(m, 2 H), 2.80–0.73 (m, 7 H); IR (NaCl) 3080, 2720, 1640, 1260, 990, 850, 810 cm^{-1}.

8: ^{13}C NMR ($Me_4Si/CDCl_3$) δ 139.4 (d), 114.8 (t), 51.2 (d), 49.5 (d), 44.6 (d), 42.0 (d), 37.5 (d), 30.8 (t), 27.4 (t); ^1H NMR ($Me_4Si/CDCl_3$) δ 5.80 (m, 1 H), 5.00 (m, 2 H), 3.15 (m, 2 H), 2.30 (m, 3 H), 1.95–0.64 (m, 4 H); IR (NaCl) 2950, 1640, 1440, 1275, 905, 850 cm^{-1}.

15: ^{13}C NMR ($Me_4Si/CDCl_3$) δ 133.2 (s), 129.6 (d), 64.6 (d), 25.7 (q), 23.7 (q), 18.0 (q); ^1H NMR ($Me_4Si/CDCl_3$) δ 5.26–4.92 (m, 1 H), 4.70–4.18 (q, 1 H), 2.22 (s, 1 H), 1.66 (s, 6 H), 1.18 (d, 3 H); IR (NaCl) 3400, 3000, 2950, 1650, 1450, 1380, 1070, 950, 870 cm^{-1}.

16: ^{13}C NMR ($Me_4Si/CDCl_3$) δ 68.5 (d), 66.9 (d), 59.2 (s), 24.9 (q), 19.2 (q), 19.1 (q); ^1H NMR ($Me_4Si/CDCl_3$) δ 3.54 (m, 2 H), 2.66 (d, 1 H), 1.30 (s, 6 H), 1.19 (d, 3 H); IR (NaCl) 3400, 2960, 1460, 1380, 1110, 1070, 1040, 880, 820 cm^{-1}.

18: ^{13}C NMR ($Me_4Si/CDCl_3$) δ 71.5 (d), 68.4 (d), 55.6 (d), 54.6 (d), 45.1 (t), 43.6 (t), 36.4 (t), 35.7 (t), 18.6 (t), 14.1 (q); ^1H NMR ($Me_4Si/CDCl_3$) δ 3.90–3.20 (m, 1 H), 3.13–2.60 (m, 3 H), 2.30 (s, 1 H), 1.70–1.23 (m, 4 H), 1.23–0.75 (m, 3 H); IR (NaCl) 3430, 2950, 1470, 1380, 920, 860 cm^{-1}.

19: ^{13}C NMR ($Me_4Si/CDCl_3$) δ 134.4 (d), 126.3 (d), 72.7 (d), 39.5 (t), 18.7 (t), 17.6 (q), 14.0 (q); ^1H NMR ($Me_4Si/CDCl_3$) δ 5.66–5.33 (m, 2 H), 3.27 (s, 2 H), 1.67 (d, 3 H), 1.60–1.23 (m, 4 H), 1.10–0.80 (m, 3 H); IR (NaCl) 3430, 2970, 1630, 1450, 1380, 970, 950 cm^{-1}.

20: ^{13}C NMR ($Me_4Si/CDCl_3$) δ 71.2 (d), 68.6 (d), 62.9 (d), 62.0 (d), 52.9 (d), 51.2 (d), 36.4 (t), 35.7 (t), 18.6 (t), 17.2 (q), 14.1 (q); ^1H NMR ($Me_4Si/CDCl_3$) δ 4.00–3.55 (m, 1 H), 3.55–3.10 (m, 1 H), 3.10–2.76 (m, 1 H), 2.76–2.50 (m, 1 H), 1.73–1.44 (m, 4 H), 1.28 (d, 3 H), 1.10–0.70 (m, 3 H); IR (NaCl) 3450, 2950, 1470, 1390, 880, 760 cm^{-1}.

46: ^{13}C NMR ($Me_4Si/CDCl_3$) δ 72.4 (d), 66.7 (t), 33.1 (t), 31.8 (t), 29.4 (t), 25.6 (t), 22.6 (t), 14.0 (q); ^1H NMR ($Me_4Si/CDCl_3$) δ 4.33 (s, 2 H), 3.80–3.23 (m, 3 H), 1.63–1.06 (m, 10 H), 1.06–0.53 (t, 3 H); IR (NaCl) 3400, 2930, 1470, 1070 cm^{-1}.

50: ^{13}C NMR ($Me_4Si/CDCl_3$) δ 74.8 (d), 70.3 (d), 31.8 (t), 31.7 (t), 25.7 (t), 22.5 (t), 16.3 (q), 13.9 (q); ^1H NMR ($Me_4Si/CDCl_3$) δ 3.93–3.36 (m, 4 H), 1.80–1.23 (m, 8 H), 1.23–0.66 (m, 6 H); IR (NaCl) 3400, 2930, 1460, 1060 cm^{-1}.

52: ^{13}C NMR ($Me_4Si/CDCl_3$) δ 75.1 (s), 67.6 (t), 34.8 (t), 28.0 (t), 25.5 (t), 23.3 (t), 14.0 (q), 7.8 (q); ^1H NMR ($Me_4Si/CDCl_3$) δ 3.36 (s, 4 H), 1.73–1.06 (m, 8 H), 1.06–0.66 (m, 6 H); IR (NaCl) 3350, 2930, 1460, 1140, 1040 cm^{-1}.

