by a Cottrell grant from the Research Corporation and a grant from the Petroleum Research Fund, administered by the American Chemical Society. We also acknowledge the thoughtful advice of the referees concerning this manuscript.

Supplementary Material Available: Preparative detail and complete spectral and analytical data for (*E*)-3-tetradecen-1-ol, 1-(benzyloxy)-3-hexyne, 1-(benzyloxy)-3-pentyne, (*E*)-1-(benzyloxy)-3-hexene, (*E*)-1-(benzyloxy)-3-tetradecene, (*E*)-1-methoxy-3-hexene, (*E*)-1-(*tert*-butyldimethylsiloxy)-3-tetradecene, (*Z*)-1-(benzyloxy)-3-hexene, (*Z*)-1-(*tert*-butyldimethylsiloxy)-3-hexene, and (*Z*)-1-(benzyloxy)-3-pentene (4 pages). Ordering information is given on any current masthead page.

Study of Reactions Leading to Sulfine Formation. 3. Competition of Reaction Pathways in the Reaction of Methoxide Ion with Methyl 1-Naphthylmethanesulfinates[1]

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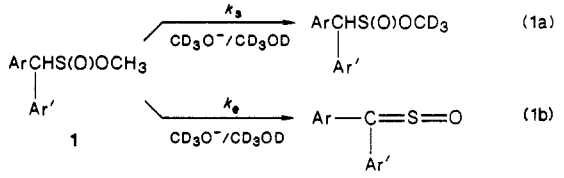
In CD_3O^-/CD_3OD methyl 1-naphthylmethanesulfinates, $NpCH_2S(O)OCH_3$ (**2**), undergo both exchange of CH_3O by CD_3O by substitution at the sulfinyl group and elimination to form the sulfine, NpCH=S=O. With use of methyl (2-methoxy-1-naphthyl)methanesulfinate (**2a**) it has been shown that formation of the sulfine takes place by an $(E1cB)_{irrev}$ mechanism. The rates of substitution (k_s) and elimination (k_e) of a series of **2** have been determined in CD_3O^-/CD_3OD by ^1H NMR spectroscopy, and the effect of several reaction variables on the competition between substitution and elimination has been examined. Salient results are as follows: (1) the rate of elimination is markedly increased by the presence of electron-withdrawing substituents on the aromatic ring, but the rate of substitution is increased only modestly by the same substituents; (2) substituents at the 2-position of the naphthyl group cause a large decrease in k_s (steric hindrance to substitution at S=O) but have little effect on k_e (elimination rate not sensitive to steric requirements of ortho substituents); (3) the activation energy for elimination is almost 9 kcal/mol greater than the activation energy for substitution. This large difference in activation energy contrasts with the 1–2 kcal/mol difference for elimination vs substitution found[14] with alkyl halides.

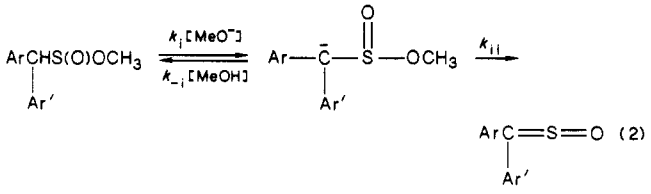
When treated with CD_3O^- in CD_3OD a methyl diarylmethanesulfinate (**1**) can undergo two reactions: (a) replacement of the CH_3O group by CD_3O via nucleophilic substitution at the sulfinyl group (eq 1a) and (b) elimination to form the corresponding sulfine (eq 1b).[2] This



(1a)

(1b)

latter elimination takes place[1b,2] by an $(E1cB)_{irrev}$ mechanism (eq 2, $k_{ii} > k_{-i}$[MeOH]) rather than the $(E1cB)_{rev}$ mechanism ($k_{ii} < k_{-1}$[MeOH]) that is observed in analogous sulfene-forming eliminations of arylmethanesulfonates[3,4] with leaving groups of comparable pK_a.



(2)

We originally planned to explore the effect of various reaction variables on the competition between substitution (k_s) and sulfine-forming elimination (k_e) by measuring (k_s/k_e) for various **1** under a variety of reaction conditions. However, because the exchange reaction (eq 1a) turned out to be considerably slower than sulfine formation (eq 1b) the 1-CD_3O^- system proved to be a less than optimal one for this purpose. To have adequate experimental flexibility in such studies it is necessary to have a system where $k_s > k_e$ under most reaction conditions.

Comparison of the rate constant for eq 1a with that for the analogous exchange involving a phenylmethanesulfinate ($PhCH_2S(O)OCH_3 + CD_3O^- \rightarrow PhCH_2S(O)OCD_3 + CH_3O^-$) showed the latter process was ~40 times faster. This suggested that the proper substrate for studies of the competition between substitution and sulfine-forming elimination would be a methyl *monoarylmethanesulfinate* that gave a reasonably stable sulfine upon elimination. Since 2-methoxynaphthalene-1-thiocarbaldehyde *S*-oxide (**8a**) was known[5] and had been isolated as a pure compound, methyl (2-methoxy-1-naphthyl)methanesulfinate (**2a**) was chosen for initial examination. When this showed that $k_s > k_e$ for **2a**, additional 1-naphthylmethanesulfinates (**2b–e**) were prepared and studied in similar fashion. The present paper reports the results of this work and what has been learned from it about the effect of various reaction variables on the competition between substitution at S=O and sulfine-forming elimination for such sulfinate esters.

Results

Synthesis of Methyl 1-Naphthylmethanesulfinates (2). Esters **2a–d** were prepared from (chloromethyl)-naphthalenes **3a–d** via the five-step sequence shown in

(1) (a) This research supported by the National Science Foundation, Grant CHE-8610116. (b) Paper 2: Kice, J. L.; Lotey, H. *J. Org. Chem.* **1988**, *53*, 3593.
(2) Kice, J. L.; Rudzinski, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 2414.
(3) King, J. F.; Beatson, R. P. *Tetrahedron Lett.* **1975**, *973*.
(4) Davy, M. B.; Douglas, K. T.; Loran, J. S.; Stettner, A.; Williams, A. *J. Am. Chem. Soc.* **1977**, *99*, 1196.
(5) Strating, J.; Thijs, L.; Zwanenburg, B. *Recl. Trav. Chim. Pays-Bays* **1964**, *83*, 631.

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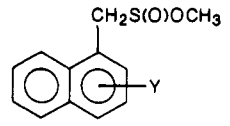
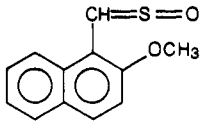


2a: Y = 2-MeO
2b: Y = 2-Me
2c: Y = H
2d: Y = 4-MeO
2e: Y = 3-NO_2



8a

Scheme I. With methyl (3-nitro-1-naphthyl)methanesulfinate (**2e**) the last three steps were also as shown in Scheme I, but the required β-(((3-nitro-1-naphthyl)methyl)thio)propionitrile (**5e**) was prepared by reaction of β-mercaptopropionitrile with 3-nitro-1-(bromomethyl)naphthalene[6] rather than by base-catalyzed addition of the thiol to acrylonitrile.

The key reaction in Scheme I is the generation of the anion of **7** by treatment of a β-(1-naphthylmethylsulfonyl)propionitrile (**6**) with a weak base ($PhCH_2S^-$). This method of generating a sulfinate ion was first described by Truce and Roberts[7] and has been used by Strating et al.[5] to synthesize **7a**.

