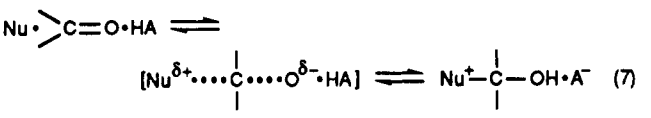
to be sensitive to the presence of substituents on the benzaldehyde, with $\rho^+ = 0.70$ (Figure 3).

The reversible addition of nitrogen nucleophiles to an eletrophilic center such as carbonyl oxygen frequently proceeds with general acid–base catalysis, according to the class of rections[20] involving proton transfer to and from an electrophilic reagent.

The structure–reactivity behavior for this reaction can be described by the reaction coordinate–energy diagram[18,29-31] in Figure 5. The axes of this diagram are defined such that the $x$ axis corresponds to the progress of proton transfer from the acid to the carbonyl group, as measured by the Brønsted coeficient, $\alpha$, and the $y$ axis to the progress of C–N bond formation, as measured by $\beta_{nuc}$ (the slope of a plot of log $k$ against $pK_{nuc}$).

It appears to be well established[3,4] that general acid catalyzed solution reactions of moderately basic nitrogen nucleophiles to reactive carbonyl compounds generally occur by a mechanism that involves formation of a zwitterionic intermediate, $T^{\pm}$ (Figure 5), which is then trapped by a kinetically significant general acid catalyzed proton transfer to the oxygen of $T^{\pm}$. Alternative mechanisms for catalysis should become significant as the stability and lifetime of $T^{\pm}$ are decreased, for example, by decreasing the basicity of the nucleophile[5,6] or the eletrophilic character of the carbonyl compound.[3,25] The addition of a weakly basic nucleophile corresponds to the pathway along the diagonal of the diagram (Figure 5). The intermediate $T^{\pm}$ does not exist or is too unstable to be able to participate in a preassociation mechanism.

The addition of weakly basic nucleophiles to benzaldehydes is assisted by stabilization of the developing charge on the carbonyl oxygen atom by hydrogen bonding to a buffer acid (eq 7).



(7)

The general acid catalysis of carbinolamine formation between Girard T reagent and para-substituted benzaldehydes must proceed by a reaction coordinate corresponding to a pathway that is predominantly diagonal.[18,21,32] Increasing the strength of the acid would be expected to shift the transition state to an earlier position along the reaction coordinate, with a corresponding decrease in the extent of C–N bond formation; perpendicular to the reaction coordinate, the effect would be to increase the extent of O–H bond formation (Figure 5). The overall effect, in particular, the decreased extent of C–N bond formation, could account for the smaller value of $\rho^+$ for the reaction catalyzed by hydronium ion, which is insensitive to the substituent effect.

The carbinolamine formation from Girard T reagent and para-substituted benzaldehydes exhibits an increase in the Brønsted $\alpha$ values (0.19–0.37) for general catalysis as the carbonyl compound becomes less reactive. The overall effect of increasing the reactivity of substituted benzaldehyde would be to decrease the extent of O–H bond formation in the transition state, which could account for the smaller values of $\alpha$ (see Figure 5).

Thus, it is not clear whether the hydronium ion and buffer catalysis occur by a qualitatively different mechanism. Indeed, the different $\sigma^+$ values may simply reflect suitable differences in the structure of the transition state and location of the reaction trajectory on the energy diagram.

**Acknowledgment.** We are indebted to Dr. Frank H. Quina for helpful comments concerning this work.

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# Methoxide-Catalyzed Decomposition of Diarylmethyl (Arylsulfonyl)methyl Sulfoxides: A Sulfine-Forming Elimination on the $(E1cB)_{rev}/(E1cB)_{irrev}$ Borderline[1]

John L. Kice* and Lidia Kupczyk-Subotkowska

*Department of Chemistry, University of Denver, Denver, Colorado 80208*

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In 7:3 $CH_3OH$–DMSO (v/v) in the presence of methoxide ion, diarylmethyl (arylsulfonyl)methyl sulfoxides ($Ar_2CHS(O)CH_2SO_2Ar'$) **4**, undergo elimination remarkably easily to afford the diarylsulfine and the aryl methyl sulfone (eq 4). Comparison of the rate of cleavage of **4** ($k_{elim}$) and the rate of disappearance of the $^1H$ NMR signal ($k_{CHSO}$) for the $Ar_2CHS(O)$ proton in $CD_3OD$–DMSO shows that the mechanism for the elimination is on the $(E1cB)_{rev}/(E1cB)_{irrev}$ borderline, ($k_{CHSO}/k_{elim}$) ranging from 1.2 to 5.2, depending on the nature of the Ar and Ar' groups in **4**. Slight changes in structure can shift the mechanism from $(E1cB)_{rev}$ to $(E1cB)_{irrev}$ as a result of their effect on the partitioning of the $\alpha$-sulfinyl carbanion intermediate ($Ar_2CS(O)CH_2SO_2Ar'$) **5**, between cleavage to diarylsulfine plus $ArSO_2CH_2^-$ (step $k_{ii}$, eq 8) and protonation to regenerate **4** (step $k_{-i}$). Structural changes that make $Ar'SO_2CH_2$ a better leaving group increase $k_{ii}/k_{-i}$[MeOD] and shift the mechanism toward $(E1cB)_{irrev}$ as does also an increase in the percentage of DMSO in the solvent. Structural changes in Ar that enhance the stability of **5** decrease $k_{ii}/k_{-i}$[MeOD] and shift the mechanism toward $(E1cB)_{rev}$. It is also shown that for **4** in general $k_{ii}$ appears larger than would be expected for a leaving group of the basicity of $Ar'SO_2CH_2^-$. Repulsion between the dipoles of the S(O) and $SO_2$ groups in **5** is thought to be responsible.

Earlier work[2,3] on base-catalyzed, sulfine-forming eliminations of (diarylmethyl)sulfinyl compounds has revealed that while the methoxide-induced elimination of methyl diarylmethanesulfinates **1**, eq 1, takes place by an

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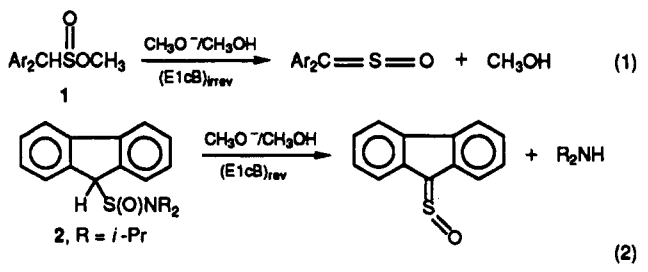
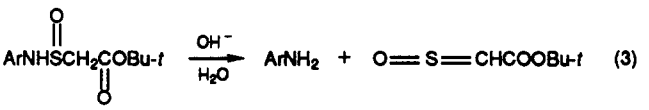


(1)



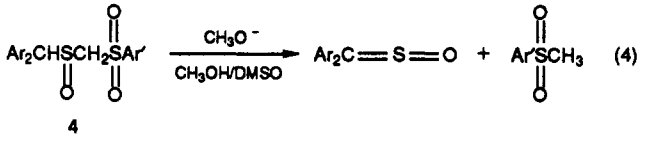
(2)

