Elimination Reactions of Alkanesulfenyl Derivatives: Effect of Structure on Reactivity in Thioketone-Forming Eliminations of Diarylmethyl Thiosulfonates

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The reaction of a group of diarylmethyl arenethiosulfonates, $ArAr'CHSSO_2Ar''$ (2), with (a) two alkoxide ions (i-PrO^- and MeO^-), (b) a series of secondary and tertiary amines of differing base strength, and (c) phenoxide ion has been examined. For each system both the overall rate of disappearance of 2 and the fraction (α_{elim}) converted to thioketone were determined. Salient results are as follows: (1) The ρ values for thioketone-forming elimination of $ArAr'CHSSO_2C_6H_4CH_3$-p with either isopropoxide (+3.4) or piperidine (+3.5) are large and positive, while the ρ value associated with variation of the substituent in Ar'' in the elimination of Ph_2CHSSO_2Ar'' with i-PrO^- is quite modest (+1.3). (2) The Brønsted β for the elimination reaction of p-nitrobenzhydryl p-toluenethiosulfonate with the series of amines is close to +1.0. (3) While plots of the elimination rate constant (k_{elim}) vs. [amine] for any of the amine-induced eliminations in amine–amineH^+ buffers are linear, plots of k_{elim} vs. [PhO^-] for the phenoxide-induced elimination in PhO^-–PhOH buffers exhibit very pronounced downward curvature (Figure 4). These various results can be explained by assuming that the different eliminations proceed by different variants of an ElcB mechanism: for the elimination involving amines and 2 a reversible $(ElcB)_{ion\ pr}$ mechanism (eq 13) is suggested; in the elimination with phenoxide ion the reaction proceeds by an ordinary $(ElcB)_{reversible}$ mechanism (eq 9, $k_i[PhOH] > k_{ii}$); in the elimination involving isopropoxide the mechanism becomes $(ElcB)_{irreversible}$ (eq 9, $k_{-i}[i\text{-}PrOH] < k_{ii}$). Comparison of selected data on the rates of thioketone-forming eliminations of 2 with amines with data obtained previously (ref 6) on the rates of sulfene-forming eliminations of aralkyl α-disulfones with amines indicates that an arylalkanesulfonyl compound undergoes elimination approximately 300 million times faster than the equivalently substituted arylalkanesulfenyl derivative.

Many substitution reactions of nucleophiles with alkanesulfonyl derivatives RCH_2SO_2Y, especially where R = Ar, proceed by an elimination–addition mechanism (eq 1a) involving a sulfene intermediate ($RCH=SO_2$), rather than by direct substitution at sulfur (eq 1b).[1] Quantitative data

$$RCH_2SO_2Y + Nu^- \xrightarrow{k_e,\ \text{elimination}} Y^- + NuH + [RCH{=}SO_2] \xrightarrow[\text{addition}]{NuH} RCH_2SO_2Nu \quad (1a)$$

$$RCH_2SO_2Y + Nu^- \xrightarrow[\text{direct substitution}]{k_{ds}} Y^- + RCH_2SO_2Nu \quad (1b)$$

are available[2-6] on the effect of various structural parameters (nature of R, Y, and Nu^-) on the rate of such eliminations and on the competition between elimination and direct substitution (k_e/k_{ds}). When combined with such information as the occurrence,[2] or nonoccurrence,[2,3] of exchange of CH_2SO_2 group protons prior to reaction, such data enable the mechanisms for most eliminations of alkanesulfonyl derivatives to be specified in detail.

In contrast to the situation for reactions of alkanesulfonyl derivatives and nucleophiles, where elimination is encountered frequently, elimination (eq 2a) is observed only infrequently in reactions of nucleophiles with alkanesulfenyl derivatives, and information on reactivity, mechanism, etc. for such reactions is quite limited.

That elimination (eq 2a) is encountered much less frequently with alkanesulfenyl derivatives is not surprising, since there are two reasons why it should compete with substitution (eq 2b) far less effectively than in the corresponding alkanesulfonyl system. First, with a given nucleophile, the rate of substitution at a sulfenyl (–SY) group is orders of magnitude faster than at a sulfonyl ($-SO_2Y$) group.[7] Second, rates for elimination will increase with increasing acidity of the hydrogens on the carbon adjacent to the sulfur, and hydrogens adjacent to a sulfonyl group are estimated to be 8–10 pK units more acidic than those adjacent to a sulfenyl sulfur.[8]

$$\begin{matrix} R \\ R' \end{matrix}\!\!>\!CHSY + Nu^- \xrightarrow{k_e} NuH + \begin{matrix} R \\ R' \end{matrix}\!\!>\!C{=}S + Y^- \quad (2a)$$

$$\begin{matrix} R \\ R' \end{matrix}\!\!>\!CHSY + Nu^- \xrightarrow{k_{ds}} \begin{matrix} R \\ R' \end{matrix}\!\!>\!CHSNu + Y^- \quad (2b)$$

With suitable alkanesulfenyl substrates elimination can, however, become the dominant reaction pathway, as is demonstrated by the fact that reaction of diphenylmethyl thiocyanate (1) with isopropoxide ion leads to the formation of thiobenzophenone in over 90% yield (eq 3).[9]

$$\underset{1}{Ph_2CHSCN} + i\text{-}PrO^- \rightarrow \underset{(95\%)}{Ph_2C{=}S} + i\text{-}PrOH + CN^- \quad (3)$$

In the present work we have examined the reaction of a series of diarylmethyl arenethiosulfonates, $ArAr'CHSSO_2Ar''$ (2), with two alkoxide ions (i-PrO^- and MeO^-), with a series of amines of differing base strength, and with phenoxide ion, determining for each system both the overall rate of disappearance of 2 and the fraction converted to thioketone. By providing quantitative data on the effect on the rate of elimination of systematic variations in Ar, Ar', $Ar''SO_2$, and basicity of nucleophile the results furnish information relevant to the timing of

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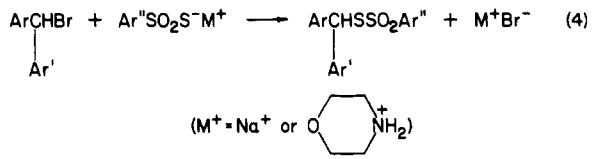
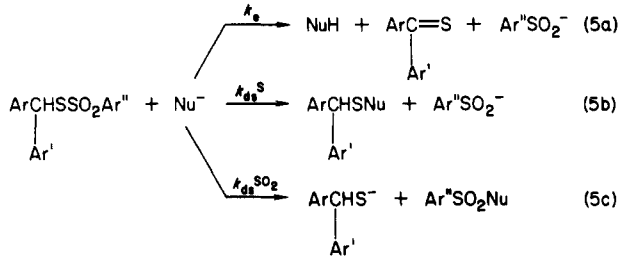
bond breaking and bond making in an elimination of an alkanesulfenyl derivative (eq 2a, R = Ar, R′ = Ar′, Y = Ar″SO_2) and the question of which of the various possible elimination mechanisms (E2, $ElcB_i$, $ElcB_r$) is operative. In addition, comparison of selected rates of elimination for **2** with those determined in earlier work[6] for eliminations of certain alkyl α-disulfones (eq 1a, R = Ar, Y = $ArCH_2SO_2$) affords an estimate of the magnitude of the difference in rates for elimination of alkanesulfenyl (eq 2a) vs. alkanesulfonyl (eq 1a) derivatives.