Kinetics of Changes in the ^1H NMR Spectrum of 2 in CD_3O^-/CD_3OD. In the ^1H NMR spectrum of each methyl 1-naphthylmethanesulfinate (**2**) there is a sharp singlet, due to the protons of the $CH_3OS(O)$ group, in the region δ 3.70–3.77. There is also a quartet in the region δ 4.38–4.59 due to the protons of the $CH_2S(O)$ group; these are, of course, diastereotopic because of the chiral nature of the S=O group. When **2** is dissolved in CD_3OD, and CD_3O^- is added, both of these signals begin to decrease in intensity and eventually disappear completely. The kinetics of the disappearance of each was followed by measuring its integrated intensity (I) relative to that of an internal standard as a function of time. The experimental first-order rate constant for the disappearance of a given signal under a particular set of conditions was obtained from the slope of a plot of log (I/I_0) for that signal vs time. The experimental first-order rate constants, k'_{OCH_3} (for the disappearance of the CH_3O signal) and k'_{CH_2} (for the disappearance of the $CH_2S(O)$ signal), for the various runs are given in Table III (supplementary material).[8]

For each ester plots of k'_{OCH_3} and k'_{CH_2} vs $[CD_3O^-]$ were linear, verifying the anticipated first-order dependence of the rate of both processes on $[CD_3O^-]$. Second-order rate constants for the disappearance of the CH_3O (k_{OCH_3}) and $CH_2S(O)$ signals (k_{CH_2}) were obtained from the slopes of these plots and are shown in Table I.

Formation and Behavior of Sulfine 8a in CD_3O^-/CD_3OD. Although sulfine **8a**[5] is reasonably stable in CD_3OD alone, it disappears quite rapidly when CD_3O^- is added. (This contrasts with the behavior of the diarylsulfines, ArAr′C=S=O, resulting from the elimination of 1 (eq 1b),[2] all of which are quite stable in basic solution in methanol.) The rate of disappearance of **8a**, followed by observing the disappearance of the absorption maximum for the sulfine at 398 nm ($\epsilon = 1.4 \times 10^4$), is proportional to $[CD_3O^-]$, as can be seen from the folllowing data obtained at 25.0 °C($[CD_3O^-]$, k_1): 0.031 M, 0.96×10^{-3} s^{-1}; 0.041 M, 1.16×10^{-3} s^{-1}; 0.050 M, 1.44×10^{-3} s^{-1}. Treatment of **8a** with an equimolar amount of methoxide in methanol showed no evidence (^1H NMR) for the formation of **2a** (base-catalyzed addition of methanol to the sulfine);

(6) Adcock, W.; Dewar, M. J. S.; Golden, R.; Zeb, M. A. *J. Am. Chem. Soc.* **1975**, *97*, 2198.
(7) Truce, W. E.; Roberts, F. E., Jr. *J. Org. Chem.* **1963**, *28*, 593.
(8) See paragraph at the end of the paper regarding supplementary material.

Scheme I. Synthesis of Methyl 1-Naphthylmethanesulfinates (2)

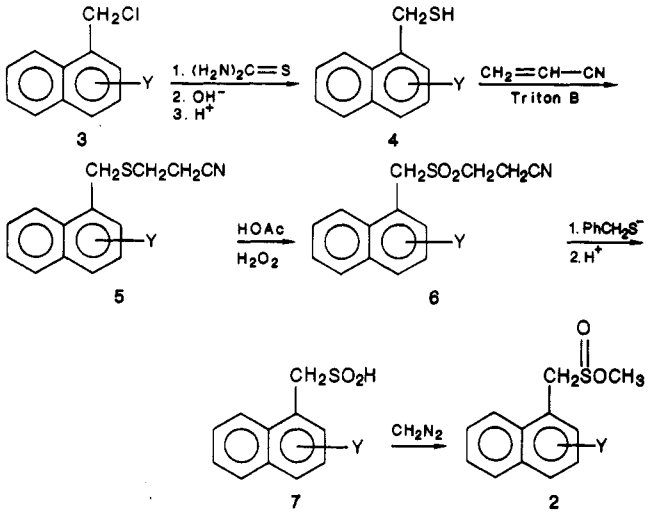
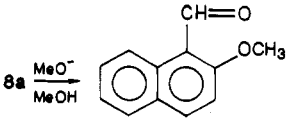


Table I. Rate Constants for Disappearance of ^1H NMR Signals for 2 in CD_3O^-/CD_3OD

sulfinate ester	temp, °C	k_{OCH_3},[a] M^{-1} s^{-1}	k_{CH_2},[b] M^{-1} s^{-1}
2a	25.0	0.0045	0.0018
2b	25.0	0.0073	0.0019
2c	25.0	0.113	0.0293
	10.0	0.0382	0.0053
	0.0	0.020	0.00176
2d	25.0	0.112	0.0024
2e	25.0	1.25	1.03

[a] Second-order rate constant for the disappearance of the signal for the $CH_3OS(O)$ group. [b] Second-order rate constant for disappearance of the signal for the $CH_2S(O)$ group.

the principal final product was, in fact, 2-methoxy-1-naphthaldehyde (**9a**).



9a

Ester **2a** (7.7×10^{-5} M) in CD_3OD was treated with CD_3O^- (0.031–0.050 M), and the absorbance of the solution was monitored as a function of time at 398 nm (λ_{max} for **8a**). In each instance the absorbance at this wavelength rose from an initial vaue of 0.00 to a maximum of about 0.06 and then fell off more gradually to a final value of 0.00. The maximum absorbance (A_{max}) at 398 nm was independent of $[CD_3O^-]$, but the time to reach this maximum (t_{max}) was not, being shorter the higher the concentration of CD_3O^-. This behavior and the shape of the curve for absorbance at 398 nm vs time were those expected[9] for the formation of **8a** as an intermediate in a sequence of two consecutive pseudo-first-order reactions (eq 3) where k_b

$$\mathbf{2a} \xrightarrow{k_{elim}[CD_3O^-]} \mathbf{8a} \xrightarrow{k_b[CD_3O^-]} \text{products} \qquad (3)$$

$> k_{elim}$. For this type of kinetic situation it is known[9] that β_{max} and τ_{max} are related to $\kappa(\kappa = k_b/k_{elim})$ as follows:

$$\beta_{max} = \kappa^{\kappa/(1-\kappa)}$$

$$\tau_{max} = \frac{1}{\kappa - 1} \ln \kappa$$

(9) Frost, A. A.; Pearson, R. G. *Kinetics and Mechanism*, 2nd ed.; John Wiley and Sons, Inc.: New York, 1961; pp 166–169.

where $\beta_{max} = [8a]_{max}/[2a]_o$ and $\tau_{max} = k_{elim}[CD_3O^-]t_{max}$. The equation for τ_{max} can be rewritten as:

$$\left(\frac{\kappa}{\kappa - 1}\right) \ln \kappa = k_b[CD_3O^-]t_{max}$$

The value of k_b (0.029 M^{-1} s^{-1}) is available from the kinetic study of the disappearance of **8a** in the presence of CD_3O^- outlined earlier. Multiplication of $[CD_3O^-]t_{max}$ by k_b gives $[\kappa/(\kappa - 1)] \ln \kappa$; this was found to be equal to 2.6 ± 0.1. This corresponds to $\kappa = 11 \pm 2$. From the maximum absorbance (0.060 ± 0.005) at 398 nm and ϵ for **8a** at this wavelength, β_{max} was calculated as 0.055 ± 0.005. This corresponds to $\kappa = 15 \pm 3$. Since there is some uncertainty, because of the flat character of the curve for A vs time in the region of the maximum, in estimating t_{max}, the values of κ, as estimated by the two methods, are considered to be in satisfactory agreement. That obtained from β_{max} is considered the more accurate.

