are 1.50 and 1.69 Å at the sites of the complexes A and B, respectively. Although these values are intermediate between those of **1** and **3**, they are closer to those of **3**, indicating that the van der Waals interaction between 12-crown-4 molecules and γ-CDs of **2** is comparable to that of **3**.

The bond distances of K^+–O are 2.80 (8) and 2.99 (9) Å at the sites of the complexes A and B, respectively. The average value of these bond distances is almost normal compared with the K^+–O distances of 2.77–2.83 Å in the (18-crown-6)·KSCN complexes.[21]

The (12-crown-4)$_2$·cation complex in **2** has an approximate S_8 symmetry, while that in **1** has an approximate D_4 symmetry. In **2**, the chirality of the 12-crown-4 ring in the complex A is opposite to that in the complex B in spite of the same chirality of the two γ-CDs. Since the γ-CD A is in a near cylindrical form and γ-CD B has a more cone-like structure in both **1** and **2**, van der Waals interactions between the 12-crown-4 molecules and the γ-CDs in the complexes A and B differ. In **2**, where the 12-crown-4 molecule of the complex B is deeply included in the cavity of the γ-CD B because of the large diameter of K^+, the closer contacts between the 12-crown-4 molecule and the γ-CD B may be the reason why the chirality of the 12-crown-4 molecules of the complex B is inverted with respect to that in **1**.

Conclusion

It is confirmed by this X-ray study that cations can exist in hydrophobic environment by forming the inclusion complexes between the crown ethers·cation complexes and γ-CDs.

The interactions between 12-crown-4 molecules and γ-CDs affect the cation–oxygen distances of the 12-crown-4·cation complexes and the chirality of 12-crown-4 molecules. Thus, each 12-crown-4 molecule suffers from particular constraints depending on the geometry of γ-CD which includes it. This is reflected in the location and the orientation of the guest molecule in the cavity and also influences the structures of 12-crown-4·cation complexes.

These inclusion complexes might be able to exhibit ion selectivity because of the complicated interaction among cations, crown ethers, and CDs. Since in **1** unusually long distances of Li^+–O and few short contacts between 12-crown-4 and γ-CD molecules are found, while in **2** normal K^+–O distances and many short contacts to γ-CDs are found, we assume that the former would be less stable than the latter. The present X-ray results suggest that the cation diameter of K^+ is just small enough that complexes with 12-crown-4 fit into the cavities of γ-CD.

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Supplementary Material Available: Tables of complete bond distances and bond angles for **1** and **2** (8 pages); listing of observed and calculated structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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Elimination Reactions of Alkanesulfinyl Derivatives: Mechanism and Reactivity in Base-Induced Sulfine Formation from Methyl Diarylmethanesulfinates

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Abstract: Upon treatment in methanol at room temperature with methoxide ion methyl diarylmethanesulfinates, ArAr′CHS(O)OCH$_3$ (**1**), and methyl 9-fluorenesulfinate (**2**) undergo elimination readily to afford the corresponding sulfines (**3** and **4**) in quantitative yield. Studies in CD_3O^-/CD_3OD show that, surprisingly, elimination of **1** to give **3** is significantly faster than nucleophilic substitution by methoxide ion at the sulfinyl group (exchange of CH_3O by CD_3O). Even more unexpected, the kinetic isotope effect for elimination of **2**-*9-d* (k_H/k_D = 6.1) and the absence of detectable H/D exchange of the methine proton of **1** in CD_3OD prior to sulfine formation establish that, even though the leaving group is MeO^-, the elimination takes place by either an irreversible ElcB or an E2 mechanism, rather than the reversible ElcB mechanism found (ref 4 and 7) for the analogous sulfene-forming elimination of arylmethanesulfonate esters with oxyanion leaving groups of comparable pK_a. Reaction of amines with **2** in methanol also gives sulfine **4**, and the amine-induced elimination, which has a large Brønsted β, also proceeds by either an $(ElcB)_{irrev}$ or an ElcB-like E2 mechanism. Why sulfine-forming eliminations of **1** and **2** favor an $(ElcB)_{irrev}$ or E2 mechanism whereas sulfene-forming eliminations of arylmethanesulfonates with even better leaving groups proceed by an $(E1cB)_{rev}$ mechanism is considered and a possible explanation presented.

Base-induced eliminations of sulfinyl compounds leading to the formation of sulfines ($B^- + >CHS(O)Y \rightarrow BH + >C{=}S{=}O + Y^-$) have been known since 1964.[2,3] For analogous *sulfene*-forming eliminations of alkanesulfonyl derivatives ($B^- + >CHS(O)_2Y \rightarrow BH + >C{=}SO_2 + Y^-$), considerable information is available,[4-8] regarding the effect of various parameters (nature of B^-, Y, and structure of the alkanesulfonyl group) on rate of elimination, competition between elimination and substitution at

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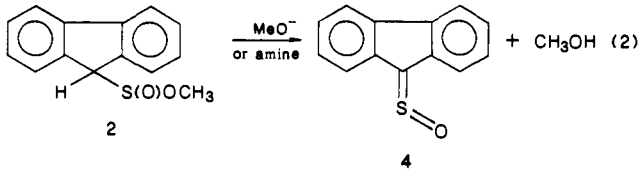
SO_2, and the exact mechanism (E2, $ElcB_{irrev}$, or $ElcB_{rev}$) used for elimination. In contrast, essentially nothing of this kind is known about sulfine-forming eliminations.

The objective of the present work was to rectify this situation. To this end we have examined the facile, methoxide-induced elimination (eq 1) of a series of methyl diarylmethanesulfinates (**1**) and a similar elimination (eq 2) of methyl 9-fluorenesulfinate (**2**) induced by either amines or methoxide ion. These reactions, which afford the sulfines in quantitative yield, are tailor-made

$$ArAr'CHS(O)OCH_3 \xrightarrow[MeOH]{MeO^-} ArAr'C{=}S{=}O + CH_3OH \quad (1)$$

1a: Ar = *p*-ClC_6H_4; Ar' = *p*-ClC_6H_4
1b: Ar = *p*-ClC_6H_4; Ar' = C_6H_5
1c: Ar = C_6H_5; Ar' = C_6H_5
1d: Ar = *p*-$CH_3C_6H_4$; Ar' = C_6H_5
1e: Ar = *p*-$CH_3OC_6H_4$; Ar' = C_6H_5
1f: Ar = *p*-$CH_3OC_6H_4$; Ar' = *p*-$CH_3OC_6H_4$



2 4 + CH_3OH (2)

for straightforward investigation of mechanism and reactivity. Quantitative comparison of the rate of elimination and the rate of direct substitution by the nucleophile (base) at the sulfinyl group of **1** is also possible via measurement of the rate of exchange of the ester methoxy group in CD_3O^-/CD_3OD ($ArAr'CHS(O)OCH_3 + CD_3O^- \rightarrow ArAr'CHS(O)OCD_3 + CH_3O^-$).

Comparison of the behavior of eq 1 and 2 with the results of earlier studies[4,7] of *sulfene*-forming eliminations of aryl arylmethanesulfonates ($ArCH_2SO_2OAr'$) reveals that eliminations of alkanesulfinates and alkanesulfonates exhibit significant, and unexpected, differences in mechanism.

Results

The various methyl diarylmethanesulfinates (**1a**–f, **2**) were synthesized by esterification of the corresponding sulfinic acids with diazomethane in ether ($ArAr'CHSO_2H + CH_2N_2 \rightarrow ArAr'CHS(O)OCH_3 + N_2$). The sulfinic acids were obtained by acidification of solutions of their sodium and potassium salts.