Results

Synthesis of the diarylmethyl arenethiosulfonates (**2**) was effected by reaction of the appropriate diarylmethyl bromide and the sodium or morpholinium salt of the arenethiosulfonate (eq 4).



Thiosulfonates **2** can react with a nucleophile in three different ways: (a) elimination to form the thioketone and Ar″SO_2^- (eq 5a), (b) nucleophilic substitution at the dicoordinate sulfur (eq 5b), and (c) nucleophilic substitution at the sulfonyl sulfur (eq 5c). The amount of thioketone formed under a given set of reaction conditions (easily ascertained from the final optical density, A_∞, of the solution at the wavelength in the 600-nm region corresponding to λ_{max} for the thioketone) indicates the fraction (α_{elim}) of the substrate reacting via the elimination pathway (eq 5a).



All kinetic studies of the reactions of **2** with nucleophiles were carried out with the nucleophile present in considerable stoichiometric excess over **2**. Under these conditions disappearance of **2** follows first-order kinetics and a plot of log ($A_\infty - A$) vs. time gives k_{tot}, the overall rate of disappearance of **2**. Multiplication of k_{tot} by α_{elim} provides k_{elim}, the experimental first-order rate constant for elimination (**2** → ArAr′C=S + Ar″SO_2^-).

Reaction of 2 with Isopropoxide. The kinetics of the reaction of **2** (0.002 M) with excess sodium isopropoxide (0.01–0.05 M) in 2-propanol at 25 °C were studied by using stopped-flow spectrophotometry. The results are summarized in Table I. The fraction of the thiosulfonate undergoing elimination varies significantly with the structure of **2**, ranging from a high of 1.0 (*p*-$O_2NC_6H_4CH$(Ph)SSO_2Ar″) down to 0.30 ($Ph_2CHSSO_2C_6H_4NO_2$-*p*). For all **2**, both k_{elim} and ($k_{tot} - k_{elim}$) are proportional to [*i*-PrO^-]. Rate constants for eq 5a (Nu^- = *i*-PrO^-), $k_e = k_{elim}/[i\text{-}PrO^-]$, are tabulated in the rightmost column of the Table.

Figure 1 shows a plot of log k_e for *p*-$CH_3C_6H_4SO_2SCH(C_6H_4Y)C_6H_4X$ vs. ($\sigma_X + \sigma_Y$); it is linear, with a slope, ρ, equal to +3.4. The fact that the point for X = *p*-NO_2, Y = *p*-H does not deviate from the correlation line shows that the data for log k_e are correlated much better by σ than by σ^-. The open circles in Figure 2 are a plot of log k_e for

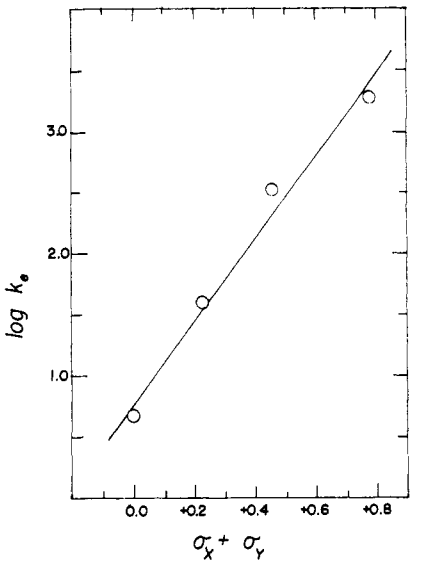


Figure 1. Plot of log k_e for *p*-$CH_3C_6H_4SO_2SCH(C_6H_4Y)C_6H_4X$ vs. ($\sigma_X + \sigma_Y$) for the thioketone-forming elimination of diarylmethyl *p*-toluenethiosulfonates with sodium isopropoxide in 2-propanol. Slope, ρ, equals +3.4.

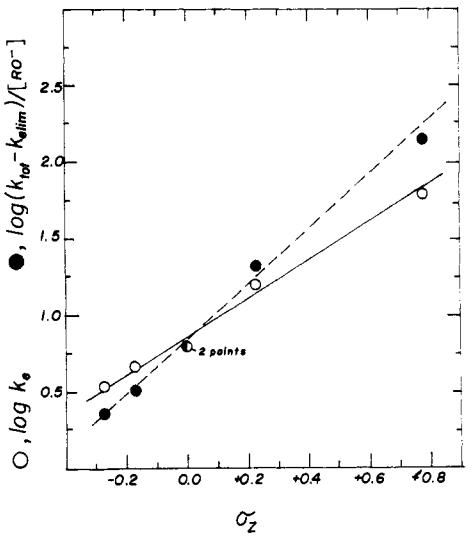


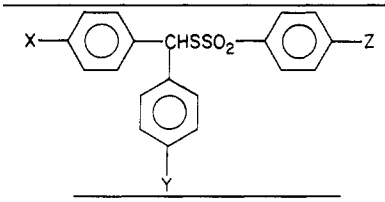
Figure 2. Reaction of diphenylmethyl arenethiosulfonates ($Ph_2CHSSO_2C_6H_4Z$) with sodium isopropoxide in 2-propanol. Plot of log k_e vs. σ_z (○), slope = 1.3; plot of log $\{(k_{tot} - k_{elim})/[i\text{-}PrO^-]\}$ vs. σ_Z (●), slope = +1.8.

$Ph_2CHSSO_2C_6H_4Z$ vs. σ_Z; the slope, ρ, is +1.3. The closed circles in Figure 2 are a plot of log $(k_{tot} - k_{elim})/[i\text{-}PrO^-]$ for the same group of substrates vs. σ_Z; this slope is +1.8.

Reaction of 2 with Methoxide. The fraction of thiosulfonate undergoing elimination upon treatment with sodium methoxide (0.01–0.04 M) in methanol at 25 °C is significantly smaller (α_{elim} = 0.15 for $Ph_2CHSSO_2C_6H_4CH_3$-*p*, α_{elim} = 0.73 for *p*-$O_2NC_6H_4CH$(Ph)$SSO_2C_6H_4CH_3$-*p*) than for the reaction of the same substrates with isopropoxide. Because of this, the kinetics of the reaction with methoxide were examined only for these two thiosulfonates. Both k_{tot} and k_{elim} were found to be proportional to [MeO^-]. From $k_{elim}/[MeO^-]$ the values of k_e for eq 5a (Nu^- = MeO^-) are: $Ph_2CHSSO_2C_6H_4CH_3$, 0.29 M^{-1} s^{-1}; *p*-$O_2NC_6H_4CH(Ph)$-$SSO_2C_6H_4CH_3$, 94 M^{-1} s^{-1}. In both cases k_e for the reaction with methoxide ion in methanol is roughly 1/20th k_e for the corresponding elimination with isopropoxide ion in 2-propanol (Table I).

