Study of Reactions Leading to Sulfine Formation. 4. Evidence for a Reversible E1cB Mechanism for Base-Induced Elimination of *N,N*-Diisopropyl-9-fluorenesulfinamide[1]

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Previous examination[2] of base-catalyzed sulfine formation from methyl diarylmethanesulfinates, $Ar_2CHS(O)OMe$, has shown that the elimination takes place by an $(E1cB)_{irrev}$ mechanism, even though MeO is not a good leaving group. It raised the question as to whether base-catalyzed sulfine formation would be possible with substrates $Ar_2CHS(O)Y$ where Y was an even poorer leaving group, and if so, at what point the mechanism would shift to $(E1cB)_{rev}$. In the present study *N,N*-diisopropyl-9-fluorenesulfinamide (**3**) has been found to undergo H/D exchange of the 9-H in CD_3OD in the presence of methoxide 120 times faster than it undergoes elimination to give 9-thiofluorenone *S*-oxide (**4**). This shows that when the leaving group is R_2N sulfine formation is still possible but that the mechanism is now $(E1cB)_{rev}$. The solvent isotope effect associated with the formation of **4** from **3** indicates that expulsion of R_2N from the intermediate carbanion (**7**) must be accompanied by the transfer of a proton from the solvent to the leaving group, so that it departs as R_2NH rather than R_2N^-.

Previous studies[2] have shown that the base-catalyzed, sulfine-forming elimination of methyl diarylmethanesulfinates (**1**), eq 1, takes place by an $(E1cB)_{irrev}$ mechanism

$$\underset{\mathbf{1}}{ArAr'CHS(O)OCH_3} \xrightarrow{MeO^-} \underset{\mathbf{2}}{ArAr'C{=}S{=}O} + CH_3OH \quad (1)$$

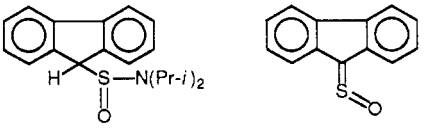
(eq 2, $k_{ii} > k_{-1}[MeOH]$) rather than by the $(E1cB)_{rev}$ mechanism (eq 2, $k_{ii} < k_{-1}[MeOH]$) that would have been anticipated from the behavior[3,4] of analogous sulfene-forming eliminations of aryl methanesulfonates ($MeO^- + ArCH_2SO_2OR \rightarrow MeOH + PhCH{=}SO_2 + RO^-$) with leaving groups of pK_a comparable to CH_3O^-.

$$ArAr'CHS(O)OCH_3 \underset{k_{-1}[MeOH]}{\overset{k_1[MeO^-]}{\rightleftharpoons}} ArAr'\bar{C}\text{-}S(O)OCH_3 \xrightarrow{k_{ii}} ArAr'C{=}S{=}O + CH_3O^- \quad (2)$$

That an elimination where the leaving group is the conjugate base of a very weak acid (pK_a of MeOH = 15.2)[5] would proceed by an $(E1cB)_{irrev}$ mechanism was surprising and unexpected. It contrasts not only with the behavior of sulfene-forming eliminations of $ArCH_2SO_2OR$ but also with that of elimination of phenoxide ion from β-substituted (X = $PhSO_2$, PhS(O), etc.) ethyl phenyl ethers (B: + $XCH_2CH_2OPh \rightarrow BH^+ + XCH{=}CH_2 + PhO^-$), for which Crosby and Stirling[6] have shown an $(E1cB)_{rev}$ mechanism is operative. Among eliminations where the leaving group is phenoxide or an alkoxide ion the mechanistic behavior of eq 1 is certainly atypical, and it suggested that further systematic examination of the mechanism of sulfine-forming eliminations was highly desirable.

Among the questions warranting investigation was whether or not alkoxide-induced sulfine formation is possible with substrates $Ar_2CHS(O)Y$, where Y is a much poorer leaving group than CH_3O, and if so, what is its mechanism. Such studies could establish at what point, if any, sulfine formation from $Ar_2CHS(O)Y$ substrates becomes an $(E1cB)_{rev}$ process. The substrates $Ar_2CHS(O)Y$ used should be ones where the acidity of the C*H*S(O) proton is not markedly lower than in $Ar_2CHS(O)OCH_3$ and where reactions with MeO^- other than sulfine formation (and exchange of the C*H*S(O) proton in deuterated medium) do not complicate matters.