Treatment of 9-thiofluorenone *S*-oxide (**4**) with potassium hydroxide in ethanol gave potassium 9-fluorenesulfinate in good yield. However, similar treatment of the other sulfines (**3a–f**) failed to give satisfactory yields of potassium diarylmethanesulfinates. These therefore had to be prepared by other routes. Except for the di-*p*-methoxy compound this was done by forming an *S*-benzyl diarylmethanethiosulfonate (**5**) through reaction of α-toluenethiol and sulfur dioxide with the appropriate diaryldiazomethane (eq 3a)[9] and then reacting the thiosulfonate with the anion of α-toluenethiol (eq 3b).[10a]

$$ArAr'C{=}N_2 \xrightarrow[PhCH_2SH]{SO_2} ArAr'CH(SO_2SCH_2Ph) \quad (3a)$$

5

$$ArAr'CHSO_2SCH_2Ph + PhCH_2S^- \rightarrow ArAr'CHSO_2^- + PhCH_2SSCH_2Ph \quad (3b)$$

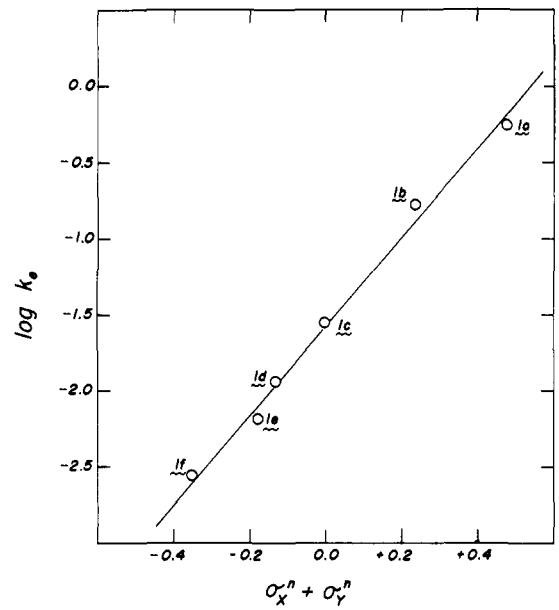


Figure 1. Plot of log k_e for $CH_3OS(O)CH(C_6H_4Y)C_6H_4X$ vs. $(\sigma_x^n + \sigma_y^n)$ for the sulfine-forming elimination of **1** with methoxide ion in methanol at 25 °C. Slope, ρ, equals +2.8.

Because reaction 3a fails when Ar = Ar' = *p*-$CH_3OC_6H_4$, sodium 4,4'-dimethoxydiphenylmethanesulfinate could not be synthesized by the route shown in eq 3. It was generated instead by treatment of β-(4,4'-dimethoxydiphenylmethanesulfonyl)-propionitrile, $(p\text{-}CH_3OC_6H_4)_2CHSO_2CH_2CH_2CN$ (**6**), with base. This is the type of elimination first described by Truce and Roberts[10b] and used by Zwanenburg et al.[10a] to prepare sodium 9-fluorenesulfinate from β-(9-fluorenesulfonyl)propionitrile. Compound **6** was synthesized by addition of 4,4'-dimethoxydiphenylmethanethiol to acrylonitrile followed by oxidation of the resulting sulfide to the sulfone.

Methoxide-Induced Formation of Sulfines from 1 and 2. Treatment of any of the methyl diarylmethanesulfinates (**1a**–f, **2**) with methoxide ion in methanol led to the appearance of a strong absorption maximum in the 320–360-nm region due to the formation of the corresponding sulfine (**3a**–f, **4**). The yield of sulfine, estimated from the optical density at λ_{max} and ϵ for the sulfine, was uniformly >95%. Confirmation of the high yield of sulfine was provided in selected cases by actual physical isolation of the sulfine from the reaction solution.

The kinetics of the methoxide ion induced formation of the sulfines from the methyl esters were studied at 25 °C in methanol over a range of methoxide ion concentrations. The reactions were followed by monitoring the increase with time in the optical density (A) at λ_{max} for the sulfine. Plots of log $(A_\infty - A)$ vs. time were linear in every case. The experimental first-order rate constants, k_{elim}, obtained from the slopes of the plots are shown in Table I. For each ester a plot of k_{elim} vs. $[MeO^-]$ shows excellent linearity. The second-order rate constant, $k_e = k_{elim}/[MeO^-]$, for sulfine formation, obtained from the slope of such a plot, is given for each ester.

Figure 1 shows a plot of log k_e for **1a**–f vs. $\Sigma\sigma^n$ for the substituents in the two aryl groups. The correlation is excellent (r = 0.995) with a slope, ρ, of +2.8. In a similar plot with regular σ constants an equally good correlation (r = 0.996; ρ = +2.8) obtains for esters **1a–e**, but the data point for ester **1f** shows a significant positive deviation from the correlation line for the other esters.

The data in Table I for 9-protio- and 9-deuterio-**2** reveal that there is a large kinetic isotope effect (k_H/k_D = 6.1) associated with the methoxide-induced formation of **4** from methyl 9-fluorenesulfinate.

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Table I. Kinetics of Mexthoxide-Induced Sulfine Formation from **1** and **2** in Methanol at 25 °C

sulfinate ester	10^5[ester]$_0$, M	10^2[MeO$^-$], M	$10^3 k_{elim}$, s^{-1}	$k_e = k_{elim}/$[MeO$^-$],[a] M^{-1} s^{-1}
1a	5.5	1.27	7.1	
		1.02	5.7	
		0.64	3.6	0.56
		0.55	2.9	
		0.26	1.46	
		0.13	0.75	
1b	8.2	5.0	8.4	
		4.0	6.8	
	5.2	3.0	4.8	
	8.2	2.2	3.6	0.17
	5.2	0.60	0.95	
	8.2	0.38	0.68	
		0.15	0.26	
		0.076	0.126	
1c	4.0	2.7	0.81	
		2.3	0.66	
		0.86	0.24	0.028
		0.31	0.084	
		0.28	0.077	
1d	5.8	5.7	0.67	
	7.2	5.0	0.58	
	5.7	3.8	0.44	0.0116
	7.3	2.9	0.33	
		1.0	0.12	
1e	6.2	6.9	0.45	
		5.8	0.38	
		3.4	0.22	
		3.1	0.21	0.0065
		1.9	0.12	
		1.25	0.082	
		0.53	0.034	
1f	5.0	22.8	0.62	
		16.2	0.45	
		12.4	0.34	
		6.5	0.19	0.0027
	10.0	4.6	0.125	
	5.0	3.6	0.089	
		2.7	0.069	
2	3.7	0.071	4.4×10^2	
		0.148	9.3×10^2	
		0.33	1.9×10^3	6.1×10^2
		0.66	4.0×10^3	
		1.26	7.8×10^3	
2-9-d	4.0	0.050	45	
		0.22	2.0×10^2	
		0.41	4.1×10^2	1.0×10^2
		0.62	6.2×10^2	
		0.81	8.3×10^2	

[a] Obtained from a plot of k_{elim} vs. [MeO$^-$].

Comparison of k_e for **1c** and **2** shows that the fluorenesulfinate undergoes elimination approximately 20000 times faster than the diphenylmethanesulfinate.

Competition between Methoxide-Induced Elimination and Substitution at Sulfinyl Sulfur. Quantitative comparison of the rate of methoxide-induced elimination of **1** and the rate of substitution of the same nucleophile at the sulfinyl group of the ester is possible by measurement of the rate of exchange of the methoxy group of the ester in CD_3O^-/CD_3OD (eq 4) under conditions where the rate of elimination of **1** to form **3** is also determined.

$$ArAr'CHS(O)OCH_3 + CD_3O^- \xrightarrow{k_s} ArAr'CHS(O)OCD_3 + CH_3O^- \quad (4)$$

In the ^{1}H NMR of each ester **1** there is a sharp singlet (δ 3.60–3.66) associated with the $CH_3OS(O)$ group. The rate of disappearance of this signal in the presence of CD_3O^- in CD_3OD at 25.5 °C was measured for **1c–f**. Since both exchange of CH_3O^- by CD_3O^- (eq 4; k_{sub}) and conversion of ester to sulfine (eq 1; k_{elim}) result in the loss of $CH_3OS(O)$ groups, the experimental first-order constants, shown in the third column of Table II, are equal to ($k_{sub} + k_{elim}$). Rates of sulfine formation (k_{elim}), shown in the fourth column, were measured simultaneously, these being determined for **1d–f** by using the shift in the position of the $CH_3C_6H_4$ or $CH_3OC_6H_4$ singlet that accompanies formation of sulfine from ester and for **1c** by monitoring the appearance of a signal (δ 7.65–7.9) in the aromatic proton region that is part of the ^{1}H NMR spectrum of sulfine **3c**. The accuracy of k_{elim} for **1c** as measured by this ^{1}H NMR procedure was confirmed by determining the rate of formation of the sulfine under the same conditions spectrophotometrically at 328 nm.