$(E1cB)_{irreversible}$ mechanism,[2b] the corresponding elimination of an *N,N*-dialkyl-9-fluorenesulfinamide (2), eq 2, where the leaving group, $R_2N$, is much poorer than MeO, proceeds by an $(E1cB)_{reversible}$ pathway.[3] An $(E1cB)_{rev}$ mechanism has also been established for another elimination (eq 3), leading to the formation of a sulfine from a sulfinamide.[4]



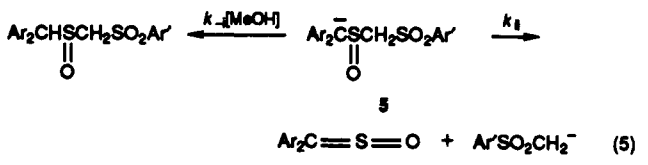
(3)

We were curious as to whether methoxide-catalyzed sulfine formation could be observed with (diarylmethyl)-sulfinyl derivatives where the leaving group would be some type of stabilized carbanion and, if so, what would be the mechanism of the elimination? This led us to examine the behavior of diarylmethyl (arylsulfonyl)methyl sulfoxides ($Ar_2CHS(O)CH_2SO_2Ar'$) 4. We have found that these compounds undergo elimination (eq 4) surprisingly easily



(4)

in the presence of methoxide ion in $CH_3OH$–DMSO. The mechanism for this facile elimination turns out to be perched on the $(E1cB)_{irrev}/(E1cB)_{rev}$ borderline, leading to a situation where suitable alteration in Ar or Ar′ results in a switch from a reaction proceeding by an $(E1cB)_{reversible}$ mechanism to one that proceeds by an essentially $(E1cB)_{irreversible}$ mechanism. Equation 4 therefore presents a system where the effect of changes in structure of Ar and Ar′, and other reaction variables, on the partitioning of the intermediate carbanion (5) between pathways $k_{ii}$ and $k_{-i}$ (eq 5) can be probed with precision. The information on

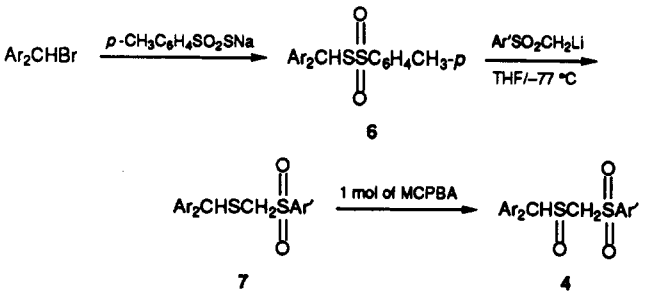


(5)

$(k_{ii}/k_{-i})$ so obtained provides insight into the effect of various reaction variables on the behavior of α-sulfinyl carbanion intermediates in sulfine-forming eliminations.

The present paper summarizes and discusses the results of our study of the elimination of 4 shown in eq 4.

**Scheme I. Synthesis of Diarylmethyl (Arylsulfonyl)methyl Sulfoxides 4**



## Results

**Synthesis of 4.** The various diarylmethyl (arylsulfonyl)methyl sulfoxides 4 used as substrates were synthesized by the reaction sequence shown in Scheme I. The appropriate *S*-diarylmethyl *p*-toluenethiosulfonate (6), prepared by reaction[5] of sodium *p*-toluenethiosulfonate with the diarylmethyl bromide, was treated in tetrahydrofuran (THF) at −77 °C with the α-lithio derivative of the aryl methyl sulfone (generated by reaction of the sulfone with *n*-butyllithium). The resulting diarylmethyl (arylsulfonyl)methyl sulfide (7) was then converted to 4 by oxidation with 1 molar equiv of *m*-chloroperoxybenzoic acid (MCPBA).

In the $^1H$ NMR spectrum of 4 in $CDCl_3$ the C*H*S(O) proton is a singlet at δ 5.15–5.30, while the methylene group between the S(O) and $SO_2$ groups appears as an AB quartet ($J_{AB}$ = 14 Hz) at δ 3.9–4.3.

**Methoxide-Induced Cleavage of 4. Products.** Upon treatment at room temperature in $CH_3OH$–DMSO (7:3 v/v) with methoxide ion (0.02 M), all of the diarylmethyl (arylsulfonyl)methyl sulfoxides 4 underwent cleavage according to eq 4 very readily ($t_{1/2}$ = 20–300 s, depending on Ar and Ar′). Workup of the final reaction solution afforded the methyl aryl sulfone ($Ar'SO_2CH_3$) in 80–94% yield. Quantitative formation of the diarylsulfine, $Ar_2C{=}S{=}O$, was established by measuring the increase in optical density of the solution at the wavelength in the 330-nm region corresponding to $\lambda_{max}$ for the sulfine. Once formed the sulfine slowly underwent decomposition in the basic solution, with the major organic product being the diaryl ketone ($Ar_2C{=}O$). However, this base-induced decomposition of the sulfine was so much slower than its rate of formation from 4 that it did not interfere with accurate estimation of the total yield of sulfine formed by eq 4.

**Kinetics.** The kinetics of eq 4 were studied in $CH_3OH$–DMSO (7:3 v/v) and $CD_3OD$–DMSO (7:3 v/v) by following the increase with time in the optical density (*A*) of the solution at $\lambda_{max}$ for the diarylsulfine ($Ar_2C{=}S{=}O$). Plots of log $(A_\infty - A)$ vs time showed excellent linearity. The experimental first-order rate constants, $k_1$, obtained from the slopes of these plots for the different runs are tabulated in Table II (supplementary material).[6] For each 4 a plot of $k_1$ vs $[MeO^-]$ was linear, and the second-order rate constants, $k_{elim} = k_1/[MeO^-]$, for the different substrates in both $CH_3OH$–DMSO (7:3 v/v) and $CD_3OD$–DMSO (7:3) at 25 °C obtained from the slopes of these plots are shown in the second and third columns of Table I. The solvent isotope effect, $k_{elim}(MeOD)/k_{elim}(MeOH)$, associated with eq 4 for each substrate is tabulated in the

(1) (a) Paper 5. Study of Reactions Leading to Sulfine Formation. Previous paper: *J. Org. Chem.* **1990**, *55*, 1523. (b) This research was supported by the National Science Foundation, Grants CHE-8610116 and CHE-9000175.

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

**Table I. Rate Constants for Methoxide-Catalyzed Elimination and Exchange of 4 in 7:3 Methanol-Dimethyl Sulfoxide at 25 °C**

| $Ar_2CHS(O)CH_2SO_2Ar'$ (4) | | $k_{elim}$,[a] $M^{-1}$ $s^{-1}$ | | | | |
|---|---|---|---|---|---|---|
| Ar | Ar' | in $CH_3OH$ | in $CD_3OD$ | $\frac{k(MeOD)}{k(MeOH)}$ | $k_{CHSO}$[b] ($M^{-1}$ $s^{-1}$) in $CD_3OD$ | ($k_{CHSO}/k_{elim}$) in $CD_3OD$ |
| $p$-$ClC_6H_4$ | Ph (**4a**) | 1.6 | 3.9 | 2.4 | 20 | 5.2 |
| $p$-$CH_3C_6H_4$ | Ph (**4b**) | 0.11 | 0.28 | 2.5 | 0.38 | 1.4 |
| Ph | Ph (**4c**) | 0.31 | 0.77 | 2.4 | 1.15 | 1.5 |
| Ph | $p$-$ClC_6H_4$ (**4d**) | 0.79 | 1.7 | 2.2 | 2.0 | 1.2 |
| Ph | $p$-$CH_3C_6H_4$ (**4e**) | 0.17 | 0.41 | 2.4 | 0.91 | 2.2 |
| Ph | $p$-$CH_3OC_6H_4$ (**4f**) | 0.11 | 0.26 | 2.4 | 0.91 | 3.5 |

[a] Slope of plot of $k_1$ for eq 4 vs [$MeO^-$]. [b] Slope of plot of $k_d$ for the disappearance of the $^1H$ NMR signal for $Ar_2CHS(O)$ vs [$MeO^-$].

fourth column of the same table; it ranges from 2.2 to 2.5.

