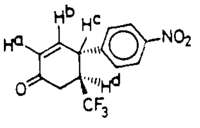
J. Org. Chem. **1982**, *47*, 2055–2060

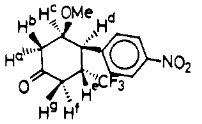
h. ^{19}F NMR analysis (standard $C_6H_5CF_3$) showed that cycloadduct **15** was formed in 63% yield (*cis,trans*-**15**/*trans,trans*-**15** ratio of 83/17). The reaction mixture was submitted to methanolysis in a manner similar to that for the desilylation of **14**.

Treatment of the reaction mixture with MeOH-TsOH at 0 °C for 2 h gave **17** in 89% yield (^{19}F NMR analysis). Compound **17**

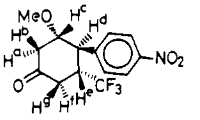


17

was isolated by a column chromatography on silica gel (eluent $CHCl_3$); mp 82–83 °C (from benzene–hexane). Desilylation by treating with MeOH–$NaHCO_3$ at 50 °C for 3 h afforded **19** in 91% yield (^{19}F NMR analysis; *cis,trans*-**19**/*trans,trans*-**19** ratio of 83/17). Both *cis,trans*-**19** and *trans,trans*-**19** were isolated by



cis,trans-19



trans,trans-19

a column chromatography on silica gel (eluent $CHCl_3$): *cis,trans*-**19**, mp 127–131 °C; *trans,trans*-**19**, mp 117.5–118.5 °C.

17: $^1H\{^{19}F\}$ NMR ($CDCl_3$) δ 2.48–3.26 (m, 3 H), 4.08 (d of t, $J_{H^a-H^c} = j_{H^b-H^c} = 2.5$ Hz, $J_{H^c-H^d} = 8$ Hz, 1 H), 6.30 (dd, $J_{H^a-H^b} = 10$ Hz, $J_{H^b-H^c} = 2.5$ Hz, 1 H), 6.76 (dd, $J_{H^a-H^b} = 10$ Hz, $J_{H^a-H^c} = 2.5$ Hz, 1 H), 7.46 (d, $J = 8$ Hz, 2 H), 8.28 (d, $J = 8$ Hz, 2 H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ −70.35 (d, $J = 7.5$ Hz); IR (KBr) 1690 ($\nu_{C=O}$), 1600 ($\nu_{C=C}$) cm^{-1}; mass spectrum, *m/e* 285 (M^+). Anal. Calcd for $C_{13}H_{10}F_3O_3N$: C, 54.74; H, 3.53; N, 4.91. Found: C, 54.78; H, 3.63; N, 4.88.

cis,trans-**19**: $^1H\{^{19}F\}$ NMR ($CDCl_3$) δ 2.46 (dd, $J_{H^f-H^g} = 15$ Hz, $J_{H^e-H^f} = 10.5$ Hz, 1 H), 2.53 (dd, $J_{H^a-H^b} = 15$ Hz, $J_{H^a-H^c} = 2.5$ Hz, 1 H), 2.82 (ddd, $J_{H^f-H^g} = 15$ Hz, $J_{H^g-H^e} = 5$ Hz, $J_{H^g-H^b} = 1.8$ Hz, 1 H), 2.96 (ddd, $J_{H^a-H^b} = 15$ Hz, $J_{H^b-H^c} = 3.6$ Hz, $J_{H^b-H^g} = 1.8$ Hz, 1 H), 3.26 (dd, $J_{H^d-H^e} = 11$ Hz, $J_{H^d-H^c} = 1.5$ Hz, 1 H), 3.45 (ddd, $J_{H^e-H^f} = 10.5$ Hz, $J_{H^e-H^g} = 5$ Hz, $J_{H^e-H^d} = 11$ Hz, 1 H), 3.73 (ddd, $J_{H^c-H^a} = 2.5$ Hz, $J_{H^c-H^b} = 3.6$ Hz, $J_{H^c-H^d} = 1.5$ Hz, 1 H), 7.59 (d, $J = 8$ Hz, 2 H), 8.18 (d, $J = 8$ Hz, 2 H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ −70.2 (d, $J = 7.5$ Hz); IR (KBr) 1720 ($\nu_{C=O}$) cm^{-1}; mass spectrum, *m/e* 231 (M^+). Anal. Calcd for $C_{14}H_{14}F_3O_4N$: C, 53.00; H, 4.45; N, 4.41. Found: C, 52.94; H, 4.37; N, 4.43.

trans,trans-**19**: $^1H\{^{19}F\}$ NMR ($CDCl_3$) δ 2.50 (dd, $J_{H^a-H^b} = 14$ Hz, $J_{H^a-H^c} = 9.5$ Hz, 1 H), 2.55 (dd, $J_{H^f-H^g} = 14$ Hz, $J_{H^f-H^e} = 12$ Hz, 1 H), 2.75 (ddd, $J_{H^g-H^f} = 14$ Hz, $J_{H^g-H^e} = 4.5$ Hz, $J_{H^g-H^b} = 1.2$ Hz, 1 H), 2.83 (ddd, $J_{H^e-H^d} = 10$ Hz, $J_{H^e-H^f} = 12$ Hz, $J_{H^e-H^g} = 4.5$ Hz, 1 H), 2.95 (ddd, $J_{H^b-H^a} = 14$ Hz, $J_{H^b-H^c} = 4$ Hz, $J_{H^b-H^g} = 1.2$ Hz, 1 H), 3.12 (s, 3 H), 3.22 (dd, $J_{H^d-H^c} = 9$ Hz, $J_{H^d-H^e} = 10$ Hz, 1 H), 3.58 (ddd, $J_{H^c-H^a} = 9.5$ Hz, $J_{H^c-H^b} = 4$ Hz, $J_{H^c-H^d} = 9$ Hz, 1 H), 7.38 (d, $J = 9$ Hz, 2 H), 8.20 (d, $J = 9$ Hz, 2 H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ −69.5 (d, $J = 7$ Hz); IR (KBr) 1730 ($\nu_{C=O}$) cm^{-1}; mass spectrum, *m/e* 231 (M^+). Anal. Calcd for $C_{14}H_{14}F_3O_4N$: C, 53.00; H, 4.45; N, 4.41. Found: C, 53.05; H, 4.46; N, 4.36.