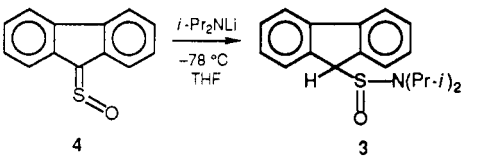
The present paper examines the behavior of *N,N*-diisopropyl-9-fluorenesulfinamide (**3**) in methanol-d_4 in the presence of sodium methoxide. The results show that 9-thiofluorenone *S*-oxide (**4**) can be formed from **3** under such conditions but that the rate at which this happens is much slower than the rate of H/D exchange of the 9-proton of **3**.



3 **4**

Results

Synthesis of 3 and 5. *N,N*-Diisopropyl 9-fluorenesulfinamide (**3**) could be synthesized successfully, albeit in only 40% yield, by reaction of $i\text{-}Pr_2NLi$ (generated from reaction of *n*-butyllithium with diisopropylamine) with sulfine **4** at −78 °C in tetrahydrofuran as solvent (eq 3). *N,N*-Diisopropyl-1,1-bis(*p*-chlorophenyl)methanesulfinamide, $(p\text{-}ClC_6H_4)_2CHS(O)N(Pr\text{-}i)_2$ (**5**), was synthesized in 60% yield in similar fashion from $(p\text{-}ClC_6H_4)_2C{=}S{=}O$.



4 **3** (3)

We originally hoped to synthesize other 9-fluorenesulfinamides with a variety of alkyl and aryl groups on the nitrogen by analogous reactions of other RR'NLi with **4**, but in our hands attempts to do this were not successful. It is not clear why reactions of such species as $CH_3N(Ph)Li$ or Et_2NLi with **4** give vanishingly small yields of the desired sulfinamide, when reaction of $i\text{-}Pr_2NLi$ with **4** proceeds satisfactorily.

We also found, not unexpectedly, that reaction of 9-fluorenesulfinyl chloride[7] with secondary amines results in elimination to form **4** when the amine is reasonably

(1) (a) Paper IV: Study of Reactions Leading to Sulfine Formation. Previous paper: *J. Org. Chem.* **1989**, *54*, 3596. (b) This research supported by the National Science Foundation, Grant CHE-8610116.

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Table I. Kinetics of Disappearance of ^1H NMR Signal of C*H*S(O) of 3 and 5 in CD_3OD

sulfinamide[a]	temp, °C	base	[base], M	$k'_{diss} \times 10^4$, s^{-1}	$k_{diss} = k'_{diss}/[base]$, $M^{-1}\ s^{-1}$
3	25.0	1:1 i-Pr_2ND/i-$Pr_2ND_2^+$	0.02	0.69	0.0034
		1:1 quinuclidine/quinuclidine-D^+	0.0050	1.8	0.036
			0.0070	2.4	0.034
			0.010	3.6	0.036
	-15.0	CD_3O^-	0.0020	9.9	0.50
			0.0040	20.1	0.50
	-20.0	CD_3O^-	0.0020	7.6	0.38
			0.0040	15	0.38
	-30.0	CD_3O^-	0.0020	4.17	0.21
			0.0040	6.76	0.17
5	25.0	CD_3O^-	0.05	0.13	0.00026
			0.07	0.20	0.00029
			0.09	0.23	0.00024

[a] Concentration of sulfinamide, 0.05 M.

basic, and in no reaction when the amine is one like Ph_2NH that is not at all basic.

The failure of these other syntheses left us with 3 as the only *N,N*-dialkyl-9-fluorenesulfinamide available for study.

Behavior of 3 in CD_3OD in the Presence of Bases. Two different phenomena can be monitored kinetically when 3 is dissolved in CD_3OD in the presence of a base (amines or CD_3O^-). The first is the disappearance of the singlet at δ 5.18 in the ^1H NMR associated with the proton on the 9-carbon. The second is the increase in the absorbance of the solution at 360 nm (λ_{max} for 4).

In an earlier study[2a] of the formation of 4 from methyl 9-fluorenesulfinate (6) and bases the rate of formation of the sulfine from the ester was much faster than the rate of subsequent base-catalyzed disappearance of the sulfine. Under such conditions formation of 4 from ester 6 was complete before there was any detectable disappearance of the sulfine. However, because the formation of 4 from 3 is much slower, disappearance of 4 in the basic CD_3OD solutions is competitive in rate with its formation from the sulfinamide, and in the present system the absorbance at 360 nm goes through a maximum. Detailed analysis of the kinetics is simplified by the fact that the rate of disappearance of 4 in the presence of base under a given set of reaction conditions can be measured independently.