In addition to the studies of eq 4 in 7:3 $CH_3OH$–DMSO at 25 °C, summarized in Table I, we also investigated, using $Ph_2CHS(O)CH_2SO_2C_6H_4CH_3$-$p$ (**4e**) as substrate, the effect on $k_{elim}$ of a change in solvent from 7:3 $CH_3OH$–DMSO to 5:5 $CH_3OH$–DMSO. For **4e**, $k_{elim}$ in 5:5 $CH_3OH$–DMSO was 1.9 $M^{-1}$ $s^{-1}$ (or 11 times faster than that in 7:3 $CH_3OH$–DMSO), while in 5:5 $CD_3OD$–DMSO it was 4.1 $M^{-1}$ $s^{-1}$ (or 10 times larger than that in 7:3 $CD_3OD$–DMSO).

The activation parameters for $Ph_2CHS(O)CH_2SO_2Ph$ (**4c**) were evaluated by determining $k_{elim}$ for **4c** in 7:3 $CH_3OH$–DMSO at 40 °C (1.7 $M^{-1}$ $s^{-1}$), 25 °C (0.31 $M^{-1}$ $s^{-1}$), and 10 °C (0.047 $M^{-1}$ $s^{-1}$). From these data, $\Delta H^{\ddagger}$ = 20.2 kcal/mol and $\Delta S^{\ddagger}$ = +7.0 eu for **4c** undergoing the elimination in eq 4 in 7:3 $CH_3OH$–DMSO as solvent.

**Kinetics of the Disappearance of the $^1H$ NMR Signal for the $Ar_2CHS(O)$ Proton in 4.** As noted earlier, in **4** the $Ar_2CHS(O)$ proton appears in the $^1H$ NMR spectrum as a singlet ($\delta$ 5.15–5.30 in $CDCl_3$) and the $S(O)CH_2SO_2$ group as an AB quartet (between $\delta$ 3.9 to 4.3 in $CDCl_3$).

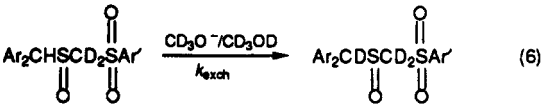
When **4** are dissolved in 7:3 $CD_3OD$–DMSO and base is added, the AB quartet of the $S(O)CH_2SO_2$ group disappears immediately due to the very rapid H/D exchange of these quite acidic protons. The disappearance of the $Ar_2CHS(O)$ signal is much slower, however, and can be studied kinetically. We followed the kinetics of the disappearance of the singlet for the $Ar_2CHS(O)$ proton 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 the $CHS(O)$ singlet, $k_d$, was obtained from the slope of a plot of log ($I/I_0$) for that resonance vs time. The values of $k_d$ for the runs with the different **4** under the various reaction conditions (methoxide concentration, temperature, etc.) are given in Table III (supplementary material).[6]

With each **4** plots of $k_d$ vs [$MeO^-$] were linear, demonstrating the first-order dependence of the process on methoxide concentration, and second-order rate constants, $k_{CHSO} = k_d/[MeO^-]$, were determined from the slopes of these plots. The values of $k_{CHSO}$ for the different **4** at 25 °C in 7:3 $CD_3OD$–DMSO are presented in column six of Table I.

The effect of a change in solvent from 7:3 $CD_3OD$–DMSO to 5:5 $CD_3OD$–DMSO on $k_{CHSO}$ was evaluated by using **4e** as the substrate, the same compound employed to assess the effect of this solvent change on $k_{elim}$; in 5:5 $CD_3OD$–DMSO $k_{CHSO}$ for **4e** at 25 °C was 6.2 $M^{-1}$ $s^{-1}$ (or 6.8 times larger than that in 7:3 $CD_3OD$–DMSO).

The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ associated with $k_{CHSO}$ were determined for several different **4**. In 7:3 $CD_3OD$–DMSO $\Delta H^{\ddagger}$ = 19.2 kcal/mol and $\Delta S^{\ddagger}$ = +6.1 eu for **4c**, and $\Delta H^{\ddagger}$ = 18.1 kcal/mol and $\Delta S^{\ddagger}$ = +8.2 eu for $(p\text{-}ClC_6H_4)_2CHS(O)CH_2SO_2Ph$ (**4a**). In 5:5 $CD_3OD$–DMSO $\Delta H^{\ddagger}$ = 19.6 kcal/mol and $\Delta S^{\ddagger}$ = +10.8 eu for **4e**.

Both elimination to give the diarylsulfine (eq 4) and prior H/D exchange of the $Ar_2CHS(O)$ proton (eq 6) lead



(6)

to the disappearance of the $^1H$ NMR signal for that proton. Therefore in Table I

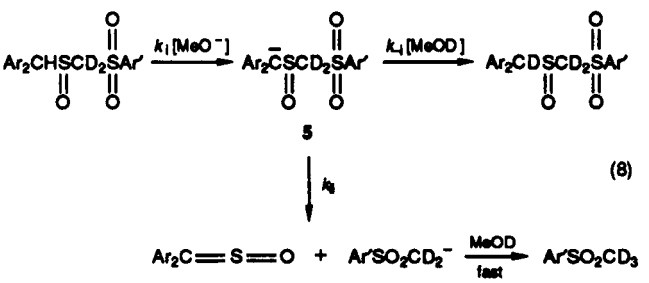
$$k_{CHSO} = k_{elim}^{CD_3OD} + k_{exch} \quad (7)$$

From the values of $k_{CHSO}/k_{elim}$ in $CD_3OD$ shown in the last column of Table I, it is apparent that for some **4** (such as **4a** or **4f**) $k_{exch} > k_{elim}$, while for others (such as **4b** or **4d**), exactly the reverse is true, i.e., $k_{exch} < k_{elim}$.

## Discussion

**Mechanism of the Methoxide-Catalyzed Elimination of 4.** On treatment with methoxide in $CH_3OH$–DMSO (7:3 v/v), diarylmethyl (arylsulfonyl)methyl sulfoxides **4** undergo cleavage (eq 4) to a diarylsulfine and a methyl aryl sulfone easily and quantitatively. This elimination reaction shows a straightforward, first-order dependence on methoxide concentration under all conditions; there is no sign of a less than first-order dependence on [$MeO^-$] at higher methoxide concentrations. In every case $k_{elim}$ (the rate constant for eq 4) is *less* than $k_{CHSO}$ (the rate constant for the disappearance of the $^1H$ NMR signal for the $Ar_2CHS(O)$ proton in **4** in $CD_3OD$/DMSO), although in some cases, such as **4b** or **4d**, the difference is only 20–40%. The solvent isotope effect, $k_{elim}(CD_3OD)/k_{elim}(CH_3OH)$, for eq 4 ranges from 2.2 to 2.5.

