Study of Reactions Leading to Sulfine Formation. 6. Base-Catalyzed Decomposition of Di-9-fluorenyl Sulfoxide[1]

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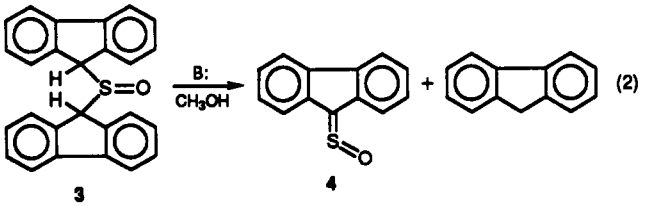
When treated with CH_3ONa in CH_3OH–CH_2Cl_2, di-9-fluorenyl sulfoxide (3) undergoes elimination readily to afford 9-thiofluorenone *S*-oxide (4) and fluorene (eq 2). Comparison of the rate of the elimination to the rate of disappearance in the presence of CD_3OD of the ^1H NMR signal for the 9-H in 3 shows that the mechanism of this sulfine-forming elimination is $(E1cB)_{rev}$, the rate of cleavage of the intermediate α-sulfinyl carbanion 7 to give 4 and a 9-fluorenyl carbanion being over 100 times slower than the rate at which 7 is protonated to regenerate 3. The $(E1cB)_{rev}$ behavior of this elimination is contrasted with the $(E1cB)_{rev}/(E1cB)_{irrev}$ borderline behavior of the elimination of diarylmethyl (arylmethyl)sulfonyl sulfoxides 1,[2] and a reason for this at first sight unexpected difference in behavior is presented.

The facile, methoxide-catalyzed decomposition of diarylmethyl (arylsulfonyl)methyl sulfoxides ($Ar_2CHS(O)CH_2SO_2Ar'$) 1 to a diarylsulfine and an aryl methyl sulfone (eq 1) is the subject of the accompanying paper.[2] Interestingly, the mechanism for this elimination turns out to be situated on the $(E1cB)_{rev}/(E1cB)_{irrev}$ borderline, meaning that cleavage of the intermediate α-sulfinyl carbanion $Ar_2\bar{C}S(O)CH_2SO_2Ar'$ 2 to sulfine and $Ar'SO_2CH_2^-$ is closely competitive in rate to its protonation by solvent to regenerate 1. This is quite remarkable, given that the leaving group ($Ar'SO_2CH_2^-$) is a carbanion whose conjugate acid ($Ar'SO_2CH_3$) has a pK_a (in DMSO) of 28–30.[3]

$$Ar_2CHS(O)CH_2SO_2Ar' \xrightarrow[CH_3OH/DMSO]{CH_3O^-} Ar_2C{=}S{=}O + Ar'SO_2CH_3 \quad (1)$$

The behavior of eq 1 suggested that other sulfine-forming eliminations where the leaving group was a carbanion of lower pK_a than $Ar'SO_2CH_2^-$ ought to be observable and that their mechanism might well be $(E1cB)_{irrev}$. A substrate for study that immediately came to mind was di-9-fluorenyl sulfoxide (3).

This paper reports the results of our study of the base-catalyzed decomposition of 3. We find that 3 does indeed undergo decomposition in the presence of base quite readily to afford thiofluorenone *S*-oxide (4) and fluorene (eq 2). However, the mechanism for this elimination is $(E1cB)_{rev}$, rather than $(E1cB)_{irrev}$, even though a 9-fluorenyl carbanion is a significantly more stable carbanion (pK_a of fluorene = 22.6),[3] and therefore presumably a better leaving group, than $Ar'SO_2CH_2^-$ (pK_a of $PhSO_2CH_3$ = 29.0).[3] This indicates, as had already been suspected,[2] that there are special aspects of the structure of the α-sulfinyl carbanion 2 that markedly enhance its rate of cleavage to $Ar_2C{=}S{=}O$ and $Ar'SO_2CH_2^-$.



3 4 (2)

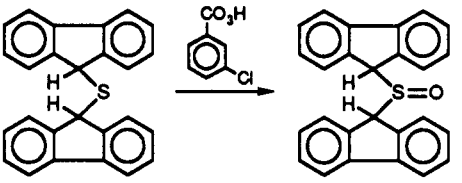
Table I. Kinetics of Formation and Disappearance of 4 When 3 Is Treated with Methoxide Ion at 25 °C in 1:3 CH_3OH–CH_2Cl_2[a]

$[MeO^-]$, 10^3 M	$\beta_{max} = [4]_{max}/[3]_0$	t_{max}, s	κ^b from β_{max} (eq 5a)	κ^b from t_{max} (eq 5b)
0.89	0.73	2400	0.14	0.16
1.33	0.72	1680	0.15	0.17
1.76	0.70	1290	0.17	0.17
2.20	0.69	1050	0.17	0.17
			av = 0.16 ± 0.01	

[a] All runs with $[3]_0$, 3.3×10^{-5} M. [b] $\kappa = k_b/k_{elim}$.

