Kinetic Study of Substituent Effects on the Mechanism of β-Elimination of Arenethiol from *trans*-2,3-Bis(arylthio)-4-nitro-2,3-dihydrothiophenes in Toluene

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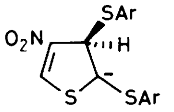
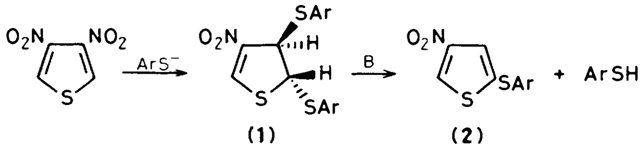
The 2,3-dihydrothiophene derivatives (**1b**—**f**) readily undergo, in toluene, regiospecific tributylamine-promoted *syn*-elimination of arenethiol to give the 2-(arylthio)-4-nitrothiophenes (**2b**—**f**). For the rather complex kinetic behaviour displayed by each member of the series, a rationalisation is proposed based on a stability of the substrate's conjugate base sufficient to allow formation of non-negligible concentrations of an intermediate ion pair along the reaction co-ordinate. The system allows direct conclusions to be drawn concerning the leaving-group expulsion step: an advanced extent of bond cleavage between carbon and the leaving group can be postulated in the transition state.

Carbanion stability is an important feature of base-promoted elimination reactions, not only because of its direct influence on choice of mechanism,[1] but also because of its bearing on the possibility of separating matters relevant to leaving-group departure from concomitant processes.[2]

We have recently carried out a detailed kinetic investigation of the ready base-promoted regiospecific β-elimination of mesitylenethiol from the 2,3-dihydrothiophene derivative (**1a**),[3] which is the last step of the overall *cine*-substitution reaction between 3,4-dinitrothiophene and mesitylenethiolate in methanol (Scheme 1).[4] In toluene, with tributylamine as the base, the proposed reversible $(E1cB)_{ip}$ pathway is allowed by the relatively high stability of the carbanion (**3a**), which ensures for the $Bu^n_3NH^+$·(**3a**) ion pair a lifetime sufficient for equilibration with substrate before elimination.[3]



(**3**)



(1) (2)

a; Ar = mesityl
b; Ar = 4 - methoxyphenyl
c; Ar = 4 - methylphenyl
d; Ar = phenyl
e; Ar = 4 - chlorophenyl
f; Ar = 3 - chlorophenyl

Scheme 1.

In order to investigate the effect of substituents in SAr of structure (**1**) on the reaction mechanism, we have prepared the substrates (**1b**—**f**) and carried out a kinetic analysis of their regiospecific β-elimination reactions, in the same base–solvent system as used for (**1a**).

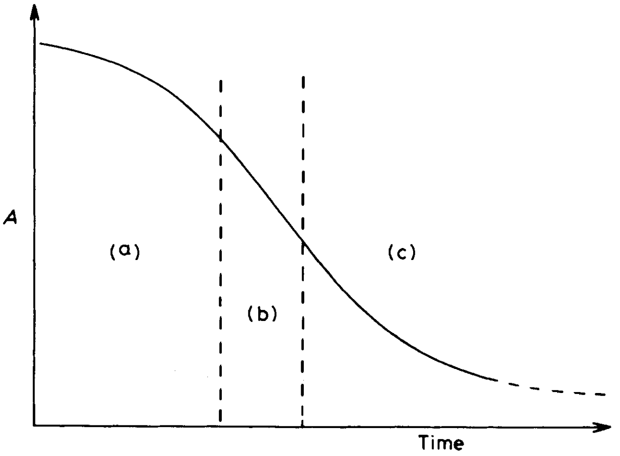


Figure. Typical absorbance (*A*) variation (λ 340 nm) for the reaction between (**1b**—**f**) and Bu^n_3N in toluene