All of these observations are consistent with the mechanism for eq 4 being as shown in eq 8, with $k_{ii} < k_{-i}$[MeOD]



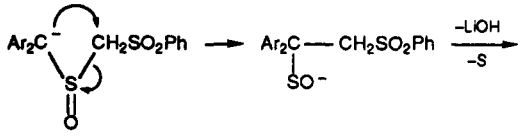
(8)

for some **4** (such as **4a** and **4f**) but with $k_{ii} > k_{-i}$[MeOD] for other **4** (such as **4b** or **4d**). The reaction is an E1cB elimination whose mechanism is perched on the $(E1cB)_{rev}/(E1cB)_{irrev}$ borderline. In some instances, such as **4a** or **4f**, where $k_{ii} < k_{-i}$[MeOD], it is $(E1cB)_{reversible}$, but in others, such as **4b** or **4d**, where $k_{ii}$ is slightly greater than $k_{-i}$[MeOD], it approaches being $(E1cB)_{irreversible}$.

Before discussing the results in Table I in detail in terms of the mechanism in eq 8, we need to digress briefly in order to point out (a) that an alternative mode of breakdown of carbanion **5** that has been suggested in the lit-

erature[7] is not a factor under our reaction conditions and (b) that the p$K_a$ of the protons in the $S(O)CH_2SO_2$ group in **4** (the most acidic in the molecule) is not quite low enough to complicate the kinetic behavior of the elimination.

Zwanenburg and co-workers[7] have examined the addition of $PhSO_2CH_2Li$ to diarylsulfines ($Ar_2C{=}S{=}O$). They found that a good yield of $Ar_2CHS(O)CH_2SO_2Ph$ was obtained only when 2 mol of $PhSO_2CH_2Li$ were used per mole of sulfine. Under those conditions the second mole of the lithium reagent converts the initial adduct anion $Ar_2\bar{C}S(O)CH_2SO_2Ph$ to the dianion $Ar_2\bar{C}S(O)\bar{C}HSO_2Ph$. If only 1 mol of $PhSO_2CH_2Li$ per mole of sulfine was used, the principal product was $Ar_2C{=}CHSO_2Ph$. Zwanenburg[7] suggested that this arose via the following path




$Ar_2C{=}CHSO_2Ph$ (9)

We believe that the reason we do not see this mode of breakdown of **5** in our system is as follows. Under the reaction conditions used by Zwanenburg et al. the cleavage of **5** to $Ar_2C{=}S{=}O$ and $PhSO_2CH_2^-$ would be reversible, and elimination to form sulfine followed by readdition of $PhSO_2CH_2^-$ to regenerate **5** probably occurs many times for every time that the alternate mode of collapse of **5** (eq 9) occurs. Under our reaction conditions the cleavage of **5** to form $Ar_2C{=}S{=}O$ and $Ar'SO_2CH_2^-$ is *not* reversible, because $Ar'SO_2CH_2^-$ is converted to $Ar'SO_2CH_3$ as soon as it is formed. Thus we observe only the pathway for collapse of **5** shown as step $k_{ii}$ in eq 8, with it being much faster than the alternative in eq 9.

The most acidic protons in **4** are those in the $S(O)CH_2SO_2$ group. Initially we worried that their p$K_a$ might be low enough that a significant fraction of **4** would be present at equilibrium as $Ar_2CHS(O)\bar{C}HSO_2Ar'$ ($\mathbf{4}^-$), especially in the solutions having the highest methoxide concentrations. Given the observation[7] that dianion $Ar_2\bar{C}S(O)\bar{C}HSO_2Ar$ apparently does not undergo cleavage, or does so only with great difficulty, if a significant fraction of **4** were present at equilibrium as $\mathbf{4}^-$ at higher [$MeO^-$], this should lead to a less than first-order dependence of $k_{elim}$ on [$MeO^-$] at higher methoxide concentration. The fact that this is not observed shows that no more than a small fraction (10% of less) of **4** is present at equilibrium as $\mathbf{4}^-$ in any of the solutions used and the p$K_a$ of the $S(O)CH_2SO_2$ group in **4** in each case is at least 1 p$K$ unit greater than the $H_-$ of the reaction solution.

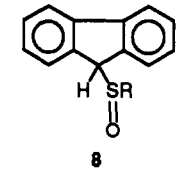
Based on the p$K_a$s (in DMSO)[8] of the methylene groups in $PhSO_2CH_2SO_2Ph$ (12.2) and $PhSCH_2SO_2Ph$ (20.3), and the fact that the p$K_a$ for $PhS(O)CH_2SO_2Ph$ should be intermediate between those values (given that a sulfinyl group in other systems has less of an acidifying effect on adjacent protons than a sulfonyl group),[8] we estimate that the p$K_a$ for $Ph_2CHS(O)CH_2SO_2Ph$ (**4c**) is probably between 14.5 and 16. The most basic solutions employed in the present study (0.02 M $MeO^-$ in 19.5 mol % DMSO) have an $H_-$ of 13.5.[9] It is therefore reasonable that the p$K_a$ of **4** is at least 1 p$K$ unit greater than $H_-$ in even the most basic solutions used and that the fraction of **4** present at equilibrium as $\mathbf{4}^-$ is too small to have a detectable impact on the kinetic behavior of the elimination.

**Origin of the Relatively Rapid Rates of Elimination for 4.** We now return to a discussion of the significance of our results in terms of the mechanism in eq 8. From this mechanism the rate constant ($k_{elim}$) for the elimination of **4** in $CD_3OD$ will be as shown in eq 10.

$$k_{elim} = k_i\left[\frac{k_{ii}}{k_{ii} + k_{-i}[MeOD]}\right] \qquad (10)$$

As noted earlier, the rates of elimination of **4** are surprisingly rapid. As will be outlined in succeeding paragraphs, it can be shown that this is *not* due to $k_i$ being unexpectedly fast but rather to $k_{ii}/k_{-i}$[MeOD] being larger than might have been anticipated based purely on the p$K_a$ of the conjugate acid of the leaving group $Ar'SO_2CH_2^-$ (p$K_a$ of $PhSO_2CH_3$ = 29.0).[10]

For each **4** $k_i$ should be equal to $k_{CHSO}$. For **4c** this means that $k_i$ = 1.15 $M^{-1}$ $s^{-1}$ in 7:3 $CD_3OD$–DMSO (v/v) at 25 °C (see Table I). From data for other (diarylmethyl)sulfinyl derivatives, we can also estimate what $k_i$ for **4c** might be predicted to be. For methyl diphenylmethanesulfinate $Ph_2CHS(O)OMe$, $k_i$ for methoxide-induced $\alpha$-sulfinyl carbanion formation is 0.085 $M^{-1}$ $s^{-1}$ at 25 °C in $CD_3OD$.[2a] Based on the variation in $k_{CHSO}$ with change in solvent from 7:3 $CD_3OD$–DMSO to 5:5 $CD_3OD$–DMSO seen in the current study and the variation in $H_-$ for a given methoxide concentration associated with a solvent change from $CD_3OD$ to 7:3 $CD_3OD$–DMSO (v/v),[9] we estimate that $k_i$ for $Ph_2CHS(O)OMe$ should be approximately 10 times larger, or 0.85 $M^{-1}$ $s^{-1}$, in 7:3 $CD_3OD$–DMSO than it is in $CD_3OD$. For a series of 9-fluorenylsulfinyl compounds (**8**), $k_i$ for base-catalyzed re-




**8**

moval of the 9-H has been shown to be dependent on $\sigma^*$ for R, and $k_i$ for **8** with R = $CH_2CN$ is about 1.5 times larger than $k_i$ for the case where R = $OCH_3$.[2b] Since $\sigma^*$ for $PhSO_2CH_2$ is approximately equal to $\sigma^*$ for $CH_2CN$,[11] $k_i$ for methoxide-catalyzed formation of **5c** from **4c** should probably be about 1.5 times faster than that for the formation of the $\alpha$-sulfinyl carbanion from $Ph_2CHS(O)OCH_3$. So the predicted $k_i$ for methoxide-catalyzed formation of **5c** from **4c** in 7:3 $CD_3OD$–DMSO at 25 °C is 1.3 $M^{-1}$ $s^{-1}$; this is very close to the actual observed value of 1.15 $M^{-1}$ $s^{-1}$.