Registry No. 1, 677-21-4; **2**, 38053-91-7; **3a**, 81206-63-5; **3b**, 81206-64-6; **4**, 70901-64-3; **5a**, 81206-65-7; **5b**, 81206-66-8; **6**, 59414-23-2; *trans*-**7**, 81206-67-9; *cis*-**7**, 81206-68-0; **8**, 81206-69-1; *trans*-**9**, 81206-70-4; *cis*-**9**, 81206-71-5; **10**, 78622-58-9; **11**, 78622-57-8; **12a**, 81206-72-6; **12b**, 81206-73-7; **13a**, 81206-74-8; **13b**, 81206-75-9; *cis,trans*-**14**, 81206-76-0; *trans,trans*-**14**, 81244-93-1; *cis,trans*-**15**, 81206-77-1; *trans,trans*-**15**, 81244-94-2; **16**, 81206-78-2; **17**, 81206-79-3; *cis,trans*-**18**, 81206-80-6; *trans,trans*-**18**, 81244-95-3; *cis,trans*-**19**, 81206-81-7; *trans,trans*-**19**, 81244-96-4; 1-methylidene-4-(trifluoromethyl)cyclohexane, 81206-82-8; 4-(methoxycarbonyl)iodobenzene, 619-44-3; 4-nitro iodobenzene, 636-98-6; 4-(trifluoromethyl)cyclohexan-1-one, 75091-99-5; 3-(trifluoromethyl)cyclohexan-1-one, 585-36-4.

Rate and Equilibrium Constants for the Reaction of Thiolate Ions with Dibenzo[*c*,*e*]-1,2-dithiin and Naphtho[1,8-*cd*]-1,2-dithiole 1,1-Dioxides

Bogdan Boduszek and John L. Kice*

Department of Chemistry, Texas Tech University, Lubbock, Texas 79409

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In aqueous dioxane the cyclic thiosulfonate dibenzo[*c*,*e*]-1,2-dithiin 1,1-dioxide (**1**) reacts rapidly with thiolate ions and undergoes opening of the thiosulfonate ring (eq 2), forming disulfide **3a**. Acidification of solutions of **3a** with carboxylic acid buffers of appropriate pH leads to facile reversal of the ring-opening reaction and the quantitative regeneration of **1**. Since this reversal of ring opening is not acid-catalyzed, it must take place via a simple intramolecular displacement of RS^- by the sulfinate (SO_2^-) group present in **3a** and is therefore the microscopic reverse of the ring-opening reaction. Rate constants have been determined for both ring opening (k_{RS}) and reversal of ring opening (k_{-RS}) for a series of alkanethiolates of varying pK_a. From these data one may also calculate the equilibrium constant, K_{eq} (= k_{RS}/k_{-RS}), for reaction of each thiolate with **1**. From comparison of the log K_{eq}'s with previously determined equilibrium constants for reaction of cyanide and sulfite ions with **1** one obtains quantitative information on the thermodynamics of reactions of the type ArSSR + $CN^- \rightleftharpoons$ ArSCN + RS^- and ArSSR + $SO_3^{2-} \rightleftharpoons ArSSO_3^-$ + RS^- that should be of considerable value for predicting the magnitude of equilibrium constants for cyanide–disulfide and sulfite–disulfide equilibria. Plots of log K_{eq}, log k_{RS}, and log k_{-RS} vs. the pK_a of RSH reveal that $\beta_{eq} = 1.25$, $\beta_{RS} = 0.26$, and $\beta_{-RS} = -0.99$. These β values show that the transition state for eq 2 is quite unsymmetrical, with a structure $[RS^{\Delta-} \cdots S\text{-}SO_2^{\delta-}]$ where the RS–S bond is only ~20% formed. The β_{RS} and β_{-RS} values are compared with the β values for several other previously studied displacements involving disulfides. The reaction of naphtho[1,8-*cd*]-1,2-dithiole 1,1-dioxide (**2**) with thiolates behaves in a fashion analogous to that of the reaction of RS^- with **1**. Comparison of K_{eq}, k_{RS}, and k_{-RS} for an equilibrium involving **2** and a thiolate with those for the corresponding thiolate reacting with **1** allows one to assess how a change from a six- to a five-membered thiosulfonate ring influences K_{eq}, k_{RS}, and k_{-RS}. The major effects are that k_{-RS} is much larger and K_{eq} is considerably smaller.

Chau and Kice[1] have shown that the cyclic thiosulfonates **1** and **2**, like ordinary open-chain aryl thiosulfonates, are cleaved readily by excess cyanide or sulfite ion (as shown for **1** in eq 1, step k_{Nu}). However, in dramatic contrast to the behavior of open-chain thiosulfonates, upon acidification of the final reaction solution with buffers sufficiently acidic to protonate CN^- or SO_3^{2-}, the reaction can be reversed (step k_{-Nu}) and the cyclic thiosulfonate rapidly and quantitatively regenerated. The reason that

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(1) Chau, M. M.; Kice, J. L. *J. Org. Chem.* **1978**, *43*, 914.

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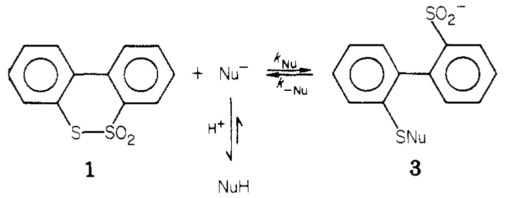
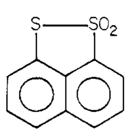


(1)

$K_{eq} = k_{Nu}/k_{-Nu}$



2

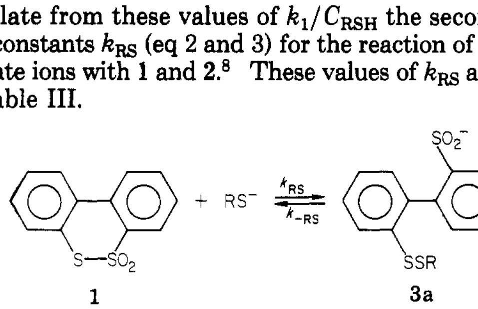
step k_{-Nu} can be readily observed with 3 at appropriate pH's, when the analogous reaction of $ArSO_2^-$ with ArSNu cannot, is because the *intramolecular* character of the displacement in the case of 3 makes the reaction many orders of magnitude faster than the *intermolecular* reaction of $ArSO_2^-$ with ArSNu.