Kinetics of the Disappearance of the 9-H Signal of 3 in CD_3OD. The kinetics of the disappearance of the singlet for the 9-H of 3 in the presence of base in CD_3OD were examined both in two 1:1 amine/amine-D^+ buffers (diisopropylamine and quinuclidine) and in solutions of CD_3O^-. The disappearance of the 9-H signal obeyed good first-order kinetics; the experimental first-order rate constants (k'_{diss}) for the different runs are collected in Table I.

In the amine buffers k'_{diss} for 3 is proportional to [amine], showing that the reaction is amine-catalyzed, rather than specific base catalyzed. The rate of disappearance of the 9-H signal of 3 in the presence of 0.002–0.004 M CD_3O^- was too rapid to be conveniently measurable at room temperature by repetitive monitoring of the ^1H NMR spectrum. Runs with CD_3O^- and 3 were therefore carried out at much lower temperatures (-15 to -30 °C). At these lower temperatures k'_{diss} was measurable and was proportional to $[CD_3O^-]$. From a plot of log k_{diss} ($k_{diss} = k'_{diss}/[CD_3O^-]$) vs $1/T$ for these runs, k_{diss} at 25 °C was estimated to be 5.0 ± 1.0 $M^{-1}\ s^{-1}$ (E_a for k_{diss} = 9.0 ± 0.5 kcal/mol).

The rate of disappearance of the C*H*S(O) signal for sulfinamide 5 in the presence of CD_3O^- in CD_3OD was also determined. This was much slower than k_{diss} for 3, and was measured at 25 °C in the presence of 0.05–0.09 M CD_3O^-; the results are shown in Table I.

Table II. Kinetics of Disappearance of Sulfine 4 in the Presence of Methoxide Ion at 25 °C[a]

solvent	$[MeO^-] \times 10^2$, M	$k'_b \times 10^4$,[b] s^{-1}	$k_b = k'_b/[MeO^-]$,[c] $M^{-1}\ s^{-1}$
CH_3OH	0.40	1.9 ± 0.1	
	0.60	3.05 ± 0.05	0.051
	1.0	4.50 ± 0.05	
	2.0	10.4 ± 0.05	
CD_3OD	0.32	3.8	
	0.55	6.4	
	0.70	7.5	0.107
	1.1	12.1	
	2.5	26	

[a] Initial concentration of 4, 3.3×10^{-5}. [b] Rate constants in CH_3OH are average of several runs; those in CD_3OD are single determinations. [c] Slope of plot of k'_b vs $[MeO^-]$.

Kinetics of the Formation of 4 from 3 in the Presence of Bases. At room temperature in methanol in the presence of methoxide ion (0.004–0.011 M) the build up of 4 to its maximum concentration is reasonably rapid (maximum reached in less than 1.5 h), and the process can be conveniently followed kinetically. On the other hand, in 10:1 quinuclidine/quinuclidine-H^+ buffers, with [quinuclidine] = 0.10–0.2 M the process is much, much slower, and the maximum concentration of 4 is not reached even after 20 h. The disappearance of 4 in the quinuclidine buffers is also much, much slower than in solutions containing 0.004–0.011 M methoxide ion, so much so that there was some question as to whether some of the decomposition of 4 under such conditions might be due to other processes than simply straightforward reaction with the amine (or MeO^- from the buffer). Therefore, although 4 is clearly formed from 3 in amine/amine-H^+ buffers, this system seemed far less suited for accurate kinetic study than the one using methoxide ion in methanol, and all quantitative examination was carried out using 3 and methoxide ion in methanol.

The kinetics of the disappearance of 4 in the presence of methoxide ion in methanol were studied at 25 °C under conditions where methoxide ion (0.003–0.025 M) was present in huge stoichiometric excess over 4 (3.3×10^{-5} M). The decrease in absorbance (A) at 360 nm (λ_{max} for 4) was followed; A_∞ was < 0.01. The experimental first-order rate constant for the disappearance of 4 (k'_b) was obtained from a plot of log $(A - A_\infty)$ vs time. Runs were carried out for both CH_3O^-/CH_3OH and CD_3O^-/CD_3OD solutions. The results are summarized in Table II.