The relatively rapid rates of elimination ($k_{elim}$) of **4** are therefore *not* due to $k_i$ being faster than would be expected from the rates of $\alpha$-sulfinyl carbanion formation of other (diarylmethyl)sulfinyl compounds.

For **4** $k_{ii}/k_{-i}$[MeOD], which is equal to $1/[(k_{CHSO}/k_{elim}) - 1]$, varies from 0.24 (**4a**) to 5.3 (**4d**). The behavior of $PhSO_2CH_2$ as a leaving group with respect to $k_{ii}/k_{-i}$-

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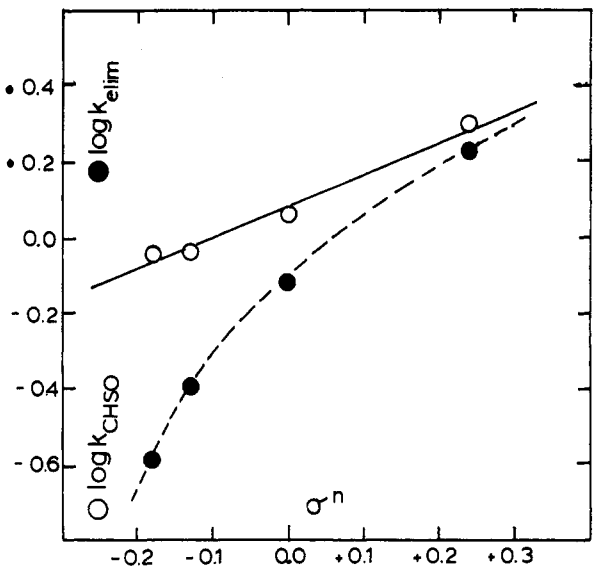
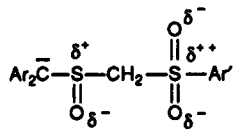



**Figure 1.** Plot of log $k_{CHSO}$ (○) and log $k_{elim}$ (●) for $Ph_2CHS(O)CH_2SO_2Ar'$ vs $\sigma^n$ for substituent in Ar'; reactions in 7:3 $CD_3OD$–DMSO at 25 °C.

[MeOD] is thus closer to that of $CH_3O$ in **1** (where $k_{ii}/k_{-i}$[MeOD] ≥ 10)[2a] than to that of $R_2N$ in **2** (where $k_{ii}/k_{-i}$[MeOD] = 0.008),[3] whereas on the basis of the p$K_a$s of $CH_3OH$ (15.2 in $H_2O$[12a]) $PhSO_2CH_3$ (29.0 in DMSO),[10] and $R_2NH$ (36 in THF,[12b] ~40 in DMSO,[12c]), it might have been expected to be closer to $R_2N$ than $CH_3O$ in behavior.

We believe the values of $k_{ii}/k_{-i}$[MeOD] for **5** are larger than might be expected from the p$K_a$ of $ArSO_2CH_3$ because $k_{ii}$ is larger than expected. We suggest that the reason for this is the existence in **5** of a significant inductive



**5**

repulsion between the dipoles of the sulfinyl and sulfonyl groups that is relieved by the expulsion of $Ar'SO_2CH_2^-$.

**Effect of Structure on $k_{ii}/k_{-i}$[MeOD] for 5.** Figure 1 shows a plot of log $k_{CHSO}$ and log $k_{elim}$ for $Ph_2CHS(O)CH_2SO_2Ar'$ vs $\sigma^n$ for Ar'. The plot of log $k_{CHSO}$ (remember that $k_{CHSO} = k_i$) vs $\sigma^n$ is linear with a slope ($\rho$) of +0.82, showing that, as might be anticipated because of their distance from the reaction site, substituents in Ar' have only a modest effect on the rate of proton removal from the CHS(O) group in **4**. The plot of log $k_{elim}$ vs $\sigma^n$ is curved, since for substituents like *p*-Cl $k_{ii} > k_{-i}$[MeOD], while for those like *p*-$CH_3O$ or *p*-$CH_3$ $k_{ii} < k_{-i}$[MeOD]. As noted above

$$(k_{ii}/k_{-i}[\text{MeOD}]) = \frac{1}{(k_{CHSO}/k_{elim}) - 1} \qquad (11)$$

The ($k_{CHSO}/k_{elim}$) in Table I lead to the following values for $k_{ii}/k_{-i}$[MeOD]) for the different Ar' groups:

| Ar' | $k_{ii}/k_{-i}$[MeOD] |
|---|---|
| *p*-$ClC_6H_4$ | 5.8 |
| $C_6H_5$ | 2.0 |
| *p*-$CH_3C_6H_4$ | 0.83 |
| *p*-$CH_3OC_6H_4$ | 0.40 |

The presence of an electron-withdrawing substituent like *p*-Cl in Ar' should increase $k_{ii}$ (because it will make $Ar'SO_2CH_2^-$ a better leaving group). Presumably it should also decrease $k_{-i}$, since it should stabilize the carbanion intermediate (**5d**) relative to the starting compound (**4d**). However, in view of the small $\rho$ (+0.8) associated with the effect of substituents in Ar' on $k_i$, their effect on $k_{-i}$ is likely to be modest at best. The effect of electron-donating substituents in Ar' (such as *p*-$CH_3$ or *p*-$CH_3O$) should be just the opposite; they should decrease $k_{ii}$ significantly and increase $k_{-i}$ by a small amount. The observed changes in $k_{ii}/k_{-i}$[MeOD] with change in the substituent in Ar' are clearly in accord with these expectations.

For $Ar_2CHS(O)CH_2SO_2Ph$ **4a–c** a plot of log $k_{CHSO}$ (log $k_i$) vs $\Sigma\sigma^n$ for the substituents in the two Ar groups has a slope ($\rho$) of +2.5, a value quite similar to the dependence ($\rho$ = +2.8) of rate on $\Sigma\sigma^n$ found[2a] for $k_i$ for methoxide-catalyzed formation of $Ar_2\bar{C}S(O)OMe$ from $Ar_2CHS(O)OMe$. Values of $k_{ii}/k_{-i}$[MeOD] for **4a–c**, as calculated from eq 11 and the ($k_{CHSO}/k_{elim}$) values in Table I are

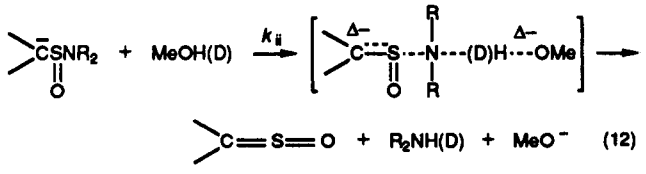
| Ar | $k_{ii}/k_{-i}$[MeOD] |
|---|---|
| *p*-$ClC_6H_4$ | 0.24 |
| $C_6H_5$ | 2.0 |
| *p*-$CH_3C_6H_4$ | 2.8 |

These data suggest that substituents in Ar like *p*-Cl that are electron-withdrawing (and stabilize carbanion **5**) apparently slow down $k_{ii}$ much more than they reduce $k_{-i}$. The effect of an electron-donating (and carbanion destabilizing) substituent like *p*-$CH_3$ is opposite.

