Rotations about Mo–N bonds may be monitored as a function of temperature on the ^1H NMR time scale, which allows an estimate of $\Delta G^{\ddagger}$, the barrier to rotation, to be placed at 16.5 kcal mol^{-1}. This is comparable to that in $Mo_2Cl_2(NMe_2)_4$.

Hexane solutions of $W_2Cl_2(NMe_2)_4$ and $(THF)_3LiSi(SiMe_3)_3$[11] (2 equiv) yield an orange crystalline compound that, on the basis of spectroscopic characterization, is formulated as the silicon analogue 1,2-$W_2(Si(SiMe_3)_3)_2(NMe_2)_4$. In similar reactions, 1,2-$M_2Cl_2(NMe_2)_4$ compounds have been found to react with potassium and tetra-*n*-butylammonium salts[12] of $CpFe(CO)_2^-$ in toluene to give orange microcrystalline compounds that, on the basis of infrared[13] and ^1H NMR characterization, are formulated as 1,2-$M_2(Fe(Cp)(CO)_2)_2(NMe_2)_4$ compounds, where M = Mo and W. These compounds contain the connectivity Fe—M≡M—Fe, and in toluene-d_8, they exist as a mixture of anti and gauche rotamers with respect to the central $M_2Fe_2N_4$ moeity in the ratio 1:2, respectively.

This work leads us to predict that it should be possible to subtend a wide variety of metal–metal bonds from dinuclear centers containing the $(M{\equiv}M)^{6+}$ unit where M = Mo and W.[14]

Registry No. $Mo_2(Sn(SnMe_3)_3)_2(NMe_2)_4$, 84521-33-5; $W_2(Sn(SnMe_3)_3)_2(NMe_2)_4$, 84521-34-6; 1,2-$Wa(Si(SiMe_3)_3)_2(NMe_2)_4$, 84521-35-7; 1,2-$Mo_2(Fe(Cp)(CO)_2)_2(NMe_2)_4$, 84537-06-4; 1,2-$W_2(Fe(Cp)(CO)_2)_2(NMe_2)_4$, 84521-36-8; $Mo_2Cl_2(NMe_2)_4$, 63301-82-6; $W_2Cl_2(NMe_2)_4$, 63301-81-5; $(THF)_3LiSn(SnMe_3)_3$, 60552-34-3; $(THF)_3LiSi(SiMe_3)_3$, 81859-95-2; $KCpFe(CO)_2$, 60039-75-0; $[Bu_4N]CpFe(CO)_2$, 65836-70-6.

Supplementary Material Available: Listings of fractional coordinates and isotropic thermal parameters (3 pages). Ordering information is given on any current masthead page.

(10) ^1H NMR data (220 MHz, 16 °C, toluene-d_8) for $Mo_2(Sn(SnMe_3)_3)_2(NMe_2)_4$: δ (NMe) 3.96 (12 H), 2.50 (12 H); δ ($SnMe_3$) 0.38 ppm (54 H). $J(^{119}Sn–C–H)$ = 45.4 Hz, $J(^{117}Sn–C–H)$ = 43.6 Hz, and $J(^{117,119}Sn–Sn–C–H)$ = 9.4 Hz. For $W_2(Sn(SnMe_3)_3)_2(NMe_2)_4$: δ (NMe) 4.00 (12 H), 2.38 (12 H); δ ($SnMe_3$) 0.40. $J(^{119}Sn–C–H)$ = 45.6 Hz, $J(^{117}Sn–C–H)$ = 44.0 Hz, and $J(^{117,119}Sn–Sn–C–H)$ = 9.8 Hz.

(11) Gutekunst, G.; Brook, A. G. *J. Organomet. Chem.* **1982**, *225*, 1.

(12) Ellis, J. E.; Flom, E. A. *J. Organomet. Chem.* **1975**, *99*, 213.

(13) The IR spectrum recorded as a Nujol mull shows two ν(C≡O) bands: 1950 (s) and 1892 (vs) cm^{-1} (M = Mo); 1953 (s) and 1885 (vs) cm^{-1} (M = W).

(14) We thank the National Science Foundation and the Wrubel Computing Center for support.