The behavior of 1 and 2 with CN^- and SO_3^{2-} suggested that ring-opening reactions of these thiosulfonates with other nucleophiles that would also be protonated upon acidification on the reaction solution (such as RS^-) would also prove to be reversible and that suitable study of such systems could provide information about the characteristics of reactions such as $ArSO_2^- + ArSSR \rightarrow ArSO_2SAr + RS^-$ not otherwise likely to be accessible to study.

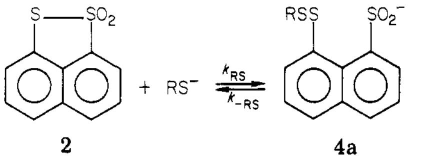
The present paper reports the results of the study of the reaction of thiolate ions with dibenzo[*c*,*e*]-1,2-dithiin and naptho[1,8-*cd*]-1,2-dithiole 1,1-dioxides (1 and 2, respectively) and of the reversal of these reactions upon acidification of the reaction solution. The data it affords on k_{Nu}, k_{-Nu}, and K_{eq} (Nu = RS) are of interest not only in their own right but also in relation to the data for certain nucleophilic displacements on aryl disulfides that have been studied by Hupe,[2] Overman,[3a] and others.[3b]

Results

When equal volumes of 60% dioxane (v/v) solutions of 1 (1.0×10^{-4} M) and a 6:1 K_2HPO_4–KH_2PO_4 buffer (pH 10)[4] containing excess alkanethiol (0.002–0.02 M) are mixed, there is a very rapid disappearance of 1 that can be followed by monitoring the disappearance of the absorption maximum for 1 at 296 nm with stopped-flow spectrophotometry. Reaction of 2 with a thiol can be followed in a similar fashion at 304 nm. The disappearance of 1 (or 2) under such conditions follows good first-order kinetics. The experimental first-order rate constants, k_1, for the various runs using different thiols and thiol concentrations are tabulated in Table I. One sees that for a given thiol and cyclic thiosulfonate k_1/C_{RSH} is a constant. Since the pH of the phosphate buffer is known[4] and the pK_a's for the various thiols in 60% dioxane are either known or can be estimated sufficiently accurately,[5] one can calculate from these values of k_1/C_{RSH} the second-order rate constants k_{RS} (eq 2 and 3) for the reaction of different thiolate ions with 1 and 2.[8] These values of k_{RS} are shown in Table III.



(2)



(3)

Measurements of k_{-RS} can be achieved as follows. The thiosulfonate (1×10^{-4} M) is treated with a sufficient amount [total thiol, $C_{RSH} = (2.1–8.4) \times 10^{-4}$ M] of a 1:1 mixture of RS^- and RSH to cause it to be converted completely to 3a (or 4a, in the case of 2). Acidification of this solution by addition of either a formic acid–sodium formate or a chloroacetic acid–sodium chloroacetate buffer leads to the essentially quantitative reversion of 3a to 1 (or 4a to 2), and the rate of this process may be followed by monitoring the increase in the optical density of the solution with time at 296 nm (or 304 nm in the case of 2). Plots of log $(A_\infty - A)$ vs. time show excellent linearity in every case; their slopes give the experimental first-order rate constant, k_{-1}, for the reversion of 3a to 1 (or 4a to 2) under the various conditions. The results for 3a are given in Table II. Reversion of 4a to 2 was studied only for the case where R = *t*-Bu. In a 1:1 chloroacetic acid–sodium chloroacetate buffer (pH 5.48)[6a] the results are as follows (C_{RSH}, k_{-1}): 3.8×10^{-4} M, 0.057 s^{-1}; 7.6×10^{-4} M, 0.057 s^{-1}. For a 1:1 formic acid–sodium formate buffer (pH 6.10)[6a] one finds the following (C_{RSH}, k_{-1}; 3.8×10^{-4} M, 0.069 s^{-1}; 7.6×10^{-4} M, 0.070 s^{-1}.

The first three entries in Table II, which show that k_{-1} does not increase with an increase in buffer concentration, demonstrate that general-acid catalysis by buffer is not important in the reversion of 3a to 1. The fact that k_{-1} does not increase with decreasing buffer pH shows that specific hydrogen ion catalysis is not important either.[9]

As measured, k_{-1} is not always exactly equal to k_{-RS}. First, previous work[1] has indicated that in 60% dioxane the pK_a of the SO_2^- group in 3a should be about 4.5 and that SO_2H is unreactive as nucleophile compared to SO_2^-. Therefore, the measured rate of reversion of 3a to 1 will be equal to $k_{-RS}(K_a^{3a}/K_a^{3a} + a_{H^+})$, rather than to k_{-RS}. Second, the equilibrium constants for eq 2 are such that in certain cases (R = *t*-Bu especially) the reversion of 3a to 1 is not quite complete at equilibrium. In those cases k_{-1} as measured will be equal to the sum of the rates of

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[2] (a) Hupe, D. J.; Wu, D. *J. Org. Chem.* **1980**, *45*, 3100. (b) Freter, R.; Pohl, E. R.; Wilson, J. M.; Hupe, D. J. *Ibid.* **1979**, *44*, 1771. (c) Wilson, J. M.; Bayer, R. J.; Hupe, D. J. *J. Am. Chem. Soc.*, **1977**, *99*, 7922.

[3] (a) Overman, L. E.; Matzinger, D.; O'Connor, E. M.; Overman, J. D. *J. Am. Chem. Soc.* **1974**, *96*, 6081. (b) Harper, D. A. R.; Mitchell, J. W.; Wright, G. J. *Aust. J. Chem.* **1973**, *26*, 121.

[4] Kice, J. L.; Lee, T. W. S. *J. Am. Chem. Soc.* **1978**, *100*, 5094.

[5] the pK_a's of thiophenol (9.48)[6a] and *t*-BuSH (13.72)[6b] in 60% dioxane have been determined experimentally. Since ΔpK_a for these two thiols in 60% dioxane (4.24 pK units) is closely similar to their ΔpK_a (4.5 pK units) in water,[7] it seems reasonable to assume that for the other thiols in Table I pK_a (*t*-BuSH) - pK_a (RSH) in 60% dioxane $\simeq$ pK_a(*t*-BuSH) - pK_a(RSH) in water. We have assumed that pK_a(*t*-BuSH) - pK_a(RSH) in 60% dioxane will be equal to 0.95[pK_a(*t*-BuSH) - pK_a(RSH)] in water.