Reaction of 2 with Amines. Reaction of *p*-nitrobenzhydryl *p*-toluenethiosulfonate (**2a**), *p*-$O_2NC_6H_4CH$-

Table I. Kinetics of the Reaction of Diarylmethyl Arenethiosulfonates (2) with Sodium Isopropoxide in 2-Propanol at 25 °C



X	Y	Z	$10^3[2]_0$, M	$10^2[i\text{-PrO}^-]$, M	k_{tot},[a] s^{-1}	α_{elim}	$k_{elim} = k_{tot}\alpha_{elim}$, s^{-1}	$k_e = k_{elim}/[i\text{-PrO}^-]$, $M^{-1}\ s^{-1}$
NO_2	H	CH_3	2.0	1.14	22.9	1.00	22.9	2.0×10^3
				2.40	43.2	1.00	43.2	1.8×10^3
Cl	Cl	CH_3	2.0	1.14	4.6	0.83	3.8	3.3×10^2
				2.40	9.4	0.84	7.9	3.3×10^2
Cl	H	CH_3	2.1	1.14	0.60	0.74	0.45	39
				2.40	1.27	0.74	0.94	39
H	H	CH_3	2.0	1.20	0.095	0.59	0.056	4.7
				2.20	0.172	0.59	0.103	4.7
				4.40	0.347	0.59	0.206	4.7
H	H	CH_3O	2.1	2.25	0.134	0.59	0.079	3.5
				4.50	0.238	0.62	0.147	3.3
H	H	H	2.1	2.25	0.29	0.48	0.141	6.3
				4.50	0.55	0.51	0.28	6.2
H	H	Cl	2.0	2.25	0.83	0.43	0.36	16
				4.50	1.62	0.43	0.70	16
H	H	NO_2	1.9	2.25	4.7	0.30	1.41	63
				4.50	8.7	0.31	2.70	60

[a] Fraction of 2 undergoing elimination (α_{elim}) calculated from final absorbance of solution (A_∞) and ϵ for thioketone at the same wavelength by using the relation: $\alpha_{elim} = A_\infty/\epsilon[2]_0$.

$(Ph)SSO_2C_6H_4CH_3$-*p*, with a series of secondary and tertiary amines in amine–amineH^+ buffers in 2-propanol at 25 °C results in the conversion of **2a** to thioketone in yields ranging from 58–100%. The kinetics of the reactions of these amines with **2a** were determined. Values of $k_{elim} = k_{tot}\alpha_{elim}$ for the different reaction conditions may be found in the first section of Table II and are proportional to [amine] for each amine. The rightmost column lists $k_e = k_{elim}/[amine]$, the rate constants for the elimination reaction (eq 5a, $Nu^- = R_2NH$ or R_3N) of **2a** with the different amines. A plot (Figure 3) of log k_e vs. the $pK_a(H_2O)$ of the conjugate acid of the amine is linear, with a slope, β, of $+0.70 \pm 0.05$.

Kinetic data for the reaction of bis(*p*-chlorophenyl)-methyl (**2b**) and *p*-chlorobenzhydryl (**2c**) *p*-toluenethiosulfonates with piperidine in piperidine–piperidineH^+ buffers in *i*-PrOH at 25 °C are also given in the first section of Table II. Note that α_{elim} is markedly dependent on buffer concentration. This is because, although $k_{elim} = k_{tot}\alpha_{elim}$ is, as before, proportional to [amine], the rate constant for the disappearance of **2** by routes other than elimination is dependent on both [amine] and [amineH^+], i.e., $(k_{tot} - k_{elim}) = k[amine] + k'[amine][amineH^+]$. Whether the dependence of $(k_{tot} - k_{elim})$ on [amineH^+] is the result of a salt effect, or, alternatively, of acid catalysis due to amineH^+, is not known. (Since the focal point of our interest was the rate of the elimination reaction (eq 5a), the matter was not investigated further.) Values of $k_e = k_{elim}/[amine]$ for eq 5a (Nu^- = piperidine) for **2b** and **2c** are listed in Table II. A plot of log k_e for **2a**, **2b**, and **2c** vs. $(\sigma_X + \sigma_Y)$ for the two *p*-substituents in the diarylmethyl group $p\text{-}XC_6H_4CH(C_6H_4Y\text{-}p)$ is linear with a slope, ρ, equal to +3.5, a value quite similar to ρ for the elimination reaction of **2** with isopropoxide ion (vide supra).

Reaction of **2** with amines in 60% dioxane as solvent leads to a significantly smaller fraction of elimination (α_{elim}) than in 2-propanol. Because of this we limited kinetic investigation of such reactions to only three examples—the reaction of morpholine with either **2a** or **2b** and the reaction of piperidine with **2b**. The results, shown in the second section of Table II, indicate that $k_{elim} = k_{tot}\alpha_{elim}$ is proportional to [amine] and that the value of $k_e = k_{elim}/$

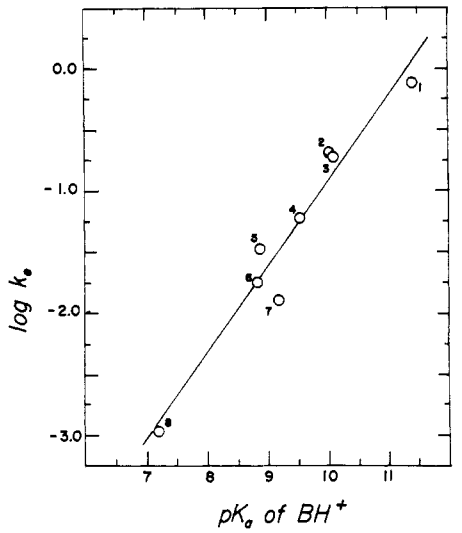
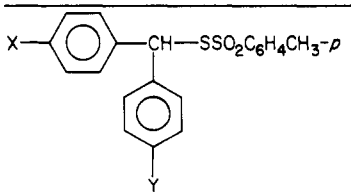


Figure 3. Plot of log k_e for the reaction of secondary and tertiary amines with **2a** vs. the pK_a (H_2O) of the conjugate acid of the amine: 1 = piperidine; 2 = piperazine; 3 = 3-quinuclidinol; 4 = benzylmethylamine; 5 = morpholine; 6 = diallylamine; 7 = DABCO; 8 = imidazole. Slope, β, equals +0.70. Plotted values of k_e for piperazine and Dabco are statistically corrected, i.e., plotted value of $k_e = k_e/2$.

[amine] is from 1.1 (**2a**–morpholine) to 1.8 (**2b**–piperidine) larger in 60% dioxane than in 2-propanol. The decreased fraction of elimination in 60% dioxane results, therefore, not from a decrease in the rate of elimination, but rather from the fact that, on going from *i*-PrOH to 60% dioxane the rate of disappearance of **2** by routes other than elimination increases by a considerably larger factor than does the rate of elimination.

Reaction of 2b with Phenoxide Ion. Reaction of **2b** with excess sodium phenoxide in phenol–phenoxide buffers in 2-propanol at 25 °C led to the formation of thioketone in >90% yield. Kinetic data for the reaction in two different PhOH–PhO^- buffers are presented in Table III. Figure 4 shows a plot of k_{elim} vs. [PhO^-] for the runs in the 3.5:1 PhOH:PhO^- buffer; it is clearly *not* linear, exhibiting pronounced downward curvature. A plot of k_{elim} vs. [PhO^-]

Table II. Kinetics of the Reaction of Diarylmethyl *p*-Toluenethiosulfonates with Amines in 2-Propanol and 60% Dioxane at 25 °C