Both ($k_{sub} + k_{elim}$) and k_{elim} are, as expected, proportional to [CD_3O^-]. Second-order rate constants for eq 4, $k_s = k_{sub}/$[CD_3O^-], and for eq 1, $k_e = k_{elim}/$[CD_3O^-], are shown in columns 5 and 6 of Table II, and values of (k_s/k_e) are given in column 7. From these data it is evident that the rate of substitution (eq 4) is *slower* by a factor of from 3 to 7 (depending on the nature of Ar and Ar') than the rate of sulfine-forming elimination (eq 1).

Precise estimation of the solvent isotope effect for k_e is complicated by the fact that the rates in MeOD (Table II) are for 25.5 °C while those in MeOH (Table I) are for 25.0 °C. We assume for each ester that at 25.0 °C k_e is ~10% smaller than at 25.5 °C. With that assumption k_{MeOD}/k_{MeOH} for **1c–f** ranges from 2.5 to 2.7. From solvent isotope effect theory[11] $k_{MeOD}/k_{MeOH} = \phi_{\ddagger}^p/\phi_{OMe}^m$, where m and p are the number of methanol molecules specifically solvating methoxide ion and transition state, respectively, and ϕ_{OMe} and $\phi_{\ddagger}$ are their deuterium fractionation factors. It seems well established[11] that $m = 3$, and the current preferred[11c] value for ϕ_{OMe} is 0.70. The predicted *maximum* solvent isotope effect (either $\phi_{\ddagger} = 1.0$ or $p = 0$) for a reaction involving methoxide ion in methanol is therefore $(0.70)^{-3}$, or 2.9; k_{MeOD}/k_{MeOH} for eq 1 approaches this upper limit and is larger than the solvent isotope effects[11b,c] for most reactions involving methoxide ion.

The exchange of the methoxy group of methyl phenylmethanesulfinate (**7**) in CD_3O^-/CD_3OD (eq 5) was also examined kinetically. In this case the exchange (eq 5) occurs much faster

$$\underset{\mathbf{7}}{PhCH_2S(O)OCH_3} + CD_3O^- \xrightarrow{k'_s} PhCH_2S(O)OCD_3 + CH_3O^- \quad (5)$$

than any other reactions involving **7**. From ^{1}H NMR measurements the rate of disappearance of the singlet for the CH_3O, k'_s for eq 5, was found to be 0.40 M^{-1} s^{-1} at 25.5 °C, or ~40 times faster than the rate constant for the analogous exchange of **1c** with CD_3O^- (eq 4, Ar = Ar' = Ph).

Absence of Exchange of the Methine Proton of 1 Prior to Sulfine Formation. The ^{1}H NMR of each of the methyl diarylmethanesulfinates (**1**) has a singlet at δ ~5.0 due to the methine proton (>C*H*S(O)OMe). The disappearance of this signal was also monitored during each of the experiments in CD_3O^-/CD_3OD shown in Table II. Within experimental error the rate constant for loss of the methine proton signal was identical with the rate at which the ester underwent sulfine formation (k_{elim}). This shows that in CD_3O^-/CD_3OD exchange of the methine proton of the diarylmethanesulfinates prior to sulfine formation is not occurring to any significant extent, a result of significance with respect to the detailed mechanism for eq 1.

Amine-Induced Sulfine Formation from 2. Treatment of methyl 9-fluorenesulfinate (**2**) with a variety of amines in amine–amineH$^+$ buffers in methanol at 25 °C led to the formation of sulfine **4** in >95% yield. The only exception was 2,2,2-trifluoroethylamine where the yield of **4** was only 60%.

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Table II. Relative Rates of Substitution and Elimination in the Reaction of CD_3O^- with Methyl Diarylmethanesulfinates in CD_3OD at 25.5 °C[a]

ArAr'CHS(O)OCH$_3$		$10^2[CD_3O^-]$,	$10^3(k_{sub} + k_{elim})$,	10^3k_{elim},	$k_s = k_{sub}/[CD_3O^-]$,	$k_e = k_{elim}/[CD_3O^-]$,	
Ar	Ar'	M	s^{-1}	s^{-1}	M^{-1} s^{-1}	M^{-1} s^{-1}	(k_s/k_e)
C_6H_5	C_6H_5	0.30	0.302 ± 0.015	0.264 ± 0.010	0.0125	0.088	0.14
		0.79		0.67[b]		0.085[b]	
		1.03	0.942 ± 0.040	0.828 ± 0.034	0.011	0.080	0.14
		2.05	1.97 ± 0.09	1.73 ± 0.07	0.012	0.084	0.14
p-$CH_3C_6H_4$	C_6H_5	2.3	0.93 ± 0.06	0.73 ± 0.06	0.0089	0.032	0.28
		4.3	1.64 ± 0.11	1.33 ± 0.12	0.0074	0.031	0.24
		5.7	2.4 ± 0.14	1.89 ± 0.16	0.0083	0.033	0.25
p-$CH_3OC_6H_4$	C_6H_5	0.95	0.212 ± 0.015	0.161 ± 0.013	0.0054	0.017	0.32
		6.3	1.64 ± 0.11	1.33 ± 0.10	0.0049	0.020	0.25
		10.1	2.5 ± 0.1	1.9 ± 0.1	0.0055	0.019	0.29
p-$CH_3OC_6H_4$	*p*-$CH_3OC_6H_4$	5.0	0.54 ± 0.07	0.39 ± 0.03	0.0030	0.0078	0.38
		11.8	1.3 ± 0.1	0.98 ± 0.05	0.0026	0.0083	0.31
		18.5	2.0 ± 0.2	1.5 ± 0.14	0.0027	0.0081	0.33

[a] Initial concentration of **1**, 0.2 M. Rate of elimination and combined rates of elimination and substitution measured by ^1H NMR (see Experimental Section). [b] Rate of elimination measured spectrophotometrically by following appearance of sulfine; initial concentration of **1c**, 4×10^{-5} M.

Table III. Rate Constants for Amine-Induced Sulfine Formation from **2** in Methanol at 25 °C

amine	pK_a (H_2O)	k_e,[a] M^{-1} s^{-1}
quinuclidine	11.5[b]	33
piperidine	11.4[c]	29
piperazine	10.1[c]	16
3-quinuclidinol	10.1[b]	14
diazabicyclooctane	9.2[b]	2.2
morpholine	8.9[c]	2.0
glycine ethyl ester	7.9[c]	0.063
imidazole	7.21[c]	0.0099
2,3-lutidine	6.57[d]	0.0027
2-ethylpyridine	5.89[d]	0.0011
trifluoroethylamine	5.84[c]	0.0016
pyridine	5.52[c]	0.00026

[a] Obtained as slope of a plot of k_{elim} vs. [amine] for runs with a given amine; k_e is independent of amine:amineH$^+$ buffer ratio. [b] Satterthwait, A. C.; Jencks, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 7018. [c] Jencks, W. P.; Gilchrist, M. *J. Am. Chem. Soc.* **1968**, *90*, 2622. [d] *Handbook of Chemistry and Physics*, 61st ed.; Chemical Rubber Publishing Co.: Cleveland, 1981; p D-161.

The kinetics of the formation of **4** from **2** in the presence of the amines were followed under conditions where the amine was present in large stoichiometric excess over **2**. The formation of **4** followed good first-order kinetics. The experimental first-order rate constants, k_{elim}, for the various runs are collected in Table IV (supplementary material).[12] For each amine a plot of k_{elim} vs. [amine] was linear. Most of the studies were done in 1:1 amine–amineH$^+$ buffers, but in several cases where a 10:1 amine–amineH$^+$ buffer was also employed identical plots of k_{elim} vs. [amine] were obtained. This shows that formation of the sulfine is due to the reaction of the amine itself with **2**.

The second-order rate constants, k_e, obtained from the slopes of the plots of k_{elim} vs. [amine] for the twelve different amines studied are found in Table III. Figure 2 is a plot of log k_e vs. the pK_a (H_2O) for amineH$^+$. The data can be accommodated reasonably well by a single correlation line with a slope, Brønsted β, of 0.89 ± 0.05.