Using $\kappa = 15$ and $k_b = 0.029$ M^{-1} s^{-1}, k_{elim} for **2a** is calculated to be 1.9×10^{-3} M^{-1} s^{-1}. Inspection of Table I shows that this is the same, within experimental error, as k_{CH_2} for **2a** (1.8×10^{-3} M^{-1} s^{-1}). For **2a** the rate of disappearance of the $CH_2S(O)$ quartet in the ^1H NMR (k_{CH_2}) and the rate at which **2a** undergoes elimination to form sulfine **8a** (k_{elim}) are the same.

Discussion

In CD_3OD in the presence of CD_3O^- the ^1H NMR signals for both the $CH_3OS(O)$ and $CH_2S(O)$ protons of methyl 1-naphthylmethanesulfinates (**2**), $NpCH_2S(O)OCH_3$, disappear with time. The experimental first-order rate constants for the disappearance of these signals are in each case proportional to $[CD_3O^-]$. Table I gives the second-order rate constants ($k_1/[CD_3O^-]$) for the disappearance of the CH_3O (k_{OCH_3}) and $CH_2S(O)$ signals (k_{CH_2}) for the various **2**.

Both substitution of CH_3O by CD_3O at the S=O group of the ester (eq 4a) and formation of sulfine from **2** by elimination (eq 4b) result in the loss of CH_3O groups. Therefore $k_{OCH_3} = k_s + k_e$.

$$\text{NpCH}_2\text{S(O)OCH}_3 + \text{CD}_3\text{O}^- \xrightarrow{k_s} \text{NpCH}_2\text{S(O)OCD}_3 + \text{CH}_3\text{O}^- \quad (4a)$$

$$\text{NpCH}_2\text{S(O)OCH}_3 + \text{CD}_3\text{O}^- \xrightarrow{k_e} \text{NpCH=S=O} + \text{CD}_3\text{OH} + \text{CH}_3\text{O}^- \quad (4b)$$

2 → **8**

If sulfine formation takes place by an $(ElcB)_{irrev}$ mechanism (eq 5, $k_{ii} > k_{-i}[CD_3OD]$), the rate constant for disappearance of the $CH_2S(O)$ signal, k_{CH_2}, will be *equal* to k_e. On the other hand, if sulfine formation occurs via an $(ElcB)_{rev}$ mechanism (eq 5, $k_{ii} < k_{-i}[CD_3OD]$), k_{CH_2} will be *larger* than k_e.

$$\text{NpCH}_2\text{S(O)OMe} \xrightarrow{k_i[CD_3O^-]} \text{NpCHS(O)OMe} \xrightarrow{k_{-i}[CD_3OD]} \text{NpCHDS(O)OMe}$$

$$\text{NpCHS(O)OMe} \xrightarrow{k_{ii}} \text{MeO}^- + \text{NpCH=S=O} \quad (5)$$

The naphthyl sulfines (**8**) unfortunately are not stable in CD_3O^-/CD_3OD and react further at a relatively rapid rate, making direct determination of k_e by spectrophotometric measurement of the appearance of **8** a challenge. However, in the case of **2a** we were able unambiguously to detect sulfine **8a**[5] spectrophotometrically as an intermediate and to treat the kinetics of the formation of **8a** and its subsequent disappearance as a sequence of two consecutive pseudo-first-order reactions[9] (eq 3). From this analysis, k_e for **2a** in CD_3O^-/CD_3OD at 25 °C was determined to be 0.0019 M^{-1} s^{-1}. This is the same, within experimental error, as the value of k_{CH_2} for this ester (Table I). For **2a**, therefore, $k_{CH_2} = k_e$, and formation of the sulfine (eq 4b) takes place by an $(ElcB)_{irrev}$ mechanism.[10] This conclusion is corroborated by the behavior of the $CH_2S(O)$ region in the ^1H NMR of **2a** when that substrate is treated with CD_3O^-/CD_3OD. The $CH_2S(O)$ quartet, while decreasing in intensity, otherwise retains its shape unaltered. In particular, there is no detectable intrusion at any stage of a tight 1:1:1 triplet for a CHD group, as would be required if NpCHDS(O)OMe were being formed from **2a** by exchange of a methylene proton.[11] The same behavior—disappearance of the $CH_2S(O)$ quartet without any detectable signal for CHDS(O)—was also seen with each of the other **2** in CD_3O^-/CD_3OD. This indicates that *none* of the 1-naphthylmethanesulfinates undergo elimination by an $(ElcB)_{rev}$ mechanism. We therefore believe it is reasonable to assume that $k_{CH_2} = k_e$ for each **2** studied.

If $k_{CH_2} = k_e$ for every **2**, then values of k_s and k_e for each ester can be calculated from the data for k_{OCH_3} and k_{CH_2} in Table I using the relationships:

$$k_e = k_{CH_2}$$

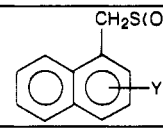
and

$$k_s = k_{OCH_3} - k_e = k_{OCH_3} - k_{CH_2}$$

Values of k_s and k_e derived in this way are presented in Table II.

Let us consider first the effect of substituents on the rates of substitution and elimination. The data for the three esters without an ortho substituent, i.e., **2c**, **2d**, and **2e**, provide information on the strictly inductive effect of substituents on k_e and k_s. They show that k_e is markedly dependent on the inductive effect of substituents, a

Table II. Rates of Substitution (k_s) and Sulfine-Forming Elimination (k_e) of Methyl 1-Naphthylmethanesulfinates (2) in CD_3O^-/CD_3OD[a]



ester		temp, °C	k_s, M^{-1} s^{-1}	k_e, M^{-1} s^{-1}
2c	unsubst (Y = H)	0.0	0.0182	0.0018
		10.0	0.033	0.0053
		25.0	0.084	0.029
2a	Y = 2-OMe	25.0	0.0027	0.0018
2d	Y = 4-OMe	25.0	0.109	0.0024
2b	Y = 2-Me	25.0	0.0054	0.0019
2e	Y = 3-NO_2	25.0	0.22	1.03

[a] Calculated from k_{OCH_3} and k_{CH_2} values in Table I assuming (as has been proven for **2**) that $k_{CH_2} = k_e$.

(10) An $(ElcB)_{irrev}$ mechanism, rather than an E2 mechanism, has been established[1b,2] for methoxide-induced, sulfine-forming eliminations of methyl diarylmethanesulfinates. A referee has noted that this does not rule out an E2 mechanism for the elimination of **2a**, since, in his opinion, the 1-naphthylmethyl system, where a less stable carbanion would be involved, might be more prone to react via a concerted mechanism for sulfine formation than a diarylmethanesulfinate. We would agree that an ElcB-like E2 mechanism is a tenable alternative to an $(Elcb)_{irrev}$ mechanism for formation of **8a** from methoxide ion and **2a**. This does not alter any of the important conclusions of the present study, however.

(11) In the event that one of the $CH_2S(O)$ hydrogens (call it H_A) exchanges, there will be a CHD signal (a closely spaced triplet) for H_B centered at the chemical shift for H_B. If both H_A and H_B exchange at comparable rates, two such triplets (one for CH_AD_B and one for CD_AH_B) will appear. The failure to see any CHD signal(s) when **2a** is treated with MeO^- in MeOD shows that conversion of $NpCH_2S(O)OMe$ to NpCHDS(O)OMe is not occurring to an extent detectable by NMR.

strongly electron-withdrawing substituent (**2e**, Y = 3-NO_2) leading to elimination being 40 times faster than for the unsubstituted compound (**2c**, Y = H), while an electron-donating substituent (**2d**, Y = 4-OMe) causes elimination to be about 10 times slower than for **2c**. On the other hand, k_s, the rate constant for substitution (eq 4a), is much less sensitive to the inductive effect of substituents, k_s for **2e** being only about 3 times larger than k_s for **2c**.