[6] (a) Kice, J. L.; Rogers, T. E. *J. Am. Chem. Soc.* **1974**, *96*, 8015. (b) Ju, T.-L., M. S. Thesis, Texas Tech University, 1979.

[7] Kreevoy, M. M.; Harper, E. T.; Duvall, R. E.; Wilgus, H. S.; Ditsch, L. T. *J. Am. Chem. Soc.* **1960**, *82*, 4899.

[8] Kinetic data with other phosphate buffers of different pH show that reaction of undissociated thiol with 1 or 2 is of absolutely no importance kinetically in this pH range. The observed rate is entirely due to the reaction of thiolate ion. This was expected from what had been found previously[6a] regarding the relative reactivity of RSH vs. RS^- toward phenyl benzenethiosulfonate.

[9] Were acid catalysis to play a role, it would be expected to be most prominent for the reaction of 3a when R = *t*-Bu, since *t*-BuS$^-$ is the most basic thiolate. The fact that acid catalysis is not detectable for the case where R = *t*-Bu indicates that it is almost certainly unimportant for the other cases as well.

Table I. Kinetics of the Reaction of Thiols with Cyclic Thiosulfonates 1 and 2 in a 6:1 K_2HPO_4-KH_2PO_4 Buffer in 60% Dioxane at 25 °C

thiosulfonate[a]	thiol	10^2C_{RSH}, M	k_1, s^{-1}	k_1/C_{RSH}, M^{-1} s^{-1}
1	*t*-BuSH	0.60	2.7	4.5×10^2
		1.20	5.1	4.3×10^2
		1.95	8.1	4.1×10^2
	n-BuSH	0.60	20	3.4×10^3
		1.07	38	3.5×10^3
		1.70	54	3.2×10^3
	$HOCH_2CH_2SH$	0.29	59	2.0×10^4
		0.57	1.14×10^2	2.0×10^4
		1.69	3.3×10^2	2.0×10^4
	$PhCH_2SH$	0.195	47	2.4×10^4
		0.395	85	2.2×10^4
		0.755	1.6×10^2	2.2×10^4
	$EtOOCCH_2SH$	0.086	1.9×10^2	2.2×10^5
		0.12	2.0×10^2	2.4×10^5
		0.17	4.7×10^2	2.7×10^5
2	*t*-BuSH	0.60	21	3.5×10^3
		1.20	39	3.2×10^3
		1.95	63	3.3×10^3

[a] At a concentration of 5×10^{-5} M.

Table II. Kinetics of the Reversion of 3a to 1 upon Acidification of an Alkaline Solution of Thio plus 3a with Carboxylic Acid Buffers[a]

R in 3a	buffer (pH)	C_{RCOOH}, M	10^4C_{RSH}, M	10^2k_{-1}, s^{-1}
t-Bu	1:1 $ClCH_2COOH$-$ClCH_2COO^-$ (5.48)	0.01	4.5	0.0147
		0.02	4.5	0.0138
		0.04	4.5	0.0131
		0.01	7.8	0.0157
			16.1	0.0173
	1:1 HCOOH-$HCOO^-$ (6.10)	0.01	4.5	0.0170
			7.8	0.0185
			16.1	0.0208
n-Bu	1:1 $ClCH_2COOH$-$ClCH_2COO^-$ (5.48)	0.01	2.2	0.216
			4.2	0.216
			8.4	0.219
	1:1 HCOOH-$HCOO^-$ (6.10)	0.01	2.1	0.258
			4.2	0.265
			8.4	0.269
$HOCH_3CH_2$	1:1 $ClCH_2COOH$-$ClCH_2COO^-$ (5.48)	0.01	2.1	2.65[b]
	1:1 HCOOH-$HCOO^-$ (6.10)	0.01	2.1	2.75[b]
$PhCH_2$	1:1 $ClCH_2COOH$-$ClCH_2COO^-$ (5.48)	0.01	2.1	0.97
			4.2	0.96
	1:1 HCOOH-$HCOO^-$ (6.10)	0.01	2.1	1.2
$EtOOCCH_2$	1:1 $ClCH_2COOH$-$ClCH_2COO^-$ (5.48)	0.01	2.2	80[b]
	1:1 HCOOH-$HCOO^-$ (6.10)	0.01	2.2	92[b]

[a] All runs in 60% dioxane at 25 °C; 1 (1×10^{-4} M) was first treated with a 1:1 mixture of RS^- and RSH, (total thiol = [CRSH]) and then acidified with the indicated buffer to initiate the reversion of 3a to 1. [b] Average of three runs.

Table III. Rate and Equilibrium Constants for the Reaction of Thiolate Ions with Cyclic Thiolsulfonates 1 and 2 at 25 °C in 60% Dioxane

thiolsulfonate	RS^-	pK_a for RSH[a]	k_{RS}, M^{-1} s^{-1}	k_{-RS}, s^{-1}	K_{eq} ($=k_{RS}/k_{-RS}$), M^{-1}	$\Delta G°$, kcal/mol[b]
1	*t*-BuS^-	13.72	2.3×10^6	0.00016	1.4×10^{10}	−13.8
	n-BuS^-	13.34	7.4×10^6	0.0025	3.0×10^9	−12.9
	$HOCH_2CH_2S^-$	12.17	3.0×10^6	0.029	1.0×10^8	−10.9
	$PhCH_2S^-$	12.17	3.3×10^6	0.012	2.7×10^8	−11.4
	$EtO_2CCH_2S^-$	10.75	1.6×10^6	0.97	1.6×10^6	−8.5
2	*t*-BuS^-	13.72	1.8×10^7	0.071	2.5×10^8	−11.4

[a] See ref 5 for the method of estimation of pK_a's of thiols in 60% dioxane. [b] Standard free-energy change for reaction of RS^- with thiolsulfonate; $\Delta G° = -RT \ln K_{eq}$.