Results and Discussion

The substrates (**1b**—**f**), isolated as intermediates in the reaction between 3,4-dinitrothiophene and the corresponding arenethiolates in methanol, undergo, like (**1a**),[3] a Bu^n_3N-promoted β-elimination in toluene to give the final *cine*-substitution products (**2b**—**f**) (Scheme 1). The *trans*-configuration of (**1b**—**f**) is confirmed by values of $J_{2,3}$ (see Experimental section) which are very low [5] and similar to that for (**1a**), the *trans*-configuration of which has been unequivocally confirmed by an *X*-ray analysis.[3]

Kinetic runs were always carried out under pseudo-first-order conditions (excess of amine); the absorbance (*A*) decrease was monitored at 340 nm (in a region where the substrates show a strong absorption band). In every case complex behaviour was observed (typically reproduced in the Figure): an induction period (a) was followed by an intermediate region (b) showing linear variation of *A* with time. In the final region (c), covering not less than 25% of the overall *A* variation observed, good pseudo-first-order plots of $\ln(A_t - A_\infty)$ *versus* time could be obtained; observed pseudo-first-order rate constants (k_Ψ/s^{-1}) are reported in Table 1.

Plots of k_Ψ *versus* base concentration ([B]) showed, for each substrate, a definite, although not strongly marked, downward curvature, the saturation effect towards a plateau region at high [B] being confirmed by the good linearity, with intercepts

Table 1. Observed rate constants for the reactions between (**1b**—**f**) and $\mathrm{Bu^n{}_3N}$ in toluene[a]