Comparison of the data for **2a** (Y = 2-OMe) and **2d** (Y = 4-OMe) shows that, although having the substituent ortho rather than para has little effect on k_e, it has a large effect on k_s, the rate of substitution being approximately 40 times slower for the 2-OMe compound than for the 4-OMe compound. The rate constants for **2b** (Y = 2-Me) indicate that this ortho substituent also causes a marked reduction in the rate of substitution but has little effect on k_e.

Steric hindrance to substitution at the sulfinyl group provided by the ortho substituent presumably accounts for the sizable retardation in k_s. Earlier measurements[2] of the relative rates of substitution of $PhCH_2S(O)OCH_3$ and $Ph_2CHS(O)OCH_3$ by CD_3O^-, which showed that the presence of the second phenyl group reduced the rate of substitution by a factor of 40, have indicated that substitutions at the sulfinyl group of arylmethanesulfinate esters can be subject to substantial steric retardation. Examination of molecular models of **2a** and **2b** suggests that the ortho substituents in these esters could easily exert significant steric hindrance to nucleophilic substitution at the S=O group of the ester.

The fact that ortho substituents have little impact, beyond their inductive effect, on k_e shows that the free energy of the transition state of the rate-determining step for the elimination (step k_i) is not affected by the steric requirements of substituents on the aromatic ring ortho to the $CH_2S(O)$ group.

For **2c** k_s and k_e have been measured at three temperatures in the range 0.0–25.0 °C (Table II) thereby allowing the activation parameters for both substitution (eq 4a) and elimination (eq 4b) to be determined. For substitution (k_s): $\Delta H^\ddagger$ = 9.2 kcal/mol; $\Delta S^\ddagger$ = −32.6 eu. For elimination (k_e): $\Delta H^\ddagger$ = 17.7 kcal/mol; $\Delta S^\ddagger$ = −6.2 eu. The difference in $\Delta H^\ddagger$ for the two reactions is quite large, 8.5 kcal/mol. Because $\Delta H^\ddagger$ for the elimination is this much larger than $\Delta H^\ddagger$ for substitution, modest increases in temperature enable elimination to compete much more effectively with substitution. Thus, although k_s is 10 times faster than k_e at 0.0 °C, at 50 °C k_e is now slightly faster than k_s.

Even though $\Delta H^\ddagger$ for elimination is much larger than $\Delta H^\ddagger$ for substitution, the two reactions are competitive in rate for the methoxide/**2c** system because $\Delta S^\ddagger$ for substitution (−32.6 eu) is much more negative than $\Delta S^\ddagger$ for elimination (−6.2 eu). That the entropies of activation for the two reactions should differ by this much is not surprising. The alkaline hydrolysis of methyl benzenesulfinate (eq 6) is a substitution at S=O closely analogous to eq 4a. It has a $\Delta S^\ddagger$ of −36.6 eu.[12] Given that $\Delta S^\ddagger$ for eq 6 is this

$$PhS(O)OCH_3 + OH^- \xrightarrow[\text{determining}]{\text{rate}} PhS(O)OH + CH_3O^- \xrightarrow{\text{fast}} PhSO_2^- + CH_3OH \quad (6)$$

negative, a $\Delta S^\ddagger$ for eq 4a of −32.6 eu is certainly reasonable. Also worth noting is the fact that $\Delta S^\ddagger$ for the exchange of the methoxy group in a series of methyl benzoates in CD_3O^-/CD_3OD (eq 7) ranges from −23 to −29 eu.[13]

$$ArC(O)OCH_3 + CD_3O^- \xrightarrow{CD_3OD} ArC(O)OCD_3 + CH_3O^- \quad (7)$$

The entropy of activation for the sulfene-forming elimination shown in eq 8 is +0.7 eu,[14] while $\Delta S^\ddagger$ for the methoxide ion induced elimination of 2-phenylethyl halides (eq 9) is about −6 eu.[15] These data for other eliminations suggest that an entropy of activation of −6.2 eu for eq 4b is certainly plausible.

$$OH^- + PhCH_2SO_2OPh \rightarrow H_2O + PhCH{=}SO_2 + PhO^- \quad (8)$$

$$CH_3O^- + PhCH_2CH_2X \rightarrow CH_3OH + PhCH{=}CH_2 + X^- \quad (9)$$

It is interesting to compare the difference in $\Delta H^\ddagger$ for substitution and elimination for **2c** with the behavior of other systems. For 2-hexyl halides reacting with methoxide ion $\Delta H^\ddagger$ for elimination (E2) is larger than $\Delta H^\ddagger$ for substitution (S_N2),[16] but only by 1–2 kcal/mol. The difference in $\Delta H^\ddagger$ for elimination and substitution for **2c** (8.5 kcal/mol) is therefore much larger than for a secondary alkyl halide. The situation with arylalkanesulfonyl compounds, on the other hand, appears closer to the behavior of **2c**. Thus $\Delta H^\ddagger$ for the sulfene-forming elimination in eq 8 is 23.4 kcal/mol.[14] Although $\Delta H^\ddagger$ for substitution by OH^- at the sulfonyl group of $PhCH_2SO_2OPh$ can't be measured, that for the related substitution of $PhSO_2OPh$ ($OH^- + PhSO_2OPh \rightarrow PhSO_2OH + PhO^-$) is 17.3 kcal/mol.[14] The difference between $\Delta H^\ddagger$ for elimination and substitution for $PhCH_2SO_2OPh$ is likely, in all probability, to be 1–2 kcal/mol less than the 6 kcal/mol difference between $\Delta H^\ddagger$ for eq 8 and this reaction. The reason is that direct displacements of arenesulfonyl compounds (such as $ArSO_2Cl$) are typically an order of magnitude or more faster than those of alkanesulfonyl compounds ($MeSO_2Cl$, $PhCH_2SO_2Cl$).[17] If the same holds true for the relative rate of displacements of $PhSO_2OPh$ vs $PhCH_2SO_2OPh$, and if the rate difference is due to a difference in $\Delta H^\ddagger$, the difference between $\Delta H^\ddagger$ for elimination and substitution for $PhCH_2SO_2OPh$ will be less than 5 kcal/mol.

The present study has examined the effect of several reaction variables on the competition between substitution at the sulfinyl group and sulfine-forming elimination for the reaction of methoxide ion with methyl arylmethanesulfinates. The significant results may be summarized as follows: (1) The activation energy for elimination is almost 9 kcal/mol larger than for substitution, so that modest changes in reaction temperature have a marked effect on the competition between the two reactions; (2) elimination is accelerated much more than substitution by the presence of electron-withdrawing substituents on the aromatic ring; (3) ortho substituents on the ring exert substantial steric hindrance to substitution but have little steric effect on the rate of elimination.

Experimental Section

Of the (chloromethyl)naphthalenes (**3a–d**) needed, **3a** and **3b** are commercially available (Aldrich). 2-Methoxy-1-(chloromethyl)naphthalene (**3c**), mp 121–122 °C dec (lit.[18] mp 119–121

(12) Najam, A. A.; Tillett, J. G. *J. Chem. Soc., Perkin Trans. 2* **1975**, 858.