Stereochemistry of the Electrophilic Fragmentation–Cyclization of Allenic Sulfones and Sulfinates: Stereoselective Synthesis of Chiral α,β-Unsaturated γ-Sultines

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Received June 16, 1982

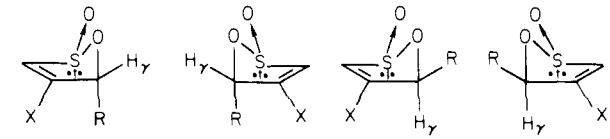
The electrophilic cyclization of a variety of functionalized allenes to heterocyclic systems[1-4] has received considerable attention due to its synthetic utility and remarkable stereoselectivity.[1a,f,2,3b,4a] In a continuation to our previous report on the electrophilic fragmentation–cyclization of allenic sulfones and sulfinates to α,β-unsaturated γ-sultines,[5] we have investigated the stereochemistry of this reaction.

Table I. Cyclization of Chiral Allenic Sulfones and Sulfinates to Chiral γ-Sultines

substrate	$[\alpha]^{25}_D$, deg	X^+	γ-sultine	$[\alpha]^{25}_D$, deg	yield, %
(−)-**2**[a]	−97.6	Br^+	(−)-**9**	−73.7 (*c* 2.7)	87
(+)-**2**[a]	+41.7	Br^+	(+)-**9**	+14.6 (*c* 1)	85
(+)-**2**[b]	+32.0	MeS^+	(+)-**11**	+20.5 (*c* 2.2)	35
(−)-**7**[c]	−47.5	Br^+	(+)-**9**	+16.9 (*c* 1.2)	87
(−)-**8**[d]	−58.5	Br^+	(+)-**10**	+15.6 (*c* 3.6)[f]	55
(−)-**7**[b]	−47.5	MeS^+	(+)-**11**	+23.7 (*c* 6.2)	80
(−)-**8**[b]	−63.5	MeS^+	(+)-**12**	+15.9 (*c* 6.1)	73

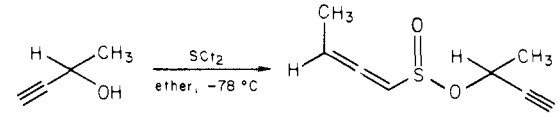
[a] In CCl_4 at 25 °C. [b] In CH_2Cl_2 at −20 °C. [c] In CCl_4 at −10 °C. [d] In CCl_4 at −20 °C. [e] In acetone. [f] Contains some 8% of sulfone.

Chart I



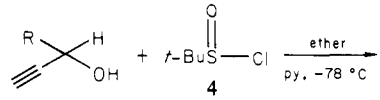
A $(R)^C$-$(S)^S$ A $(S)^C$-$(R)^S$ B $(S)^C$-$(S)^S$ B $(R)^C$-$(R)^S$

Treatment of (*R*)-(+)-1-butyn-3-ol ((+)-**1**[6], $[\alpha]^{25}_D$ +17.7° (*c* 1.0, dioxane)) and of (*S*)-(−)-**1**,[6] $[\alpha]^{25}_D$ −49.4° (*c* 3.2, dioxane) with sulfur dichloride, as previously described,[7] afforded sulfinates (+)-**2** ($[\alpha]^{25}_D$ +41.7° (*c* 1.0, acetone, yield 80%)) and (−)-**2** ($[\alpha]^{25}_D$ −97.6° (*c* 1.7, acetone, yield 80%)), respectively (eq 1).

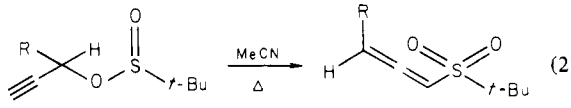


1 2 (1)

Racemic γ-methyl- and γ-*tert*-butylallenyl *tert*-butyl sulfones (**7**, **8**)[8] were prepared by a previously reported method[9] (eq 2).