The kinetic isotope effects associated with three of the tertiary amine-induced eliminations were also determined (using 9-deuterio-**2** as substrate). The values of k_H/k_D were the following: quinuclidine, 3.8; 3-quinuclidinol, 2.8; 2-ethylpyridine, 3.1.

Measurements of the rate of reaction of 9-protio-**2** with imidazole in CH_3OD vs. CH_3OH indicated that the *solvent* isotope effect for this elimination was very small (k_{MeOD}/k_{MeOH} = 0.90). That the solvent isotope effect associated with this amine-catalyzed elimination should be very different than that for the methoxide-induced reaction would be expected from solvent isotope effect theory.[11]

(12) See paragraph at the end of the paper regarding supplementary material.

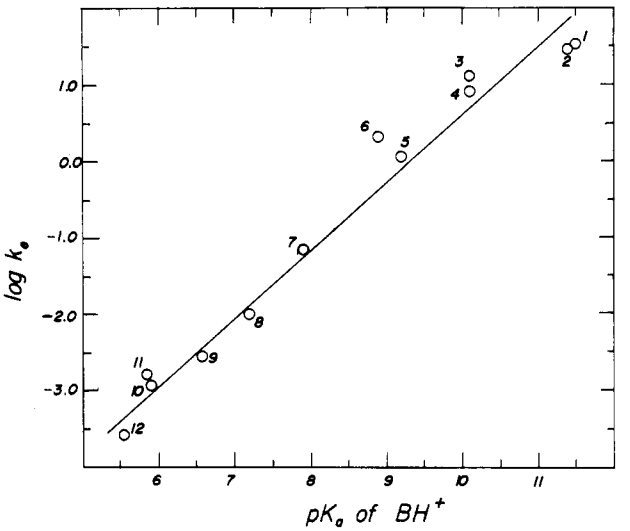

Figure 2. Plot of log k_e for the sulfine-forming elimination of **2** with amines in methanol vs. pK_a (H_2O) of the conjugate acid of the amine: 1 = quinuclidine; 2 = piperidine; 3 = 3-quinuclidinol; 4 = piperazine; 5 = DABCO; 6 = morpholine; 7 = glycine ethyl ester; 8 = imidazole; 9 = 2,3-lutidine; 10 = 2-ethylpyridine; 11 = trifluoroethylamine; 12 = pyridine. Slope, β, equals +0.9. Plotted values of k_e for piperazine and DABCO are statistically corrected, i.e., plotted value of $k_e = k_e/2$.

Rates of amine-induced elimination of **1** were so much slower than those of **2** as to make study of their kinetics impractical.

Absence of Exchange of Methine Proton of 2 Prior to Sulfine Formation. For **4** the ^1H NMR signal for one of the protons in the aromatic ring that is syn to the S=O group appears at lower field (δ 8.4–8.6) than the signals for either the other protons in **4** or the aromatic ring protons of ester **2** (δ 7.15–7.85). The methine proton (>C*H*S(O)OMe) of **2** is a sharp singlet at δ 5.07.

The decrease with time in the intensity of the methine proton singlet at δ 5.07 and the increase in the sulfine proton signal at δ 8.4–8.6 were measured simultaneously for the reaction of **2** with several of the amines in CD_3OD at 25.5 °C. The latter provides a measurement of the rate of sulfine formation from **2** (k_{elim}) while the former measures the rate of sulfine formation plus the rate of H/D exchange (k_{exch}) of the C-9 proton of **2** prior to sulfine formation. In all cases investigated the rate of disappearance of the methine proton signal, within experimental error (10–15%), did *not* exceed k_{elim}, showing that exchange of the C-9 proton in **2** was not occurring to any significant extent.

Discussion

Before discussing the results of the present investigation it is pertinent to review the mechanistic behavior of the related, sulfene-forming elimination of aryl arylmethanesulfonates (eq 6).

When Ar'O⁻ is the anion of a highly acidic phenol (pK_a of Ar'OH

$$B^- + ArCH_2SO_2OAr' \rightarrow BH^+ + [ArCH{=}SO_2] + Ar'O^- \quad (6)$$

< 6), the elimination proceeds by an irreversible ElcB (eq 7, $k_{ii} > k_{-1}[BH^+]$),[4] or perhaps a very ElcB-like E2,[7,13] mechanism; $(k_H/k_D) = 4.0$ for OH^--induced elimination of $PhCD_2SO_2OAr'$ (Ar' = 2,4-dinitrophenyl),[7] variation of substituents in Ar gives

$$ArCH_2SO_2OAr' \underset{k_{-1}[BH^+]}{\overset{k_1[B]}{\rightleftharpoons}} Ar\bar{C}H{-}SO_2OAr' \xrightarrow{k_{ii}} ArCH{=}SO_2 + Ar'O^- \quad (7)$$

a ρ value of from +2.4 to +2.7,[4] and in a deuteriated solvent medium exchange of the methylene protons of the ester prior to sulfene formation is not observed.[4,7] On the other hand, when Ar'O⁻ is the anion of a less acidic phenol (pK_a of Ar'OH > 7) the mechanism for elimination changes to $(ElcB)_{rev}$ (eq 7, $k_{ii} < k_{-1}[BH^+]$),[4,7] and H/D exchange of the methylene protons of the ester prior to sulfene formation is observed.[4,7] For the $(ElcB)_{rev}$ mechanism variation of the substituents in Ar leads to a ρ value of only +0.54,[4] presumably because the transition state for its rate-determining step (step k_{ii}) is close to [ArCH=SO_2 + Ar'O⁻] in structure, and there is little carbanion character associated with the carbon α to the Ar group.

Given that CH_3O^- is the anion of a significantly weaker acid than phenol (pK_a of MeOH = 15.2),[14] the behavior of the sulfene-forming eliminations of the arylmethanesulfonates would lead one to anticipate that the mechanism for the sulfine-forming eliminations in eq 1 and 2 would almost certainly also be $(ElcB)_{rev}$. However, the behavior of eq 1 and 2 shows clearly that this is not the case. First, there is no H/D exchange in MeOD of the >CHS(O) proton prior to sulfine formation in either the MeO⁻-induced elimination of **1** (eq 1) or the amine-induced elimination of **2** (eq 2). Second, the kinetic isotope effect (k_H/k_D = 6.1) for the methoxide-promoted elimination of 9-deuterio-**2** is so large as to require a mechanism for this reaction where the C–D bond is broken in the rate-determining step. If the mechanism for the reaction were $(ElcB)_{rev}$, the C–D bond would be broken *prior* to the rate-determining step, and a large kinetic isotope effect would not be observed. The isotope effects (k_H/k_D = 2.8 to 3.8) for several amine-induced eliminations of **2**, while smaller than k_H/k_D for the elimination with MeO⁻, are still large enough to suggest that the C–D bond is being broken in the rate-determining step of these eliminations as well.

These results clearly indicate that, despite the high pK_a of the conjugate acid of the leaving group (MeO⁻), the mechanism for the sulfine-forming eliminations of **1** and **2** in eq 1 and 2 is either $(ElcB)_{irrev}$ (eq 8) or E2 (eq 9). Given the behavior of the related base-induced elimination of aryl arylmethanesulfonates (eq 6), this is both unexpected and noteworthy. It shows that the specific

$$Ar_2CHS(O)OCH_3 \underset{k_{-1}[BH^+]}{\overset{k_1[B]}{\rightleftharpoons}} Ar_2\bar{C}{-}S(O)OCH_3 \xrightarrow{k_{ii}} Ar_2C{=}S{=}O + CH_3O^- \quad (8)$$

$$B = CH_3O^-, R_3N, \text{ or } R_2NH;\ k_{ii} > k_{-1}[BH^+]$$

mechanistic behavior of sulfene-forming eliminations of alkanesulfonyl compounds cannot be used to predict the mechanism for analogous sulfine-forming eliminations of alkanesulfinyl com-

$$B + Ar_2CHS(O)OCH_3 \xrightarrow{k_{E2}} \left[\begin{array}{c} Ar \\ | \\ B^{\delta+}\cdots H\cdots C^{\delta-}\cdots S(O)\cdots O^{\delta-}CH_3 \\ | \\ Ar \end{array}\right] \longrightarrow \underset{\text{transition state}}{} BH^+ + Ar_2C{=}S{=}O + CH_3O^- \quad (9)$$

pounds. Speculation as to why sulfine-forming eliminations of **1** and **2** take place by an $(ElcB)_{irrev}$ or E2 mechanism, whereas sulfene-forming eliminations of arylmethanesulfonates with even better leaving groups proceed by an $(ElcB)_{rev}$ mechanism, will be deferred to the end of the Discussion.