(13) Jones, M. B.; Sloane, T. M. *Tetrahedron Lett.* **1966**, 831.

(14) Laleh, A.; Ranson, R.; Tillett, J. G. *J. Chem. Soc., Perkin Trans. 2* **1980**, 610.

(15) DePuy, C. H.; Bishop, C. A. *J. Am. Chem. Soc.* **1960**, *82*, 2535.

(16) Bartsch, R. A.; Bunnett, J. F. *J. Am. Chem. Soc.* **1968**, *90*, 408.

(17) See, for example: Robertson, R. E. *Prog. Phys. Org. Chem.* **1967**, *4*, 213.

(18) Badger, R. A.; Carruthers, W.; Cook, J. W. *J. Chem. Soc.* **1949**, 1768.

°C dec), was prepared by the procedure outlined by Badger, Carruthers, and Cook:[18] ^{1}H NMR ($CDCl_3$) δ 4.00 (s, 3 H), 5.18 (s, 2 H), 7.25–8.10 (m, 6 H). 4-Methoxy-1-(chloromethyl)-naphthalene (**3d**) was synthesized from 4-methoxy-1-naphthaldehyde (Aldrich). The aldehyde was reduced to 4-methoxynaphthyl carbinol, mp 79–80 °C (lit.[19] mp 76–77 °C) as described by Gonzalez-Trigo and co-workers,[19] and the carbinol was converted to **3d** by reaction with thionyl chloride:[20] ^{1}H NMR ($CDCl_3$) δ 3.98 (s, 3 H), 5.01 (s, 2 H), 6.72 (d, 1 H), 7.40 (m, 3 H), 8.06 (d, 1 H), 8.31 (d, 1 H).

Preparation of 1-Naphthylmethanethiols (4). The following procedure was employed for the conversion of **3** to the corresponding 1-naphthylmethanethiols (**4**). A mixture of **3** (30 mmol) and thiourea (30 mmol) in 15 mL of 95% ethanol was refluxed for 2 h. At the end of that time 5 mL of 9.5 N aqueous sodium hydroxide was added, and refluxing was continued for an additional hour under a nitrogen atmosphere. Except for the case of **4c**, where the workup procedure of Strating et al.[5] was used, the thiol (**4**) was isolated by removal of the solvents from the final reaction mixture under reduced pressure, addition of a small amount of water to the residue, acidification of the aqueous layer to pH 2 by addition of 4 M sulfuric acid, and extraction with benzene to separate the thiol. Removal of the benzene from the extract gave quite pure **4** (≥90%) as judged by ^{1}H NMR spectroscopy.

1-Naphthylmethanethiol (4a) was obtained in 67% yield as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.84 (t, 1 H), 4.12 (d, 2 H), 7.3–8.1 (m, 7 H).

(2-Methyl-1-naphthyl)methanethiol (4b), isolated in 80% yield, was also an oil at room temperature: ^{1}H NMR ($CDCl_3$) δ 1.73 (t, 1 H), 2.54 (s, 3 H), 4.18 (d, 2 H), 7.27–8.10 (m, 6 H).

(2-Methoxy-1-naphthyl)methanethiol (4c). Crystallization of the product from aqueous methanol gave **4c** (78%): mp 76–77 °C (lit.[5] mp 75–76 °C); ^{1}H NMR ($CDCl_3$) δ 1.64 (t, 1 H), 3.95 (s, 3 H), 4.16 (d, 2 H), 7.10–7.95 (m, 6 H).

(4-Methoxy-1-naphthyl)methanethiol (4d) was isolated in 55% yield as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.85 (t, 1 H), 3.98 (s, 3 H), 4.15 (d, 2 H), 6.72 (d, 1 H), 7.25–7.62 (m, 3 H), 8.02 (d, 1 H), 8.31 (d, 1 H).

Conversion of 4 to 5. The general procedure for conversion of the 1-naphthylmethanethiols (**4**) to β-((1-naphthylmethyl)-thio)propionitriles (**5**) was as follows. A solution of 0.42 g (8 mmol) of acrylonitrile in 4 mL of benzene was added dropwise to a stirred solution of **4** (5.7 mmol) and two drops of Triton B in 10 mL of benzene at a rate such that the temperature of the solution did not rise above 45 °C. The reaction mixture was then left overnight at room temperature. The basic Triton B catalyst was removed by washing the benzene solution with dilute acid. The benzene solution was then dried ($MgSO_4$) and concentrated under reduced pressure. The residue of **5** so obtained, if solid, was purified by dissolving it in diethyl ether at room temperature and cooling the solution to −20 to −30 °C. Isolated yields of pure **5** were generally from 75–80%.

β-((1-Naphthylmethyl)thio)propionitrile (5a) was an oil at room temperature: ^{1}H NMR ($CDCl_3$) δ 2.46 (t, 2 H), 2.66 (t, 2 H), 4.22 (s, 2 H), 7.36–8.15 (m, 7 H); IR (neat) 2240 cm^{-1} (CN). Its purity was judged to be ≥90% from the ^{1}H NMR spectral determination.

β-(((2-Methyl-1-naphthyl)methyl)thio)propionitrile (5b): mp 77–78 °C; ^{1}H NMR ($CDCl_3$) δ 2.5 (t overlapping with a singlet, 5 H), 2.85 (t, 2 H), 4.33 (s, 2 H), 7.25–8.15 (m, 6 H); IR (Nujol) 2240 cm^{-1} (CN). Anal. Calcd for $C_{15}H_{15}NS$: C, 74.64; H, 6.27. Found: C, 74.94; H, 6.43.

β-(((2-Methoxy-1-naphthyl)methyl)thio)propionitrile (5c): mp 47–48 °C (lit.[5] mp 45–46 °C); ^{1}H NMR ($CDCl_3$) δ 2.66 (overlapping t, 4 H), 3.98 (s, 3 H), 4.28 (s, 2 H), 7.25–8.05 (m, 6 H); IR (Nujol) 2240 cm^{-1} (CN).

β-(((4-Methoxy-1-naphthyl)methyl)thio)propionitrile (5d): mp 46–47 °C; ^{1}H NMR ($CDCl_3$) δ 2.46 (t, 2 H), 2.67 (t, 2 H), 3.99 (s, 3 H), 4.18 (s, 2 H), 6.72 (d, 1 H), 7.26 (d, 1 H), 7.46–7.61 (m, 3 H), 8.05 (d, 1 H), 8.31 (d, 1 H); IR (Nujol) 2240 cm^{-1} (CN). Anal. Calcd for $C_{15}H_{15}ONS$: C, 70.00; H, 5.88. Found: C, 70.07; H, 5.94.

Synthesis of β-(((3-Nitro-1-naphthyl)methyl)thio)-propionitrile (5e). 3-Nitro-1-(bromomethyl)naphthalene was prepared from 3-nitro-1,8-naphthalic anhydride (Aldrich) via a four-step reaction sequence.

3-Nitro-1,8-naphthalic anhydride (21.8 g, 90 mmol) was dissolved in 550 mL of water containing 14.4 g of sodium hydroxide. To the resulting solution was added a solution prepared by dissolving 25.1 g of yellow mercuric oxide in a mixture of 75 mL of water and 25 mL of glacial acetic acid. The mixture was refluxed for 4 days, cooled, and then filtered to isolate the mercurated product. The mercurated product was washed with cold water and dried at 50–60 °C. The mercurated product (36 g) was then refluxed in 700 mL of 5 M HCl for 3 h, and the cream-colored precipitate was filtered off, washed with cold water, dried, and recrystallized from hot acetic acid, giving 12 g (64%) of 3-nitro-1-naphthoic acid, mp 271–272 °C (lit.[21] mp 270.5–271.5 °C).