When sulfinamide 3 (3.3×10^{-5} M) was treated with methoxide ion (0.004–0.011 M) in methanol the shape of

Table III. Kinetics of Formation and Disappearance of 4 When 3 Is Treated with Methoxide Ion at 25 °C[a]

solvent	$[MeO^-] \times 10^2$, M	$\beta_{max} = [4]_{max}/[3]_o$	t_{max}, s	κ^b from β_{max}	κ^b from t_{max}
CH_3OH	0.40	0.43	4800	0.73	0.82
	0.60	0.41	3000	0.81	0.89
	1.0	0.40	1800	0.83	0.88
CD_3OD	0.80	0.18	1750	3.3	2.4
		0.21	1750	2.6	2.4
	1.1	0.21	1320	2.6	2.6

[a] All runs with $[3]_o = 3.3 \times 10^{-5}$ M. [b] $\kappa = k_b/k_{elim}$ (eq 4).

the curve for the rise and fall of the absorbance at λ_{max} for 4 matched that anticipated[8] for the formation of 4 as an intermediate in a pair of consecutive pseudo first-order reactions (eq 4). Values of β_{max} ($\beta_{max} = [4]_{max}/[3]_o$) and

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

t_{max}, the time at which the maximum concentration of 4 is achieved, are presented in Table III for the different runs. These are supposed[8] to be related to κ ($\kappa = k_b/k_{elim}$) as follows:

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

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

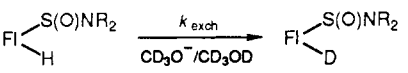
In accord with expectations, variation in $[MeO^-]$ does not result, within experimental error, in any variation in β_{max}, while t_{max} is inversely proportional to $[MeO^-]$. The values of κ calculated for each run from both β_{max} and t_{max} are also shown in Table III. From the average of all values κ for the runs in CH_3OH is 0.83 ± 0.04, while κ for the runs in CD_3OD is 2.6 ± 0.2.

Using these values of κ and the values of k_b for 4 from Table II, $k_{elim} = 0.061 \pm 0.002$ M^{-1} s^{-1} for 3 in CH_3OH at 25 °C, while in CD_3OD $k_{elim} = 0.041 \pm 0.003$ M^{-1} s^{-1}. Note that the solvent isotope effect, $k(CD_3OD)/k(CH_3OH)$, for $k_{elim} = 0.66$, while that for $k_b = 2.1$.

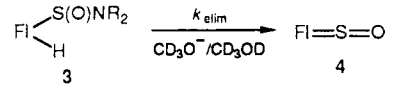
Comparison of k_{elim} for 3 in CD_3OD at 25 °C with k_{diss} for the disappearance of the C*H*S(O) signal for the sulfinamide at this temperature in CD_3OD shows that $k_{diss}/k_{elim} = 120$; disappearance of the C*H*S(O) signal for 3 therefore takes place over 100 times faster than the rate at which 3 forms sulfine 4.

Discussion

In methanol-d_4 in the presence of methoxide both base-catalyzed H/D exchange of the 9-H of sulfinamide 3 (eq 5) and CD_3O^--induced conversion of 3 to 4 (eq 6) will lead to the disappearance of the ^1H NMR signal for the 9-proton. The rate constant ($k'_{diss} = k_{diss}[CD_3O^-]$) for the disappearance of the 9-H signal ($k_{diss} = 5.0 \pm 1.0$ M^{-1} s^{-1} at 25 °C) is 120 times larger than the rate constant for eq 6 ($k_{elim} = 0.041 \pm 0.003$ M^{-1} s^{-1} at 25 °C).



3 3-d (5)



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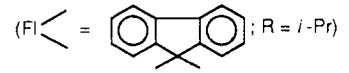
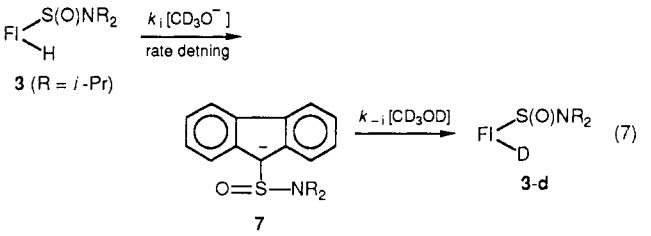


This demonstrates that the exchange (eq 5), which presumably takes place by the mechanism:



(7)

is much faster than the elimination yielding the sulfine (eq 6). If the formation of 4 from 3 also proceeds through 7 (eq 8), this means that the elimination must be proceeding by an $(E1cB)_{rev}$ mechanism ($k_{-i}[CD_3OD] \gg k_{ii}$). The present study establishes that when Y in $Ar_2CHS(O)Y$ becomes as poor a leaving group as R_2N, base-catalyzed formation of a sulfine from $Ar_2CHS(O)Y$ is still possible but that the mechanism shifts from an $(E1cB)_{irrev}$ pathway ($k_{ii} > k_{-i}[CD_3OD]$) to an $(E1cB)_{rev}$ pathway.

$$\underset{3}{Fl[H(D)]S(O)NR_2} \underset{k_{-i}[CD_3OD]}{\overset{k_i[CD_3O^-]}{\rightleftharpoons}} \underset{7}{\bar{F}lS(O)NR_2} \xrightarrow{k_{ii}} Fl{=}\underset{4}{S}{=}O + R_2ND \quad (8)$$

$$(k_{ii} \ll k_{-i}[CD_3OD])$$

A possible alternative mechanism for the formation of 4 from 3 (eq 9) would appear to be able to be ruled out. This mechanism has 3 undergoing rate-determining, base-catalyzed methanolysis to form ester 6, which is

$$\underset{3}{Fl[H(D)]S(O)NR_2} \xrightarrow[\text{rate detning}]{CD_3O^-/CD_3OD} \underset{6}{Fl[H(D)]S(O)OMe} \xrightarrow[\text{fast}]{CD_3O^-} Fl{=}\underset{4}{S}{=}O + MeOD \quad (9)$$

known from earlier work[2a] to undergo very rapid ($k_2 = 1.0 \times 10^2$ M^{-1} s^{-1} for reaction of MeO^- with 6-*d* at 25 °C) elimination to 4 in the presence of methoxide. Biasotti and Andersen[9] have measured the rate of alkaline hydrolysis of *N*-mesitylbenzenesulfinamide in aqueous ethanol ($PhS(O)NHAr + OH^- \rightarrow PhSO_2^- + ArNH_2$; Ar = mesityl). The rate constant for this alkaline hydrolysis ($k_2 = 1.4 \times 10^{-4}$ M^{-1} s^{-1} at 30 °C) should be a good indicator of what the rate constant for the first (and rate-determining) step of eq 9 might be anticipated to be. The fact that it is ~300 times *slower* than the rate constant at which 3 forms 4 ($k_{elim} = 0.041$ M^{-1} s^{-1} at 25 °C) shows that the first step of the mechanism in eq 9 would not have a rapid enough rate to be consistent with the observed rate at which sulfine 4 is formed from 3 in methanol in the presence of methoxide.

The solvent isotope effect, K_{MeOD}/K_{MeOH}, for the equilibrium in eq 8 between 3 and carbanion 7 will be equal

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

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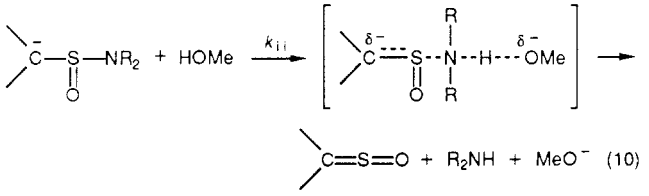
to ϕ_7^p/ϕ_{MeO}^m, where m and p are the number of methanol molecules specifically solvating methoxide ion and **7**, respectively, and ϕ_{MeO} and ϕ_7 are their deuterium fractionation factors.[10] For methoxide $m = 3$ and $\phi_{MeO} = 0.70$,[10c] so that $K_{MeOD}/K_{MeOH} = 2.9 \times \phi_7^p$. The solvent isotope effect ($K_{MeOD}/K_{MeOH} = 2.6$) for another equilibrium ($ArOMe + MeO^- \rightleftarrows Ar(OMe)_2^-$)[11] where MeO^- is replaced by a carbanion suggests that ϕ_7^p will not be much less than one, and therefore that K_{MeOD}/K_{MeOH} for the equilibrium between **3** and **7** will be *significantly larger than one*, most likely ≥ 2.0. Also consistent with that expectation is the fact that $k_{MeOD}/k_{MeOH} = 2.5$–2.7 for the methoxide-catalyzed formation of $Ar_2C{=}S{=}O$ from $Ar_2CHS(O)OMe$;[2a] the solvent isotope effect for the equilibrium formation of **7** from **3** would be anticipated[12] to be similar in magnitude to the kinetic solvent isotope effect for the $(E1cB)_{irrev}$ formation of the sulfine from a methyl diarylmethanesulfinate.