The effect of an increase in the DMSO content of the solvent on $k_{ii}/k_{-i}$[MeOD] was also examined. Data for **4e** show that $k_{ii}/k_{-i}$[MeOD] increases from 0.83 in 7:3 MeOD–DMSO to 2.0 in 5:5 MeOD–DMSO. We suggest that this increase results from the fact that the decreased proton-donating power, including lower [MeOD], of 5:5 MeOD–DMSO vs 7:3 MeOD–DMSO decreases $k_{-i}$[MeOD]. At the same time this solvent change has negligible impact on $k_{ii}$, a reaction in which one carbanion (**5e**) is converted to another, *p*-$CH_3C_6H_4SO_2CH_2^-$.

**Solvent Isotope Effect.** One final point worth discussion is the solvent isotope effect, $k_{elim}$(MeOD)/$k_{elim}$(MeOH), for eq 4 and the way it contrasts with what has been found[3] for a sulfine-forming elimination of a sulfinamide, a reaction that also involves a leaving group ($R_2N$) whose conjugate acid has a high p$K_a$.

For the $(E1cB)_{rev}$ elimination of sulfinamide **2** (eq 2), $k$(MeOD)/$k$(MeOH) = 0.66.[3] Since the solvent isotope effect, $K_{MeOD}/K_{MeOH}$, for the equilibrium ($k_i/k_{-i}$) between **2** and the α-sulfinyl carbanion can be shown[3] to be ≥2.0, this means that $k_{ii}$(MeOD)/$k_{ii}$(MeOH) for this elimination is ≤0.3 and that there is a sizeable *primary* kinetic isotope effect associated with the $k_{ii}$ step. The explanation[3] is that because $R_2N^-$ is such a strongly basic anion, expulsion of $R_2N$ from the α-sulfinyl carbanion (eq 12) is accompanied




(12)

by the transfer of a proton from the solvent to the leaving group, so that it departs, in effect, as $R_2NH$ rather than $R_2N^-$. We had anticipated that we might find similar behavior in the eliminations involving **4** since $Ar'SO_2CH_2^-$ is also a strongly basic anion (p$K_a$ of $PhSO_2CH_3$ = 29).[10] However, the solvent isotope effect data in Table I indicate otherwise. Both those eliminations that are clearly

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$(E1cB)_{rev}$ ($k_{ii}$ rate-determining), like those of **4a** or **4f**, and those that are effectively $(E1cB)_{irrev}$ ($k_i$ rate-determining), like those of **4b** or **4d**, exhibit the same solvent isotope effect, $k_{elim}(MeOD)/k_{elim}(MeOH) = 2.2$ to 2.4. Furthermore a solvent isotope effect of this magnitude for the $(E1cB)_{rev}$ reactions is that expected for $k_{ii}(MeOD)/k_{ii}(MeOH) \cong 1.0$.[13]

We conclude therefore that although $Ar'SO_2CH_2^-$ is a leaving group whose conjugate acid has a $pK_a \cong 30$, it is expelled from **5** in the $k_{ii}$ step of eq 8 as $Ar'SO_2CH_2^-$ and *not* in a process (akin to eq 12) where a proton is transferred to it from the solvent synchronous with its departure.

**Summary.** The present study demonstrates that sulfine-forming eliminations where the leaving group is a stabilized carbanion are indeed possible and, in the case of **4**, surprisingly facile.

Mechanistically the methoxide-catalyzed eliminations of **4** are located on the $(E1cB)_{rev}/(E1cB)_{irrev}$ borderline, and slight changes in structure can shift the mechanism from $(E1cB)_{rev}$ to $(E1cB)_{irrev}$ as a result of their effect on the partitioning ($k_{ii}/k_{-i}[MeOD]$) of the intermediate $\alpha$-sulfinyl carbanion **5** in eq 8. Structural changes in $Ar'SO_2CH_2$ that make it a better leaving group increase $k_{ii}/k_{-i}[MeOD]$ and shift the mechanism toward $(E1cB)_{irrev}$, as does also an increase in the percentage of DMSO in the $CH_3OH$–DMSO solvent mixture used as reaction solvent. Structural changes in Ar that enhance the stability of the intermediate $\alpha$-sulfinyl carbanion $Ar_2\bar{C}S(O)CH_2SO_2Ar'$ decrease $k_{ii}/k_{-i}[MeOD]$ and shift the mechanism toward $(E1cB)_{rev}$.

The present results raise the possibility of other relatively easy sulfine-forming eliminations where the leaving group is a carbanion. One of these, the base-catalyzed decomposition of di-9-fluorenyl sulfoxide, is discussed in the accompanying paper.

## Experimental Section

**Synthesis of Diarylmethyl (Arylsulfonyl)methyl Sulfides 7.** Needed starting materials for the synthesis of **7** were diarylmethyl *p*-toluenethiosulfonates **6** and aryl methyl sulfones. Thiosulfonates **6** were prepared by the reaction of the diarylmethyl bromide ($Ar_2CHBr$) with an equimolar amount of sodium *p*-toluenethiosulfonate in acetonitrile by using the procedure of Kice and Weclas.[5] The preparation and properties of 4,4′-dichlorodiphenylmethyl (**6a**) and diphenylmethyl (**6c**) *p*-toluenethiosulfonates have been described earlier.[5] 4,4′-Dimethyldiphenylmethyl *p*-toluenethiosulfonate (**6b**) was obtained in 52% yield, mp 123–125 °C: IR (KBr) 1315 and 1130 $cm^{-1}$ ($SO_2$); $^1H$ NMR ($CDCl_3$) $\delta$ 2.27 (s, 6 H), 2.35 (s, 3 H), 5.82 (s, 1 H), 6.94–7.37 (m, 12 H).

The different aryl methyl sulfones were prepared by the reaction of the sodium arenesulfinate ($Ar'SO_2Na$) with excess methyl iodide in DMSO at room temperature. At the completion of the reaction, the reaction mixture was poured into water and the sulfone, which precipitated, was filtered off and recrystallized from ethyl acetate–hexane. The yields and mp's of the sulfones were as follows: phenyl methyl sulfone (60%), mp 83–85 °C (lit.[16] mp 89 °C); *p*-chlorophenyl methyl sulfone (67%), mp 92–95 °C (lit.[17] mp 96 °C); *p*-tolyl methyl sulfone (43%), mp 84–86 °C (lit.[18] 87–88 °C); *p*-anisyl methyl sulfone (61%), mp 118–120 °C (lit.[19] 120 °C). Sodium benzenesulfinate and *p*-toluenesulfinate were commercially available (Aldrich). Sodium *p*-chlorobenzenesulfinate was prepared from *p*-chlorobenzenesulfonyl chloride (Aldrich) by the procedure of Kulka,[20] and sodium *p*-methoxybenzenesulfinate was prepared from *p*-methoxybenzenesulfonyl chloride (Aldrich) by the procedure of Overberger and Godfrey.[21]

The general procedure for the synthesis of **7** from **6** and an aryl methyl sulfone was as follows. All reactions were carried out under nitrogen.