The 3-nitro-1-naphthoic acid was dissolved in 1,2-dimethoxyethane and treated with excess ethereal diazomethane. The solvents were removed under reduced pressure, and the residue was crystallized from methylene chloride–petroleum ether, giving methyl 3-nitro-1-naphthoate, mp 139–140 °C (lit.[22] mp 139–141 °C) in 90% yield.

The methyl ester was then reduced to 3-nitro-1-naphthyl carbinol by the procedure described by Dixon et al.[23] with some modifications. Lithium aluminum hydride (1.6 g, 0.042 mol) was suspended in 40 mL of anhydrous diethyl ether. Anhydrous $AlCl_3$ (5.6 g, 0.042 mmol) in 65 mL of anhydrous ether was added quickly to the vigorously stirred suspension (*caution*: very energetic reaction). A suspension of 4.0 g (17.3 mmol) of methyl 3-nitro-1-naphthoate in 75 mL of ether was then added dropwise over 15 min, and the mixture was stirred for an additional 10–15 min following the completion of the addition. Ice-cold water (75 mL) was added cautiously to the mixture with external cooling. The aqueous and organic layers were separated, and the aqueous layer was extracted with a mixture of ethyl acetate and methanol. The combined organic layers were concentrated to dryness, and the residue was crystallized from ligroin–benzene 9:1, giving 2.5 g (67%) of 3-nitro-1-naphthyl carbinol, mp 132–133 °C (lit.[23] mp 132–134 °C).

3-Nitro-1-naphthyl carbinol (4.75 g, 21.9 mmol) was dissolved with warming in 200 mL of anhydrous benzene, and 4.8 mL of phosphorus tribromide (26.3 mmol) was added, followed by the addition of a few drops of anhydrous pyridine. The mixture was stirred for 1 h at room temperature and then poured onto ice. The benzene layer was separated, and the aqueous phase was extracted with benzene. The combined organic layer was washed sequentially with water, cold dilute sodium bicarbonate, and water. It was dried over $MgSO_4$, and the solvent was removed, giving 4.34 g (75%) of 3-nitro-1-(bromomethyl)naphthalene, mp 148–149 °C (lit.[6] mp 149–151.5 °C).

Nitrile **5e** was synthesized by reaction of 3-nitro-1-(bromomethyl)naphthalene with β-mercaptopropionitrile. β-Mercaptopropionitrile[24] (1.74 g, 20 mmol) was dissolved under nitrogen in a mixture of dimethyl sulfoxide (60 mL) and aqueous sodium hydroxide (0.73 g NaOH in 5 mL of H_2O). To this was added a solution of 4.83 g (18.3 mmol) of 3-nitro-1-(bromomethyl)-naphthalene in 20 mL of dimethyl sulfoxide. The mixture was stirred at room temperature under nitrogen for 20 min, poured into 250 mL of water, and stirred vigorously for 0.5 h. The resulting precipitate was filtered off, washed with water, and air-dried. Recrystallization from diethyl ether gave 3.9 g (80%) of **5e**: mp 127–129 °C; ^{1}H NMR ($CDCl_3$) δ 2.65 (t, 2 H), 2.78 (t, 2 H), 4.34 (s, 2 H), 7.65–7.84 (m, 2 H), 8.05 (d, 1 H), 8.20 (d, 2 H), 8.76 (s, 1 H); IR (Nujol) 2240 (CN), 1530 and 1345 cm^{-1} (NO_2). Anal. Calcd for $C_{14}H_{12}N_2O_2S$: C, 61.75; H, 4.42. Found: C, 61.41; H, 4.72.

Conversion of 5 to 6. The following general procedure was used. To an ice-cold solution of **5** (2.84 mmol) in 6 mL of glacial acetic acid was added 1.0 g of 30% hydrogen peroxide. (In the

(19) Gonzalez-Trigo, G.; Alvarez-Builla, J.; de la Cuesta Elosequi, E. *Annales de Quimica* **1979**, *75*, 765.
(20) Marchini, P.; Belleau, B. *Can. J. Chem.* **1958**, *36*, 581.
(21) Leuck, G. J.; Perkins, R. P.; Whitmore, F. C. *J. Am. Chem. Soc.* **1929**, *51*, 1831.
(22) Adcock, N.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1967**, *89*, 386.
(23) Dixon, E. A.; Fischer, A.; Robinson, F. P. *Can. J. Chem.* **1981**, *59*, 2629.
(24) Welsh, T. L. *J. Org. Chem.* **1961**, *26*, 1443.

case of **5e** its lower solubility required the use of 19 mL of acetic acid, and slightly more, 1.23 g, of 30% H_2O_2). After 2 days (4 days in the case of **5e**) a crystalline product (**6**) had separated. This was filtered off and recrystallized from ethyl alcohol. The yields of **6** obtained after recrystallization ranged from 65 to 75%.

β-((1-Naphthylmethyl)sulfonyl)propionitrile (6a): mp 143–144 °C; IR (Nujol) 2240 (CN), 1320 and 1130 cm^{-1} (SO_2). Anal. Calcd for $C_{14}H_{13}NO_2S$: C, 64.84; H, 5.05. Found: C, 64.60; H, 5.09.

β-(((2-Methyl-1-naphthyl)methyl)sulfonyl)propionitrile (6b): mp 192–193 °C; IR (Nujol) 2240 (CN), 1290 and 1130 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.68 (s, 3 H), 2.77 (t, 2 H), 3.20 (t, 2 H), 5.00 (s, 2 H), 7.40–8.10 (m, 6 H). Anal. Calcd for $C_{15}H_{15}NO_2S$: C, 65.90; H, 5.53. Found: C, 66.00; H, 5.65.

β-(((2-Methoxy-1-naphthyl)methyl)sulfonyl)propionitrile (6c): mp 132–133 °C (lit.[5] mp 131–132 °C); IR (Nujol) 2240 (CN), 1300 and 1130 cm^{-1} (SO_2).

β-(((4-Methoxy-1-naphthyl)methyl)sulfonyl)propionitrile (6d): mp 141–142 °C; IR (Nujol) 2240 (CN), 1310 and 1110 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.73 (t, 2 H), 3.15 (t, 2 H), 4.04 (s, 3 H), 4.79 (s, 2 H), 6.80 (d, 1 H), 7.51–7.70 (m, 3 H), 8.01 (d, 1 H), 8.37 (d, 1 H). Anal. Calcd for $C_{15}H_{15}NO_3S$: C, 62.26; H, 5.22. Found: C, 62.37; H, 5.25.

β-(((3-Nitro-1-naphthyl)methyl)sulfonyl)propionitrile (6e): mp 224–225 °C; IR (Nujol) 2260 (CN), 1540 and 1340 (NO_2), 1300 and 1130 cm^{-1} (SO_2); ^1H NMR (acetone-d_6) δ 3.14 (t, 2 H), 3.76 (t, 2 H), 5.31 (s, 2 H), 7.73–7.92 (m, 2 H), 8.34 (d, 1 H), 8.47 (m, 2 H), 9.00 (s, 1 H). Anal. Calcd for $C_{14}H_{12}N_2O_4S$: C, 55.25; H, 3.97. Found: C, 55.34; H, 4.01.