Distinction between $(ElcB)_{irrev}$ and E2 mechanisms for an elimination is frequently not easy, and in the case of the present sulfine-forming eliminations the necessary experimental information (leaving group effect for eliminations of $Ar_2CHS(O)OR$, or (k_{16}/k_{18}) for elimination of $Ar_2CHS(O)^{18}OCH_3$) needed to attempt such a decision is not yet at hand. However, the ρ value (+2.8) for the methoxide-induced elimination of **1** (eq 1) suggests that the α-carbon to the sulfinyl group possesses significant carbanionic character in the rate-determining transition state. This suggests that if the mechanism is E2 it is of the ElcB-like E2 variety with cleavage of the C–H bond running in advance of cleavage of the S–OCH_3 bond. Note that the ρ value for eq 1 is quite similar to the ρ value found[4] for eq 6 for arylmethanesulfonates that undergo elimination via an $(ElcB)_{irrev}$[4] (or ElcB-like E2[7,13]) mechanism and is much larger than the ρ value (+0.54)[4] for arylmethanesulfonates that undergo elimination by an $(ElcB)_{rev}$ mechanism. This further supports the view that the sulfine-forming eliminations of **1** and **2** proceed by other than an $(ElcB)_{rev}$ mechanism.

Comparison of the rates of MeO⁻-induced elimination of **1c** and **2** shows that the 9-fluorenesulfinate reacts ~20 000 times faster than the diphenylmethanesulfinate. Given the much greater stability of a 9-fluorenyl carbanion relative to a benzhydryl carbanion (fluorene is 9.7 pK units stronger acid than diphenylmethane),[15] and the indication from the ρ value for eq 1 of significant carbanionic character for the α-carbon to the sulfinyl group in the rate-determining transition state, the much greater reactivity of **2** is expected.

The apparent Brønsted β (+0.89 ± 0.05) associated (Figure 2) with amine-induced sulfine formation from **2** is large and would seem to suggest that the >CHS(O) proton is almost completely transferred to the amine by the time the transition state is reached. It is interesting to note that very large β's (0.85–1.0) have been found[17] for E2 eliminations of certain (2-arylethyl)quinuclidinium ions. These particular reactions are ones where inadequate stabilization of a carbanion intermediate enforces a concerted mechanism, but where the relatively poor nature of the leaving group (as compared to a halide or tosylate ion) leads to the transition state occurring at a point on the three-dimensional reaction coordinate-energy contour diagram (More O'Ferrall plot[18]) where the bond to the leaving group is virtually intact (β_{lg} = −0.1 to −0.3) while the C–H bond is almost completely broken (β = 0.85 to 1.0). This contrasts with E2 eliminations of the corresponding 2-arylethyl halides and tosylates where both bonds are broken to roughly the same extent in the transition state.

We had anticipated that substitution of CD_3O^- at the >S(O) group of **1** (eq 4) might be much faster than methoxide-induced sulfine formation from the same substrate (eq 1). However, the results in Table II show that this is not the case and that, in actuality, k_s is slower than k_e by a factor of from 3 to 7. Comparison of the rate of substitution for **1c** with the rate of substitution for $PhCH_2S(O)OCH_3$ (eq 5) shows that introduction of the second phenyl group slows substitution by a factor of about 40. This is somewhat larger than the ~10-fold reduction in rate seen in the alkaline hydrolysis of $Ph_2CHC(O)OMe$ vs. $PhCH_2C(O)OMe$.[19] In both cases the decrease in rate of substitution attending the introduction of the second phenyl group is presumably due to increased steric hindrance to attack of the

(13) Williams and co-workers[7] prefer to picture these eliminations as taking place by an extremely ElcB-like E2 mechanism with an unusually "unsymmetrical" timing for bond cleavage, rather than proceeding by the standard $(ElcB)_{irrev}$ mechanism favored by King and Beatson.[4]

(14) Reeve, W.; Erikson, C. M.; Alutto, P. F. *Can. J. Chem.* **1979**, *57*, 2747.

(15) In Me_2SO the pK_a for fluorene is 22.6 while that for diphenylmethane is 32.3.[16]

(16) (a) Bordwell, F. G.; Bartmess, J. E.; Drucker, G. E.; Margolin, Z.; Matthews, W. S. *J. Am. Chem. Soc.* **1975**, *97*, 3226. (b) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, G. J.; Vanier, N. R. *Ibid.* **1975**, *97*, 7006.

(17) Gandler, J. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 1937.

(18) More O'Ferrall, R. A. *J. Chem. Soc. B* **1970**, 274.

(19) Taft, R. W., Jr. *J. Am. Chem. Soc.* **1952**, *74*, 3120.

nucleophile on the >S=O or >C=O group.

Table II shows that (k_s/k_e) increases from 0.14 to 0.33 as the substrate changes from **1c** to **1f**. Electron-donating substituents in the aryl groups of the diarylmethanesulfinate therefore decrease the rate of nucleophilic substitution at the sulfinyl group less than they decrease the rate of elimination. This is as would be expected.

We had originally hoped to be able to use (k_s/k_e) for **1** as a means of probing the effect of a variety of other reaction variables (temperature, solvent, etc.) on the competition between substitution and elimination for an alkanesulfinyl compound. However, the fact that $k_s < k_e$ for **1** makes the diarylmethanesulfinates unsuited for this purpose, since in order to have sufficient experimental flexibility for such studies it is necessary to have a system where $k_s > k_e$ under most reaction conditions.

We return now to the question of why sulfine-forming eliminations of **1** and **2** take place by an $(ElcB)_{irrev}$, or ElcB-like E2, mechanism whereas sulfene-forming eliminations of arylmethanesulfonates with a comparable leaving group proceed by an $(ElcB)_{rev}$ mechanism. The similarity in the pK_a's of $Ph_2CHS(O)Ph$ (24.5)[20] and $PhCH_2SO_2Ph$ (23.4)[20] indicates the carbanion intermediates $Ar_2C^-S(O)OMe$ and ArC^-HSO_2OMe should be approximately equal in energy, with the carbanion from the sulfinate ester being slightly less stable. On the other hand, the elimination products ($Ar_2C{=}S{=}O$ and $ArCH{=}SO_2$) of the two reactions differ greatly in their relative stability with the *diarylsulfine being much the more stable*. Thus, monoarylsulfenes ($ArCH{=}SO_2$) are reactive, unstable intermediates that are not isolable and react readily with nucleophiles to afford substitution products ($ArCH{=}SO_2 + NuH \rightarrow ArCH_2SO_2Nu$),[4-8] while diarylsulfines ($Ar_2C{=}S{=}O$) are easily isolable species that are stable for an extended period of time in the presence of nucleophiles such as OH^- or MeO^-. Given the similar energies of $Ar_2C^-S(O)OMe$ and ArC^-HSO_2OMe, this marked difference in the stability of $Ar_2C{=}S{=}O$ vs. $ArCH{=}SO_2$ could easily lead to $\Delta G^{\ddagger}$ for loss of MeO^- from $Ar_2C^-S(O)OMe$ (step k_{ii}, eq 8) being enough smaller than $\Delta G^{\ddagger}$ for loss of the same leaving group from ArC^-HSO_2OMe (eq 7, Ar'O = MeO) so that, although $k_{ii} < k_{-1}[BH^+]$ for ArC^-HSO_2OMe, $k_{ii} > k_{-i}[BH^+]$ for $Ar_2C^-S(O)OMe$.