54 (methyl ester): ^{13}C NMR ($Me_4Si/CDCl_3$) δ 173.5 (s), 51.4 (q), 33.7 (t), 24.4 (t); ^1H NMR ($Me_4Si/CDCl_3$) δ 3.76 (s, 6 H), 2.66–2.20 (m, 4 H), 1.90–1.50 ((m, 4 H); IR (NaCl) 2960, 1740, 1440, 1200 cm^{-1}.

55: ^{13}C NMR ($Me_4Si/CDCl_3$) δ 74.8 (d), 71.6 (s), 36.9 (t), 30.3 (t), 26.5 (q), 23.2 (t), 21.6 (t); ^1H NMR ($Me_4Si/CDCl_3$) δ 3.46–3.20 (t, 1 H), 2.85 (s, 2 H), 1.76–1.30 (m, 8 H), 1.21 (s, 3 H); IR (NaCl) 3400, 2940, 1450, 1370, 750 cm^{-1}.

56: ^{13}C NMR ($Me_4Si/CDCl_3$) δ 209.3 (s), 178.5 (s), 43.1 (t), 33.7 (t), 29.8 (q), 24.1 (t), 23.1 (t); ^1H NMR ($Me_4Si/CDCl_3$) δ 10.10 (s, 1 H), 2.64–2.24 (m, 4 H), 2.16 (s, 3 H), 1.76–1.50 (m, 4 H); IR (NaCl) 3400–2900, 2960, 1720, 1410, 1370 cm^{-1}.

57: ^{13}C NMR ($Me_4Si/CDCl_3$) δ 141.3 (t), 114.1 (d), 74.9 (d), 71.3 (d), 36.3 (d), 36.3 (t), 28.3 (t), 27.8 (t); ^1H NMR ($Me_4Si/CDCl_3$) δ 6.10–5.50 (q, 1 H), 5.16–4.95 (m, 1 H), 4.95–4.75 (m, 1 H), 4.24 (s, 2 H), 3.77–3.10 (m, 2 H), 2.70–1.75 (m, 7 H); IR (NaCl) 3400, 2910, 1640, 1450, 1220, 1060 cm^{-1}.

58: ^{13}C NMR ($Me_4Si/CDCl_3$) δ 178.5 (s), 177.2 (s), 139.3 (t), 116.5 (d), 39.6 (d), 39.6 (t), 31.6 (t), 28.9 (t); ^1H NMR ($Me_4Si/CDCl_3$) δ 8.22 (s, 2 H), 5.80–5.40 (m, 1 H), 5.20–4.92 (m, 2 H), 2.64–2.15 (m, 4 H), 1.95–1.40 (m, 3 H); IR (NaCl) 3400–2900, 2950, 1710, 1650, 1420, 930 cm^{-1}.

62 (methyl ester): ^{13}C NMR ($Me_4Si/CDCl_3$) δ 173.3 (s), 51.6 (q), 33.1 (t), 20.2 (t); ^1H NMR ($me_4Si/CDCl_3$) δ 3.76 (s, 6 H), 2.66–2.26 (t, 4 H), 2.26–1.80 (m, 2 H); IR (NaCl) 2960, 1740, 1440, 1200 cm^{-1}.

Rates of H/D Exchange of 9-Fluorenyl Sulfoxides: Evidence for an Irreversible E1cB Mechanism for Base-Induced Sulfine Formation from Methyl Diarylmethanesulfinates[1]

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A previous study[2] had shown that the base-catalyzed, sulfine-forming eliminations of methyl 9-fluorenesulfinate (**4**) and other methyl diarylmethanesulfinates take place by either an E1cB-irreversible or an E2 mechanism, rather than the E1cB-reversible mechanism that had been expected. In the present work the rates (k_{exch}) of DABCO (diazabicyclooctane)-catalyzed H/D exchange of the 9-H in a series of 9-fluorenyl sulfoxides (**3**) have been determined at 25 °C in CD_3OD. From a plot of log k_{exch} vs σ* for R in **3** the anticipated rate for the DABCO-catalyzed formation of the 9-fluorenyl carbanion from **4** (eq 3, R = OCH_3) can be estimated. Comparison of this rate with the actual rate (k_{elim}) of the DABCO-catalyzed, sulfine-forming elimination of **4** (eq 5) indicates that the elimination does *not* take place by an E2 mechanism in which there is a significant degree of cleavage of the S(O)–OCH_3 bond in the rate-determining transition state. The results are, however, entirely consistent with an E1cB-irreversible mechanism for the elimination.

A recent study[2] has shown that methyl diarylmethanesulfinates (**1**) undergo base-catalyzed elimination (eq 1)

$$\underset{\mathbf{1}}{ArAr'CHS(O)OCH_3} \xrightarrow[MeOH]{base} \underset{\mathbf{2}}{ArAr'C{=}S{=}O} + CH_3OH \quad (1)$$

in methanol to form the corresponding sulfine (**2**) in quantitative yield. The absence of detectable H/D exchange of the C*H*S(O) proton in MeOD prior to reaction and the kinetic isotope effects for both the methoxide-induced (k_H/k_D = 6.1) and amine-induced (k_H/k_D = 3.8 for quinuclidine) eliminations of methyl 9-fluorenesulfinate-*9-d* demonstrated that eq 1 proceeds by either an $(E1cB)_{irrev}$ or an E2 mechanism, rather than the $(E1cB)_{rev}$ mechanism that might have been anticipated based on the behavior of related sulfene-forming eliminations of arylmethanesulfonates.[3]

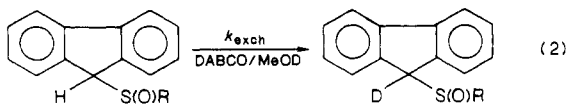
(1) This research was supported by the National Science Foundation (Grant CHE-8610116).