1, R = Me
3, R = *t*-Bu



5, R = Me (64%)
6, R = *t*-Bu (67%)

7, R = Me (95%)
8, R = *t*-Bu (100%) (2)

Optically active sulfones (−)-**7** ($[\alpha]^{25}_D$ −47.5° (*c* 1.4, acetone, yield 70%)) and (−)-**8** ($[\alpha]^{25}_D$ −58.5° (*c* 2.8, acetone, yield 66%), mp 87–88 °C) were obtained by the elegant method of kinetic resolution.[10] Treatment of optically active sulfinate **2** and sulfones

(1) (a) Jacobs, T. L.; Macomber, R.; Zunker, D. *J. Am. Chem. Soc.* **1967**, *89*, 7001. (b) Toda, F.; Komoda, T.; Akagi, K. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1493. (c) Hoff, S.; Brandsma L. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 845. (d) Gelin, R.; Gelin, S.; Albrand, M. *Bull. Soc. Chim. Fr.* **1972**, 720. (e) Ollson, L.; Claeson, A. *Synthesis* **1979**, 743. (f) Beaulieu, P. L.; Morisset, V. M.; Garratt, D. G. *Tetrahedron Lett.* **1980**, *21*, 129.

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(3) (a) Macomber, R. S.; Kennedy, E. R. *J. Org. Chem.* **1976**, *41*, 3191. (b) Macomber, R. S. *J. Am. Chem. Soc.* **1977**, *99*, 3072.

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(8) All new compounds gave satisfactory elemental analysis and/or IR, NMR, and mass spectra data in accord with the assigned structures.

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(10) Cinquini, M.; Colonna, S.; Cozzi, F. *J. Chem. Soc., Perkin Trans. 1* **1978**, 247.

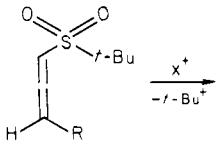
0002-7863/83/1505-1061$01.50/0

Table II. ^{1}H NMR Data[a] and Optical Rotations[b] of γ-Sultine Diastereomers

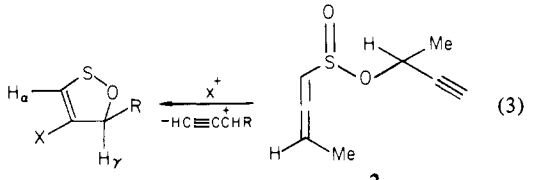
γ-sultine	diastereo-isomer	H_α	H_γ	CH_3	t-Bu	CH_3S	$[\alpha]^{25}_D$, deg
9	A	6.85 (d, J = 2)	5.65 (q, J = 8)[c]	1.60 (d, J = 8)			
	B	6.85 (d, J = 2)	5.25 (q, J = 8)[c]	1.75 (d, J = 8)			
10	A	6.88 (d, J = 2)	5.35 (d, J = 2)		1.12 (s)		−17.90
	B	6.80 (d, J = 2)	4.90 (d, J = 2)		1.20 (s)		+75.76
11	A	6.15 (d, J = 1)	5.75 (q, J = 6)[c]	1.52 (d, J = 2)		2.50 (s)	
	B	6.15 (d, J = 1)	5.28 (q, J = 6)[c]	1.72 (d, J = 2)		2.50 (s)	
12	A	6.15 (d, J = 2)	5.38 (d, J = 2)		1.09 (s)	2.49 (s)	+32.16
	B	6.05 (d, J = 2)	4.85 (d, J = 2)		1.18 (s)	2.46 (s)	+66.07

[a] 60-MHz spectra in $CDCl_3$ with internal Me_4Si; J values given in hertz. [b] In acetone. [c] Each signal shows allylic coupling, J = 2 Hz.

7 and 8 with bromine and methanesulfenyl chloride gave optically active γ-sultines 9–12 (eq 3) as summarized in Table I.



7, 8



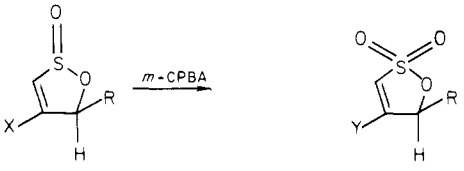
(3)

2

9, X = Br; R = Me
10, X = Br; R = t-Bu
11, X = MeS; R = Me
12, X = MeS; R = t-Bu

All the γ-sultines were obtained as diastereomeric mixtures (ca. 1:1, by NMR). While each one of γ-sultines (+)-10 and (+)-12 (R = t-Bu) was separated into two diastereomers A and B by means of column chromatography (silica, CH_2Cl_2), the structural assignment of the two diastereomers of (+)-9 and (+)-11 could only be obtained by double irradiation ^{1}H NMR. Irradiation of each one of the H_γ quartets showed a change to a singlet of the related methyl doublet. The results are summarized in Table II.