It is also conceivable that the markedly greater stability of the diarylsulfine could result in the energy of [$Ar_2C{=}S{=}O + MeO^-$] being low enough relative to $Ar_2C^-S(O)OMe$ that the energy contours of the More O'Ferrall plot[18] for the sulfine-forming elimination would be such that the carbanion did not represent a discrete energy minimum on the energy surface. In that case sulfine formation would perforce proceed via a *concerted* (E2) pathway, and it is quite reasonable that the transition state for this pathway would be found in the same domain (large β, relatively small β_{lg}) of the More O'Ferrall diagram as the transition states for the E2 eliminations of (2-arylethyl)quinuclidinium ions studied by Gandler and Jencks.[17] As noted earlier, an ElcB-like E2 mechanism for the sulfine-forming eliminations of **1** and **2** is consistent with the experimental data so far at hand.

Crosby and Stirling[21] have shown that the elimination of phenoxide from β-substituted (X = $PhSO_2$, PhS(O), etc.) ethyl phenyl ethers ($B + XCH_2CH_2OPh \rightarrow BH^+ + XCH{=}CH_2 + PhO^-$), like sulfene formation from phenyl arylmethanesulfonates (eq 6, Ar' = Ph), takes place by an $(ElcB)_{rev}$ mechanism. This further emphasizes that among eliminations where the leaving group is phenoxide or an alkoxide ion the mechanistic behavior of the sulfine-forming eliminations of **1** and **2** is definitely atypical. It clearly indicates that further systematic mechanistic study of sulfine-forming eliminations of additional substrates is highly desirable.

Experimental Section

Preparation and Purification of Methyl Esters of Diarylmethanesulfinic Acids. The methyl esters were synthesized by esterification of the corresponding diarylmethanesulfinic acids with diazomethane in ether solution. The sulfinic acids (white, unstable solids) were obtained by acidification of cold aqueous solutions of their potassium or sodium salts with 2 N sulfuric acid. The sulfinic acid that precipitated was filtered off, washed with a little cold water, and then dissolved in ether. The ether solution was washed once with cold water, and diazomethane (generated from Aldrich Diazald) was passed into the cold ether solution until a yellow color persisted. The ether was then evaporated and the residue of crude sulfinate ester was purified by either preparative thin-layer or flash chromatography on silica gel with use of dichloromethane–chloroform mixtures as eluants. The purified esters, which were obtained from the sulfinate salts in 45–65% yield, were further purified in most cases by recrystallization.

Methyl diphenylmethanesulfinate (1c) was recrystallized twice from benzene–petroleum ether: mp 79–80 °C (lit.[22] mp 79–80 °C); IR (KBr) 1120 and 977 cm^{-1} (>S(O)O); ^1H NMR (CD_3OD) δ 3.62 (s, 3 H), 5.10 (s, 1 H), 7.2–7.6 (m, 10 H); mass spectrum, *m/e* 246 (M^+).

Methyl 9-fluorenesulfinate (2) was crystallized from benzene–hexane: mp 49–50.5 °C (lit.[22] mp 47–48 °C); IR (KBr) 1149 and 997 cm^{-1} (>S(O)O); ^1H NMR (CD_3OD) δ 3.80 (s, 3 H), 5.07 (s, 1 H), 7.15–7.85 (m, 8 H); mass spectrum, *m/e* 244 (M^+).

Methyl 9-fluorenesulfinate-*9-d* was purified similarly: mass spectrum, *m/e* 245 (M^+).

Methyl bis(4-chlorophenyl)methanesulfinate (1a) was crystallized from chloroform–hexane: mp 83–84 °C; IR (KBr) 1126 and 981 cm^{-1} (>S(O)O); ^1H NMR (CCl_4) δ 3.60 (s, 3 H), 4.80 (s, 1 H), 7.0–7.5 (m, 8 H). Anal. Calcd for $C_{14}H_{12}Cl_2O_2S$: C, 53.34; H, 3.84. Found: C, 53.24; H, 3.97.

Methyl (4-chlorophenyl)phenylmethanesulfinate (1b) was recrystallized from dichloromethane–petroleum ether: mp 96.5–97.5 °C; IR (KBr) 1126 and 987 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.66 (s, 3 H) 4.95 (s, 1 H), 7.0–7.8 (m, 9 H). Anal. Calcd for $C_{14}H_{13}ClO_2S$: C, 59.89; H, 4.67. Found: C, 60.00; H, 4.86.

Methyl (4-methylphenyl)phenylmethanesulfinate (1d) was obtained as an oil: IR (neat) 1124 and 989 cm^{-1}; ^1H NMR (CD_3OD) δ 2.30 (s, 3 H), 3.60 (s, 3 H), 5.08 (s, 1 H), 7.1–7.6 (m, 9 H). Anal. Calcd for $C_{15}H_{16}O_2S$: C, 69.20; H, 5.81. Found: C, 69.23; H, 6.03.

Methyl (4-methoxyphenyl)phenylmethanesulfinate (1e) was recrystallized from ether–petroleum ether: mp 62.5–64 °C; IR (KBr) 1128 and 988 cm^{-1}; ^1H NMR (CD_3OD) δ 3.63 (s, 3 H), 3.75 (s, 3 H), 5.07 (s, 1 H), 6.8–7.7 (m, 9 H). Anal. Calcd for $C_{15}H_{16}O_3S$: C, 65.19; H, 5.84. Found C, 64.84; H, 5.75.

Methyl bis(4-methoxyphenyl)methanesulfinate (1f) was recrystallized from ether–petroleum ether: mp 74–75 °C; IR (KBr) 1127 and 986 cm^{-1}; ^1H NMR (CD_3OD) δ 3.63 (s, 3 H), 3.75 (s, 6 H), 5.0 (s, 1 H), 6.8–7.6 (m, 8 H). Anal. Calcd for $C_{16}H_{18}O_4S$: C, 62.73; H, 5.92. Found: C, 62.50; H, 5.80.

Preparation of Salts of Diarylmethanesulfinic Acids. The salts of all the diarylmethanesulfinic acids except bis(4-methoxyphenyl)methanesulfinic acid and 9-fluorenesulfinic acid were prepared from the appropriate benzyl diarylmethanethiosulfonate, $ArAr'CHSO_2SCH_2Ph$, by reaction of the thiosulfonate with an equimolar amount of sodium α-toluenethiolate ($PhCH_2SNa$) in methanol solution following the procedure outlined by Zwanenburg and co-workers[10a] for the synthesis of Ph_2CHSO_2Na. After being refluxed for 10 minutes the reaction mixture was cooled, water was added, and the benzyl disulfide that had formed was removed by filtration. The filtrate was subjected to rotary evaporation at room temperature to remove much of the methanol and was then washed with both dichloromethane and ether. The remaining aqueous solution of the diarylmethanesulfinate was then kept under nitrogen at 0 °C until the sulfinic acid was liberated by acidification (vide supra).

Sodium bis(4-methoxyphenyl)methanesulfinate was generated from β-(bis(4-methoxyphenyl)methanesulfonyl)propionitrile, $(p\text{-}CH_3OC_6H_4)_2CHSO_2CH_2CH_2CN$, by treatment of this compound with an equimolar amount of sodium α-toluenethiolate in methanol following the procedure used by Zwanenburg et al.[10a] for the preparation of sodium 9-fluorenesulfinate from β-(9-fluorenesulfonyl)propionitrile. After removal of the solvent the residue was washed with ether and then dissolved in water. The aqueous solution of the sulfinate was washed with both dichloromethane and ether and the sulfinic acid was liberated from it by acidification in the same manner as for the other diarylmethanesulfinates.

The potassium salt of 9-fluorenesulfinic acid was prepared by adding 2.1 g (10 mmol) of 9-thiofluorenone *S*-oxide (**4**)[10a] to a stirred solution of potassium hydroxide (0.84 g, 15 mmol) dissolved in 50 mL of ethanol and kept at 0 °C. The mixture was allowed to stir for 1 h, poured into water, and extracted with ether to remove water-insoluble byproducts. Acidification of the aqueous layer resulted in the precipitation of 9-fluorenesulfinic acid. Potassium 9-fluorenesulfinate-*9-d* resulted when

(20) Bordwell, F. G.; Bares, J. E.; Bartmess, J. E.; McCollum, G. J.; Van Der Puy, M.; Vanier, N. R.; Matthews, W. S. *J. Org. Chem.* **1977**, *42*, 321.
(21) Crosby, J.; Stirling, C. J. M. *J. Chem. Soc. B* **1970**, 679.
(22) Gibbs, C. G. Ph.D. Thesis, Texas Christian University, 1973.

the 9-thiofluorenone *S*-oxide was allowed to react with potassium deuterioxide in CH_3OD. This method of synthesis of potassium 9-fluorenesulfinate was first described by Gibbs.[22]

Synthesis of Benzyl Diarylmethanethiosulfonates. The various benzyl diarylmethanethiosulfonates were synthesized from benzyl mercaptan, sulfur dioxide, and the appropriate diaryldiazomethane, $ArAr'C{=}N_2$, using the general procedure outlined by Kloosterziel, Boerma, and Backer[9] for the synthesis of alkyl diphenylmethanethiosulfonates, including benzyl diphenylmethanethiosulfonate,[9] mp 143–145 °C. To obtain reasonable yields of the thiosulfonate by this procedure from certain of the substituted diphenyldiazomethanes it was necessary to modify the procedure by including a tertiary amine (either pyridine or triethylamine) as a catalyst. The crude thiosulfonates were purified by either crystallization from dichloromethane–methanol or flash chromatography (using chloroform as eluant).