(2) Kice, J. L.; Rudzinski, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 2414.

(3) (a) King, J. F.; Beatson, R. P. *Tetrahedron Lett.* **1975**, 973. (b) Davy, M. B.; Douglas, K. T.; Loran, J. S.; Stettner, A.; Williams, A. *J. Am. Chem. Soc.* **1977**, *99*, 1196.

0022-3263/88/1953-3593$01.50/0

Although distinction between an $(E1cB)_{irrev}$ and an E2 mechanism for an elimination is sometimes difficult, the objective of the present work was to do so if possible for eq 1. The approach used was to measure the rates of base-catalyzed H/D exchange (eq 2, DABCO = diazabicyclooctane) of the 9-H for a series of 9-fluorenyl sulfoxides

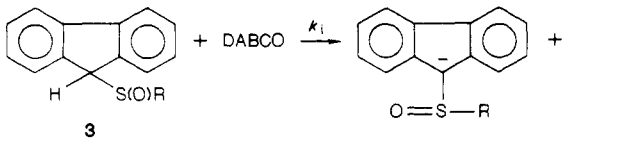


(2)

3 3-d

a, R = CH_3 **c**, R = Ph **e**, R = $CH_2C(O)OMe$
b, R = $PhCH_2$ **d**, R = CH_2CH_2F **f**, R = CH_2CN

(**3a–f**), where R is a poor enough leaving group that sulfine formation is not observed. A plot of log k_{exch} vs σ^* for R provides ρ^* for the exchange, a reaction whose rate-determining step is presumably abstraction of the 9-proton by the base (eq 3). From ρ^* for the exchange and σ^* for



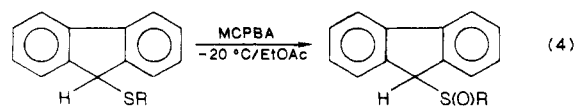
3

DABCO-H^+ (3)

CH_3O, the anticipated value of k_i for methyl 9-fluorenesulfinate (4) (eq 3, R = OCH_3) can be estimated. If this and the actual rate constant for DABCO-induced sulfine formation from **4** are closely comparable, this is consistent with an $(E1cB)_{irrev}$ mechanism for the elimination. On the other hand, if the elimination takes place by an E2 mechanism, where removal of the proton, departure of the CH_3O group, and formation of the sulfine are *concerted*, the rate constant for sulfine formation is likely to be much larger than the k_i estimated for **4**. As will be seen, the results in the present system are consistent with an $(E1cB)_{irrev}$ mechanism.

Results

The 9-fluorenyl sulfoxides (**3a–f**) needed for the exchange studies were synthesized by oxidation of the corresponding sulfides (**5a–f**) with *m*-chloroperoxybenzoic acid (MCPBA) in ethyl acetate solution at −20 °C (eq 4).



(4)

5 3

Two of the sulfoxides, **3b**[4] and **3c**,[5] have been reported previously. Fluorenyl sulfides **5a,d,f** were prepared by reaction of 9-fluorenethiol[6] with the appropriate alkyl halide or tosylate in alkaline solution in methanol, while sulfides **5b,c,e** were obtained by reaction of 9-bromofluorene with the appropriate thiolate in the same solvent.

Kinetics of H/D Exchange of the 9-H of 9-Fluorenyl Sulfoxides in CD_3OD. Each of the sulfoxides (**3**) has a singlet due to the proton on the 9-position in the region δ 5.2–5.5 in the ^1H NMR spectrum. In CD_3OD addition of a base leads to the disappearance of this singlet as a result of base-catalyzed exchange of the 9-H by D. The rate of disappearance of the singlet depends on the strength of the base and its concentration.

Table I. Rates of H/D Exchange of 9-Fluorenyl Sulfoxides (3) in DABCO Buffers in CD_3OD at 25 °C

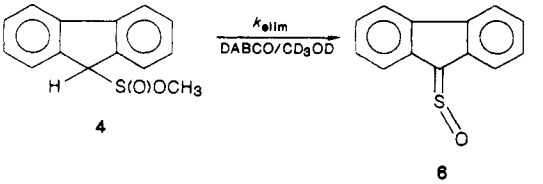
sulfoxide	sulfoxide concn, M	10^3[DABCO],[a] M	$k_1 \times 10^4$, s^{-1}	$k_{exch} = k_1/$[DABCO],[b] $M^{-1}\ s^{-1}$
3a	0.22	5.0	2.8	0.061
		2.5	1.3	
		1.5	0.69	
3b	0.016	1.5	3.0	0.21
		1.0	2.05	
		0.70	1.5	
3c	0.22	1.0	2.8	0.28
		0.70	2.1	
		0.50	1.2	
3d	0.15	1.0	4.4	0.46
		0.80	3.9	
		0.50	1.9	
		0.30	1.6	
3e	0.22	0.80	5.9	0.83
		0.50	3.2	
		0.30	1.6	
3f	0.099	0.50	17	3.4
		0.30	9.2	
		0.20	7.2	

[a] Runs for **3a–e** in buffers with [DABCO] = [DABCO-D^+]; those for **3f** in buffers with [DABCO] = 0.5[DABCO-D^+]. [b] Obtained from a plot of k_1 vs [DABCO].