				[(**1b**)] 1.40 × 10^{-4}M, *T* 25.0 °C						
$10[\mathrm{B}]/\mathrm{M}$	13.2	11.0	9.45	7.94	5.29	2.65	1.32	0.662		
$10^4k_\Psi/\mathrm{s}^{-1}$	11.9	11.6	9.85	8.74	6.65	4.02	2.42	1.25		
				[(**1c**)] 1.18 × 10^{-4}M, *T* 25.0 °C						
$10[\mathrm{B}]/\mathrm{M}$	12.4	10.4	8.88	7.46	6.22	4.15	2.07	1.04	0.518	
$10^4k_\Psi/\mathrm{s}^{-1}$	21.4	17.8	16.5	14.8	12.3	8.56	4.62	2.51	1.31	
$10^8k_0/\mathrm{mol\ l^{-1}\ s^{-1}}$	10.7	8.52	7.18	6.09	4.82	3.15	1.57	0.895	0.472	
$10^6[(\mathrm{I})]/\mathrm{M}$	21.3	17.0	14.3	12.1	9.60	6.27	3.13	1.78	0.940	
$10^4k_\Psi/\mathrm{s}^{-1}$[b]		15.6						2.16		
				[(**1c**)] 1.18 × 10^{-4}M, *T* 36.8 °C[c]						
$10[\mathrm{B}]/\mathrm{M}$	12.4	10.4	8.88	7.46	4.97	2.49	1.24	0.622		
$10^4k_\Psi/\mathrm{s}^{-1}$	25.9	22.1	20.0	16.6	12.6	6.91	3.53	1.86		
$10^8k_0/\mathrm{mol\ l^{-1}\ s^{-1}}$	11.3	8.52	7.18	6.00	4.33	2.38	1.25	0.666		
$10^6[(\mathrm{I})]/\mathrm{M}$	16.1	12.2	10.2	8.56	6.18	3.40	1.78	0.950		
				[(**1c**)] 1.18 × 10^{-4}M, *T* 49.4 °C[c]						
$10[\mathrm{B}]/\mathrm{M}$	12.4	10.4	8.88	7.46	4.97	2.49	1.24	0.622		
$10^4k_\Psi/\mathrm{s}^{-1}$	32.5	26.5	25.9	21.8	15.1	7.94	4.29	2.09		
$10^8k_0/\mathrm{mol\ l^{-1}\ s^{-1}}$	12.6	10.1	8.86	7.52	5.24	2.57	1.36	0.710		
$10^6[(\mathrm{I})]/\mathrm{M}$	8.69	6.97	6.11	5.19	3.61	1.77	0.938	0.490		
				[(**1d**)] 1.19 × 10^{-4}M, *T* 25.0 °C						
$10[\mathrm{B}]/\mathrm{M}$	12.5	10.4	7.48	6.23	4.16	2.08	1.04	0.520		
$10^3k_\Psi/\mathrm{s}^{-1}$	6.56	5.79	4.30	3.81	2.61	1.34	0.703	0.364		
$10^7k_0/\mathrm{mol\ l^{-1}\ s^{-1}}$	3.40	2.72	1.90	1.59	1.00	0.496	0.256	0.130		
$10^6[(\mathrm{I})]/\mathrm{M}$	15.5	12.4	8.64	7.23	4.55	2.25	1.16	0.591		
				[(**1e**)] 1.01 × 10^{-4}M, *T* 25.0 °C						
$10[\mathrm{B}]/\mathrm{M}$	12.4	10.4	6.22	4.14	2.07	1.04	0.518	0.207		
$10^3k_\Psi/\mathrm{s}^{-1}$	31.5	27.9	22.1	16.8	9.60	5.15	2.71	1.09		
$10^7k_0/\mathrm{mol\ l^{-1}\ s^{-1}}$	12.7	11.8	7.94	6.26	3.22	1.78	0.979	0.392		
$10^6[(\mathrm{I})]/\mathrm{M}$	19.1	17.7	11.9	9.41	4.84	2.68	1.47	0.589		
				[(**1f**)] 1.07 × 10^{-4}M, *T* 25.0 °C						
$10[\mathrm{B}]/\mathrm{M}$	13.3	11.1	9.50	7.98	5.32	2.66	1.33	0.665	0.266	0.133
$10^2k_\Psi/\mathrm{s}^{-1}$		7.57	6.68	5.92	4.28	2.56	1.33	0.701	0.275	0.138
$10^7k_0/\mathrm{mol\ l^{-1}\ s^{-1}}$		32.9	28.9	25.2	17.6	9.57	5.07	2.81	1.00	0.497
$10^6[(\mathrm{I})]/\mathrm{M}$		12.1	10.6	9.23	6.45	3.51	1.86	1.03	0.366	0.182
$10^3k_\Psi/\mathrm{s}^{-1}$[d]	36.2	31.3	27.7	24.3	17.4	10.5	5.10	2.47		0.495
				[(**1f**)] 1.07 × 10^{-4}M, *T* 37.0 °C[c]						
$10[\mathrm{B}]/\mathrm{M}$	10.9	9.35	7.85	5.24	2.64	1.31	0.665	0.266		
$10^2k_\Psi/\mathrm{s}^{-1}$	9.60	8.23	6.98	5.12	2.73	1.34	0.726	0.286		
$10^7k_0/\mathrm{mol\ l^{-1}\ s^{-1}}$	37.1	32.5	27.2	19.5	10.1	4.91	2.64	1.04		
$10^6[(\mathrm{I})]/\mathrm{M}$	7.67	6.71	5.62	4.03	2.09	1.01	0.545	0.215		
				[(**1f**)] 1.07 × 10^{-4}M, *T* 49.8 °C[c]						
$10[\mathrm{B}]/\mathrm{M}$	10.9	9.35	7.85	5.24	2.64	1.31	0.665	0.266		
$10^2k_\Psi/\mathrm{s}^{-1}$	11.1	9.18	7.59	5.32	2.59	1.36	0.685	0.274		
$10^7k_0/\mathrm{mol\ l^{-1}\ s^{-1}}$	41.5	34.3	28.1	18.7	9.23	4.66	2.27	0.908		
$10^6[(\mathrm{I})]/\mathrm{M}$	2.20	1.81	1.49	0.989	0.488	0.247	0.120	0.0480		