Conversion of 6 to Methyl 1-Naphthylmethanesulfinates (2). The procedure employed was as follows. A methanol solution of sodium α-toluenethiolate was prepared under nitrogen by adding 12.5 mmol of $PhCH_2SH$ (Aldrich) to 25 mL of methanol containing 12.5 mmol of sodium methoxide. A suspension of 12.5 mmol of the sulfonylpropionitrile (**6**) in 20 mL of methanol was then added to this in one portion, and the resulting reaction mixture was heated for 0.5 h, by which time a homogeneous solution was obtained. The solvent was then removed under reduced pressure, and the residue was washed with 30 mL of diethyl ether before being dissolved in a mixture of 25 mL of water and 15 mL of methanol. This solution was extracted first with ether (25 mL) and then with 40–60 °C petroleum ether (15 mL). It was then cooled in ice and acidified with *cold* 4 M sulfuric acid. The precipitate of the 1-naphthylmethanesulfinic acid (**7**) that formed was filtered off and dried, either under vacuum or between filter papers under pressure. After drying it was immediately subjected to the esterification procedure outlined below.

Depending upon its solubility, the freshly prepared sulfinic acid (**7**) was dissolved either in diethyl ether, 1,2-dimethoxyethane, or a mixture of the two solvents. Ethereal diazomethane (generated from Diazald) was added to the cooled sulfinic acid solution until a yellow color persisted. The solvent was then removed under reduced pressure, and the crude methyl 1-naphthylmethanesulfinates (**2**) were purified as outlined below:

Methyl 1-naphthylmethanesulfinate (2a) was purified by flash chromatography with 10:1 CH_2Cl_2/EtOAc as eluent: mp 106–108 °C; IR (Nujol) 1110 cm^{-1} (S=O); ^1H NMR ($CDCl_3$) δ 3.73 (s, 3 H) 4.48 (quartet, 2 H), 7.49–8.10 (m, 7 H). Anal. Calcd for $C_{12}H_{12}O_2S$: C, 65.44; H, 5.49. Found: C, 65.70; H. 5.56.

Methyl (2-methyl-1-naphthyl)methanesulfinate (2b) was purified by flash chromatography with 13:1 CH_2Cl_2/EtOAc as eluent: mp 64–65 °C; IR (Nujol) 1110 cm^{-1} (S=O); ^1H NMR ($CDCl_3$) δ 2.60 (s, 3 H) 3.70 (s, 3 H), 4.59 (quartet, 2 H), 7.32–8.10 (m, 6 H). Anal. Calcd for $C_{13}H_{14}O_2S$: C, 66.65; H, 6.02. Found: C, 66.44; H, 6.07.

Methyl (2-methoxy-1-naphthyl)methanesulfinate (2c) was purified by flash chromatography with 10:1 CH_2Cl_2/EtOAc as eluent: mp 57–58 °C; IR (Nujol) 1110 cm^{-1} (S=O); ^1H NMR ($CDCl_3$) δ 3.71 (s, 3 H), 4.00 (s, 3 H), 4.58 (quartet, 2 H), 7.27–8.07 (m, 6 H). Anal. Calcd for $C_{13}H_{14}O_3S$: C, 62.39; H, 5.64. Found: C, 62.24; H, 5.70.

Methyl (4-methoxy-1-naphthyl)methanesulfinate (2d) was purified by flash chromatography with 16:1 CH_2Cl_2/EtOAc as eluent. The purified material solidifies at −70 °C but liquifies on warming to room temperature: IR (neat) 1110 cm^{-1} (S=O); ^1H NMR ($CDCl_3$) δ 3.73 (s, 3 H), 4.00 (s, 3 H), 4.38 (quartet, 2 H), 6.80 (d, 1 H), 7.36–7.62 (m, 3 H), 7.96 (d, 1 H), 8.33 (d, 1 H). Anal. Calcd for $C_{13}H_{14}O_3S$: C, 62.39; H, 5.64. Found: C, 61.87; H, 5.79.

Methyl (3-Nitro-1-naphthyl)methanesulfinate (2e). The product after removal of the solvent was found to be pure by TLC (CH_2Cl_2/MeOH, 6:1): mp 92–94 °C; IR (Nujol) 1530 and 1340 (NO_2), 1110 cm^{-1} (S=O); ^1H NMR ($CDCl_3$) δ 3.77 (s, 3 H), 4.54 (quartet, 2 H), 7.66–7.84 (m, 2 H), 8.08–8.20 (m, 2 H), 8.27 (s, 1 H), 8.81 (s, 1 H). Anal. Calcd for $C_{12}H_{11}NO_4S$: C, 54.33; H, 4.18. Found: C, 54.30; H, 4.49.

Preparation of 2-Methoxynaphthalene-1-thiocarbaldehyde *S*-Oxide (8). This was prepared according to the procedure described by Strating *et al.*[5] Purification of the crude product was accomplished by flash chromatography rather than by recrystallization because of the considerable loss of product that accompanies the latter procedure: ^1H NMR ($CDCl_3$) δ 10.61 (s, 1 H), 7.26–8.00 (m, 6 H), 4.16 (s, 3 H); UV (CD_3OD) λ_{max} 398 nm ($\epsilon = 1.4 \times 10^4$).

Kinetics of the Disappearance of the $CH_3OS(O)$ and $CH_2S(O)$ Signals of 2 in the ^1H NMR Spectrum. Each of the methyl 1-naphthylmethanesulfinates (**2**) has a singlet, due to the $CH_3OS(O)$ protons, in the region δ 3.70–3.77 and a quartet, resulting from the diastereotopic $CH_2S(O)$ group, in the region δ 4.38–4.59. In CD_3OD upon addition of CD_3O^- these two signals decrease in intensity and eventually disappear, although not at the same rate. The disappearance of both these signals was monitored by measuring their integrated intensity relative to that of an internal standard as a function of time. The internal standard was a measured amount of cyclohexane (δ 1.43) that was added to the solution of the ester in CD_3OD prior to the addition of any methoxide ion.

The specific procedure for the kinetic runs was as follows. The desired amount of sulfinate ester (**2**) was weighed out and dissolved in 0.86–0.98 mL of methanol-d_4. To this was then added 10 μL of a stock solution of cyclohexane in CD_3OD. The solution was placed in an NMR tube in the thermostated probe of a Chemagnetics A200 NMR spectrometer, and the reactions leading to the disappearance of the $CH_3OS(O)$ and $CH_2S(O)$ NMR signals were initiated by the addition of an amount (5–150 μL) of a stock solution of CD_3ONa (0.10–0.65 M) in CD_3OD that would give the concentration of CD_3O^- desired for a particular run. At appropriate time intervals after the initiation of the reaction, spectra were obtained and stored. After sufficient time both the singlet in the region δ 3.70–3.77 and the quartet centered in the region δ 4.38–4.59 disappeared completely. A plot of log (I/I_o) vs time was made for each signal, where I and I_o are the integrated intensities of the particular signal relative to the internal standard at times t and zero, respectively. The experimental first-order rate constant for the disappearance of the signal (k_1) was then evaluated from the slope of this plot. In cases where the rates of disappearance of the $CH_3OS(O)$ and $CH_2S(O)$ signals are reasonably comparable, data for both reactions could be obtained from a run at a given $[CD_3O^-]$. In cases where the $CH_3OS(O)$ signal disappears much faster than the $CH_2S(O)$ signal, it was necessary to use runs with considerably higher $[CD_3O^-]$ than those used for measuring k_1 for the disappearance of the $CH_3OS(O)$ signal in order to determine k_1 for the disappearance of the $CH_2S(O)$ signal accurately.