Preliminary studies showed that conveniently measurable rates of exchange for **3** at 25 °C could be achieved in 1:1 DABCO/DABCO-D^+ buffers.[7] The integrated intensity (I) of the singlet for the 9-H relative to an internal standard was determined as a function of time. Plots of log (I/I_0) vs time showed excellent linearity in all cases. Their slope is k_1, the experimental first-order rate constant. The data for the various sulfoxides are collected in Table I. For each sulfoxide k_1 was proportional to [DABCO], and values of k_{exch}, the second-order rate constant for the DABCO-catalyzed exchange, were obtained from plots of k_1 vs [DABCO]. These are shown in the rightmost column of Table I.

The methylene protons ($S(O)CH_2COOMe$ and $S(O)CH_2CN$) in sulfoxides **3e** and **3f** underwent exchange much faster than the 9-H. While quantitative measurement of the rates of exchange of these methylene groups was not attempted, in both cases the signal for the CH_2 group was almost completely gone by the time 20% of the protons at C-9 of the sulfoxide had undergone exchange. On the other hand, with sulfoxides **3b** and **3d** no significant exchange of the $PhCH_2$ and $S(O)CH_2CH_2F$ protons was observed during the time period required for complete exchange of the 9-H.

Rate of DABCO-Induced Sulfine Formation from Methyl 9-Fluorenesulfinate (4) in CD_3OD. The rate constant (k_{elim}) for DABCO-induced formation of sulfine **6** from **4** in CD_3OD (eq 5) is needed for the comparison



(5)

4 6

outlined in the introduction. The rate of formation of **6** was measured spectrophotometrically in the manner described previously[2] in 1:1 DABCO–DABCO-D^+ buffers in

(4) Bavin, P. M. G. *Can. J. Chem.* **1962**, *40*, 220.
(5) Nishi, S.; Matsuda, M. *J. Am. Chem. Soc.* **1979**, *101*, 4632.
(6) Pan, H.-L. Fletcher, T. L. *Chem. Ind. (London)* **1968**, 546.

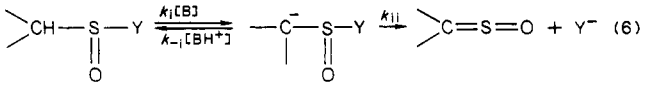
(7) Rates of exchange in solutions containing 0.001 M or greater CD_3O^- were too fast (exchange complete in 5 min or less) to be followed conveniently by NMR.

CD_3OD at 25 °C with the following results ([DABCO], k_1): 0.0026 M, 5.25×10^{-3} s^{-1}; 0.00133 M, 2.64×10^{-3} s^{-1}; 0.00067 M, 1.36×10^{-3} s^{-1}. These results show k_1 is strictly proportional to [DABCO] and a value of 2.0 M^{-1} s^{-1} for $k_{elim} = k_1/[DABCO]$.

Since k_{elim} for DABCO and **4** in MeOH is 2.2 M^{-1} s^{-1},[2] the solvent isotope effect for the elimination in eq 5 is $k_{MeOD}/k_{MeOH} = 0.91$. This is the same as the solvent isotope effect (0.90) for the imidazole-catalyzed elimination of **4**.[2]

Discussion

The general mechanism for an E1cB elimination of an alkanesulfinyl derivative is shown in eq 6. If protonation



(6)

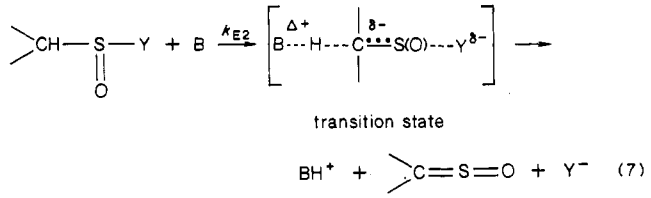
7

$(E1cB)_{rev}$: $k_{-i}[BH^+] > k_{ii}$
$(E1cB)_{irrev}$: $k_{ii} > k_{-i}[BH^+]$

of the carbanion intermediate (**7**) is faster than loss of the leaving group ($k_{-i}[BH^+] > k_{ii}$), the mechanism will be $(E1cB)_{rev}$. When departure of the leaving group occurs more rapidly than protonation of the carbanion ($k_{ii} > k_{-i}[BH^+]$), the mechanism becomes $(E1cB)_{irrev}$.

In a reaction proceeding by an $(E1cB)_{irrev}$ mechanism the rate-determining step is the formation of the carbanion (**7**) from the substrate. The variation in rate with variation in Y should simply be that associated with the effect of Y on the ease of formation of **7**.

The difference between an $(E1cB)_{irrev}$ and an E2 elimination (eq 7) is that in the latter the cleavage of the S-



transition state

(7)

(O)–Y and C–H bonds is concerted, and carbanion **7** is not an intermediate on the reaction coordinate. For those eliminations that proceed by an E2 mechanism the concerted pathway provides a lower activation energy than would the analogous E1cB pathway going through a carbanion as an intermediate.[8] Consistent with this, eliminations proceeding via an E2 mechanism normally show rates much faster than the estimated rate at which a carbanion should be formed from the substrate under the same conditions (step k_i of an E1cB mechanism).