[a] k_Ψ Values are pseudo-first-order rate constants from region (c) of the Figure; k_0 values are zero-order rate constants from region (b) of the Figure; [(I)] values were obtained as k_0/k_2, where k_2 is the extrapolated plateau value of k_Ψ (see Table 2). [b] [2,3,5-^{2}H$_3$]-(**1c**) 1.18 × 10^{-4}M. [c] Rate values not corrected for solvent expansion. [d] [2,3,5-^{2}H$_3$]-(**1f**) 1.07 × 10^{-4}M.

significantly different from zero, of double reciprocal (k_Ψ^{-1} *versus* $[\mathrm{B}]^{-1}$) plots (see later).

A reasonable explanation for this saturation effect is the formation, with increasing [B], of increasing amounts of an intermediate (I) along the reaction co-ordinate of the elimination process [Scheme 2; $k_1[\mathrm{B}]$ not $\ll (k_{-1} + k_2)$]. This explanation could also offer a rationale for the complex overall variation of *A* if it is assumed that equilibration between substrate and intermediate is not fast, and therefore equilibrium is not reached at the very beginning of the reaction (k_{-1} not $\gg k_2$), *i.e.* time is required for the relatively slow accumulation of the intermediate. The following observations support this view: (*a*) addition of base does not appreciably alter, at very short times, the u.v. spectrum of the substrates in the 280—450 nm region, but (*b*) a gradual shift of an isosbestic point in the 290—300 nm region, during reactions carried out at high [B], can be taken as evidence for the formation of non-negligible amounts of at least one intermediate.

Theoretical equations, obtained for a system like that depicted in Scheme 2 with assumption of all rate constants as first-order (or pseudo-first-order),[6] allow one to reproduce, at least qualitatively, the behaviour observed: an induction period

$$(1) \underset{k_{-1}}{\overset{k_1[\mathrm{B}]}{\rightleftharpoons}} (\mathrm{I}) \xrightarrow{k_2} \text{products}$$

Scheme 2.

Table 2. Kinetic and activation parameters for the reaction between (**1b**—**f**) and $Bu^n{}_3N$ in toluene[a]

Substrate	T/°C	k'/l mol^{-1} s^{-1}	k_2/s^{-1}	k'/k_2(l mol^{-1})
(**1b**)	25.0	$(2.02 \pm 0.03) \times 10^{-3}$	$(2.01 \pm 0.16) \times 10^{-3}$	1.00 ± 0.08
(**1c**)	25.0	$(2.58 \pm 0.02) \times 10^{-3}$	$(5.02 \pm 0.58) \times 10^{-3}$	0.51 ± 0.06
	36.8	$(3.06 \pm 0.02) \times 10^{-3}$	$(7.01 \pm 0.63) \times 10^{-3}$	
	49.4	$(3.44 \pm 0.03) \times 10^{-3}$	$(1.45 \pm 0.40) \times 10^{-2}$	
		$E_a = 2.24 \pm 0.23$ kcal mol^{-1}	$E_a = 8.25 \pm 1.78$ kcal mol^{-1}	
		$\Delta H^‡ = 1.65 \pm 0.23$ kcal mol^{-1}	$\Delta H^‡ = 7.66 \pm 1.78$ kcal mol^{-1}	
		$\Delta S^‡ = -64.8 \pm 0.8$ cal mol^{-1} K^{-1}	$\Delta S^‡ = -43.5 \pm 5.7$ cal mol^{-1} K^{-1}	
(**1d**)	25.0	$(7.08 \pm 0.04) \times 10^{-3}$	$(2.20 \pm 0.32) \times 10^{-2}$	0.32 ± 0.05
(**1e**)	25.0	$(5.37 \pm 0.02) \times 10^{-2}$	$(6.65 \pm 0.56) \times 10^{-2}$	0.81 ± 0.07
(**1f**)	25.0	$(1.04 \pm 0.00) \times 10^{-1}$	$(2.73 \pm 0.66) \times 10^{-1}$	0.38 ± 0.09
	37.0	$(1.08 \pm 0.01) \times 10^{-1}$	$(4.84 \pm 1.62) \times 10^{-1}$	
	49.8	$(1.03 \pm 0.00) \times 10^{-1}$	1.89 ± 1.15	
		$E_a = -0.07 \pm 0.25$ kcal mol^{-1}	E_a *ca.* 15 kcal mol^{-1}	
		$\Delta H^‡ = -0.66 \pm 0.25$ kcal mol^{-1}	$\Delta H^‡$ *ca.* 14 kcal mol^{-1}	
		$\Delta S^‡ = -65.2 \pm 0.8$ cal mol^{-1} K^{-1}	$\Delta S^‡$ *ca.* -14 cal mol^{-1} K^{-1}	
[$^2H_3$]-(**1f**)	25.0	$(3.73 \pm 0.01) \times 10^{-2}$	$(2.64 \pm 1.57) \times 10^{-1}$	