Benzyl (4-Methylphenyl)phenylmethanethiosulfonate. Reaction of 1.8 g (8.8 mmol) of (4-methylphenyl)phenyldiazomethane with 1.03 mL of benzyl mercaptan in the presence of sulfur dioxide in 10 mL of ether at −10 °C gave 2.8 g (88%) of the thiosulfonate as an oil: IR (neat) 1317 and 1126 cm^{-1} (>SO_2); ^1H NMR ($CDCl_3$) δ 2.27 (s, 3 H), 3.53 (s, 2 H), 4.9 (s, 1 H), 6.8–7.7 (m, 14 H).

Benzyl (4-methoxyphenyl)phenylmethanethiosulfonate was obtained in a yield of 90% (0.95 g) from the reaction of sulfur dioxide in 10 mL of ether at −30 °C with 0.54 g (2.7 mmol) of (4-methoxyphenyl)phenyldiazomethane and 0.37 mL of benzyl mercaptan in the presence of 0.25 mL of triethylamine as catalyst. The thiosulfonate as initially isolated was an oil: IR (neat) 1319 and 1128 cm^{-1} (>SO_2); ^1H NMR δ 3.75 (s, 3 H), 3.85 (s, 2 H), 4.9 (s, 1 H), 6.8–7.6 (m, 14 H).

Benzyl (4-Chlorophenyl)phenylmethanethiosulfonate. Passage of sulfur dioxide through a solution of 0.85 mL of benzyl mercaptan and 1.63 g (7.15 mmol) of (4-chlorophenyl)phenyldiazomethane in 10 mL of ether at −10 °C gave a crude yield of 2.4 g (88%) of benzyl (4-chlorophenyl)phenylmethanethiosulfonate as an oil: IR (neat) 1325 and 1125 cm^{-1} (>SO_2); ^1H NMR ($CDCl_3$) δ 4.0 (s 2 H), 4.9 (s, 1 H), 6.8–7.7 (m, 14 H).

Benzyl bis(4-chlorophenyl)methanethiosulfonate, mp 95–98 °C, was obtained in 25% yield (0.20 g), after crystallization from methylene chloride–methanol, from passage of sulfur dioxide through an ether solution (10 mL) containing 0.55 g (2.1 mmol) of bis(4-chlorophenyl)diazomethane, 0.3 mL of benzyl mercaptan, and 2 mL of pyridine: IR 1329 and 1126 cm^{-1} (>SO_2); ^1H NMR (acetone-d_6) δ 4.25 (s, 2 H), 5.55 (s, 1 H), 7.1–7.8 (m, 13 H).

Preparation of Diaryldiazomethanes. Diphenyldiazomethane was prepared by the standard procedure.[23] (4-Methyl-,[24] (4-methoxy-,[24] and (4-chlorophenyl)phenyldiazomethane[24] were all prepared in 40–55% yield from the corresponding *p*-toluenesulfonyl hydrazones by the general procedure described by Farnum,[25] with the modification that benzene–dioxane rather than pyridine was used as the solvent. Bis(4-chlorophenyl)diazomethane was obtained in 70% yield by oxidation of 4,4′-dichlorobenzophenone hydrazone with *m*-chloroperoxybenzoic acid.[26] The diaryldiazomethanes were crystallized from ether, recrystallized from pentane, and then used immediately for the synthesis of the benzyl diarylmethanethiosulfonates.

Synthesis of β-(Bis(4-methoxyphenyl)methanesulfonyl)propionitrile. 4,4′-Dimethoxybenzhydrol (Aldrich) was converted to 4,4′-dimethoxybenzhydryl bromide in 65% yield with use of the procedure of Dolbier and co-workers:[27] ^1H NMR ($CDCl_3$) δ 3.8 (s, 6 H), 5.8 (s, 1 H), 6.5–7.0 (m, 8 H). The bromide (4.1 g, 12.7 mmol) in 10 mL of methanol was added to 15 mL of 2 M aqueous sodium trithiocarbonate, and the mixture was heated for 5 h at 60 °C. Workup gave 1.63 g (49%) of bis(4-methoxyphenyl)methanethiol as an oil: IR (neat) 2541 (w, SH), 1251 (vs) cm^{-1}. To 1.62 g (6.2 mmol) of the thiol was added 25 mg of commercial sodium methoxide powder and then, dropwise, excess acrylonitrile. The mixture was allowed to stand overnight. The excess acrylonitrile was removed under reduced pressure and the residue was chromatographed on silica gel (chloroform–methylene chloride as eluant) to give 1.46 g (76%) of β-(bis(4-methoxyphenyl)methylthio)propionitrile: IR (neat) 2254 (CN), 1252 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.3–2.65 (m, 4 H), 3.75 (s, 6 H), 5.2 (s, 1 H), 6.6–7.5 (m, 8 H). Oxidation of β-(bis-(4-methoxyphenyl)methylthio)propionitrile (1.41 g, 4.5 mmol) with *m*-chloroperoxybenzoic acid (1.88 g, 9 mmol) in chloroform at 0 °C for 10 h, followed by 15 h at room temperature, gave, after column chromatography on silica gel ($CHCl_3$ as eluant), 0.73 g (47%) of β-(bis(4-methoxyphenyl)methanesulfonyl)propionitrile as an oil: IR (neat) 2262 (CN), 1322 and 1130 (SO_2), and 1248 (COC) cm^{-1}.

Formation of Sulfines from 1 and 2. Methyl bis(4-chlorophenyl)-methanesulfinate (**1a**), 1.0 mmol, was dissolved in 25 mL of methanol containing 0.01 M sodium methoxide. After 20 min the solution was neutralized, and the methanol was removed under reduced pressure. Purification of the residue by flash chromatography on silica gel with benzene–ether as eluant gave, after recrystallization, 0.21 g (75%) of 4,4′-dichlorothiobenzophenone *S*-oxide (**3a**), mp 79–80 °C (lit.[27] mp 78–80 °C), identical in all respects with a known sample[28] of this sulfine. Similar treatment of **2** yielded 9-thiofluorenone *S*-oxide (**4**)[10a] in 80% yield after workup and recrystallization.

The success in preparing and isolating **3a** and **4** by the procedure just described led us to employ it also for the preparation of sulfines **3b**, **3d**, and **3e** from sulfinate esters **1b**, **1d**, and **1e**, respectively. In each case the sulfine was obtained pure in 70–80% yield upon workup.

With sulfinate esters **1c** and **1f** the formation of the expected sulfine (**3c** or **3f**) was demonstrated by comparison of the absorption spectrum of the final reaction solution with that of an authentic sample[10a] of **3c** and **3f**.

In methanol each of the sulfines has a characteristic long wavelength absorption maximum in the 320–360-nm region. The location of λ_{max} and its extinction coefficient (log ϵ) for the different sulfines are as follows: **3a**, 332 nm (4.17); **3b**, 330 nm (4.09); **3c**, 328 nm (4.08); **3d**, 332 nm (4.12); **3e**, 351 nm (4.13); **3f**, 345 nm (4.19); **4**, 360 nm (4.19).

Kinetics of Sulfine Formation as Followed by UV Spectrophotometry. The formation of the sulfine from the methyl ester of the sulfinic acid was followed in each case by measuring the increase with time in the optical density of the solution at the wavelength (see tabulation above) corresponding to the long wavelength λ_{max} for the sulfine.