This provides the basis for one experimental approach for distinguishing between an E2 and an $(E1cB)_{irrev}$ mechanism for a particular elimination. If a reliable estimate can be made of the expected rate constant for carbanion formation (k_i), this can then be compared with the actual rate constant at which the compound undergoes elimination (k_{elim}). If k_{elim} is much faster than k_i, an E2 mechanism is definitely indicated for the elimination. Conversely, $k_{elim} \simeq k_i$ is consistent with an $(E1cB)_{irrev}$ mechanism. This experimental approach requires that a method for accurately estimating k_i be available.

9-Fluorenyl sulfoxides **3a–f** undergo exchange (eq 2) of their 9-H in the presence of base in CD_3OD. There is no evidence of other chemical change in the time period required for complete H/D exchange. The rate-determining step for the exchange is presumably the abstraction of the 9-H from the sulfoxide by the base. The rate constant (k_{exch}, Table I) for the DABCO-catalyzed H/D exchange of **3** in DABCO–DABCO-D^+ buffers in CD_3OD can therefore be equated with k_i (eq 3), the rate constant for the formation of the 9-fluorenyl α-sulfinyl carbanion from **3** by reaction with DABCO.

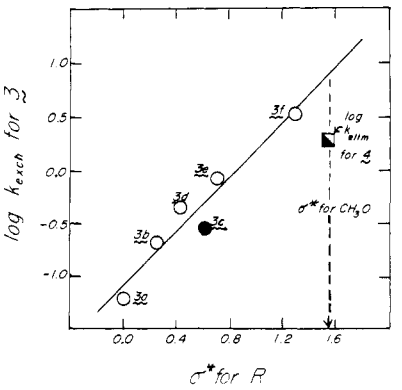
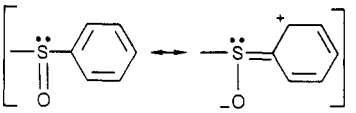


Figure 1. Plot of log k_{exch} for DABCO-catalyzed exchange of 9-H in 9-fluorenyl sulfoxides (**3**) vs σ^* for R in **3**. The rate (log k_{elim}) of DABCO-catalyzed elimination of methyl 9-fluorenesulfinate (**4**, R = OCH_3) is also shown (◪).

Figure 1 is a plot for **3** of log k_{exch} vs σ^* for R (calculated from tabulated[9] σ_I values as outlined in footnote 10). The correlation line shown in Figure 1 ($\rho^* = +1.28$, correlation coefficient = 0.980) is based on the data for all the sulfoxides except **3c**. The data point for the phenyl sulfoxide (**3c**) lies somewhat below this line. If the data point for **3c** is included, the slope does not change significantly ($\rho^* = +1.26$) but the correlation coefficient is somewhat lower (0.958). We think the deviation of the point for **3c** is the result of the electron density on the >S=O group being greater than would be expected from the purely inductive effect of the phenyl group, due to a mesomeric interaction of the electrons of the aromatic ring with the sulfinyl group:



Values of σ_I for CH_3O ranging between 0.23 and 0.31 can be found in the literature.[9] If a σ_I value (+0.25) near the lower end of this range is taken, $\sigma^*(CH_3O) = +1.55$, while use of a σ_I value (+0.29) close to the upper end leads to $\sigma^*(CH_3O) = +1.80$.

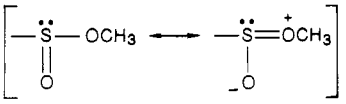
From the correlation line in Figure 1 k_i for eq 3 for a sulfinyl compound **3** having an R group with $\sigma^*(R) = +1.55$ is estimated as 7.9 M^{-1} s^{-1}; that for an R group with $\sigma^*(R) = +1.8$ is estimated as 17.8 M^{-1} s^{-1}. The rate constant (k_{elim}) for DABCO-catalyzed formation of sulfine **6** from **4** in CD_3OD (eq 5) is 2.0 M^{-1} s^{-1}. Depending upon which σ^* value for CH_3O is used, this is either 4.0 or 8.8 times smaller than the correlation line value. Since an elec-

(8) Saunders, W. H., Jr. *Acc. Chem. Res.* **1976**, *9*, 19.

(9) (a) Exner, O. In *Advances in Linear Free Energy Relationships*; Chapman, N. B., Shorter, J., Eds.; Plenum: New York, 1972; pp 37–38. (b) Exner, O. In *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum: New York, 1978; pp 500–525. (c) Ritchie, C. D. *Physical Organic Chemistry*; Marcel Dekker: New York, 1975; p 111.

(10) The relationships $\sigma_I(X) = 0.45\sigma^*(CH_2X)$ and $\sigma(X) = 2.8\sigma(CH_2X)$ are well established.[9] From them comes $\sigma^*(X) = 6.2\sigma_I(X)$. We have used these relationships to calculate σ^* values for the various R groups in **3** using the following values of σ_I: $PhCH_2$, 0.04; Ph, 0.10; CH_2CN, 0.21; COOMe, 0.32; F, 0.54; MeO, 0.25. For each substituent the σ_I value used is the average of the most reliable values reported.

tron-donating resonance interaction with the sulfinyl group:



should be even more important for CH_3O than for Ph, the actual k_i for **4** (eq 3, R = OCH_3) would be expected to be smaller than predicted by the correlation line, and by a greater amount than k_{exch} for **3c** is smaller (Figure 1) than predicted by the normal inductive effect of a phenyl group. The observed value for k_{elim} is therefore quite consistent with an $(E1cB)_{irrev}$ mechanism where formation of the 9-fluorenyl carbanion from **4** (step k_i) is the rate-determining step of the elimination. It is definitely not in accord with an E2 mechanism where the S(O)–OCH_3 bond is substantially broken in the rate-determining transition state, since k_{elim} for an elimination proceeding by such a mechanism would typically be expected to be one or more orders of magnitude *faster* than k_i.