Results

Di-9-fluorenyl sulfoxide (3) was synthesized with no difficulty by peracid oxidation of di-9-fluorenyl sulfide (5), eq 3. Sulfide 5 was prepared from 9-fluorenethiol[4] and



5 3 (3)

9-bromofluorene as described by Bavin.[5]

Decomposition of Di-9-fluorenyl Sulfoxide in the Presence of Base: Products. When 3 (0.01 M) was dissolved at room temperature in 1:3 CH_3OH–CH_2Cl_2[6] containing 0.02 M CH_3O^-, it underwent decomposition. Workup of the reaction after 3 h gave fluorene (84%) and 9-fluorenone (86%). The latter compound results from methoxide-catalyzed decomposition of initially formed 9-thiofluorenone *S*-oxide (4). Base-catalyzed elimination of sulfoxide 3 to form sulfine 4 and fluorene (eq 2) obviously occurs quite easily.

Kinetics. When 3 (3.3×10^{-5} M) was treated with CH_3O^- ($0.89–2.2 \times 10^{-3}$ M) in 1:3 CH_3OH–CH_2Cl_2, the absorbance of the solution at 360 nm (λ_{max} for 4) first increased, then went through a maximum, and finally decayed to zero. This behavior and the shape of the curve for the rise and fall of the optical density at λ_{max} for 4 were consistent with a kinetic scheme where 4 was an intermediate product in a sequence of two consecutive pseudo-first-order reactions (eq 4). In this type of kinetic

(1) (a) For paper 5, see ref 2. (b) This research was supported by the National Science Foundation, Grant CHE-9000175.

(2) Kice, J. L.; Kupczyk-Subotkowska, L. *J. Org. Chem.*, previous paper in this issue.

(3) (a) Bordwell, F. G.; Matthews, W. S.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 442. (b) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. C.; Drecker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *Ibid.* **1975**, *97*, 7006.

(4) Pan, H.-L.; Fletcher, T. L. *Chem. Ind. (London)* **1968**, 546.

(5) Bavin, P. M. G. *Can. J. Chem.* **1962**, *40*, 220.

(6) Limited solubility of 3 in methanol precluded the use of pure methanol as solvent.

0022-3263/91/1956-1431$02.50/0

$$3 \xrightarrow[\text{(eq 2)}]{k_{elim}[MeO^-]} 4 \xrightarrow{k_b[MeO^-]} \text{fluorenone} \quad (4)$$

sequence β_{max} ($\beta_{max} = [4]_{max}/[3]_0$) and t_{max}, the time at which the maximum concentration of 4 occurs, are related to κ ($\kappa = k_b/k_{elim}$) as follows:[7]

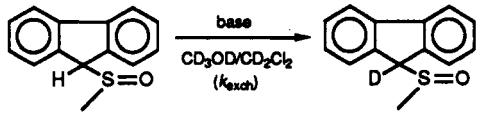
$$\beta_{max} = \kappa^{\kappa/(1-\kappa)} \quad (5a)$$

$$t_{max} = \frac{1}{k_b[MeO^-]}\left[\frac{\kappa}{\kappa - 1}\right] \ln \kappa \quad (5b)$$

The β_{max} and t_{max} values for the different runs are tabulated in the second and third columns of Table I. As expected from eqs 5a and 5b, β_{max}, within experimental error, is independent of [MeO^-], while t_{max} is inversely proportional to [MeO^-]. The calculated values of κ for each run from both β_{max} and t_{max} (using eqs 5a and 5b) are also shown in Table I. The average of all these values of κ (0.16 ± 0.01) was considered to be the best value of κ.

The first-order rate constant (k_1) for the disappearance of 4 in the presence of excess methoxide in 1:3 CH_3OH–CH_2Cl_2 at 25 °C was measured independently, and from a plot of k_1 vs [MeO^-], k_b ($k_b = k_1/[MeO^-]$) for 4 was determined to be 0.16 M^{-1} s^{-1}. From this value for k_b and the average value for κ (0.16), k_{elim} for 3 reacting with methoxide ($k_{elim} = k_b/\kappa$) is 1.0 ± 0.1 M^{-1} s^{-1} at 25 °C in 1:3 CH_3OH–CH_2Cl_2 as solvent.