Reaction of 8a with Methoxide Ion. Kinetics. To 3.0 mL of CD_3OD in a 1-cm spectrophotometer cell was added 25 μL of a 0.009 16 M solution of **8a** in CD_3OD. Such a solution has a long wavelength maximum at 398 nm (ϵ = 14 000) due to **8a**. To this was then added an amount of a 1.44 M solution of CD_3O^- in CD_3OD sufficient to give the concentration of CD_3O^- desired (0.03–0.05 M) for a particular run, and the decrease in the absorbance (A) of the solution at 398 nm was followed with time. Experimental first-order rate constants (k_1) were evaluated from the slope of a plot of log $(A - A_\infty)$ vs time. The second-order rate constant, $k_1/[CD_3O^-]$, was independent of $[CD_3O^-]$.

Products. A solution containing 1 mmol of **8a** in 10 mL of methanol was mixed with one containing 1 mmol of methoxide in 10 mL of the same solvent, and the resulting solution was stirred under nitrogen at room temperature for 1 h. At the end of that time the solvent was removed under reduced pressure, the residue was treated with a little water, the water was acidified to pH 4–5 with dilute HCl, and the mixture was extracted with methylene

chloride. The methylene chloride extracts were dried over $MgSO_4$, concentrated, and purified by preparative TLC. The major product (R_f = 0.68) isolated was a slightly impure sample, mp 73–75 °C, of 2-methoxy-1-naphthaldehyde (**9a**) whose ^1H NMR ($CDCl_3$) and IR (Nujol) spectra were identical with those of a known sample (Aldrich) of this aldehyde. There was no evidence for the formation of any **2a** upon treatment of **8a** with an equimolar amount of methoxide ion.

Formation of 8a from 2a in CD_3O^-/CD_3OD. An amount of a 1.44 M solution of CD_3O^- in methanol-d_4 sufficient to give the desired concentration (0.03–0.05 M) of CD_3O^- was added to 3.0 mL of CD_3OD contained in a 1-cm cell in the thermostated cell compartment of a UV/visible spectrophotometer. After the solution had reached thermal equilibrium, a 25-μL aliquot of a 0.009 16 M stock solution of **2a** in CD_3OD was added by microsyringe with good mixing, and the absorbance of the solution was monitored as a function of time at 398 nm, the wavelength where **8a** has its long-wavelength maximum. The absorbance at 398 nm first increased from 0.00 to about 0.06 and then declined. The maximum absorbance achieved was independent of $[CD_3O^-]$, but the time to reach the maximum was not, being shorter the higher the concentration of CD_3O^-. The data were analyzed using the expressions[9] for the behavior of the concentration of an intermediate during two consecutive pseudo-first-order reactions.

Supplementary Material Available: Tabulation of the results of individual kinetic runs for the disappearance of the ^1H NMR signals for the $CH_3OS(O)$ and $CH_2S(O)$ protons in **2** (Table III) and ^1H NMR spectra for **4a, 4b, 4d,** and **5** (6 pages). Ordering information is given on any current masthead page.

Competition between Birch Reduction and Bond Cleavage in 1,2-Bis(4-methyl-1-naphthyl)ethane

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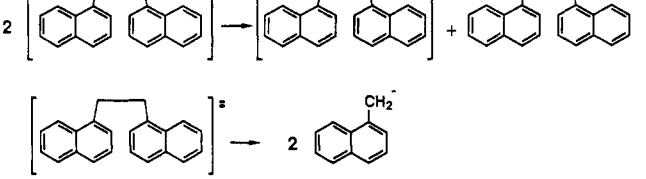
The reaction of 1,2-bis(4-methyl-1-naphthyl)ethane with Li, Na, and K in ammonia, THF, and HMPA, or mixtures thereof, has been examined with respect to the factors favoring Birch reduction of the aromatic ring and cleavage of the ethane carbon–carbon bond. Bond cleavage was found to increase relative to ring reduction in the series Li < Na < K and with the solvents NH_3 < THF < HMPA. However, the latter position of ammonia may be due to the necessarily restricted low-reaction temperature since only ring reduction was observed at temperatures at or below the boiling point of ammonia (–33 °C). A number of reduction and cleavage products were isolated and identified, and the mechanistic pathways for their formation is discussed.

A discussion of the cleavage of 1,2-diarylethanes by alkali metals, together with a historical perspective, has been provided recently by Grovenstein et al.[2] Pentaphenyl-

$$Ar_nCH_m\text{–}CH_{m'}Ar_{n'} \xrightarrow{M} Ar_nCH_m^- M^+ + Ar_{n'}CH_{m'}^- M^+$$

ethane is cleaved[3] by potassium sand in ether[3] while 1,1,2,2-tetraphenylethane may be cleaved with Na–K alloy.[4] 1,2-Diphenylethane, on the other hand, is not reactive under these conditions.[5] As noted by Grovenstein,[2] the ease of cleavage increases with increasing number of aryl groups and/or increasing stabilization of the cleavage products (benzyl anions). This was also demonstrated by Eisch[6] who found 1,1,2,2- and 1,1,1,2-tetraphenylethane to be cleaved by lithium–biphenyl in THF while 1,1,1-triphenylethane was unreactive. However, 1,2-diphenylethane reacts with Na–K alloy in glyme–triglyme at 0 °C, and so solvaton effects are also expected to be important.[5] Grovenstein also points out that cleavage of 1,2-diarylethanes should increase throughout the series aryl = anthracene < naphthalene < benzene due to the corresponding decrease in π-resonance energies between the radical anions (or dianions) and the respective arylmethyl anions.

Although the identification of the actual intermediate undergoing cleavage has been addressed in several investigations, radical anions have often been suggested without detailed kinetic evidence.[2] Szwarc et al.[8] studied the cleavage of 1,2-bis(1-naphthyl)ethane and found a rate law second order in the radical anion (at least for Li^+, Na^+, and K^+). This is consistent with the dianion as the species



undergoing cleavage. Groverstein[2] studied a number of 1,2-diarylethanes and also concluded the dianion to be the responsible intermediate. Moreover, he suggested the importance of a stereoelectronic effect that involves the alignment of the p orbitals of the benzene rings with the sp^3–sp^3 bond so as to allow interaction with the σ orbitals (this also allows maximum overlap with the developing, benzylic anionic center).

Thus it appears that dianions are the likely intermediates undergoing cleavage in the treatment of 1,2-diarylethanes with alkali metals. However, radical anions appear to play an important role in the similar reaction of diarylmethanes where sp^2–sp^3 bonds are undergoing

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(2) Grovenstein, E., Jr.; Bhatti, A. M.; Quest, D. E.; Sengupta, D.; VanDerveer, D. *J. Am. Chem. Soc.* **1983**, *105*, 6290.
(3) Bachmann, W. E. *J. Am. Chem. Soc.* **1933**, *55*, 3005.
(4) Ziegler, K.; Thielmann, F. *Chem. Ber.* **1953**, *56*, 1740.
(5) Conant, J. B.; Garvey, B. S., Jr. *J. Am. Chem. Soc.* **1927**, *49*, 2599.
(6) Eisch, J. J. *J. Org. Chem.* **1963**, *28*, 707.
(7) Collins, C. J.; Hombach, H.-P.; Maxwell, B.; Woody, M. C.; Benjamin, B. M. *J. Am. Chem. Soc.* **1980**, *102*, 851. Collins, C. J.; Hombach, H.-P.; Maxwell, B. E.; Benjamin, B. M.; McKamey, D. *J. Am. Chem. Soc.* **1981**, *103*, 1213.
(8) Lagendijk, A.; Szwarc, M. *J. Am. Chem. Soc.* **1971**, *93*, 5359.

0022-3263/89/1954-3602$01.50/0