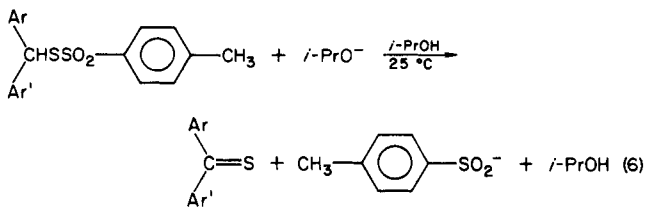
X	Y	$10^3[2]_0$, M	amine	pK_a (H_2O)	10^2[amine], M	[amine]/[amineH$^+$]	10^2k_{tot}, s^{-1}	α_{elim}[a]	10^3k_{elim}, s^{-1} [b]	$k_e = k_{elim}/$[amine], $M^{-1}\ s^{-1}$
					A. Reactions in 2-Propanol					
NO_2	H	2.2	piperidine	11.42[d]	8.83	2.0	7.3	0.94	68	0.78
					3.65	1.5	2.7	0.99	27	0.73
		2.0	piperazine	10.10[d]	4.07	9.6	2.8	0.58	16	0.40
					2.03	9.6	1.12	0.68	7.6	0.37
			3-quinuclidinol	10.01[d]	3.76	4.0	0.73	0.99	7.2	0.19
					1.88	4.0	0.37	1.00	3.7	0.20
		2.1	$PhCH_2NHMe$	9.55[e]	7.11	3.7	0.90	0.60	5.4	0.076
					3.55	3.7	0.40	0.67	2.7	0.075
		2.0	Dabco[c]	9.20[d]	1.44	13.5	0.036	0.95	0.34	0.024
					0.72	13.5	0.018	0.95	0.17	0.024
			morpholine	8.87[d]	2.28	4.7	0.089	0.85	0.76	0.033
					1.14	4.7	0.044	0.85	0.37	0.033
			diallylamine	8.85[e]	7.18	3.5	0.148	0.86	0.13	0.0177
					3.59	3.5	0.069	0.91	0.063	0.0174
			imidazole	7.21[d]	6.64	3.5	0.0079	0.88	0.070	0.0010
					3.32	3.5	0.0043	0.83	0.035	0.0011
					1.96	1.7	0.0026	0.81	0.021	0.0011
Cl	Cl	2.0	piperidine	[f]	15.2	2.3	1.24	0.40	5.0	0.033
					8.83	2.0	0.64	0.43	2.8	0.031
					4.44	2.0	0.24	0.58	1.4	0.031
Cl	H	2.0	piperidine	[f]	17.4	1.8	0.85	0.17	1.4	0.0081
					9.02	1.8	0.26	0.26	0.69	0.0076
					8.88	2.0	0.25	0.30	0.73	0.0082
					4.44	2.0	0.089	0.42	0.37	0.0083
					B. Runs in 60% Dioxane					
NO_2	H	2.0	morpholine	[f]	2.11	2.1	0.25	0.30	0.75	0.035
					1.05	2.1	0.099	0.39	0.39	0.037
					0.52	2.1	0.036	0.51	0.19	0.036
Cl	Cl	2.0	morpholine	[f]	10.6	2.1	0.40	0.037	0.015	0.0014
					2.1	2.1	0.031	0.12	0.0036	0.0017
					1.05	2.1	0.011	0.14	0.0016	0.0015
			piperidine	[f]	2.10	2.1	1.59	0.077	1.2	0.058
					1.05	2.1	0.53	0.12	0.64	0.062

[a] Fraction of **2** undergoing elimination (α_{elim}) calculated from final absorbance of solution (A_∞) and ϵ for thioketone at the same wavelength using relation, $\alpha_{elim} = A_\infty/\epsilon[2]_0$. [b] $k_{elim} = k_{tot}\alpha_{elim}$. [c] Dabco = 1,4-diazabicyclo[2.2.2.]octane. [d] Reference 16a. [e] Reference 16b. [f] See earlier entry for this amine.

for the runs in the 1.13:1 PhOH:PhO^- buffer shows analogous curvature. Such behavior is, of course, in marked contrast to the simple proportionality between k_{elim} and [Nu^-] observed in all the thioketone-forming eliminations of **2** with isopropoxide, methoxide, or amines.

Discussion

Thioketone-Forming Eliminations of 2 with Alkoxides and Phenoxide. The ρ value (+3.4) for the elimination reaction of diarylmethyl *p*-toluenethiosulfonates with sodium isopropoxide in 2-propanol (eq 6) is large and positive.



Large positive ρ values (+3.5 for eq 7, +4 for eq 8) have also been observed for two other thioketone-forming eliminations of (diarylmethyl)thio derivatives (**3** and **4**)

Table III. Kinetics of the Reaction of Sodium Phenoxide with Bis(*p*-chlorophenyl)methyl *p*-Toluenethiosulfonate in 2-Propanol at 25 °C

$10^3[2b]_0$, M	[PhOH]/[PhO^-]	10^2[PhO^-], M	10^2k_{elim}, s^{-1}
2.1	1.13	0.61	1.45
		0.91	1.93
		1.22	2.3
		1.68	2.7
		2.45	3.3
		2.90	3.8
		3.65	4.3
2.0	3.5	0.57	1.06
		0.862	1.35
		1.13	1.7
		1.72	2.0
		2.27	2.6
		3.45	2.8
		3.98	3.0
		4.57	3.5

with isopropoxide ion.[9,10] Ceccon and co-workers[9,10] pointed out that these values of ρ are larger than those found in most eliminations, and they have considered them indicative of a large amount of carbanionic character for

(10) Miotti, U.; Tonellatto, U.; Ceccon, A. *J. Chem. Soc. B* **1970**, 325.

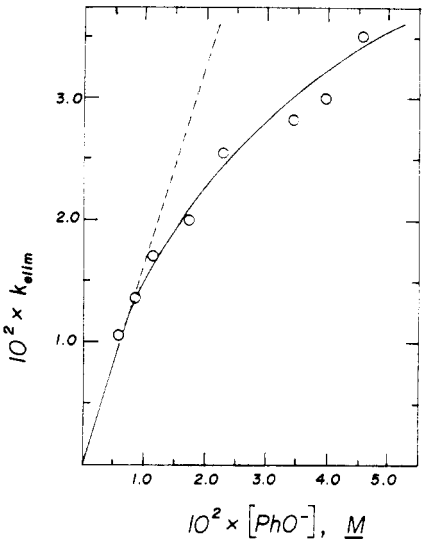
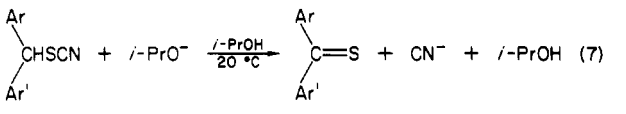
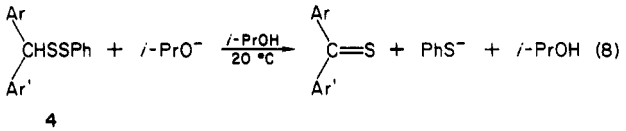


Figure 4. Plot of k_{elim} vs. [PhO^-] for the thioketone-forming elimination of **2b** with phenoxide ion in a 3.5:1 PhOH:PhO^- buffer in 60% dioxane.

the ArAr'CS carbon in the rate-determining transition state for eq 7 and 8. Because significant H/T exchange

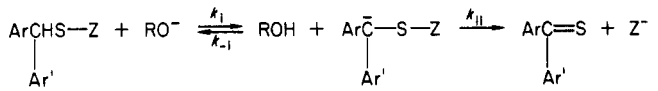


3



4

was not observed in the **3** or **4** recovered from partial reaction in *i*-PrOT and because of the magnitude of k_H/k_D (3.0 for **3**, 6.1 for **4**) for reaction of >CHS vs. >CDS in the two cases, the Italian workers preferred to view eq 7 and 8 as proceeding by an ElcB-like E2 mechanism. In our opinion, however, their data are also compatible with an irreversible ElcB mechanism (eq 9, RO^- = *i*-PrO^-, $k_{ii} > k_{-i}[i\text{-PrOH}]$) for these reactions.