the forward $[k_{RS}(K_a^{RSH}/a_{H^+})C_{RSH}]$ and reverse $[k_{-RS}(K_a^{3a}/K_a^{3a} + a_{H^+})]$ steps of eq 2 under the particular reaction conditions. Therefore, the general expression for k_{-1} is as shown in eq 4a,b.

$$k_{-1} = k_{-RS}\left(\frac{K_a^{3a}}{K_a^{3a} + a_{H^+}}\right) + k_{RS}\left(\frac{K_a^{RSH}}{a_{H^+}}\right)C_{RSH} \qquad (4a)$$

$$k_{-1} = k_{-1}^0 + k'C_{RSH} \qquad (4b)$$

For those cases where the second term in eq 4a makes a detectable contribution, a plot of k_{-1} vs. C_{RSH} gives $k_{-RS}(K_a^{3a}/K_a^{3a} + a_{H^+})$ as the intercept (k_{-1}^0) at $C_{RSH} = 0$. The fact that in all cases k_{-1}^0 is only about 10% smaller in the chloroacetate (pH 5.48) than in the formate (pH 6.10) buffer is in accord with the pK_a for **3a** being 4.5 and not significantly influenced by the nature of the R group, and we have used this pK_a for **3a** throughout to convert values of k_{-1}^0 to k_{-RS}. The values of k_{-RS} are shown in

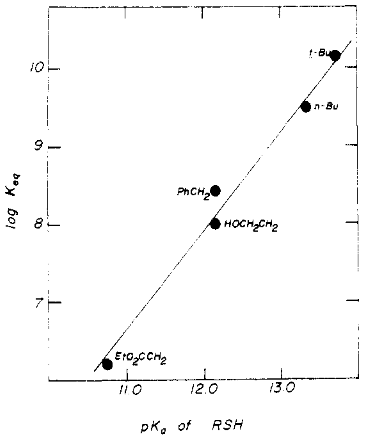


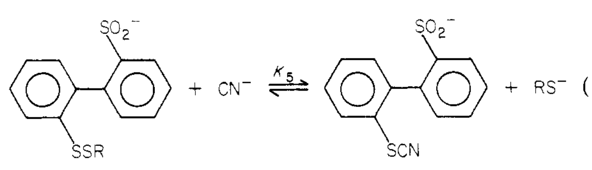
Figure 1. Plot of log K_{eq} for the reaction of thiolate ions (RS^-) with 1 (eq 2) vs. pK_a of RSH. Slope of correlation line, β_{eq}, is 1.25.

Table III, as are also the equilibrium constants, K_{eq} (= k_{RS}/k_{-RS}), and the free-energy changes, $\Delta G°$, associated with the various equilibria.

Discussion

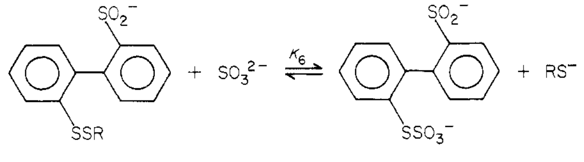
Figure 1 is a plot of log K_{eq} for eq 2 ($K_{eq} = k_{RS}/k_{-RS}$) vs. the pK_a of RSH. The fact that the point for RS = t-BuS falls on the correlation line shows that the steric bulk of the R group in RS has no significant effect on the magnitude of the equilibrium constant for eq 2. The correlation line has a slope, β_{eq}, of 1.25. On the basis of a calibrating scale where the effective charge on sulfur in RSH is taken as 0.0 and that in RS^- as −1.0, this gives the effective charge on the RS sulfur in **3a** as +0.25. Since the effective charge on the sulfur atom in a thiolacetate $RSC(O)CH_3$ is only +0.38,[10] it is interesting, and perhaps a bit unexpected, that the ArS fragment attached to the RS sulfur in **3a** has this large an effect on the electron density on that atom.

The standard free-energy change, $\Delta G_{RS}° = -RT \ln K_{eq}$, for the $1 + RS^- \rightleftharpoons$ **3a** equilibrium ranges, depending on the nature of RS^-, from −8.5 to −13.8 kcal/mol (Table III). Standard free energies, $\Delta G_{CN}°$ (−5.5 kcal/mol) and $\Delta G_{SO_3}°$ (−7.1 kcal/mol), for the reactions of 1 with cyanide (eq 1, $Nu^- = CN^-$) and sulfite ions ($Nu^- = SO_3^{2-}$), respectively, are available from previous work.[1] The difference $\Delta G_{CN}° - \Delta G_{RS}°$ will be $\Delta G°$ for the equilibrium shown as eq 5,



(5)

$$\Delta G_5° = \Delta G_{CN}° - \Delta G_{RS}°$$



(6)

$$\Delta G_6° = \Delta G_{SO_3}° - \Delta G_{RS}°$$

while $\Delta G_{SO_3}° - \Delta G_{RS}°$ is equal to $\Delta G°$ for the equilibrium shown as eq 6. Estimated values of $\Delta G_5°$ (and K_5 at 25 °C) for several RS groups are as follows: n-BuS, 7.4 (3.8×10^{-6}); $HOCH_2CH_2S$, 5.4 kcal (1.1×10^{-4}); EtO_2CCH_2S, 3.0 kcal (6.3×10^{-3}). Values of $\Delta G_6°$ (and K_6) for the same RS groups are as follows: n-BuS, 5.8 kcal (5.6×10^{-5}); $HOCH_2CH_2S$, 3.8 kcal (1.6×10^{-3}); EtO_2CCH_2S, 1.4 kcal (0.094).

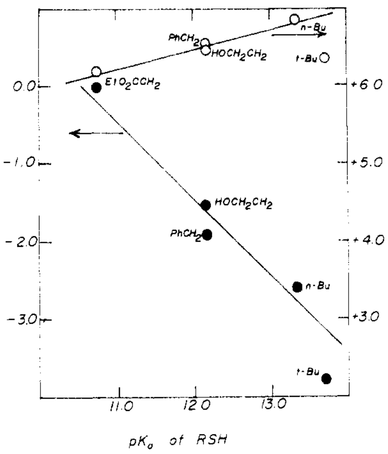


Figure 2. Plot of log k_{RS} (right ordinate) and log k_{-RS} (left ordinate) for various thiolate ions (RS^-) reacting in eq 2 vs. pK_a of RSH. Slopes of correlation lines: $\beta_{RS} = 0.26$; $\beta_{-RS} = -0.99$ (the points for $RS^- = t\text{-BuS}^-$ deviate from the correlation lines for the other thiolates because of a steric effect).