Kinetics of the Disappearance of the 9-H ^{1}H NMR Signal of 3 in the Presence of Base and CD_3OD. The 9-H protons in 3 appear in the ^{1}H NMR as a singlet at δ 4.90. When 3 is dissolved in 1:3 CD_3OD–CH_2Cl_2 and a base is added, the intensity of this singlet begins to diminish and eventually disappears completely. Both eq 2 and base-catalyzed H/D exchange of 3 (eq 6) prior to its undergoing elimination can contribute to the disappearance of the singlet at δ 4.90.



(6)

The kinetics of the disappearance of this singlet were monitored under various conditions by measuring its integrated intensity relative to an internal standard as a function of time. When the added base was methoxide ion, the disappearance of the signal was extremely rapid, being complete in less than 3 min at −25 °C with [MeO^-] = 7 × 10^{-4} M. (Study of the disappearance of the 9-H singlet at lower temperatures than −25 °C was precluded for reasons outlined in footnote 8).

Although the rate of disappearance of the 9-H signal of 3 was too fast to be measured accurately when methoxide was the base, it was slow enough in 1:1 buffers of two tertiary amines (quinuclidine and diazabicyclooctane [DABCO]) to be measurable at 25 °C. The experimental first-order rate constants (k_d) for the conditions studied are presented in Table II. These rate constants are seen in each instance to be proportional to [amine], and second-order rate constants ($k_{CHSO} = k_d/[amine]$) calculated from a plot of k_d vs [amine] are also listed in this table. It is seen that quinuclidine (k_{CHSO} = 6.9 M^{-1} s^{-1}) is about 35 times more reactive than DABCO (k_{CHSO} = 0.19 M^{-1} s^{-1}).

(7) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*, 3rd ed.; John Wiley and Sons: New York, 1981; pp 290–293.

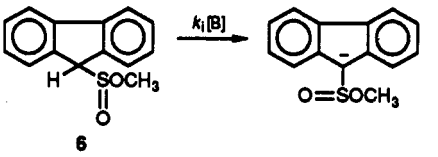
(8) The chemical shift of the proton in CD_3OH, which forms as the reactions (eqs 2 and 6) proceed, is temperature dependent. Below −25 °C, it becomes too close to δ 4.90 for reliable integration of the 9-H signal for 3.

Table II. Kinetics of the Disappearance of the 9-H ^{1}H NMR Signal of 3 in 1:3 CD_3OD–CD_2Cl_2 at 25 °C[a]

buffer	[base], 10^3 M	$10^3 k_d$, s^{-1}	$k_{CHSO} = k_d/[base]$,[b] M^{-1} s^{-1}
1:1 quinuclidine/ quinuclidine D+	0.15	1.0	
	0.25	1.8	6.9
	0.33	2.3	
1:1 DABCO/ DABCO-D+	1.1	0.24	
	1.6	0.25	0.19
	2.2	0.42	

[a] All runs with $[3]_0$, 0.01 M. [b] From a plot of k_d vs [base].

In the base-catalyzed abstraction of the 9-H in methyl 9-fluorenesulfinate (6), eq 7, quinuclidine is 15 times more



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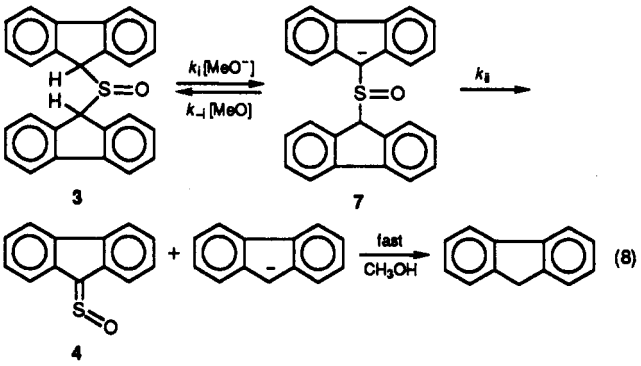
reactive than DABCO, and methoxide ion (B = CH_3O^-) is 19 times more reactive than quinuclidine.[9] The difference in reactivity between quinuclidine and DABCO as catalysts for the disappearance of the 9-H in 3 is therefore somewhat larger than their difference in reactivity in eq 7. This indicates that k_{CHSO} for CH_3O^- reacting with 3 (which, as already noted, is too fast to be measured by ^{1}H NMR) should be somewhat faster than 130 M^{-1} s^{-1} (which is 19 times that of k_{CHSO} for quinuclidine reacting with 3). Note that 130 M^{-1} s^{-1} represents a *minimum* for k_{CHSO} for CH_3O^- and 3 in 1:3 CH_3OH-CH_2Cl_2 at 25 °C. Given that ($k_{quinuclidine}/k_{DABCO}$) is roughly twice as large for 3 than for 6, k_{CHSO} for CH_3O^- and 3 could easily be as large as 300 M^{-1} s^{-1}.

