8) For references to the Lawton reaction, see ref 14 in: Saddler, J. C.; Donaldson, R. E.; Fuchs, P. L. *J. Am. Chem. Soc.* **1981**, *103*, 2110. For recent references to Lawton reactions with acyclic beta'-halo vinyl sulfones, see: (a) Anzeveno, P. B.; Mathews, D. P.; Barney, C. L.; Barbuch, R. J. *J. Org. Chem.* **1984**, *49*, 3134. (b) Knochel, P.; Normant, J. F. *Tetrahedron Lett.* **1985**, *26*, 425.

(9) The ((*tert*-butyl*dimethyl*silyl)oxy)ammonium salt had been previously prepared[3] but was not routinely isolated. Although the tetrafluoroborate counterion was used throughout this entire study, we have found that the crude triflate precursor to **8** affords *cis*-**11a** in identical yield and stereoselectivity.

(10) For all HPLC analyses, a normal phase econosphere silica 5 μm, 15 cm × 4.6 mm column was used with 3.5% THF in hexane (v/v) as mobile phase. Flow rate was 2.5 mL/min with UV detection at 254 nm.

(11) Baldwin, J. E. *J. Chem. Soc., Chem. Comm.* **1976**, 734.

(12) Addition of a vinyllithium reagent to *cis*-4-(dimethylamino)-1-(silyloxy)-2-cyclopentenyl sulfone also occurs via the trans-addition mode,[3] again avoiding the 6-endo-trig[11] directed addition option.

(13) (a) Commercon-Bourgain, M.; Normant, J. P.; Villieras, J. *C. R. Seances Acad. Sci., Ser. C* **1977**, *285*, 211. (b) Decodts, G.; Dressiare, G.; Langlois, Y. *Synthesis* **1979**, 510. (c) Dressiare, G.; Langlois, Y. *Tetrahedron Lett.* **1980**, *21*, 67. (d) Langlois, Y.; VanBac, N.; Fall, Y. *Tetrahedron Lett.* **1985**, *26*, 1009.

(14) Imamoto, T.; Sugiura, Y.; Takiyama, N. *Tetrahedron Lett.* **1984**, *25*, 4233.

(15) Reaction of **8** with more basic reagents is far less satisfactory. Methylmagnesium bromide does not provide any evidence for the generation of *cis*- or *trans*-**11a**; methyllithium affords a low yield of adducts with substantially diminished stereocontrol (see Table I).

(16) It should be noted that both enantiomers of **7** are available via enantioconvergent synthesis,[8] thereby also providing efficient access to chiral material.

(17) Studies relating to the scope and generality of this ammonium ion directed S_N2' reaction are currently under active investigation.

Homogeneous Catalysis of Hydrogen Reduction of SO_2 to Sulfur and Water Using $[(\eta^5\text{-}Me_nCp)Mo(S)(SH)]_2$

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Industrial processes involving heterogeneously catalyzed reduction of SO_2 by CH_4 or H_2S are well established, and H_2 reduction on Ru/Al_2O_3 has been demonstrated under mild conditions.[1] Homogeneous studies of CO reduction by H_2 have provided a wealth of mechanistic information relevant to heterogeneous catalysis and have led to homogeneous systems that are catalytic. Similar studies of SO_2 reductions with H_2 and metal hydrides should produce information pertinent to the elementary steps and even to practical reduction chemistry. Reactions of SO_2 with hydride complexes generally terminate with the formation of metal sulfide or oxy sulfide complexes,[2] precluding standard hydrogenation methods. However, Rakowski DuBois has shown that an organometallic Mo–S complex catalyzes $^1/_8S_8 + H_2 \rightarrow$

(1) Moody, D. C.; Ryan, R. R.; Salazar, K. V. *J. Catal.* **1981**, *70*, 221.

(2) (a) Kubas, G. J.; Ryan, R. R. *Inorg. Chem.* **1984**, *23*, 3181. (b) Kubas, G. J.; Wasserman, H. J.; Ryan, R. R. *Organometallics* **1985**, *4*, 419. (c) Kubas, G. J.; Wasserman, H. J.; Ryan, R. R. *Organometallics*, in press.

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