The oxidation of γ-sultines (+)-9, obtained from both (+)-2 and (−)-7, as well as of (−)-10A, (+)-10B, and (+)-11 to the optically active sultones 13–15, which lack a chiral sulfur (eq 4), may be taken as proof that the observed optical activity in the sultines is also due to the γ-carbon.



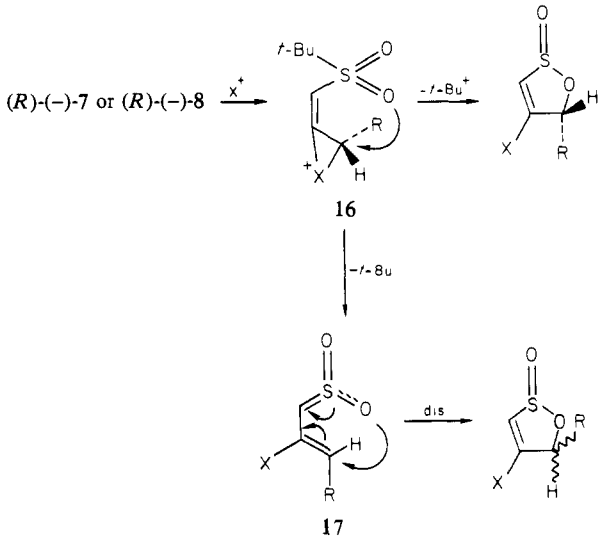
(4)

	$[\alpha]^{25}_D$, deg		$[\alpha]^{25}_D$, deg
9	+14.6	13, R = Me; Y = Br	+3.8
9	+16.9	13	+2.7
10A	−17.0	14, R = t-Bu; Y = Br	+9.8
10B	+75.8	14	+12.6
11	+23.7	15, R = Me; Y = $MeSO_2$	−3.7

The two chiral centers present in γ-sultines 9–12 give rise to four diastereomers for each sultine. These can be divided into structural types A and B, as shown in Chart I.

Since it is well-known that a γ-proton cis to the S → O bond in closely related γ-sultines is deshielded with respect to the same proton cis to a sulfur nonbonding electron pair,[11] one may conclude from the analysis of the NMR data shown in Table II that diastereomers 9A-12A have type-A structure and diastereomers 9B-12B are all of type-B structure (Chart I).

Scheme I



16

17

We suggest that the absolute configuration of (+)-2, derived from (R)-(+)-1, is (R)-(+)-α-methylpropargyl (R)-γ-methylallene-(R,S)-sulfinate, since we assume that both electron pairs on sulfur in the sulfoxylate intermediate (R,R)-[HC≡CCH-$(CH_3)O]_2S$ should be equally reactive and since the [2,3] sigmatropic rearrangement is known to occur with nearly complete transfer of chirality.[3b,12] The absolute configuration of both sulfones (−)-7 and (−)-8 was assigned as R by the use of the Lowe–Brewster rules[13] and the substituent polarizability order RSO_2 > H and alkyl > H. Further support for the assignment of the R configuration to the allenyl group in both sulfinate (+)-2 and sulfone (−)-7 comes from their cyclizations with bromine and MeSCl, which give the same γ-sultines, (+)-9 and (+)-11, respectively (Table I).

The intermediacy of vinylsulfene 17[14] in the reaction mechanism (Scheme I) appears to be excluded, since its disrotatory closure would lead to racemic γ-carbon in the product. On the other hand, the spatial arrangement of the γ-carbon in the bridged onium ion 16 will be preserved also during the nucleophilic attack by sulfonyl oxygen,[1a,f] and as a result this carbon will retain its optical activity in the γ-sultine, as actually observed.

The identity in sign and similarity in optical rotations of sultones (+)-14, obtained from (−)-10A and (+)-10B (eq 4) indicate that

(11) See, for example: Dittmer, D. C.; Henlon, R. S.; Takashina, N. *J. Org. Chem.* **1969**, *34*, 1310. Pirkle, W. H.; Hoekstra, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 1832. Hall, C. R.; Smith, D. J. *Tetrahedron Lett.* **1974**, 3633. See also ref 5a in ref 5a.