[a] The correlation coefficient of the k_Ψ^{-1} *versus* $[B]^{-1}$ plots was always $\geqslant 0.999$; activation parameters are referred to 25.0 °C.

Table 3. Effect of $Bu^n{}_3NH^+Cl^-$ on the reaction between (**1c**) or (**1f**) and $Bu^n{}_3N$ in toluene at 25 °C[a]

Substrate	$[Bu^n{}_3N]$/M	$[Bu^n{}_3NH^+Cl^-]$/M	k_Ψ/s^{-1}
(**1c**)	1.32	0	2.31×10^{-3}
		2.32×10^{-4}	2.35×10^{-3}
		5.76×10^{-4}	2.46×10^{-3}
		1.14×10^{-3}	2.46×10^{-3}
(**1c**)	2.07×10^{-1}	0	4.62×10^{-4}
		2.32×10^{-4}	5.30×10^{-4}
		5.76×10^{-4}	5.69×10^{-4}
		1.14×10^{-3}	5.55×10^{-4}
(**1f**)	2.64×10^{-1}	0	2.62×10^{-2}
		2.32×10^{-4}	2.55×10^{-2}
		5.76×10^{-4}	2.65×10^{-2}
		1.14×10^{-3}	2.79×10^{-2}

[a] [Substrate] 1.18×10^{-4}M.

(slow accumulation of the intermediate accompanied by some product formation) is followed by a region (around $[(I)]_{max.}$) characterised by a relatively constant [(I)], until a decrease in [(I)] takes over, the [(I)]:[substrate] ratio remaining constant up to the last stages of reaction.* It must be pointed out, in any case, that the final 'equilibration' between intermediate and unchanged substrate is not simply governed by $k_1[B]/k_{-1}$: a proportionality factor ($\alpha \leqslant 1$) must be introduced [equation (1)], which accounts for the impossibility of the system attaining

$$[(I)]/[\text{substrate}] = \alpha k_1[B]/k_{-1} \qquad (1)$$

'true' equilibrium due to the subsequent non-negligible product formation. With the foregoing assumption, equation (2) can be

$$k_\Psi = k_1k_2[B]\alpha/(k_{-1} + k_1[B]\alpha) \qquad (2)$$

obtained for the observed pseudo-first-order rate constant. The good linearity of the double reciprocal plots (k_Ψ^{-1} *versus* $[B]^{-1}$) over the whole [B] range explored (Table 2) argues against any major dependence of α on [B]. Thus it seems reasonable to express this proportionality factor as in equation (3), which