While results fully support an $(E1cB)_{irrev}$ mechanism for the sulfine-forming elimination in eq 5, we ought to note that a *very E1cB-like* E2 mechanism where the rate-determining transition state has the C–H bond almost fully cleaved, and the S(O)–OCH_3 bond not significantly broken, is also allowed. In such a transition state the 9-carbon will have a great deal of carbanion character and the S(O)–O-CH_3 bond will be virtually as it is in **4**; such a mechanism will exhibit a dependence of rate on structure essentially identical with that for an $(E1cB)_{irrev}$ mechanism. The rate-determining transition states for an $(E1cB)_{irrev}$ and for a very E1cB-like E2 mechanism simply do not differ enough in structure for the experimental diagnostic tests for differentiating $(E1cB)_{irrev}$ and normal E2 mechanisms to be able to distinguish between them.[11]

The present results do, however, rule out any E2 mechanism for eq 5 in which there is a significant degree of cleavage of the S(O)–OCH_3 bond in the rate-determining step.

Experimental Section

9-Fluorenethiol was prepared from 9-bromofluorene (Aldrich) by using the procedure outlined by Pan and Fletcher:[6] mp 103–105 °C (lit.[6] mp 103–106 °C); ^1H NMR ($CDCl_3$) δ 2.03 (d, 1 H), 4.9 (d, 1 H), 7.16–7.76 (m, 8 H).

Synthesis of 9-Fluorenyl Sulfides (5). 9-Fluorenyl Methyl Sulfide (5a). 9-Fluorenethiol (2.0 g, 10 mmol) was dissolved under nitrogen in 25 mL of a methanol solution 0.40 M in sodium methoxide, and excess methyl iodide (7.1 g, 50 mmol) was added. The solution was kept under nitrogen and heated at 40–50 °C for 30 min. After the mixture cooled, it was concentrated to dryness under reduced pressure and the residue was treated with approximately 20 mL of a 4:1 mixture of methylene chloride and petroleum ether. The insoluble material was filtered off. Concentration of the filtrate gave an oily residue that upon crystallization (twice) from methanol yielded 1.43 g (67%) of 9-fluorenyl methyl sulfide (**5a**): mp 46–47 °C (lit.[4] mp 47–48 °C); ^1H NMR ($CDCl_3$) δ 1.4 (s, 3 H), 4.83 (s, 1 H), 7.23–7.83 (m, 8 H).

9-Fluorenyl 2-Fluoroethyl Sulfide (5d). 2-Fluoroethyl *p*-toluenesulfonate was prepared by the procedure described by Edgell and Parts.[12] The *p*-toluenesulfonate (10 mmol) was reacted with 9-fluorenethiol (10 mmol) in methanol containing sodium methoxide (10 mmol) and worked up with the same procedure as for **5a**. The crude sulfide was purified by flash chromatography using petroleum ether–methylene chloride (2.5:1.5) as eluent. There was obtained 1.3 g (53%) of 9-fluorenyl 2-fluoroethyl sulfide (**5d**) mp 34–35 °C; IR (Nujol) 1060 cm^{-1} (C–F); ^1H NMR ($CDCl_3$) δ 2.0 (t) and 2.3 (t) (SCH_2CH_2F), 3.5 (t) and 4.28 (t) (SCH_2CH_2F), 4.85 (s, 1 H), 7.16–7.85 (m, 8 H).

9-Fluorenyl cyanomethyl sulfide (5f) was synthesized by reaction of 10 mmol of bromoacetonitrile (Aldrich) with an equivalent amount of 9-fluorenethiol in methanolic sodium methoxide using the same procedure as for the preparation of **5a**. The crude sulfide obtained upon workup was purified by flash chromatography with methylene chloride–ethyl acetate (10:1) as eluent, giving 1.54 g (65%) of 9-fluorenyl cyanomethyl sulfide (**5f**): mp 72–73 °C; IR (Nujol) 2240 cm^{-1} (CN); ^1H NMR ($CDCl_3$) δ 2.61 (s, 2 H), 5.05 (s, 1 H), 7.36–7.80 (m, 8 H).

9-Fluorenyl Benzyl Sulfide (5b). α-Toluenethiol (1.36 g, 11 mmol) was dissolved under nitrogen in 20 mL of a 0.5 M solution of sodium methoxide in methanol. To this was then added with stirring 2.45 g (10 mmol) of 9-bromofluorene. After the addition was complete the mixture was heated at 50–55 °C for 15 min. After the mixture cooled, the solvent was removed under reduced pressure at room temperature, and the residue was treated with approximately 20 mL of dichloromethane. The material that did not dissolve in dichloromethane was removed by filtration, and the dichloromethane was evaporated from the filtrate. The residue was crystallized twice from methanol, giving 1.6 g (56%) of 9-fluorenyl benzyl sulfide (**5b**): mp 68–69 °C (lit.[4] mp 66–67 °C); ^1H NMR ($CDCl_3$) δ 3.17 (s, 2 H), 4.91 (s, 1 H), 7.10–7.73 (m, 13 H).