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(13) Lowe, G. *J. Chem. Soc., Chem. Commun.* **1965**, 411. Brewster, J. H. *Top. Stereochem.* **1967**, *2*, 1. Krow, G. *Ibid.* **1970**, *5*, 31.

(14) For a review on sulfenes, see: King, J. F. *Acc. Chem. Res.* **1975**, *8*, 10. We are indebted to Professor J. F. King for the suggestion of this mechanism to us.

the absolute configuration of the γ-carbon in both sultones as well as both sultines is the same. In conclusion, we suggest that γ-sultines **9A-12A** and **9B-12B** (Chart I, Table II) may be assigned the $(R)^C$-$(S)^S$ and $(R)^C$-$(R)^S$ absolute configurations, respectively.

Registry No. (*R*)-(+)-**1**, 42969-65-3; (*S*)-(-)-**1**, 2914-69-4; (-)-**2**, 84064-97-1; (+)-**2**, 84107-52-8; (*R*)-(-)-**7**, 84064-98-2; (*R*)-(-)-**8**, 84073-44-9; **9A**, 84107-53-9; **9B**, 84107-54-0; **10A**, 84064-99-3; **10B**, 84107-55-1; **11A**, 84065-00-9; **11B**, 84107-56-2; **12A**, 84065-01-0; **12B**, 84107-57-3.

Mechanism of Proton Removal from Intramolecularly Hydrogen-Bonded (Phenylazo)resorcinol Monoanions

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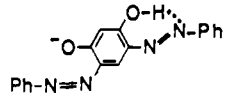
Received July 1, 1982

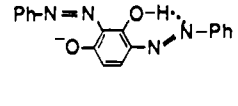
Two mechanisms have been proposed[1,2] for removal of the intramolecularly hydrogen-bonded proton from 4-phenylazoresorcinol monoanion. The mechanisms, Schemes I[1] and II[2], were based on measurements of the reciprocal relaxation time (τ^{-1}) for equilibration of the monoanion and dianion in the presence of hydroxide ion after a temperature perturbation. As the hydroxide ion concentration was varied, a minimum in the value of τ^{-1} was found as opposed to the expected linear variation.

Scheme I involves direct attack of hydroxide ion on the internally hydrogen-bonded monoanion (upper path) and a two-step process through an open form of the monoanion (lower path).[1] For other hydrogen-bonded acids it has been shown[3] that proton transfer occurs by the two-step process, and there is no evidence for direct attack on hydrogen-bonded protons. This makes Scheme I of particular interest. An alternative explanation for the unusual dependence of τ^{-1} on hydroxide ion concentration is shown in Scheme II. In the lower path, protonation of the monoanion gives a low concentration of the conjugate acid, and this is followed by formation of an isomeric form of the monoanion in which the proton is located in a site where it is unable to participate in an intramolecular hydrogen bond. The upper route involves proton removal from the monoanion by either direct attack on the hydrogen-bonded proton or by two-step reaction through an open form; the precise mechanism cannot be specified.[4]

We now report a similar dependence of reciprocal relaxation time on hydroxide ion concentration for proton removal from bis(phenylazo)resorcinol monoanions **1** and **2**.[5] Relaxation times



1



2

for the equilibration between monoanions **1** and **2** and their respective dianions in the presence of hydroxide ion were determined at 5 °C and 0.2 M ionic strength in aqueous solution by using the temperature-jump technique. The reaction was followed spectrophotometrically at ca. 520 or 440 nm, corresponding to absorbance by the dianion and monoanion, respectively. The