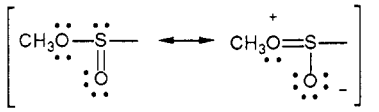
Given that $(K_{MeOD}/K_{MeOH}) \geq 2.0$ for the formation of **7** from **3** plus methoxide, the fact that the measured solvent isotope effect for the methoxide-induced formation of **4** from **3** is $(k_{MeOD}/k_{MeOH}) = 0.66$ requires that k_{ii} in eq 8 exhibit a sizeable solvent isotope effect with $k_{ii}(MeOH)$ being approximately *three times faster* than $k_{ii}(MeOD)$. The most logical way to explain an isotope effect of this magnitude for k_{ii} is to assume that expulsion of R_2N from **7** must be accompanied by the transfer of a proton from the solvent to the leaving group (eq 10) so that R_2N is



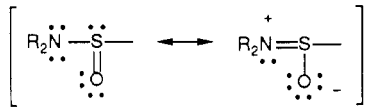
$$\rightarrow \quad C{=}S{=}O + R_2NH + MeO^- \qquad (10)$$

expelled in effect as R_2NH rather than as the very unstable R_2N^- ion. The proton transfer in eq 10 should result in k_{ii} exhibiting a primary isotope effect, $k_{MeOH}/k_{MeOD} > 1$. A similar phenomenon, with a similar effect on solvent isotope effect, is seen[13] in the basic hydrolysis of *N*-methyl-*N*-phenyltrifluoroacetamide.

There are several other aspects of the results for the present system that are worth brief discussion. First, comparison of the rate constant (Table I) for the quinuclidine-catalyzed disappearance of the 9-H signal of **3** ($k_{diss} = 0.035\ M^{-1}\ s^{-1}$) with the equivalent rate constant for the reaction of methyl 9-fluorenesulfinate (**6**) with quinuclidine ($k_e = 33\ M^{-1}\ s^{-1}$)[2a] indicates (after correcting for the fact that the rate for **3** is with CD_3OD as solvent while that for **6** is with CH_3OH)[14] that removal of the 9-proton from **3** is ~800 times slower than for ester **6**. Based on the measured[2b] ρ^* (+1.3) for amine-catalyzed H/D exchange of the 9-proton in 9-fluorenyl sulfoxides, and the difference in the σ^* values for CH_3O (+1.55)[2b] and $(CH_3)_2N$ (+0.32),[15] the rate of abstraction of the 9-H from **3** by the amine would be predicted from the purely inductive effect of the two substituents to be 40 times slower than for **6**. Two factors could be responsible for the 20-fold greater difference in reactivity actually found. First, the two branched, and somewhat bulky, isopropyl groups on the nitrogen of **3** may exert some steric hindrance to the approach of the amine to the 9-proton. Second, in the case of **6** it is known[2b] that the electron-donating resonance interaction of the CH_3O group with the sulfinyl group:



causes the actual rate for **6** to be about 5 times slower than predicted from the correlation line for simple 9-fluorenyl sulfoxides, HFlS(O)R. If an equivalent interaction of the unshared pair on nitrogen with the sulfinyl group:



is even more important in the case of **3**, this could lead to the rate constant for removal of its 9-H being significantly less than expected from the difference in σ^* for CH_3O and $(CH_3)_2N$ and the ρ^* for the proton abstraction reaction.

We can also compare the relative reactivity of methoxide and quinuclidine as bases in abstracting the 9-H of **3** with their relative reactivity in effecting the equivalent proton abstraction from **6**. For **6** $(k_{MeO}/k_{Quin}) = 19$, these data being in CH_3OH as solvent. The k_{diss} values for **3** in Table I are in CD_3OD rather than CH_3OH. The solvent isotope effect associated with the methoxide reaction is almost certainly quite large[2a] ($k_{MeOD}/k_{MeOH} \cong 2.5$) while that for the amine reaction should not be significantly different than one.[14] We would therefore estimate that in CH_3OH for **3** $(k_{MeO}/k_{Quin}) \cong 50$, i.e. $(5.1/0.035) \times (1/2.5)$. The steric demands of quinuclidine are presumably greater than those of methoxide ion. The *N*,*N*-diisopropyl group of **3** is much bulkier than the CH_3O group of **6**. It would not be surprising, then, if there was some increased steric hindrance to abstraction of the 9-H in **3** by quinuclidine that was not present in the abstraction of the proton in the other cases. This would lead to k_{Quin} for **3** being smaller, and (k_{MeO}/k_{Quin}) being larger, than would otherwise be expected.