(9)

A plot of k_{elim} vs. [PhO^-] for the phenoxide-induced, thioketone-forming elimination of **2b** in PhOH–PhO^- buffers in 2-propanol exhibits very pronounced downward curvature (Figure 4). The degree of curvature is *too great* to be able to be attributed to a decrease in phenoxide concentration with increasing buffer concentration due to the association.[11]

$$PhO^- + PhOH \overset{K}{\rightleftharpoons} PhO^-\cdots HOPh$$

The observed curvature can, however, be easily explained if the elimination reaction of **2b** with phenoxide ion takes place by an $(ElcB)_{rev}$ mechanism (eq 9, Z = Ar″SO_2, RO^- = PhO^-, $k_{ii} < k_{-i}[PhOH]$).[12]

Since the thioketone-forming elimination of **2b** with the phenoxide apparently proceeds by an ElcB mechanism, it seems reasonable that the reaction of isopropoxide with **2** (eq 6) should also be an ElcB process. The behavior of the isopropoxide-induced elimination of **3** (eq 7)[9] suggests that the mechanism for eq 6 is $(ElcB)_{irrev}$ (eq 9, Z = Ar″SO_2, $k_{ii} > k_{-i}[i\text{-PrOH}]$), rather than the $(ElcB)_{rev}$ mechanism that obtains for the phenoxide reaction. The acidity of *i*-PrOH is much less than that of PhOH. If, even though the transfer is thermodynamically favorable, the rate of proton transfer to the carbanion in eq 9 (step k_{-i}) is dependent on the pK_a of ROH, then k_{-i} when ROH = *i*-PrOH will be smaller than when ROH = PhOH. This can account for why $k_{ii} < k_{-i}[PhOH]$ but $k_{ii} > k_{-i}[i\text{-PrOH}]$.

The ρ value associated with variation of the Ar″ group in the elimination

$$Ph_2CHSSO_2Ar'' + i\text{-}PrO^- \xrightarrow[25\ °C]{i\text{-PrOH}} Ph_2C{=}S + Ar''SO_2^- + i\text{-PrOH} \quad (10)$$

is quite modest (+1.3), being smaller, in fact, than the ρ(+1.8) associated with the noneliminative reaction of Ph_2CHSSO_2Ar'' with *i*-PrO^- (eq 5b and 5c, Nu^- = *i*-PrO^-). Given the ρ = +1.9 for the removal of a proton from $PhCH_2SO_2OAr$ by Et_3N in D_2O–dimethoxyethane,[2] a value of ρ = +1.3 for eq 10 seems entirely consistent with the proposal of an $(ElcB)_{irrev}$ mechanism where the rate-determining step is

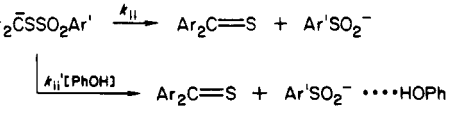
$$Ph_2CHSSO_2Ar'' + i\text{-}PrO^- \xrightarrow{k_i} i\text{-PrOH} + Ph_2C^-SSO_2Ar''$$

Comparison of the rate constants (k_e) for eq 6, 7, and 8 (Ar *p*-ClC_6H_4, *p*-ClC_3H_4, Ar′ = Ph) affords additional information on the effect of the leaving group, Z, on the rate (Z, k_e): CN, 44 M^{-1} s^{-1} (20 °C);[9] *p*-$CH_3C_6H_4SO_2$, 39 M^{-1} s^{-1} (25 °C); PhS, 0.23 M^{-1} s^{-1} (20 °C).[10] Since the σ_I values for CN (+0.56) and RSO_2 (+0.59) are almost the same[13,14] and are significantly more positive than σ_I for RS (+0.25), the variation of k_e with variation in the leaving group, Z, fits well with that anticipated if eq 6, 7, and 8 all proceed by an $(ElcB)_{irrev}$ mechanism, and the effect of leaving group on rate is determined by its effect on the acidity of the CHS proton.

Since the ArAr′CS carbon has a large amount of carbanion character in the rate-determining transition state for eq 6, it is somewhat surprising to find (Figure 1) that the rate for **2a** (Ar = *p*-$O_2NC_6H_4$, Ar′ = Ph) is correlated much better with σ for *p*-NO_2 than with σ^-. Such behavior is not unprecedented, however, in eliminations involving diarylmethyl derivatives. Thus Hammett equation plots of the kinetic data for eq 11 show that when R is equal to either H or CH_3 the rate for Ar = *p*-$O_2NC_6H_4$ correlates with σ^- for *p*-NO_2, but that when R = Ph the rate for the

(11) To achieve a satisfactory fit, i.e., $k_{elim}/[PhO^-]$ = constant, for the data in the 1.13:1 PhOH:PhO^- buffer requires a value for *K* of 200; this seems too large to be reasonable. Furthermore, this value for *K* does not give a satisfactory fit for the data for the 3.5:1 PhOH:PhO^- buffer, $k_{elim}/[PhO^-]$ increasing by more than a factor of two on going from the lowest stoichiometric phenoxide concentration to the highest.

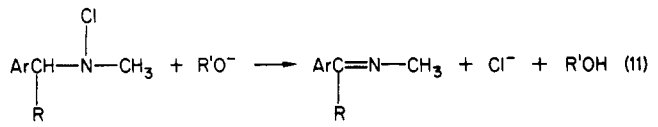
(12) For the optimum fit to the experimental data for both PhOH–PhO^- buffers it appears necessary to modify the mechanism in eq 9 slightly by including the possibility (step k_{ii}') of PhOH-catalyzed collapse of the carbanion intermediate to products, i.e.,



The data for the runs in the two different buffers are fitted by the scheme above by using the following values: k_i = 3 M^{-1} s^{-1}; k_{-i}/k_{ii} = 40 M^{-1}; k_{ii}'/k_{ii} = 5.5 M^{-1}.

(13) Taft, R. W. "Steric Effects in Organic Chemistry"; Newman, M., Ed.; John Wiley & Sons, Inc.: New York, 1956; p 595.

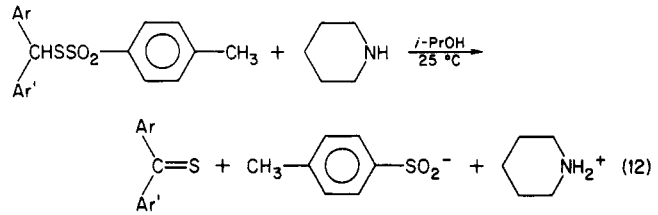
(14) Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; John Wiley & Sons, Inc.: New York, 1975; p 98.



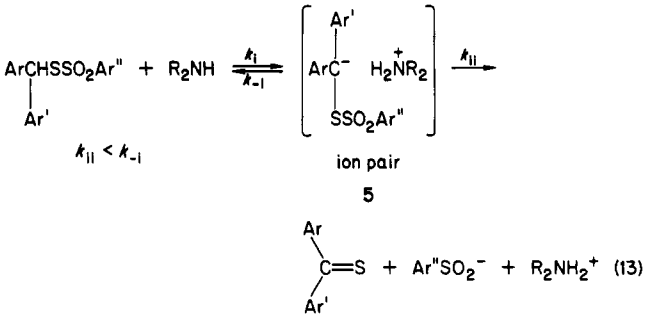
p-nitro compound correlates much better with σ for p-NO_2 than with σ^-.[15] This result, and the behavior of **2a**, suggest that in some eliminations involving proton removal from a diarylmethyl group there is apparently sufficient hindrance to coplanarity of the p orbital of the developing carbanion and the ρ orbitals of the aromatic ring containing the p-NO_2 group so that stabilization of the carbanion by the nitro group is due only to the inductive effect of that group.