While there have been some previous qualitative and semiquantitative observations[11,12] regarding equilibrium constants for processes of the type $ArSSR + CN^- \rightleftharpoons ArSCN + RS^-$ and $ArSSR + SO_3^{2-} \rightleftharpoons ArSSO_3^- + RS^-$, the data above represent, to our knowledge, the first quantitative measurements of the thermodynamics associated with such equilibria. Since we doubt that the particular aryl group in eq 5 and 6 has much effect on $\Delta G°$, we feel that $\Delta G_5°$ and $\Delta G_6°$ should be representative of the free-energy changes that may normally be expected for such equilibria for alkyl aryl disulfides and should be generally useful in predicting the magnitude of equilibrium constants for cyanide–disulfide and sulfite–disulfide equilibria.

Two indications that this is true are the following. First, the pK_a of thiophenol is ~1.3 pK units less than that of EtO_2CCH_2SH.[7] From the variation in K_5 with RS, our data would predict that when the pK_a of RSH is 1.3 pK units smaller than that for ethyl thioglycolate, $\Delta G_5° = 0.69$ kcal and $K_5 = 0.3$. This is consistent with the report[12] that treatment of PhSSPh with a 10-fold molar excess of cyanide ion results in the conversion of a sizeable fraction of the disulfide to PhSCN. Second, Stricks and Kolthoff[13] have determined $\Delta G°$ (4.5 kcal) and K_{eq} (4.7×10^{-4} at 25 °C) for the equilibrium $(^-O_2CCH_2S)_2 + SO_3^{2-} \rightleftharpoons {}^-O_2CCH_2SSO_3^- + {}^-O_2CCH_2S^-$. The p$K_a$ of $^-O_2CCH_2SH$[14] is about 0.4 pK units larger than that of $HOCH_2CH_2SH$. With that pK_a difference, our estimates for eq 6 with $RS^- = {}^-O_2CH_2S^-$ are $\Delta G_6° = 4.5$ kcal and $K_6 = 5 \times 10^{-4}$, values in striking agreement with those actually found for the sulfite–dithiodiglycolate equilibrium by Stricks and Kolthoff.[13]

Figure 2 shows plots for both log k_{RS} and log k_{-RS} in eq 2 vs. the pK_a of RSH. For all thiolates except $t\text{-BuS}^-$ there is an excellent correlation between log k_{RS} and the pK_a of RSH, with the slope, β_{RS}, of the correlation line being 0.26. Since we have seen (Figure 1) that the point for $t\text{-BuS}^-$

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[10] Hupe, D. J.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 451.

[11] Parker, A. J.; Kharasch, N. *Chem. Rev.* **1959**, *59*, 582.

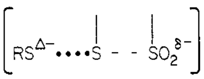
[12] Parker, A. J.; Kharasch, N. *J. Am. Chem. Soc.* **1960**, *82*, 3071.

[13] Stricks, W.; Kolthoff, I. M. *J. Am. Chem. Soc.* **1951**, *73*, 4569.

[14] Sekin, T.; Kato, K. A.; Takamori, K.; Machida, M.; Kanoaka, Y. *Biochem. Biophys. Acta* **1974**, *354*, 139.

does *not* deviate from the correlation line for log K_{eq} vs. pK_a, the point for t-BuS$^-$ on the log k_{-RS} vs. pK_a plot in Figure 2 should also deviate in a negative direction from the correlation line for the other thiolates by an amount equal to the deviation of the t-BuS$^-$ point in the log k_{RS} vs. pK_a plot, and the correlation line for log k_{-RS} in Figure 2 has been drawn accordingly; its slope, β_{-RS}, is −0.99.

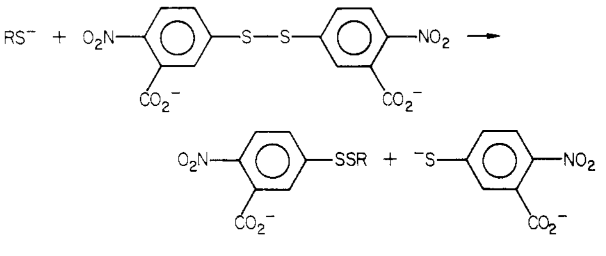
The fact that $|\beta_{RS}| \ll |\beta_{-RS}|$ indicates that the transition state for eq 2 is quite unsymmetrical with a structure of the type shown in **5**. That this should be the case is not surprising since thiolate ions are much stronger nucleophiles than an arenesulfinate ion, and one might therefore expect that in going from **1** to **3a** the transition state would be reached rather early along the reaction coordinate. The ratio β_{RS}/β_{eq}, if interpreted literally, would suggest that at the transition state the RS–S bond is only ~20% formed.



5

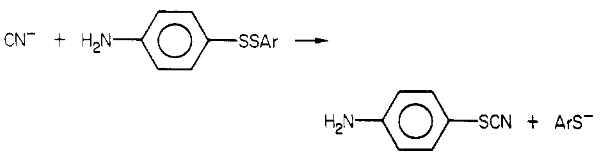
As noted earlier, the fact that the point for t-BuS$^-$ does not deviate from the correlation line for log K_{eq} shows that the particular steric requirements of a *tert*-butyl group have no effect on the free energy of **3a**. They do, however, exert some effect on the free energy of the *transition state* for eq 2 as evidenced by the negative deviation of the t-BuS$^-$ point from the correlation line for log k_{RS} (and log k_{-RS}). This steric effect is not a large one, though, the rates being slower than expected by only about a factor of 4. For that reason it is hardly surprising that the exact nature of the origin of this steric effect is not unambiguously apparent upon examination of a reasonable molecular model of the transition state for eq 2.

Hupe and co-workers[2c] have determined that β_{RS} for the reaction (eq 7) of a series of alkanethiolates with Ellman's reagent, 5,5′-dithiobis(2-nitrobenzoic acid), is 0.50.[15] The value of β_{RS} for eq 7 is approximately twice as large as the one (0.26) for eq 2. This indicates that in the transition state for eq 7 RS–S bond formation is much further advanced than it is in the transition state for eq 2. This is quite reasonable since ArSO$_2^-$ is presumably a considerably better leaving group than the Ar′S$^-$ group in eq 7, and one would expect that the transition state for eq 2 would be reached at an earlier point along the reaction coordinate for RS–S bond formation than in the displacement in eq 7.