With **6** and $(p\text{-}ClC_6H_4)_2CHS(O)OMe$ (**8**) the rate of methoxide-induced sulfine formation from **6** is 1100 times faster than the rate for **8**. We had therefore anticipated that the rate of methoxide-catalyzed H/D exchange of the >C*H*S(O) proton in **3** and **5** would show a comparable rate ratio, since the rate-determining step, like that for the reactions of **6** and **8**, would be formation of the >C̄S(O) carbanion. As the results in Table I show, the ratio of k_{diss} for **3** vs **5** is actually 2×10^4, or 20-fold larger than for **6** vs **8**. We are unclear why the change from a 9-fluorenyl to a dichlorophenylmethyl group has this much larger effect on the rates for the sulfinamides than it does on the rates for the sulfinate esters.

Experimental Section

Preparation of 3. To 2.1 g (0.02 mol) of diisopropylamine (Aldrich) in 50 mL of anhydrous tetrahydrofuran at −78 °C was added under nitrogen by syringe 8.1 mL of a 2.5 M solution of *n*-butyllithium (Aldrich) in hexane. The solution was stirred for 1 h at −78 °C, and then a solution of 2.14 g (0.01 mol) of 9-thiofluorenone *S*-oxide (**4**)[16] in 100 mL of tetrahydrofuran was

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(14) The solvent isotope effect for the reaction of **6** with quinuclidine should be $(k_{MeOD}/k_{MeOH}) = 0.9$. This is based on the measured[2] solvent isotope effects for reaction of other amines with **6**.

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slowly added. After the addition was complete the reaction mixture was stirred for 0.5 h at −78 °C and then was allowed to warm to room temperature. Saturated ammonium chloride solution (150 mL) was added. The mixture was extracted three times with ethyl acetate. The combined organic layers were washed successively with saturated ammonium chloride and water and dried over magnesium sulfate, and the organic solvents were evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using successively methylene chloride and diethyl ether as eluents. Crystallization from ether–petroleum ether gave 1.2 g (37%) of *N,N*-diisopropyl-9-fluorenesulfinamide (**3**): mp 102–103 °C; ^{1}H NMR ($CDCl_3$) δ 7.26–7.84 (m, 8 H), 5.18 (s, 1 H), 3.61–3.75 (m, 2 H), 1.27 (d, 6 H), 0.85 (d, 6 H). Anal. Calcd for $C_{19}H_{23}NOS$: C, 72.75; H, 7.45. Found: C, 72.99; H, 7.62.

Preparation of 5. To 2.52 g (0.025 mol) of diisopropylamine in 60 mL of anhydrous tetrahydrofuran kept at −62 °C was added 9.6 mL of a 2.5 M solution of *n*-BuLi in hexane. The solution was stirred for 0.5 h, and then 3.4 g (0.012 mol) of 4,4′-dichlorothiobenzophenone *S*-oxide (**9**)[17] in 100 mL of tetrahydrofuran was slowly added, the temperature being kept at −62 °C during the addition. After the addition was complete the reaction mixture was stirred for an additional hour before being poured into excess saturated ammonium chloride solution. The mixture was extracted several times with diethyl ether. The ether extracts were combined and washed twice with water. After drying over anhydrous $MgSO_4$, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using methylene chloride, followed by ethyl acetate, as eluents. The cream-colored solid so obtained (2.8 g) was further purified by recrystallization from ether–petroleum ether, giving 2.4 g (52%) of *N,N*-diisopropyl-1,1-bis(4-chlorophenyl)-methanesulfinamide (**5**): mp 127–128 °C; ^{1}H NMR ($CDCl_3$) δ 7.2–7.6 (m, 8 H), 5.03 (s, 1 H), 3.6–3.8 (m, 2 H), 1.31 (d, 6 H), 0.81 (d, 6 H). Anal. Calcd for $C_{19}H_{23}Cl_2NOS$: C, 59.40; H, 6.03. Found: C, 59.66; H, 6.10.