Thioketone-Forming Eliminations of 2 with Amines. Diarylmethyl p-toluenethiosulfonates can also undergo thioketone-forming eliminations upon reaction with secondary or tertiary amines in 2-propanol (eq 5a, Nu^- = R_2NH or R_3N), although only when the thiosulfonate is **2a** is elimination the dominant reaction pathway (see α_{elim} values in Table II).

The ρ value for the thioketone-forming elimination of **2** with piperdine (eq 12) is, like that for eq 6, large and positive (+3.5).

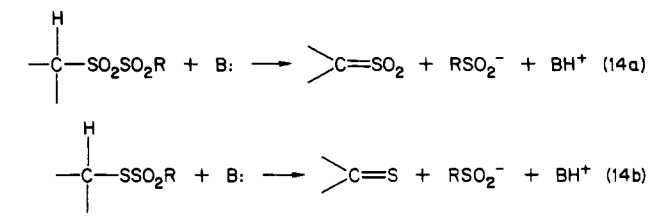


For thiosulfonate **2a** a plot (Figure 3) of log k_e (k_e is the rate constant for eq 5a) vs. the $pK_a(H_2O)$[16] of $R_2NH_2^+$ and R_3NH^+ is linear with a slope, β, of +0.70 ± 0.05. To measure accurately the extent of proton transfer from carbon to amine at the rate-determining transition state such a plot should actually use the pK_a's of the amines in i-PrOH rather than water. Unfortunately these are not known. The pK_a's for some of the amines are known in ethanol, however, or can be estimated.[16b] A plot of log k_e vs. pK_a(EtOH) gives β = +0.9 ± 0.1. This suggests that the value associated with the thioketone-forming elimination of **2a** with amines (eq 5a, Nu^- = R_2NH or R_3N, Ar = p-$O_2NC_6H_4$, Ar′ = Ph, Ar″ = p-$CH_3C_6H_4$) in i-PrOH is large enough (~+1.0) to be consistent with a mechanism for this reaction where the proton has been completely transferred to the amine by the time the rate-determining transition state is reached. A mechanism meeting this requirement is shown in eq 13. In this mechanism step k_{ii} is rate determining and, consistent with the large positive ρ for the reaction, the ArAr′CS carbon possesses a large amount of carbanion character in the rate-determining transition state. The $(ElcB)_{ion\ pr}$ mechanism in eq 13 is also consistent with the fact that in the thioketone-forming eliminations of **2a** in amine–amineH^+ buffers k_{elim}/[amine] does not decrease with increasing [amineH^+] (Table II). In the $(ElcB)_{ion\ pr}$ mechanism the molecule of $R_2NH_2^+$ that protonates the carbanion in step k_{-i} is the one formed from reaction of the amine with **2a** and not one present in the bulk of the solution. Because of this the rate of protonation of the intermediate carbanion is not affected by an increase in the bulk concentration of amineH^+ in the solution.



Whether an $(ElcB)_{ion\ pr}$, rather than a classical $(ElcB)_{rev}$, mechanism obtains for the reaction of a given **2**–base system depends upon whether protonation of the intermediate carbanion by the conjugate acid of the base (step k_{-i} in eq 13) is, or is not, faster than the equilibration by diffusion of the molecule of the conjugate acid formed in step k_i with the conjugate acid present in the bulk solution. If protonation is faster, an $(ElcB)_{ion\ pr}$ mechanism is observed; if it is not, an $(ElcB)_{rev}$ mechanism is observed. Reaction of an amine with **2** leads to an intermediate (**5**) comprised of a pair of oppositely charged ions. In a relatively low dielectric solvent like 2-propanol their diffusive separation should be significantly slower than the diffusive separation of the initially formed intermediate, [ArAr′C⁻(SSO_2Ar'')HOPh], in the reaction of phenoxide with **2**. The decreased rate of diffusive equilibration of the conjugate acid in **5** with that in the bulk solution, as compared to the situation for the phenoxide–**2** reaction, could explain the change in mechanism from $(ElcB)_{rev}$ for phenoxide to $(ElcB)_{ion\ pr}$ for the amines. Note also that ΔpK_a for a neutral acid like PhOH on transfer from H_2O to i-PrOH will be much more positive than ΔpK_a for a positively charged acid like $R_2NH_2^+$ or R_3NH^+. Therefore, even though in water phenol (pK_a = 10) is a slightly stronger acid than several of the amineH^+ ions in Table II, in *2-propanol* it should be a significantly *weaker* acid than any of them. Thus, to the extent that the rate constant for the thermodynamically favorable protonation of the intermediate carbanion is sensitive to, and increases with, decreasing pK_a of the conjugate acid it should be faster when the conjugate acid of the base is amineH^+ than when it is phenol. A faster rate of protonation of the intermediate carbanion would also favor the mechanism being $(ElcB)_{ion\ pr}$ rather than $(ElcB)_{rev}$.

Comparison of Rates of Elimination of Alkanesulfenyl vs. Alkanesulfonyl Compounds. Certain of the data on the rates of thioketone-forming eliminations of **2** with amines can be used together with previously obtained data[6] on the rates of elimination of aralkyl disulfones with amines to make a *rough* estimate of the magnitude of the difference in rates of elimination for alkanesulfonyl vs. alkanesulfenyl compounds having the same leaving group, i.e.,



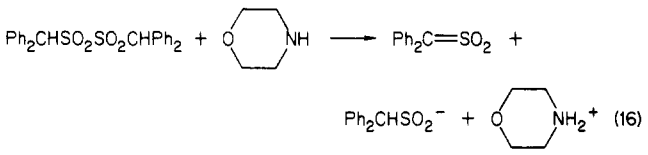
The rate constant for the reaction of benzyl α-disulfone (**6a**) with glycine ethyl ester (eq 15, amine = H_2NCH_2COOEt) in 60% dioxane at 25 °C is 94 M^{-1} s^{-1}.[6]

(15) Bartsch, R. A.; Cho, B. R. *J. Am. Chem. Soc.* **1979**, *101*, 3578. (b) Cho, B. R. Ph. D. Thesis, Texas Tech University, 1979.
(16) (a) Jencks, W. P.; Gilchrist, M. *J. Am. Chem. Soc.* **1968**, *90*, 2622. (b) Bel'skii, V. E.; Kudryavtseva, L. A.; Derstuganova, K. A.; Teitel'baum, A. B.; Ivanov, B. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 966.

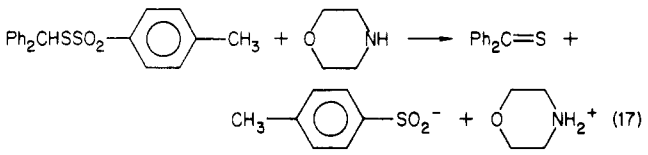
$$RCH_2SO_2SO_2CH_2R + \text{amine} \rightarrow RCH{=}SO_2 + RCH_2SO_2^- + \text{amineH}^+ \quad (15)$$

6a, R = Ph; **6b**, R = *n*-Pr; **6c**, R = H

The rate constant for eq 15 for the reaction of **6a** with morpholine would be expected, based on the relative reactivity of morpholine vs. glycine ethyl ester with **6b**,[6] to be approximately 10 times greater, or 9×10^2 M^{-1} s^{-1}. This is ~13 times larger than the rate constant (70 M^{-1} s^{-1})[6] for eq 15 for reaction of **6c** with morpholine. In **6** replacement of H by Ph therefore leads to slightly over a 10-fold increase in the rate of elimination. If it is assumed that replacement of a second hydrogen in $CH_3SO_2SO_2CH_3$ by Ph will result in a comparable additional increase in rate, the predicted rate constant for the sulfene-forming elimination shown in eq 16 is $(9 \times 10^2) \times 13 = 1 \times 10^4$ M^{-1} s^{-1} (25 °C, 60% dioxane).