To 0.054 mol of the appropriate aryl methyl sulfone ($Ar'SO_2CH_3$) dissolved in 100 mL of anhydrous tetrahydrofuran (THF) and cooled to −77 °C was slowly added 21.6 mL of a 2.5 M solution of butyllithium in hexanes (Aldrich). The mixture was stirred for 0.5 h at −77 °C and then 0.027 mol of the appropriate diarylmethyl *p*-toluenethiosulfonate **6**, dissolved in 100 mL of anhydrous THF, was added dropwise with stirring. After an additional 0.5 h at −77 °C the reaction mixture was poured into saturated ammonium chloride solution. The product **7** was extracted with ethyl acetate, the extracts were washed with brine and dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using methylene chloride–hexane mixtures as eluants. The sulfides **7** isolated from the chromatography were further purified by recrystallization.

**4,4′-Dichlorodiphenylmethyl (phenylsulfonyl)methyl sulfide (7a)** was obtained in 21% yield after recrystallization from methylene chloride–hexane, mp 121–122 °C: IR (KBr) 1300 and 1150 $cm^{-1}$ ($SO_2$); $^1H$ NMR ($CDCl_3$) $\delta$ 3.73 (s, 2 H), 5.71 (s, 1 H), 7.32–7.96 (m, 13 H). Anal. Calcd for $C_{20}H_{16}Cl_2O_2S_2$: C, 56.70; H, 3.80; S, 15.10. Found: C, 56.93; H, 3.73; S, 15.26.

**4,4′-Dimethyldiphenylmethyl (phenylsulfonyl)methyl sulfide (7b)** was recrystallized from chloroform–hexane, mp 92–94 °C (16%): IR (KBr) 1295 and 1145 $cm^{-1}$ ($SO_2$); $^1H$ NMR ($CDCl_3$) $\delta$ 2.31 (s, 6 H), 3.74 (s, 2 H), 5.49 (s, 1 H), 7.09–7.98 (m, 13 H). Anal. Calcd for $C_{22}H_{22}O_2S_2$: C, 69.07; H, 5.80; S, 16.76. Found: C, 69.01; H, 5.71; S, 16.16.

**Diphenylmethyl (phenylsulfonyl)methyl sulfide (7c)** was isolated in 40% yield after recrystallization from ether–hexane, mp 131–132 °C: IR (KBr) 1310 and 1150 $cm^{-1}$ ($SO_2$); $^1H$ NMR ($CDCl_3$) $\delta$ 3.75 (s, 2 H), 5.61 (s, 1 H), 7.22–7.98 (m, 15 H). Anal. Calcd for $C_{20}H_{18}O_2S_2$: C, 67.80; H, 5.10; S, 18.10. Found: C, 67.33; H, 5.06; S, 18.31.

**Diphenylmethyl [(*p*-chlorophenyl)sulfonyl]methyl sulfide (7d)** was obtained in 26% yield after recrystallization from methylene chloride–hexane, mp 146–147 °C: IR (KBr) 1310 and 1155 $cm^{-1}$ ($SO_2$); $^1H$ NMR ($CDCl_3$) $\delta$ 3.74 (s, 2 H), 5.71 (s, 1 H), 7.26–7.91 (m, 14 H). Anal. Calcd for $C_{20}H_{17}ClO_2S_2$: C, 61.76; H, 4.41; S, 16.49. Found: C, 62.12; H, 4.43; S, 16.26.

**Diphenylmethyl (*p*-tolylsulfonyl)methyl sulfide (7e)** was recrystallized from chloroform–petroleum ether, mp 133–134 °C (32%): IR (KBr) 1300, 1150 $cm^{-1}$ ($SO_2$); $^1H$ NMR ($CDCl_3$) $\delta$ 2.46 (s, 3 H), 3.73 (s, 2 H), 5.64 (s, 1 H), 7.25–7.86 (m, 14 H). Anal. Calcd for $C_{21}H_{20}O_2S_2$: C, 68.40; H, 5.47; S, 17.40. Found: C, 68.02; H, 5.36; S, 16.90.

**Diphenylmethyl [(*p*-methoxyphenyl)sulfonyl]methyl sulfide (7f),** mp 120–121 °C, was recrystallized from methylene chloride–hexane (36%): IR (KBr) 1320, 1150 $cm^{-1}$ ($SO_2$); $^1H$ NMR ($CDCl_3$) $\delta$ 3.72 (s, 2 H), 3.88 (s, 3 H), 5.63 (s, 1 H), 7.00–7.91 (m, 14 H). Anal. Calcd for $C_{21}H_{20}O_3S_2$: C, 65.60; H, 5.24. Found: C, 65.34; H, 5.16.

**Synthesis of Diarylmethyl (Arylsulfonyl)methyl Sulfoxides 4.** The following general procedure was used for the oxidation of **7** to the corresponding sulfoxides **4**. To 2.35 mmol of **7** dissolved in 40 mL of chloroform and cooled to 0 °C was added 2.35 mmol of *m*-chloroperoxybenzoic acid. The mixture was

(13) The solvent isotope effect for the equilibrium $4 + MeO^- \rightleftarrows 5 + MeOH$, or ($k_i/k_{-i} = K_i$, will be equal to $\phi_S^p/\phi_{MeO}^m$, where *m* and *p* are the number of methanol molecules specifically solvating $MeO^-$ and **5**, respectively, and $\phi_{MeO}$ and $\phi_S$ are their deuterium fractionation factors.[14] For methoxide $m = 3$ and $\phi_{MeO} = 0.70$,[14c] so that $K_i(MeOD)/K_i(MeOH) = 2.9\phi_S^p$. The solvent isotope effect ($K_{MeOD}/K_{MeOH} = 2.6$) of another equilibrium ($ArOMe + MeO^- \rightleftarrows Ar(OMe)_2^-$),[15] where $MeO^-$ is replaced by a carbanion suggests that $\phi_S^p$ should be slightly smaller than 1, so that the anticipated solvent isotope effect for $k_i/k_{-i}$ is in the range of 2.5.

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stirred at room temperature for 2 h. The progress of the oxidation was monitored by TLC. An additional 50 mL of chloroform was added after the oxidation was complete, and the reaction solution was then washed three times with 5% sodium bicarbonate solution, followed by three washings with water. The chloroform solution was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using methylene chloride followed by ethyl acetate as eluants. The sulfoxides 4 isolated from the chromatography were further purified by recrystallization ($CHCl_3$–hexane, **4a** and **4f**; $Et_2O$–hexane, **4c** and **4e**; $Et_2O$, **4b**; and ethyl acetate–hexane, **4d**). Yields, mp's, and other properties of the various 4 were as follows.

**4,4'-Dichlorodiphenylmethyl (phenylsulfonyl)methyl sulfoxide (4a)**: mp 114–115 °C (73%); IR (KBr) 1305, 1145 ($SO_2$), 1050 $cm^{-1}$ (S=O); $^1H$ NMR ($CDCl_3$) $\delta$ 3.86–4.25 (AB quartet, $J_{AB}$ = 14 Hz, 2 H), 5.29 (s, 1 H), 7.42–7.95 (m, 13 H). Anal. Calcd for $C_{20}H_{16}Cl_2O_3S_2$: C, 54.67; H, 3.67; S, 14.59. Found: C, 54.49; H, 3.59; S, 14.73.