Attempts to carry out similar additions of other amines ($C_6H_5NHCH_3$ or Et_2NH) to **4** or **9** using the same general procedure were unsuccessful. The reactions gave a spectrum of products and no significant amount of the desired sulfinamides.

Kinetics of the Disappearance of the CHS(O) Signal of 3 in CD_3OD in the Presence of Bases. The integrated intensity of the singlet for the 9-H of **3** at δ 5.18 relative to that of an internal standard was monitored as a function of time. The internal standard used was the signal at δ 3.3 for the small amount of CH_3OD present in the methanol-d_4 used as solvent.

One milliliter of a 0.05 M solution of **3** in CD_3OD was placed in an NMR tube in the thermostated probe of a Chemagnetics A200 NMR spectrometer. In the runs using amine buffers at 25 °C a measured amount of a 0.1 M solution of trifluoroacetic acid in methanol-d_4 was then added by microsyringe followed by an equal amount of a 0.2 M solution of the amine (quinuclidine or diisopropylamine) in CD_3OD. In the runs with methoxide ion as the base the reaction was initiated by the addition by microsyringe of an amount of a 0.1 M solution of CD_3O^- in CD_3OD appropriate to give the desired final concentration of [CD_3O^-]. The methoxide solution was cooled to the temperature of the solution in the NMR tube in the thermostated probe before being added.

At appropriate time intervals after the initiation of the reaction, spectra were obtained and stored. After a run was complete a plot of log (I/I_o) vs time was made for the signal at δ 5.18, where I and I_o are the integrated intensities of this particular signal relative to the internal standard at times t and zero, respectively. The experimental first-order rate constant for the disappearance of the singlet at δ 5.18 (k'_{diss}) was calculated from the slope of the plot.

The procedure for the runs using **5**, rather than **3**, was identical except that in that case the ^{1}H NMR signal for the C*H*S(O) proton is at δ 5.03 instead of 5.18.

Kinetics of the Disappearance of 4 in Methanol in the Presence of Methoxide Ion. A solution (3.0 mL) of **4** (3.3×10^{-5} M) in methanol was placed in a 1-cm spectrophotometer cell in the thermostated cell compartment of a UV–visible spectrophotometer. To this was then added by microsyringe with good mixing an amount of a 1.0 M solution of sodium methoxide in methanol sufficient to give the concentration of methoxide desired (0.004–0.025 M), and the decrease in the optical density (A) of the solution at 360 nm (long wavelength maximum for **4**) was then followed as a function of time. Experimental first-order rate constants (k'_b) were evaluated from the slope of a plot of log ($A - A_\infty$) vs time. The second-order rate constant k'_b/[MeO^-] was independent of methoxide ion concentration. Runs were carried out in both CD_3OD and CH_3OH.

Kinetics of the Formation of 4 from 3 in the Presence of Methoxide. A 3.3×10^{-5} M solution of **3** in methanol was placed in a 1-cm spectrophotometer cell in the thermostated cell compartment of a UV–visible spectrophotometer. After the solution had reached thermal equilibrium, the amount of a 1.0 M solution of sodium methoxide in methanol needed to give the desired final concentration of methoxide ion (0.004–0.011 M) was added by microsyringe with good mixing, and the absorbance of the solution at 360 nm (λ_{max} for **4**) was monitored as a function of time. The absorbance at 360 nm first increased from 0.00 to either about 0.20 (runs in CH_3OH) or 0.10 (runs in CD_3OD) and then subsequently decreased back to zero with the disappearance of **4**. The maximum absorbance at 360 nm was independent of [MeO^-] but the time to reach the maximum was not, being shorter the higher the concentration of methoxide. The data were analyzed using the expression for the concentration of an intermediate during two consecutive first-order reactions given by Moore and Pearson.[8]

Several runs were also carried out with **3** in CH_3OH using a 10:1 0.2 M quinuclidine/quinuclidine-H^+ buffer. These runs used a temperature of 35 °C rather than 25 °C. However, the length of time to reach a maximum in absorbance at 360 nm was so long (20–24 h) that the system was not judged to be a practical one in which to obtain accurate quantitative data on the rate constants for formation and disappearance of **4**.

Registry No. **3**, 124401-73-6; **4**, 4440-32-8; **5**, 124401-74-7; **9**, 33240-29-8; D_2, 7782-39-0.

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