From the log k_e vs. σ plot for eq 12 for the other thiosulfonates, k_e for the thioketone-forming elimination of diphenylmethyl *p*-toluenethiosulfonate with piperidine in 2-propanol at 25 °C (eq 12, Ar = Ar′ = Ph) is estimated to be 1×10^{-3} M^{-1} s^{-1}. The data in Table II for **2a** and **2b** indicate that (a) morpholine will be ~30 times *less* reactive than piperidine in such an elimination, and (b) a change in solvent from 2-propanol to 60% dioxane should have little effect on k_e. We therefore estimate that the rate constant for the elimination shown in eq 17 should be $(1 \times 10^{-3})(1/30) = \sim 3 \times 10^{-5}$ M^{-1} s^{-1} (25 °C, 60% dioxane).



The rate at which benzhydryl α-disulfone undergoes elimination with morpholine (eq 16) is thus estimated to be roughly $(1 \times 10^4)/(3 \times 10^{-5}) = \sim 3 \times 10^8$ faster than the rate at which benzhydryl *p*-toluenethiosulfonate undergoes elimination with the same base (eq 17). This 300 million-fold difference in the rates at which two equivalently substituted[17] alkanesulfonyl and alkanesulfenyl compounds undergo elimination provides a striking quantitative indication of how much more easily an alkanesulfonyl derivative will undergo elimination (eq 14a) than the corresponding alkanesulfenyl moiety (eq 14b).

Experimental Section

Preparation of Diarylmethyl Bromides. The various diarylmethyl bromides required were synthesized by the reaction of the corresponding diarylmethanol with a complex of methyl sulfide and *N*-bromosuccinimide in methylene chloride as solvent by using the procedure of Corey, Kim, and Takeda.[18] Except for *p*-nitrobenzhydrol the diarylmethanols were commercially available (Aldrich). *p*-Nitrobenzhydrol was prepared by reduction of 4-nitrobenzophenone (Aldrich) with aluminum isopropoxide by the method of Young, Hartung, and Crossley.[19] After reduction solvent 2-propanol was removed under reduced pressure, the reaction mixture was neutralized with 1 M sulfuric acid, and the *p*-nitrobenzhydrol was extracted with ether. The ether extract was washed with water and dried ($MgSO_4$), and the ether removed. Crystallization of the residue from ligroin–benzene gave *p*-nitrobenzhydrol in 90% yield, mp 74.5–75.5 °C (lit.[20] mp 74.5–75 °C).

The diarylmethyl bromides were purified by either chromatography, or flash chromatography, on silica gel with either benzene or toluene as eluant. Except for diphenylmethyl bromide (mp 45–46 °C) they were oils that were not purified further. The yields and ^1H NMR spectra ($CDCl_3$) of the various bromides were as follows: diphenylmethyl bromide (60%) δ 6.16 (s, 1 H), 7.0–7.4 (m, 10 H); 4-nitrodiphenylmethyl bromide (22%) δ 6.20 (s, 1 H), 7.2–8.2 (m, 9 H); 4-chlorodiphenylmethyl bromide (25%) δ 6.18 (s, 1 H), 6.9–7.5 (m, 9 H); 4,4′-dichlorodiphenylmethyl bromide (25%) δ 6.19 (s, 1 H), 7.0–7.7 (m, 8 H).

Preparation of Diarylmethyl *p*-Toluenethiosulfonates. These were synthesized by the reaction of stoichiometric amounts of the diarylmethyl bromide and morpholinium *p*-toluenethiosulfonate,[21] either at room temperature in anhydrous methylene chloride for 5 h (diphenylmethyl bromide) or in acetonitrile at 85 °C for 1–3 h (all other diarylmethyl bromides). After filtration to remove the precipitate of morpholinium bromide and evaporation of the filtrate, the various *p*-toluenethiosulfonates were purified in the following manner.

Diphenylmethyl *p*-toluenethiosulfonate was isolated in 42% yield after recrystallization from acetonitrile: mp 124–125 °C (lit.[22] mp 125–126 °C); IR (KBr) 1327 and 1138 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.33 (s, 3 H), 5.85 (s, 1 H), 6.8–7.5 (m, 14 H).

4-Nitrodiphenylmethyl *p*-Toluenethiosulfonate (2a). The crude product was purified by flash chromatography on silica gel with toluene as eluant. Recrystallization from diethyl ether gave 20% of **2a**: mp 97–99 °C; IR (KBr) 1328 and 1140 cm^{-1} (SO_2), 1515 and 1345 cm^{-1} (NO_2); ^1H NMR ($CDCl_3$) δ 2.33 (s, 3 H), 5.90 (s, 1 H), 6.9–8.0 (m, 13 H). Anal. Calcd for $C_{20}H_{17}NO_4S_2$: C, 60.13; H, 4.29. Found: C, 60.24; H, 4.39.

4-Chlorodiphenylmethyl *p*-Toluenethiosulfonate (2c). The crude product was purified by preparative TLC on silica gel with toluene as the developing solvent. Recrystallization from ether gave **2c** (18%): mp 105–106 °C; IR (KBr) 1312–1292 and 1130 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.32 (s, 3 H), 5.86 (s, 1 H), 6.7–7.5 (m, 13 H). Anal. Calcd for $C_{20}H_{17}ClO_2S_2$: C, 61.76; H, 4.40. Found: C, 61.56; H, 4.41.

4,4′-Dichlorodiphenylmethyl *p*-Toluenethiosulfonate (2b). Purification in the same manner as for **2c** gave **2b** (15%): mp 123–125 °C; IR (KBr) 1315–1290 and 1130 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.40 (s, 3 H), 5.82 (s, 1 H), 7.0–7.6 (m, 12 H). Anal. Calcd for $C_{20}H_{16}Cl_2O_2S_2$: C, 56.74; H, 3.81. Found: C, 56.64; H, 3.85.

Preparation of Diphenylmethyl *p*-Nitro-, *p*-Chloro-, *p*-Methoxy-, and Benzenethiosulfonates. Sodium *p*-chlorobenzenesulfinate,[23] *p*-methoxybenzenesulfinate,[24] and *p*-nitrobenzenesulfinate[24] were prepared by published procedures, and they and sodium benzenesulfinate (Aldrich) were each converted to the corresponding sodium arenethiosulfonate by the method described by Sato and co-workers.[25]

The various diphenylmethyl benzenethiosulfonates were synthesized by reacting equimolar amounts of diphenylmethyl bromide and the requisite sodium arenethiosulfonate in acetonitrile at 85 °C for 1–3 h. At the end of this time the reaction mixture was filtered and the solvent was removed by evaporation under reduced pressure. The residual diphenylmethyl arenethiosulfonates were then purified in the following manner.

Diphenylmethyl Benzenethiosulfonate. The crude product was recrystallized twice from ethyl ether giving the pure thio-

(17) The fact tha the leaving group in eq 17 is p-$CH_3C_6H_4SO_2^-$, while in eq 16 it is $Ph_2CHSO_2^-$, will not have a significant effect on the magnitude of this rate ratio.