9-Fluorenyl phenyl sulfide (5c) was synthesized from 9-bromofluorene and thiophenol in the manner described by Bavin[13] in 52% yield after two recrystallizations from methanol: mp 48–49 °C (lit.[13] mp 48–49 °C); ^1H NMR ($CDCl_3$) δ 5.24 (s, 1 H), 7.13–7.63 (m, 13 H).

Methyl α-(9-Fluorenylthio)acetate (5e). Reaction of 9-bromofluorene (10 mmol) with an equimolar amount of methyl thioglycolate in methanolic sodium methoxide following the same procedure and workup as for **5b** gave methyl α-(9-fluorenylthio)acetate (**5e**) as an oil (2.2 g, 82%), which TLC (silica gel, 2:1 petroleum ether–CH_2Cl_2) showed to be pure enough to use in the subsequent oxidation step: IR (neat) 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.66 (s, 2 H), 3.33 (s, 3 H), 4.86 (s, 1 H), 7.15–7.80 (m, 8 H).

Oxidation of 9-Fluorenyl Sulfides to Sulfoxides. The following general procedure was employed for the oxidation of the various 9-fluorenyl sulfides (**5**) to the corresponding sulfoxides (**3**). A solution of *m*-chloroperoxybenzoic acid (5 mmol) in 25 mL of ethyl acetate was added dropwise with stirring to a solution of 5.0 mmol of the 9-fluorenyl sulfide (**5**) in 35 mL of ethyl acetate at −20 °C. After the addition was complete the solution was stirred for 3 h at −20 °C. It was then washed sequentially with cold 5% sodium bicarbonate followed by brine. The organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The crude sulfoxide was purified by flash chromatography on silica gel using gradient elution.

9-Fluorenyl Methyl Sulfoxide (3a). Gradient elution, first with 10:1 and 5:1 chloroform–ethyl acetate and then with 3:17 methanol–chloroform, afforded 0.57 g (50%) of 9-fluorenyl methyl sulfoxide, mp 83–84 °C. Thin-layer chromatography (SiO_2, 4:1 $CHCl_3$–petroleum ether) showed only a single spot, R_f 0.35: IR (Nujol) 1050 cm^{-1} (S=O); ^1H NMR δ 1.55 (s, 3 H), 5.23 (s, 1 H), 7.15–7.85 (m, 8 H). Anal. Calcd for $C_{14}H_{12}OS$: C, 73.68; H, 5.26. Found: C, 73.97; H, 5.26.

9-Fluorenyl Benzyl Sulfoxide (3b). In this case the solvents used for gradient elution were 8:1 and 4:1 chloroform–petroleum ether, followed by pure chloroform. This gave 0.76 g (50%) of **3b**: mp 150–151 °C (lit.[4] mp 147–148 °C); IR (Nujol) 1050 cm^{-1} (S=O); ^1H NMR ($CDCl_3$) δ 2.85 (partially resolved doublet, 2 H), 5.44 (s, 1 H), 6.88–8.02 (m, 13 H).

9-Fluorenyl Phenyl Sulfoxide (3c). Elution with $CHCl_3$ afforded 0.77 g (53%) of 9-fluorenyl phenyl sulfoxide (**3c**): mp 104–105 °C (lit.[5] mp 107 °C); IR (Nujol) 1050 cm^{-1} (S=O); ^1H

(11) We originally hoped to further confirm the mechanistic conclusions from the study of the H/D exchange rates of **3** with a kinetic isotope effect (KIE) study (in collaboration with Prof. H. J. Shine of Texas Tech University) that would determine k_{16}/k_{18} for the elimination of **4** and its methoxy ^{18}O-labeled isomer. However, after examining the mass spectrum of **4**, Prof. Shine informed us that the relatively weak intensity of the molecular ion of **4** and the nature of its fragmentation pattern would make an accurate determination of k_{16}/k_{18} impossible.

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(13) Bavin, P. M. G. *Can. J. Chem.* **1960**, *38*, 917.

NMR ($CDCl_3$) δ 5.36 (s, 1 H), 6.64–7.66 (m, 13 H).

9-Fluorenyl 2-Fluoroethyl Sulfoxide (3d). Mixtures of methylene chloride–ethyl acetate (17:1, 12:1, and 5:1) were used for gradient elution. There was obtained 0.64 g (49%) of **3d**: mp 126–128 °C; IR (Nujol) 1060 and 1050 cm^{-1} (overlapping C–F and S=O absorptions); ^1H NMR ($CDCl_3$) δ 1.85 (complex m, 2 H), 4.5 (complex m, 2 H), 5.48 (s, 1 H), 7.32–7.95 (m, 8 H). The signals centered at δ 1.85 and 4.5 are very complex because the protons of both methylenes are diastereotopic, and there is coupling between the fluorine and each proton, as well as between protons. Anal. Calcd for $C_{15}H_{13}FOS$: C, 69.21; H, 5.03. Found: C, 68.94; H, 4.96.