**4,4'-Dimethyldiphenylmethyl (phenylsulfonyl)methyl sulfoxide (4b)**: mp 113–115 °C (69%): IR (KBr) 1300, 1140 ($SO_2$), 1050 $cm^{-1}$ (S=O); $^1H$ NMR ($CDCl_3$) $\delta$ 2.34 (s, 6 H), 3.90–4.28 (AB quartet, $J$ = 14 Hz, 2 H), 5.15 (s, 1 H) 7.17–7.96 (m, 13 H). Anal. Calcd for $C_{22}H_{22}O_3S_2$: C, 66.30; H, 5.56; S, 16.09. Found: C, 66.67; H, 5.42; S, 16.49.

**Diphenylmethyl (phenylsulfonyl)methyl sulfoxide (4c)**: mp 123–126 °C (61%): IR (KBr) 1300, 1140 ($SO_2$) 1050 $cm^{-1}$ (SO); $^1H$ NMR ($CDCl_3$) $\delta$ 3.92–4.28 (AB quartet, $J_{AB}$ = 14 Hz, 2 H), 5.24 (s, 1 H), 7.35–7.96 (m, 15 H). Anal. Calcd for $C_{20}H_{18}O_3S_2$: C, 64.80; H, 4.90; S, 17.30. Found: C, 64.68; H, 4.88; S, 17.90.

**Diphenylmethyl [(*p*-chlorophenyl)sulfonyl]methyl sulfoxide (4d)**: mp 140–142 °C (60%); IR (KBr) 1325, 1150 ($SO_2$), 1040 $cm^{-1}$ (SO); $^1H$ NMR ($CDCl_3$) $\delta$ 3.91–4.26 (AB quartet, $J_{AB}$ = 14 Hz, 2 H), 5.22 (s, 1 H), 7.36–7.89 (m, 14 H). Anal. Calcd for $C_{20}H_{17}ClO_3S_2$: C, 59.32; H, 4.23; S, 15.83. Found: C, 59.29; H, 4.21; S, 15.53.

**Diphenylmethyl (*p*-tolylsulfonyl)methyl sulfoxide (4e)**: mp 134–135 °C (73%); IR (KBr) 1310, 1145 ($SO_2$), 1050 $cm^{-1}$ (SO); $^1H$ NMR ($CDCl_3$) $\delta$ 2.45 (s, 3 H), 3.88–4.26 (AB quartet, $J_{AB}$ = 14 Hz, 2 H), 5.22 (s, 1 H), 7.34–7.83 (m, 14 H). Anal. Calcd for $C_{21}H_{20}O_3S_2$: C, 65.60; H, 5.24; S, 16.68. Found: C, 65.45; H, 5.18; S, 16.80.

**Diphenylmethyl [(*p*-methoxyphenyl)sulfonyl]methyl sulfoxide (4f)**: mp 152–154 °C (80%): IR (KBr) 1325, 1140 ($SO_2$), 1040 $cm^{-1}$ (SO); $^1H$ NMR ($CDCl_3$) $\delta$ 3.87–4.26 (m, 5 H), 5.22 (s, 1 H), 6.99–7.88 (m, 14 H). Anal. Calcd for $C_{21}H_{20}O_4S_2$: C, 62.98; H, 5.03. Found: C, 63.03; H, 5.06.

**Kinetics of the Disappearance of the $Ar_2CHS(O)$ Signal of 4 in the $^1H$ NMR Spectra.** As noted earlier each 4 has a quartet, due to the diastereotopic protons of the $S(O)CH_2SO_2$ group, at $\delta$ 3.9–4.3, and a singlet in the region 5.15–5.29, due to the $Ar_2CHS(O)$ proton. When 4 are dissolved in 7:3 $CD_3OD$/DMSO-$d_6$ and $CD_3O^-$ is added, the quartet due to the $S(O)CH_2SO_2$ group disappears almost immediately, too fast to be followed kinetically by $^1H$ NMR. This is the result of the rapid H/D exchange of these quite acidic protons. The disappearance of the singlet due to the $Ar_2CHS(O)$ proton is much slower and can be followed conveniently by $^1H$ NMR. The integrated intensity ($I$) of the singlet for the C*H*S(O) proton relative to that of an internal standard (the signal at $\delta$ 2.49 due to the small amount of undeuterated DMSO present in the DMSO-$d_6$ solvent) was monitored as a function of time, and rate constants for exchange evaluated from plots of log ($I/I_0$) vs time.

The exchange was carried out in an NMR tube in the thermostatted probe of a Chemagnetics A200 NMR spectrometer. The desired amount of 4 was weighed out, dissolved in 7:3 $CD_3OD$/DMSO-$d_6$, and placed in the NMR tube in the spectrometer, and the reaction was initiated by addition via microsyringe of the correct amount of a solution of $CD_3O^-$ in the same solvent. At appropriate time intervals after the initiation of the reaction, spectra were obtained and stored.

**Kinetics of Sulfine Formation from 4.** An anhydrous methanol–DMSO (7:3 v/v) solution (3.0 mL) containing the desired amount of methoxide ion was placed in a 1-cm spectrophotometer cell in the thermostatted cell compartment of a Beckmann DU-50 UV–vis spectrophotometer. After the solution reached thermal equilibrium, the elimination reaction was initiated by the addition via microsyringe of 20–25 $\mu$L of a 0.005 M solution of 4 in methanol–DMSO. The progress of the formation of the sulfine from 4 was monitored by following the increase in the absorbance of the solution at the wavelength corresponding to the absorption maximum for the sulfine (322 nm for **4a**, 334 nm for **4b**, and 328 nm for **4c–f**). From the absorbance at the end of the reaction ($A_\infty$) and $\epsilon$ for the sulfine,[2] the yield of sulfine formed from 4 was calculated to exceed 95% in every case.

**Formation of Aryl Methyl Sulfones in the Cleavage of 4.** To verify that aryl methyl sulfones ($Ar'SO_2CH_3$) were the other product formed besides the diarylsulfine ($Ar_2C{=}S{=}O$), the following experiments were performed. To 0.46 mmol of 4, dissolved in 40 mL of 7:3 methanol–DMSO, was added 2 mL of a 0.5 M solution of sodium methoxide in the same solvent. The solution was allowed to stand at room temperature for 1–6 h and then was acidified by the addition of dilute HCl. The mixture was extracted with ethyl acetate, the extracts were dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel using methylene chloride–hexane to elute a mixture of the diarylsulfine plus the diaryl ketone ($Ar_2C{=}O$) (a decomposition product of the sulfine), followed by ethyl acetate to elute the sulfone. The sulfones were positively identified in each instance by melting point and spectral comparison with authentic samples that had been prepared (vide supra) in connection with the synthesis of 7. The isolated yields of aryl methyl sulfone in the different cases were as follows: $PhSO_2Me$ from **4a** (84%), from **4b** (80%), from **4c** (89%); $p$-$ClC_6H_4SO_2Me$ from **4d** (85%); $p$-$CH_3C_6H_4SO_2Me$ from **4e** (80%); and $p$-$CH_3OC_6H_4SO_2Me$ from **4f** (94%).

**Supplementary Material Available:** Tabulation of the results of individual kinetic runs for the methoxide-catalyzed elimination of 4, eq 4 (Table II), and disappearance of the $^1H$ NMR signal for the $Ar_2CHS(O)$ proton in 4 (Table III) (4 pages). Ordering information is given on any current masthead page.