In the runs that were followed by conventional ultraviolet spectrophotometry 3.0 mL of an anhydrous methanol solution containing the desired amounts of the base (methoxide ion, amine) and, where appropriate, its conjugate acid were placed in a 1-cm spectrophotometer cell in the thermostated cell compartment of a Lamda 5 or Cary 17 UV–visible spectrophotometer. After the solution had reached thermal equilibrium 20–50 μL of an 0.005 M solution of the sulfinate ester in methanol was added to the cell by microsyringe with good mixing, and the progress of the elimination reaction was monitored by following the increase in the absorbance (A) of the solution at the appropriate wavelength.

In the runs followed by stopped-flow spectrophotometry a solution of the base in methanol was placed in one of the reservoir syringes of a Durrum-Gibson D-110 stopped-flow spectrophotometer and a solution of the sulfinate ester in the same solvent was placed in the other reservoir syringe. The elimination reaction was initiated by mixing the two solutions, and the increase in absorbance with time at λ_{max} for the sulfine was recorded on the storage oscilloscope.

The first-order rate constants, k_{elim}, for sulfine formation were obtained from the slopes of plots of ln ($A_\infty - A$) vs. time. Values of A_∞ were determined from absorption measurements taken after at least 7 half-lives had elapsed. The amount of sulfine formed was also determined from A_∞ and the known ϵ for the sulfine at that wavelength. In all cases except one (the reaction of **2** with trifluoroethylamine, where the yield of sulfine was only 60%) the yield of sulfine was 95–100%.

If the final reaction solution was allowed to stand for an extended period of time there was some tendency for the sulfine to disappear slowly. It was established that a major final product of the decomposition of most of the sulfines under such conditions was the corresponding ketone. In every case, however, the rate of disappearance of the sulfine was slow enough so as not to interfere with an accurate determination of A_∞.

Kinetics of Sulfine Formation and Methoxy Group Exchange as Followed by ^1H NMR. The desired amount of sulfinate ester was weighed into a 1-mL volumetric flask, 5 μL of cyclohexane was added to serve as an internal NMR standard, and the ester and hydrocarbon were dissolved in, and made up to volume with, methanol-d_4 in a drybox. A portion of this solution (0.43–0.47 mL) was transferred in the drybox to an NMR tube and placed in the probe of an NMR spectrometer. Once the solution reached the temperature of the probe 40–70 μL of a solution of CD_3O^- in methanol-d_4 was added with good mixing. At appropriate time intervals thereafter the integrated intensities of selected proton resonances in the solution were determined.

The $CH_3OS(O)$ resonance of all of the sulfinate esters is located between δ 3.60 and 3.66. The decrease in the integrated intensity of this

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signal relative to that of the internal cyclohexane standard measures the sum of the rate of exchange of CH_3O by CD_3O at the sulfinyl group (k_{sub}) and the rate of elimination of the ester to form the sulfine (k_{elim}).

With ester **1d** the signal for the CH_3 protons of the *p*-tolyl group is at δ 2.30 in the ester and at δ 2.40 in the sulfine formed on elimination. Measurement of the change (increase at δ 2.40, decrease at δ 2.30) in the integrated intensity of either of these signals relative to the cyclohexane standard gives k_{elim}.

For ester **1e** the signal for the *p*-methoxy group is at δ 3.75 in the ester and at δ 3.80 in the sulfine. Measurement of the decrease with time in the integrated intensity of the signal at δ 3.75 provided k_{elim}. With the bis(4-methoxyphenyl) ester (**1f**) a similar change in the location of the resonance for the *p*-methoxy groups takes place, and the increase in the intensity of the signal for the *p*-methoxy groups in the sulfine (δ 3.80) was used to measure k_{elim}.

The two ortho protons of the *syn*-phenyl group in **3c** (thiobenzophenone *S*-oxide) are found at lower field (δ 7.65–7.9) than either the remaining aromatic protons in **3c** or the aromatic protons of ester **1c** (δ 7.2–7.6). The increase with time in the integrated intensity of these two sulfine protons was used to determine k_{elim} for ester **1c** in the NMR experiments.

During each of the experiments outlined above the integrated intensity of the >C*H*S(O) singlet at δ 5.0–5.1 was also monitored with time. In every case the rate constant for the disappearance of this signal was identical within experimental error to the rate constant (k_{elim}) for sulfine formation. This establishes that exchange of the methine proton in the diarylmethanesulfinate ester prior to sulfine formation is not occurring to a detectable extent.

Kinetics of Methoxy Group Exchange of Methyl Phenylmethanesulfinate. The same procedure outlined in the preceding section was also used to follow the exchange of the methoxy group of methyl phenylmethanesulfinate (**7**)[29] in CD_3O^-/CD_3OD. The decrease in the integrated intensity of the C*H*$_3$OS(O) resonance for **7** at δ 3.75 relative to the internal cyclohexane standard was measured. Also monitored concurrently was the integrated intensity of the signal of the $CH_2S(O)$ group (δ 4.10). Since the rate of disappearance of the methoxy group resonance was approximately 40 times faster than the rate of disappearance of the signal for the methylene group at δ 4.10, the rate of disappearance of the methoxy signal for **7** equals the rate of exchange of CH_3O by CD_3O at the sulfinyl group (eq 5), uncomplicated by any significant contribution from other reactions.

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Relative Rates of Sulfine Formation and H/D Exchange in Reaction of 2 with Amines. The ortho proton of the syn aromatic ring in sulfine **4** appears at lower field (δ 8.4–8.6) than the other protons of the sulfine or the aromatic protons of ester **2** (δ 7.15–7.85). The increase with time in the intensity of this signal relative to an internal standard provides a means of measuring k_{elim} for sulfine formation from reaction of **2** with an amine in CD_3OD in an NMR experiment. At the same time the decrease with time in the intensity of the singlet at δ 5.07 for the >C*H*S(O) proton of **2** provides a measurement of the sum of the rate of sulfine formation (k_{elim}) and the rate of H/D exchange of the C-9 proton (k_{exch}) under the same conditions.

Preparation of the reaction solutions and initiation of the reaction for the NMR experiments was carried out in the same way as for the NMR studies with the various methyl diarylmethanesulfinates in CD_3OD.

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Registry No. 1a, 106864-84-0; **1b**, 106864-85-1; **1c**, 106864-86-2; **1d**, 106880-49-3; **1e**, 106864-87-3; **1f**, 106864-88-4; **2**, 106864-89-5; **5** (Ar = *p*-$CH_3OC_6H_4$; Ar′ = Ph), 106864-90-8; **5** (Ar = *p*-ClC_6H_4; Ar′ = Ph), 106864-91-9; **5** (Ar = Ar′ = *p*-ClC_6H_4), 106864-92-0; **5** (Ar = *p*-$CH_3C_6H_4$; Ar′ = Ph), 106864-95-3; β-(bis(4-methoxyphenyl)methanesulfonyl)propionitrile, 106864-93-1; (4-methylphenyl)phenyldiazomethane, 20359-75-5; (4-methoxyphenyl)phenyldiazomethane, 20359-74-4; (4-chlorophenyl)phenyldiazomethane, 1140-33-6; bis(4-chlorophenyl)diazomethane, 1143-92-6; 4,4′-dimethoxybenzhydrol, 728-87-0; 4,4′-dimethoxybenzhydryl bromide, 69545-37-5; bis(4-methoxyphenyl)-methanethiol, 26608-02-6; β-(bis(4-methoxyphenyl)methylthio)propionitrile, 106864-94-2; D_2, 7782-39-0; quinuclidine, 100-76-5; piperidine, 110-89-4; piperazine, 110-85-0; 3-quinuclidinol, 1619-34-7; diazabicyclooctane, 280-57-9; morpholine, 110-91-8; glycine ethyl ester, 459-73-4; imidazole, 288-32-4; 2,3-lutidine, 583-61-9; 2-ethylpyridine, 100-71-0; trifluoroethylamine, 753-90-2; pyridine, 110-86-1.

Supplementary Material Available: Tabulation of the results of individual kinetic runs for the reaction of **2** with amines (Table IV) (3 pages). Ordering information is given on any current masthead page.