Methyl α-(9-Fluorenylsulfinyl)acetate (3e). Gradient elution with 10:1 and 5:1 methylene chloride–ethyl acetate gave 0.84 g (59%) of **3e**; mp 81–83 °C; IR (Nujol) 1730 (C=O) and 1050 cm^{-1} (S=O); ^1H NMR ($CDCl_3$) δ 2.55 (quartet, 2 H), 3.57 (s, 3 H), 5.41 (s, 1 H), 7.3–8.0 (m, 8 H). Anal. Calcd for $C_{16}H_{14}O_3S$: C, 67.12; H, 4.92. Found: C, 66.79; H, 4.87.

9-Fluorenyl Cyanomethyl Sulfoxide (3f). Methylene chloride–ethyl acetate mixtures (12:1, 10:1, and 7:1) were employed for gradient elution. There was obtained 0.63 g (50%) of **3f**: mp 111–113 °C; IR (Nujol) 2240 (CN), 1050 cm^{-1} (S=O); ^1H NMR ($CDCl_3$) δ 2.58 (poorly resolved quartet, 2 H), 5.47 (s, 1 H), 7.35–8.05 (m, 8 H). Anal. Calcd for $C_{15}H_{11}NOS$: C, 71.13; H, 4.37. Found: C, 70.56; H, 4.45.

Kinetics of H/D Exchange of 3 As Followed by ^1H NMR. The sulfoxides **3** each have a singlet due to the 9-H in the region δ 5.2–5.5. The H/D exchange of this proton was monitored by measuring the integrated intensity of this signal, relative to that of an internal standard, as a function of time. In most cases the signal used as an internal standard was the singlet at δ 3.3 due to the small amount of CH_3OD present in the CD_3OD used as solvent. In those cases where other resonances in the sulfoxide might cause some interference with the accurate measurement of the integrated intensity of this peak, small amounts (10–30 μL) of a stock solution of cyclohexane in CD_3OD were added prior to the initiation of the exchange reaction and the cyclohexane singlet (δ 1.43) was used as the internal standard.

The general procedure for the kinetic runs was as follows. Diazabicyclooctane (DABCO), purified as described in an earlier publication,[14] was dissolved in CD_3OD (99.5 atom % D, Aldrich) to make a 0.10 M stock solution. A 0.10 M stock solution of CF_3CO_2D (Aldrich) in CD_3OD was also prepared. The 9-fluorenyl sulfoxide (**3**) was weighed out and dissolved in 0.90–0.99 mL of CD_3OD to which had been added 3–75 μL (depending on the DABCO-D^+ concentration desired) of the 0.10 M stock solution of CF_3CO_2D in CD_3OD. If needed 10–30 μL of the stock solution of cyclohexane in CD_3OD was added at this point. The solution was placed in an NMR tube in the thermostated probe (25 °C) of a Chemagnetics A200 NMR spectrometer, and the exchange reaction was initiated by the addition of an amount (6–150 μL) of the 0.10 M stock solution of DABCO equal to twice the volume of 0.1 M CF_3CO_2D solution added initially. In the runs with **3f** the volume of DABCO solution used was only 1.5 times the volume of CF_3CO_2D solution, since in that case a 1:2 DABCO–DABCO-D^+ buffer was desired. At appropriate time intervals after the initiation of the reaction, spectra were obtained and stored. After sufficient time the singlet for the 9-H disappeared completely. A plot of log (I/I_0) vs time was made for each run, where I and I_0 are the integrated intensities of the 9-H singlet relative to the internal standard at times t and zero, respectively. The experimental first-order rate constant for exchange (k_1) was then evaluated from the slope of this plot.

Kinetics of DABCO-Catalyzed Sulfine Formation from 4 in CD_3OD. The formation of sulfine **6** from ester **4** in CD_3OD in the presence of DABCO was studied in 1:1 DABCO–DABCO-D^+ buffers using procedures outlined in an earlier paper.[2] The rates were all measurable by conventional ultraviolet spectrophotometry.

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The Anti-Selective Michael Addition of Allylic Organometals to Ethylidenemalonates and Related Compounds

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The reaction of ethylidenemalonates **3a** and α-cyanocrotonates **3b** with crotylorganometals **2** such as B, Ti, Zr, and Sn reagents produced the anti adduct **4** predominantly. Similarly, the Michael addition of γ-alkoxy-substituted allylmetals **6** to **3** gave the anti adduct **7** preferentially. The Michael addition of crotyltin **2e** and (γ-(methoxymethoxy)allyl)tin **6d** to nitroolefins **20** again produced the anti isomers (**21** and **23**, respectively) predominantly. The anti preference was also observed in the reaction of crotyltin **2e** with α,β-unsaturated ketones. The selectivity difference between the allylic organometal additions (anti selectivity) and the enolate additions (syn or anti selectivity) is demonstrated.

The diastereofacial control between two adjacent substituents in the acylic system **1** continues to be of current

1

1a; X=Y=Me
b; X=C, Y=O, N, ···
c; X=Y=O, N, ···

importance in organic synthesis. The stereocontrol between X = carbon and Y = heteroatoms (**1b**) or between X = Y = heteroatoms (**1c**) may be achieved by various excellent methods.[1] At the outset of our work, the method for diastereofacial control between two adjacent alkyl groups, e.g., **1a**, seemed to be inadequate despite the frequent occurrence of such a stereodefined unit in important natural products.[2] One of the previous methods for this stereocontrol was based on intramolecular reactions such

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