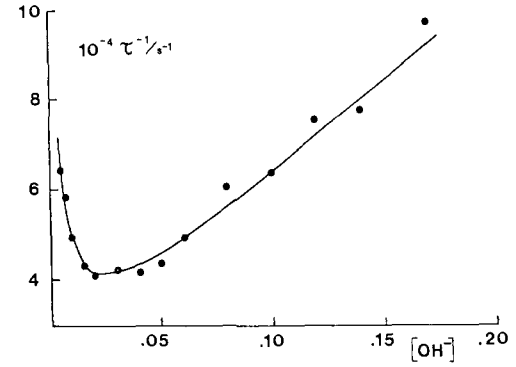
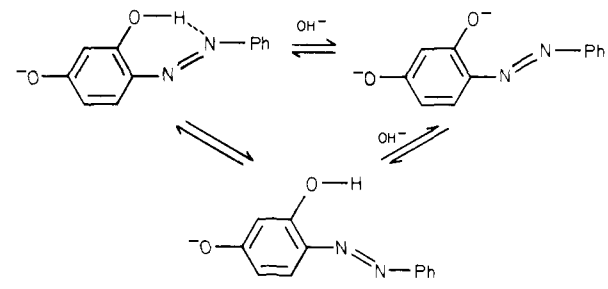
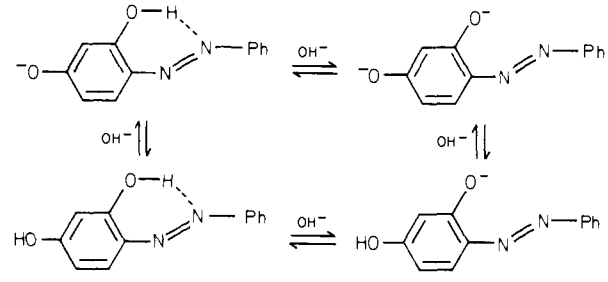


Figure 1. Dependence of reciprocal relaxation time for the equilibration between the monoanion and dianion of 2,4-bis(phenylazo)resorcinol on hydroxide ion concentration. The line is a best fit of eq 1.

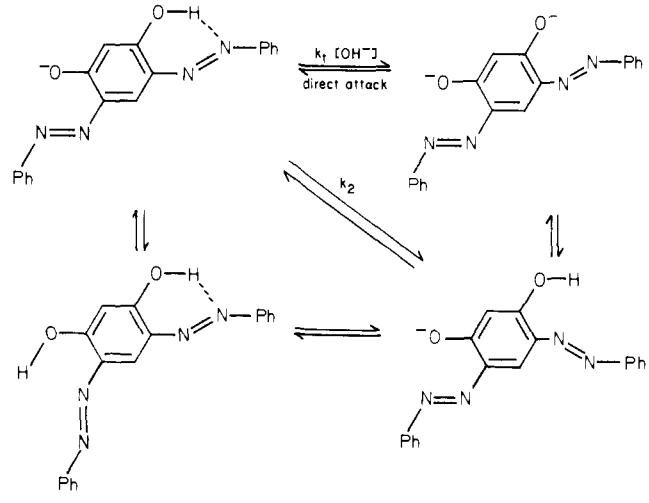
Scheme I



Scheme II



Scheme III



results for **2** are given in Figure 1, and it is clear that a minimum in τ^{-1} is observed.

Certain simplifications are possible for the bis(phenylazo)-resorcinol monoanions in attempting to explain the minimum in terms of Schemes I and II. This arises because for **1** and **2** an intermediate cannot be written where the proton is located at a site in which it is unable to participate in an intramolecular hydrogen bond. This means that if the proton is relocated in **1**

(1) Perlmutter-Hayman, B.; Sarfaty, R.; Shinar, R. *Int. J. Chem. Kinet.* **1976**, *8*, 741-751.
(2) Yoshida, N.; Fujimoto, M. *Chem. Lett.* **1977**, 1301-1304.
(3) Hibbert, F.; Awwal, A. *J. Chem. Soc., Perkin, Trans. II* **1978**, 939-945. Hibbert, F.; Robbins, H. J. *J. Am. Chem. Soc.* **1978**, *100*, 8239-8244. Kresge, A. J.; Powell, M. F. *Ibid.* **1981**, *103*, 972-973.
(4) If the upper route in Scheme II occurs by two-step reaction through an open form, it is necessary that this open form and the intermediate isomeric form of the monoanion on the lower route should differ significantly in energy in order to explain the kinetic behavior. The alternative possibility is that the upper route in Scheme II involves direct single-step attack. These arguments will be presented in detail when a full report of this work is published.
(5) Hodson, H. F.; Stamm, O. A.; Zollinger, H. *Helv. Chim. Acta* **1958**, **41**, 1816-1823.

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