$$\alpha = k_{-1}/(k_{-1} + k_2) \qquad (3)$$

represents its limiting value when $k_1[B] \ll (k_{-1} + k_2)$ [no accumulation of (I)], and which anyway satisfactorily reproduces it, in the simulated system, at [B] values such that $k_1[B] < (k_{-1} + k_2)$: the present system can therefore be placed at the borderline between steady-state and non-steady-state conditions for the intermediate (I), in good agreement with the relatively meagre curvature of the experimental k_Ψ *versus* [B] plots. From the double reciprocal plots, k_2 and k' [$= k_1k_2\alpha/k_{-1} = k_1k_2/(k_{-1} + k_2)$] can be obtained as the reciprocals, respectively, of intercept and slope (Table 2). The high standard deviation associated with the limiting rate constant (k_2) for each substrate is most likely due to the gap between the experimental and the plateau values, which is in turn a direct consequence of the not strongly marked curvature already noted. Nevertheless the activation parameters, as based on relative values, should be quite reliable and likely to give valuable information on the system. At low [B] the E_a and $\Delta S^‡$ values are easily rationalisable on the basis of a complex rate constant[3] $\{k_\Psi = k'[B] = k_1k_2[B]/(k_{-1} + k_2)\}$; at high [B], *i.e.* in the plateau region, their more 'normal' values (higher E_a and less negative $\Delta S^‡$) are in good agreement with the identification of the observed rate constant with a single kinetic constant ($k_\Psi = k_2$).

The accumulation of an intermediate, namely the carbanionic species (**3**), obtained from substrate deprotonation by $Bu^n{}_3N$, is reasonable on the grounds of the nature of the substrates themselves. The acidity of a dithioacetal such as (**1**) is well established, although the real nature of the stabilising effect of two adjacent sulphur atoms on the conjugate base is still debated.[3-7] In the present system, given the low polarity of the medium, it is conceivable that, as proposed for (**1a**),[3] further stabilisation could be achieved through formation of an ion pair between (**3**) and $Bu^n{}_3NH^+$. The following experimental evidence supports this view. (*a*) During a run the observed pseudo-first-order rate constant [Figure, region (c)] does not decrease as an effect of liberated $Bu^n{}_3NH^+$. (*b*) Added $Bu^n{}_3NH^+Cl^-$ has only a minor accelerating effect at both low and high [B] (Table 3). (*c*) No D/H exchange could be detected when treating 2,3,5-trideuterio-(**1c**) with amine in the presence of $Bu^n{}_3NH^+Cl^-$ (see Experimental section). Furthermore, as pointed out in the previous paper,[3] the nature of the leaving

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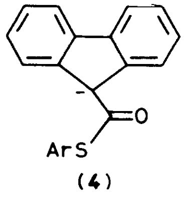
* For the simulation we chose similar values of k_1, k_{-1}, and k_2. The theoretical possibility of consecutive irreversible steps (negligible k_{-1}) seems here highly unlikely, mainly on the grounds of the nature of the k_{-1} step which will emerge from the discussion [proton transfer within an ion pair (internal return); moreover this step has been recently found to be faster than leaving-group depature for the similar system (**1a**)[3]].

group itself possibly contributes to the appreciable lifetime of the intermediate;[8] although it has been stressed that both absolute and relative nucleofugacities depend on the particular process under examination,[9] the arylthio group is commonly accepted as a relatively poor leaving group, the departing ability of which ranks rather low in alkene-forming processes.[2]