(7)

The k_{-RS} step in eq 2 is a displacement of an alkanethiolate by an arenesulfinate ion. For the displacement of a series of ArS$^-$ groups by cyanide ion in the reaction shown in eq 8 the data of Harper, Mitchell, and Wright[3b] indicate that $\beta_{lg} = -0.76$. While the β for the leaving group in the reaction of triphenylphosphine with symmetrical aryl disulfides (eq 9) is not known, the overall ρ value (3.0) for the reaction, as compared with that (4.2) for the reaction of cyanide ion with symmetrical aryl disulfides[3b] (CN$^-$ + ArSSAr → ArSCN + ArS$^-$) suggests that β_{lg} for eq 9 is probably in the range −0.5 to −0.6. The β_{lg}'s for both eq 8 and 9 are therefore significantly smaller in magnitude than the β_{lg} (−0.99) for step k_{-RS} in eq 2. That this should be the case is not surprising. An arenesulfinate is undoubtedly a much weaker nucleophile toward dicoordinate sulfur than either CN$^-$ or Ph$_3$P, as evidenced by the fact that the *intermolecular* displacement Ar′SO$_2^-$ + ArSSAr → Ar′SO$_2$SAr + ArS$^-$ has never been observed. That being so, one would expect that the transition state for step k_{-RS} in eq 2 would occur at a point on the reaction coordinate where the S–S bond of the disulfide has been cleaved to a significantly greater extent than in the transition state for eq 8 or 9.



(8)

$$\mathrm{Ph_3P + ArSSAr \rightarrow ArS{-}PPh_3^+ + ArS^-} \qquad (9)$$

In the reactions of **1** and **2** with cyanide and sulfite ions[1] comparison of rate and equilibriuim constants for the five-membered cyclic thiolsulfonate **2** with those for the six-membered cyclic thiolsulfonate **1** shows the following: $k_{Nu}{}^2/k_{Nu}{}^1 \simeq 10$; $k_{-Nu}{}^2/k_{-Nu}{}^1 \simeq 200$; $K_{eq}{}^2/K_{eq}{}^1 \simeq 0.05$. Thus the equilibrium constant for opening of the ring in **2** is about 20 times smaller than that for the opening of the ring in **1** by the same nucleophile. This results from the fact that even though k_{Nu} for **2** is 10 times larger than k_{Nu} for **1**, k_{-Nu} for **2** is about 200 times larger than k_{-Nu} for **1**. The probable reason that k_{-Nu} for **2** is so much larger than that for **1** has been discussed.[1]

One might anticipate that roughly similar behavior for **2** vs. **1** should also be observed in their reaction with thiolate ions. The data in Table III for the reaction of t-BuS$^-$ with the two thiolsulfonates indicate that this is the case: $k_{RS}{}^2/k_{RS}{}^1 = 8$; $k_{-RS}{}^2/k_{-RS}{}^1 = 440$; $K_{eq}{}^2/K_{eq}{}^1 = 0.02$. The only slight difference from the earlier data[1] for cyanide and sulfite is that the ratio ($k_{-Nu}{}^2/k_{-Nu}{}^1$) is about a factor of 2 larger in the reaction involving the thiolate.

Experimental Section

Purification of Materials. Dibenzo[*c*,*e*]-1,2-dithiin 1,1-dioxide[17] (**1**, mp 132–133 °C) was purified by recrystallization from chloroform–hexane. Naphtho[1,8-*cd*]-1,2-dithiole 1,1-dioxide[18] (**2**, mp 150–151 °C) was purified by recrystallization from isopropyl alcohol. Commercial samples (Aldrich) of the various thiols were purified by fractional distillation and were stored under either nitrogen or argon. Dioxane was purified by the procedure described by Fieser and Fieser,[19] and the freshly fractionally distilled solvent was then frozen and stored at −20 °C to prevent formation of peroxides prior to use. All water used was doubly distilled from glass. The formic and chloroacetic acids used to prepare buffers

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[15] A similar value of β_{RS} (+0.57) was also found[2b] for the reaction of RS$^-$ with the mixed disulfide HOCH$_2$CH$_2$CH$_2$SSAr′ (Ar′ = 3-carboxy-4-nitrophenyl). The lower value of β_{RS} (+0.36) reported by Whitesides[16] for eq 7 is not correct since that correlation line was established by using data for *both* alkyl and aryl thiols, and Hupe[2c] has shown that the data for aryl thiols actually fall on a separate correlation line displaced upward from that for the alkyl thiols by about 0.8 log unit. If one attempts to draw a single correlation line through both sets of data the apparent slope will be much lower than the correct β value.

[16] Whitesides, G. G.; Lilburn, J. E.; Szajewski, R. P. *J. Org. Chem.* **1977**, *42*, 3265.

[17] Chau, M. M.; Kice, J. L. *J. Org. Chem.* **1977**, *42*, 3265.

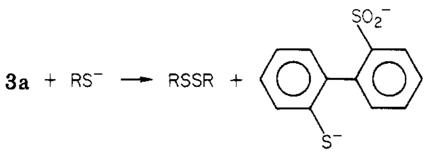
[18] Zweig, A.; Hoffman, A. K. *J. Org. Chem.* **1965**, *30*, 3997.

[19] Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 333.

were of the highest degree of purity commercially available.

Procedure for Kinetic Runs. Measurement of k_{RS}. A 1.0×10^{-4} M solution of 1 (or 2) in 60% dioxane was placed in one of the reservoir syringes of a Durrum-Gibson stopped-flow spectrophotometer. In the other reservoir syringe was placed in a solution of the thiol (0.002–0.02 M) in 60% dioxane also containing 0.03 M K_2HPO_4 and 0.005 M KH_2PO_4. The reaction was initiated by mixing the two solutions by using the stopped-flow device, and the decrease in the absorbance at 296 nm (304 nm for 2) with time was recorded on a storage oscilloscope.