(18) Corey, E. J.; Kim, C. U.; Takeda, M. *Tetrahedron Lett.* **1972**, 4339.
(19) Young, W. G.; Hartung, W. H.; Crossley, F. S. *J. Am. Chem. Soc.* **1936**, *58*, 100.
(20) Stewart, B. B.; Smith, H. A. *J. Am. Chem. Soc.* **1957**, *79*, 5457.
(21) Kurzer, F.; Powell, J. R. *J. Am. Chem. Soc.* **1952**, 3728.
(22) Olsen, C. V.; Senning, A. *Sulfur Lett.* **1982**, *1*, 29.
(23) Whitmore, F. C.; Hamilton, F. H. "Organic Syntheses"; Wiley: New York, 1941; Collect. Vol. I, p 492.
(24) Kulka, M. *J. Am. Chem. Soc.* **1950**, *72*, 1215.
(25) Sato, R.; Goto, T.; Takikawa, Y.; Takizawa, S. *Chem. Commun.* **1980**, 615.

sulfonate in 57% yield: mp 117–119 °C; IR (KBr) 1303–1282 and 1130 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 5.93 (s, 1 H), 7.2–7.6 (m, 15 H). Anal. Calcd for $C_{19}H_{16}O_2S_2$: C, 67.03; H, 4.74. Found: C, 67.07; H, 4.76.

Diphenylmethyl *p*-chlorobenzenethiosulfonate was isolated in 45% yield after recrystallization from ether: mp 103–105 °C; IR (KBr) 1312–1280 and 1128 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.93 (s, 1 H), 6.5–7.4 (m, 14 H). Anal. Calcd for $C_{19}H_{15}ClO_2S_2$: C, 60.87; H, 4.03. Found: C, 60.74; H, 4.12.

Diphenylmethyl *p*-methoxybenzenethiosulfonate was also purified by recrystallization from ether: mp 99–101 °C (42%); IR (KBr) 1300 and 1115 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 3.80 (s, 3 H), 5.88 (s, 1 H), 6.6–7.5 (m, 14 H). Anal. Calcd for $C_{20}H_{18}O_3S_2$: C, 64.84; H, 4.90. Found: C, 65.10; H, 4.89.

Diphenylmethyl *p*-Nitrobenzenethiosulfonate. The residue was chromatographed on silica gel with toluene to elute the thiosulfonate. Recrystallization of the thiosulfonate fraction from ether gave pure diphenylmethyl *p*-nitrobenzenethiosulfonate (12%): mp 142–144 °C; IR (KBr) 1330–1305 and 1135 (SO_2), 1520 and 1340 cm^{-1} (NO_2); ^1H NMR ($CDCl_3$) δ 5.96 (s, 1 H), 7.2–8.0 (m, 14 H). Anal. Calcd for $C_{19}H_{15}NO_4S_2$: C, 59.20; H, 3.92. Found: C, 59.00; H, 4.13.

Other Reagents. Reagent grade 2-propanol was dried (molecular sieves) and then twice distilled. Dioxane was purified as previously described.[26] Anhydrous methanol was obtained by treatment of absolute methanol with magnesium followed by distillation. It was then redistilled from molecular sieves. Phenol, imidazole, *N*-benzylmethylamine and diallylamine (all from Aldrich) were purified by distillation. Piperidine and morpholine were purified as previously described.[27] Piperazine and 1,4-diazabicyclo[2.2.2]octane (Aldrich) were recrystallized from ethanol–ethyl ether, and 3-quinuclidinol (Aldrich) was recrystallized from benzene–ligroin–ethanol. Solutions of sodium methoxide in methanol and of either sodium isopropoxide or sodium phenoxide in 2-propanol were prepared under nitrogen and titrated by standard procedures. All other reagents were of the highest purity commercially available and were used without further purification.

Procedure for Kinetic Runs. The appearance of the thioketone was followed by measuring the increase in the optical density of the solution at the absorption maximum for the thioketone in the 600-nm region. The λ_{max} and extinction coefficients for the different thioketones were determined by the preparation of pure samples of each thioketone from the corresponding ketone by the method described by Korver, Veenland, and DeBoer[28] followed by immediate measurement of the λ_{max} and ϵ in 2-propanol or 60% dioxane. The results in 2-propanol were as follows (substituent, λ_{max} (ϵ)): *p*-H, 595 nm (167); *p*-Cl, 600 nm (188); 4,4'-di-Cl, 607 nm (212); *p*-NO_2, 620 nm (195). The data for the *p*-H and *p*-Cl compound agree with those reported by Ceccon et al.[9] For the *p*-NO_2 compound ϵ is ~20% larger than reported earlier.[28]

In the runs that were followed by conventional spectrophotometry 3.5 mL of a solution of the nucleophile and, where appropriate, its conjugate acid were placed in a 1-cm spectrophotometer cell in the thermostated cell compartment of a Cary Model 17 spectrophotometer. Once the solution had reached thermal equilibrium the reaction was initiated by the addition via microsyringe of 20–25 μL of a concentrated solution of known concentration of the appropriate diarylmethyl arenethiosulfonate dissolved in the appropriate solvent. The increase in the absorbance of the solution at the wavelength corresponding to λ_{max} for the thioketone was then followed with time. The total amount of the thioketone formed from the thiosulfonate under a given set of reaction conditions was determined from the final absorbance (A_∞) of the solution at this wavelength, and the fraction (α_{elim}) of the thiosulfonate reacting via the elimination pathway was calculated from A_∞, ϵ and the initial concentration of the thiosulfonate, c_0: $\alpha_{elim} = A_\infty/\epsilon c_0$. The overall first-order rate constant (k_{tot}) for the disappearance of the thiosulfonate under the reaction conditions was determined from the slope of a plot of log ($A_\infty - A$) vs. time. The experimental first-order rate constant for elimination, k_{elim}, was then calculated from the relationship: $k_{elim} = k_{tot}\alpha_{elim}$.

In those runs that were so rapid that they had to be followed by stopped-flow spectrophotometry a solution of the thiosulfonate in the appropriate solvent, prepared immediately prior to use, was placed in one of the reservoir syringes of a Durrum-Gibson Model D-110 stopped flow spectrophotometer, and a solution of the nucleophile in the same solvent was placed in the other reservoir syringe. After the reactants were mixed the course of the reaction was then monitored on the storage oscilloscope at the wavelength corresponding to the λ_{max} for the thioketone. Analysis of the data was carried out in the same fashion as in the runs followed by conventional spectrophotometry.

Solutions of the thioketones in 2-propanol showed good stability with no tendency for A_∞ to drift downward with time. In methanol, on the other hand, there was some tendency for the thioketones to disappear slowly when the final reaction solution was allowed to stand for an extended period of time. The rate of disappearance of the thioketones was, however, slow enough so as not to interfere with an accurate determination of A_∞ for the runs carried out in this solvent.

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Registry No. **2** (X = Y = H, Z = CH_3), 83994-72-3; **2** (X = Y = H, Z = CH_3O), 93454-48-9; **2** (X = Y = Z = H), 93454-49-0; **2** (X = Y = H, Z = Cl), 93454-50-3; **2** (X = Y = H, Z = NO_2), 93454-51-4; **2a**, 93454-45-6; **2b**, 93454-46-7; **2c**, 93454-47-8; Dabco, 280-57-9; $PhCH_2NHMe$, 103-67-3; MeO^-, 3315-60-4; piperidine, 110-89-4; piperazine, 110-85-0; 3-quinuclidinol, 1619-34-7; morpholine, 110-91-8; diallylamine, 124-02-7; imidazole, 288-32-4; sodium phenoxide, 139-02-6; sodium isopropoxide, 683-60-3.

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