Discussion

Methoxide-catalyzed decomposition of di-9-fluorenyl sulfoxide (3) to thiofluorenone *S*-oxide (4) and fluorene (eq 2) presumably takes place by the mechanism shown in eq 8. Removal of a 9-H from 3 (step k_i) generates an



(8)

α-sulfinyl carbanion (7), which then undergoes cleavage (step k_{ii}) to 4 and a 9-fluorenyl carbanion. The latter is immediately protonated.

A key detail regarding this mechanism is whether or not breakdown of carbanion 7 to 4 and a fluorenyl carbanion is faster, $(E1cB)_{irrev}$ mechanism, or slower, $(E1cB)_{rev}$ mechanism, than protonation of 7 by methanol to regenerate 3 (step k_{-i}), i.e., is k_{ii}/k_{-i}[MeOH] greater or less than 1?

The rate constant for disappearance of the ^{1}H NMR signal for the 9-H in 3 in the presence of base (k_{CHSO}) is

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

equal to a sum of the rate constants for elimination (eq 2, k_{elim}) and H/D exchange of the 9-H (eq 6, k_{exch})

$$k_{CHSO} = k_{exch} + 2k_{elim} \quad (9a)$$

$$k_{exch} = k_{CHSO} - 2k_{elim} \quad (9b)$$

At the same time k_{exch} and k_{elim} can be expressed as follows in terms of the mechanism in eq 8:

$$k_{exch} = k_i\left(\frac{k_{-i}[MeOH]}{k_{ii} + k_{-i}[MeOH]}\right)$$

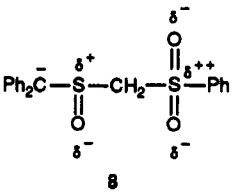
$$k_{elim} = k_i\left(\frac{k_{ii}}{k_{ii} + k_{-i}[MeOH]}\right)$$

so that

$$(k_{elim}/k_{exch}) = k_{ii}/k_{-i}[MeOH]$$

Since k_{elim} for **3** and methoxide in 1:3 CH_3OH–CH_2Cl_2 at 25 °C is 1.0 M^{-1} s^{-1}, while k_{CHSO} is ≥130 M^{-1} s^{-1}, k_{ii}/k_{-i}[MeOH] for **3** is ≤0.008, and the mechanism of the elimination in eq 2 is unequivocally $(E1cB)_{reversible}$.

The surprising aspect of this result is that although a 9-fluorenyl carbanion is a considerably more stable carbanion than $PhSO_2CH_2^-$ (pK_a of fluorene = 22.6;[3] pK_a of $PhSO_2CH_3$ = 29.0,[3] both in DMSO) and therefore should be a considerably better leaving group, k_{ii}/k_{-i}[MeOH] for **7** is ≤0.008 while k_{ii}/k_{-i}[MeOH] for $Ph_2CS(O)CH_2SO_2Ph$ (**8**) is 2.0.[2] We believe that the reason for this at first sight unexpected behavior is a strong destabilizing dipolar repulsion between the S=O and SO_2 groups in both **1** and the carbanion **8** derived from it that is relieved by the



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cleavage of **8**. This causes k_{ii} for **8** to be larger than would be anticipated from the pK_a of the conjugate acid of the leaving group.

Our results with **3** indicate that although sulfine-forming eliminations where the leaving group is a carbanion are not limited to (arylsulfonyl)methyl sulfoxides **1**, the facility with which they occur with **1** does represent a somewhat special situation.

Experimental Section

Preparation of Di-9-fluorenyl Sulfoxide (3). Di-9-fluorenyl sulfide (**5**) was prepared in 75% yield, mp 249–254 °C (lit.[5] mp 257–259 °C dec), by reaction of 9-fluorenethiol[4] with 9-bromofluorene (Aldrich) following the procedure described by Bavin.[5]

To 1.12 g (3.1 mmol) of **5** dissolved in 160 mL of chloroform was added 0.64 g of 85% *m*-chloroperoxybenzoic acid (Aldrich). The mixture was stirred at room temperature for 3 h. It was then washed three times with dilute sodium bicarbonate, followed by three washings with water, and dried ($MgSO_4$), and the chloroform was removed under reduced pressure. The crude product was purified by column chromatography on silica gel using methylene chloride followed by chloroform as the eluants. Recrystallization from chloroform–hexane gave 0.70 g (60%) of di-9-fluorenyl sulfoxide (**3**), mp 189–190 °C: IR (KBr) 1060 cm^{-1} (SO); ^1H NMR ($CDCl_3$) δ 4.90 (s, 2 H), 7.16–7.75 (m, 16 H). Anal. Calcd for $C_{26}H_{18}OS$: C, 82.51; H, 4.79. Found: C, 82.11; H, 4.73.