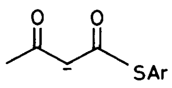
Further experimental evidence that must be viewed in the light of the proposed scheme is represented by the kinetic isotope effect. For the present system, the supposed relation between k_{-1} and k_2 (k_{-1} not $\gg k_2$) implies that [at variance with (**1a**),[3] for which $k_{-1} \gg k_2$, and $k'^{\mathrm{H}}/k'^{\mathrm{D}} = 1.0$] the primary substrate isotope effect on the experimental k_Ψ at low [B] (*i.e.* when $k_\Psi = k'[\mathrm{B}]$, or anyway when $k_\Psi < k_2$) is sizeable and increases with k_2, as a result of an increasing weight of proton transfer on the reaction co-ordinate. This expectation is fulfilled by the results for (**1c**) and (**1f**) (Tables 1 and 2), although it must be considered that any experimental isotope effect here is actually a combination of a primary (β-D) and a secondary (α-D) effect. While (**1c**) shows only a small effect (although well outside experimental error) over the whole [B] range explored ([B] = 1.04M, $k_\Psi^{\mathrm{H}}/k_\Psi^{\mathrm{D}} = 1.14$; [B] = 1.04×10^{-1}M, $k_\Psi^{\mathrm{H}}/k_\Psi^{\mathrm{D}} = 1.16$), (**1f**) displays $k'^{\mathrm{H}}/k'^{\mathrm{D}} = 2.80$. Moreover, notwithstanding the high error associated with it, the isotope effect on the plateau rate constant for (**1f**) ($k_\Psi^{\mathrm{H}}/k_\Psi^{\mathrm{D}} = 1.03 \pm 0.66$) is a further substantiation of our assumption [k_Ψ (plateau) = k_2] as any isotope effect on leaving-group departure must be a secondary effect, and therefore a low effect, either direct or inverse.[10]*

For the present system, Hammett plots show a strong dependence of both k_2 ($\rho_{k_2} = 3.18 \pm 0.21$; $n = 5$) and k' ($\rho_{k'} = 2.87 \pm 0.22$; $n = 5$) on the substituent constant.[11] As far as leaving-group depature is concerned, although the experimental ρ_{k_2} value cannot be taken, by itself, as a measure of transition-state structure, its high value suggests a rather advanced transition state, the effect of the substituent in the leaving group overwhelming the most likely opposite effect of the same substituent in the twin adjacent 2-SAr group. In this respect, the present elimination is not in accord with common activated alkene-forming eliminations. Such reactions seem to experience, at least in protic solvents, low degrees of cleavage of the carbon–leaving group bond in the transition state,[2,12] being therefore relatively insensitive to changes in the leaving group itself. The present system seems more akin to ketene-forming eliminations, for which, moreover, data on the effects of substituents on arenethiolate nucleofugacity, although in protic solvents, are directly available: β (leaving group) = −0.99 and −1.13 for ArS$^-$ expulsion in aqueous media at 25 °C from anions (**4**)[13] and (**5**),[14] respectively, indicating, in both cases, a product-like transition state.

The effect of the 2-SAr group is apparent when $k'/k_2 = k_1/(k_{-1} + k_2)$ is considered. Allowing for the uncertainty of the k_2 values, this parameter is scarcely influenced by the substituent, variations being poorly correlated with σ (Table 2). As k_2 is non-negligible with respect to k_{-1}, the substituent effect on it must be compensated by an effect (most likely due mainly to the 2-SAr group) on k_1, k_{-1}, or both. As already mentioned, the real nature of the acidifying effect of sulphur in dithioacetals is still being questioned;[7] in any case, a contribution of a conjugative effect involving the *d* orbitals of sulphur seems warranted[7c] and theoretical arguments predict that electron-attracting groups will contract the *d* orbitals, enhancing their overlapping with the *p* orbitals of the adjacent negatively charged carbon atom.[7c,15]



(**4**)



(**5**)

With regard to region (b) of the Figure, the experimental zero-order rate constant (k_0/mol l^{-1} s^{-1}; Table 1) allows, for substrates (**1c**—**f**), the evaluation, at each [B] value, of the constant concentration of the intermediate in that region [equation (4)]. Allowing for experimental error, these [(I)] values (Table 1) are scarcely dependent on substrate: this could well be the