Measurement of k_{-RS}. A concentrated solution containing equal amounts of an alkanethiol (RSH) and the corresponding alkanethiolate (RS^-) was prepared by adding the calculated amount of 1 N standard sodium hydroxide to a solution of the thiol in 60% dioxane. A measured volume of this solution, containing an amount of thiolate at least sufficient to convert the thiolsulfonate completely to **3a** (or **4a**), was then added to a 1×10^{-4} M solution of 1 (or 2) in 60% dioxane. For certain thiols, mercaptoethanol and ethyl mercaptoacetate, it was important to use no more than the minimum amount (1×10^{-4} M) of thiolate ion needed to convert 1 quantitatively to **3a**. If significantly larger amounts of thiolate were added, the further reaction of **3a** with the thiolate (eq 10) began to create problems, particularly if the solution was allowed to stand for any length of time before being acidified with a carboxylic acid buffer. With $t\text{-BuS}^-$, where reaction 10 is extremely slow due to the steric hindrance to attack on the sulfur adjacent to the *tert*-butyl group in **3a**, a large excess of thiolate ion over the minimum required to convert 1 to **3a** could be used. With $n\text{-BuS}^-$ and $PhCH_2S^-$ up to a 2-fold excess of thiolate could be used, provided care was taken to perform the subsequent acidification of the solution promptly.



(10)

For the runs with 1 and all thiols except ethyl mercaptoacetate a 3.5-mL aliquot of the solution resulting from the addition of the 1:1 RS^-/RSH solution to the solution of 1 was placed in a 1-cm spectrophotometer cell in the thermostated cell compartment of a Cary Model 17 UV spectrometer. To this was then added from 35–140 μL of a concentrated (1 M in each buffer component) 1:1 RCOOH/$RCOO^-$ buffer, using either chloroacetic or formic acid as the buffer acid, and the increase in the optical density of the solution at 296 nm was then monitored with time.

With ethyl mercaptoacetate the return of **3a** to 1 upon acidification was too rapid to be followed by conventional spectrophotometry, and the following stopped-flow procedure was employed. The solution resulting from the addition of the 1:1 RS^-/RSH solution to the solution of 1 was placed in one reservoir syringe of the stopped-flow spectrophotometer, a 1:1 RCOOH/$RCOO^-$ buffer ([RCOOH] = 0.02 M) in 60% dioxane was placed in the other syringe, and the reversion of **3a** to 1 was then initiated upon mixing the two solutions together in the stopped-flow apparatus. The reaction was followed at 296 nm. The same type of stopped-flow procedure was also used to follow the reversion of **4a** to 2. In this case a wavelength of 304 nm was used to follow the reaction.

Acknowledgment. The support of this research by the Robert A. Welch Foundation (Grant D-650) is gratefully acknowledged.

Registry No. 1, 25331-82-2; 2, 40227-43-8; t-BuSH, 75-66-1; BuSH, 109-79-5; $HOCH_2CH_2SH$, 60-24-2; $PhCH_2SH$, 100-53-8; $EtOCOCH_2SH$, 623-51-8.

Photochemical Studies of Cyclopropenes and Cyclopentadienes. Mechanistic and Exploratory Organic Photochemistry[1,2]

H. E. Zimmerman* and D. J. Kreil

Chemistry Department of the University of Wisconsin, Madison, Wisconsin 53706

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The photochemistry of two vinylcyclopropenes and one cyclopentadiene was investigated. Thus, 3-phenyl-3-(1-phenylvinyl)cyclopropene, 3-phenyl-3-(2,2-diphenylvinyl)cyclopropene, and 2,5,5-triphenylcyclopentadiene were studied. The vinylcyclopropenes were designed with the vinyl moieties being the low-energy chromophores in contrast to previously studied examples where the cyclopropene π bond is lower in energy. As with previous vinylcyclopropenes, irradiation led to cyclopentadienes and indenes. 2,5,5-Triphenylcyclopentadiene was the main photoproduct of the irradiation of the (diphenylvinyl)cyclopropene. 3-(2,2-Diphenylvinyl)indene was a lesser product that was encountered. 1,2-Diphenylcyclopentadiene, 3-(1-phenylvinyl)indene, and 3,4-diphenyl-1,2,4-pentatriene were formed from direct photolysis of the styryl cyclopropene. Interestingly, the corresponding sensitized irradiation led exclusively to 1,2-diphenylcyclopentadiene. Quantum efficiencies were determined for these reactions. Direct irradiation of 2,5,5-triphenylcyclopentadiene led to a novel ring contraction to afford the (diphenylvinyl)cyclopropene. Additionally, phenyl migration was observed, leading to formation of 1,4,5-triphenylcyclopentadiene. Sensitized reaction of 2,5,5-triphenylcyclopentadiene led only to the phenyl migration product. Again, quantum yields were determined. The (diphenylvinyl)cyclopropene was labeled in order to ascertain the skeletal change in the rearrangement. Similarly, labeling studies were carried out with 2,5,5-triphenylcyclopentadiene, thus allowing delineation of the fate of each carbon. Additionally, studies were carried out independently to generate the 3,5,5-triphenylpentadienyl carbene. The (diphenylvinyl)cyclopropene was the major product along with 2,5,5-triphenylcyclopentadiene and 3-(2,2-diphenylvinyl)indene.

A major function of organic photochemistry is the search for new reactions. Once a new reaction has been uncovered, there is need for exploration of the generality, limitations, and mechanisms of the reaction. One type of reaction which has been of interest to us[3-5] is the photo-

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(1) This is paper 133 of our "Mechanistic and Exploratory Organic Photochemistry" series.

(2) For paper 132 of the series, see Zimmerman, H. E. *Top. Curr. Chem.* **1982**, *100*, 45–73. Paper 131: Zimmerman, H. E.; Penn, J. H.; Carpenter, C. W. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 2128–2132. Paper 130: Zimmerman, H. E. In "Rearrangements in Ground and Excited States"; DeMayo, P., Ed.; Academic Press: New York, 1980.

(3) (a) Zimmerman, H. E.; Aasen, S. M. *J. Am. Chem. Soc.* **1977**, *99*, 2342–2344. (b) Zimmerman, H. E.; Aasen, S. M. *J. Org. Chem.* **1978**, *43*, 1493–1506.

(4) Zimmerman, H. E.; Hovey, M. C. *J. Org. Chem.* **1979**, *44*, 2331–2345.

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