9-Thiofluorenone *S*-oxide (4) was prepared by reaction of triphenylphosphonium fluorenylide with *N*-sulfinyl-*p*-nitroaniline using the procedure described by Saito and Motoki,[10] mp 105 °C (lit.[10] mp 105–106 °C).

Methoxide-Catalyzed Cleavage of 3: Products. Di-9-fluorenyl sulfoxide, 0.38 g (1.0 mmol), was dissolved in 100 mL of 1:3 CH_3OH–CH_2Cl_2 and 2 mL of a 1.1 M solution of sodium methoxide in methanol was added. The reaction solution was stirred at room temperature for 3 h and then acidified by the addition of dilute HCl. The organic solvents were evaporated under reduced pressure, 50 mL of water was added to the residue, and the products were extracted into ethyl acetate. The ethyl acetate extracts were dried ($MgSO_4$), and the solvent was removed under reduced pressure. The products in the residue were separated by column chromatography on silica gel using 4:1 CH_2Cl_2–hexane as the eluant. There were obtained 0.14 g (84%) of fluorene and 0.15 g (86%) of 9-fluorenone, each identical with a known sample of the same compound.

Kinetics. To 3.0 mL of 1:3 CH_3OH–CH_2Cl_2 having the desired concentration of methoxide ion, and contained in a 1-cm spectrophotometer cell in the thermostated cell compartment of a Beckman DU-50 UV–vis spectrophotometer, was added by microsyringe 25 μL of a 0.005 M solution of **3** in 1:3 CH_3OH–CH_2Cl_2, and the absorbance of the solution at 360 nm was monitored with time. The absorbance at 360 nm first increased from zero to approximately 0.36 and then fell back to zero with the disappearance of **4**.

Kinetics of the Disappearance of 4 in 1:3 Methanol–Dichloromethane in the Presence of Methoxide. Twenty microliters of a 0.005 M solution of **4** in 1:3 CH_3OH–CH_2Cl_2 was added by microsyringe to 3.0 mL of a solution containing the desired concentration of methoxide ion in 1:3 CH_3OH–CH_2Cl_2 and contained in a 1-cm spectrophotometer cell in the thermostated cell compartment of a UV–vis spectrophotometer. The decrease in the optical density (A) of the solution with time at 360 nm (λ_{max} for **4**) was then followed as a function of time. Experimental first-order rate constants (k_1) were evaluated from the slope of a plot of log ($A - A_\infty$) vs time.

Kinetics of the Disappearance of the 9-H ^1H NMR Signal of 3 in the Presence of Base in 1:3 CD_3OD–CD_2Cl_2. The integrated intensity of the singlet at δ 4.90 in the ^1H NMR of **3** was monitored as a function of time relative to an internal standard (the signal at δ 3.30 due to the small amount of CH_3OD present in the solvent mixture).

When methoxide ion was used as base at a concentration of 7×10^{-4} M at a temperature of −25 °C, disappearance of the signal at δ 4.90 was complete in 3 min. Lower temperatures than −25 °C could not be used for reasons already outlined.[8] Accurate kinetic measurement of the rate constant for the methoxide-catalyzed reaction was therefore impossible.

For the runs where either DABCO or quinuclidine was the catalyzing base, the procedure was as follows. One milliliter of a 0.01 M solution of **3** in 1:3 CD_3OD–CD_2Cl_2 was placed in an NMR tube in the thermostated probe of a Chemagnetics A200 NMR spectrometer. The reaction was then initiated by the addition via microsyringe of the desired amount of a 1:1 buffer of the tertiary amine and its conjugate acid in CD_3OD. At appropriate time intervals after the initiation of the reaction, ^1H NMR spectra were obtained and stored.

Both tertiary amines (Aldrich) were recyrstallized (DABCO, ethyl alcohol; quinuclidine, ethyl ether) before preparation of the buffers.

(10) Saito, T.; Motoki, S. *J. Org. Chem.* **1977**, *42*, 3922.