$$k_0 = k_2[(\mathrm{I})] \qquad (4)$$

result of concomitant effects of the substituent on the deprotonation equilibrium and on leaving-group departure, and matches quite well the slight variation of $k_1/(k_{-1} + k_2)$ with substituent just discussed. Interestingly, though, for (**1b**), regions (a) and (b) of the Figure are reduced, preventing the evaluation of k_0. This could be the result of a shift of the system, as a consequence of an increased k_{-1}/k_2, towards a situation where equilibration is fast ($k_{-1} > k_2$). Any substituent with a more negative σ value, causing a further decrease in both k_1 and k_2, should then lead, without any break in the Hammett correlation, to a situation where $k_1[\mathrm{B}] \ll k_{-1} \gg k_2$ (fast equilibration with no intermediate accumulation), corresponding to the experimental outcome for (**1a**).[3] In fact, the second-order rate constant for (**1a**) ($k_{\mathrm{II}} = k_1k_2/k_{-1} = 0.88 \times 10^{-4}$ l mol^{-1} s^{-1}) is only *ca.* four times lower than the value calculated from the Hammett plot relative to $k_1k_2/(k_{-1} + k_2)$ when assuming a roughly additive electronic contribution ($\sigma = 3 \times \sigma_{4\text{-Me}}$) for the three methyl groups and neglecting any steric effect of the *ortho*-methyl groups in SAr ($k_{\mathrm{calc.}} = 3.19 \times 10^{-4}$ l mol^{-1} s^{-1}).

In conclusion, the possibility of twin substitutions at C-2 and C-3 makes the present system particularly interesting in relation to a study of the influence of structural substrate variations on the kinetic outcome for the base-promoted alkene-forming β-elimination of arenethiol *via* a carbanionic intermediate. The overall substituent effect causes a progressive change of the rate-determining step as a result of an increasing weight of deprotonation on the reaction co-ordinate when going from (**1a**) to (**1f**). Nevertheless, as a consequence of parallel effects on deprotonation (due mainly to the 2-SAr substituent) and on leaving-group expulsion (due mainly to the 3-SAr substituent), no major break in the Hammett plot for the complex rate constant at low [B] (k') can be detected. Finally, the stabilising effect of electron-attracting substituents on the substrate's conjugate base, which is formed in non-negligible concentrations in all cases except (**1a**), allows the experimental extrapolation of the rate constant for leaving-group expulsion (k_2), which is of fundamental importance for the determination of both absolute and relative nucleofugacities.

Experimental

^{1}H N.m.r. spectra were recorded with a Varian FT 80 instrument (solvent CDCl$_3$; standard Me$_4$Si). Kinetic experiments and u.v. spectra (solutions in toluene) were recorded with a Perkin-Elmer 554 spectrophotometer.

Materials.—3,4-Dinitrothiophene, 2,5-dideuterio-3,4-dinitrothiophene (96% deuteriated), and tributylammonium chloride

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* The ^{1}H n.m.r. chemical shift assignments here imply, for the trideuterio derivatives, an almost complete deuteriation and a >80% deuteriation at the 2- and 3-position, respectively. Although the assignments are only tentative (see Experimental section), any error would at most imply a slight correction of the experimental isotope effect, leaving the conclusions unaffected.

were prepared as previously reported.[3] Benzenethiols (Aldrich or Fluka) were distilled before use. Tributylamine (Schuchardt) was distilled and stored as reported.[3] CH_3OD was a commercial (Merck) product. Toluene (Hoechst) was refluxed over sodium and distilled before use.

2,3-Bis(arylthio)-4-nitro-2,3-dihydrothiophenes (**1b**—**f**) *and 2,3-Bis(arylthio)-2,3,5-trideuterio-4-nitro-2,3-dihydrothiophenes*, [2,3,5-$^2H_3$]-(**1c**) *and* (**1f**).—A solution of sodium arenethiolate (5 mmol) in CH_3OH (or CH_3OD) (5 cm^3) was added to a solution of 3,4-dinitrothiophene (or 2,5-dideuterio-3,4-dinitrothiophene) (10 mmol) in the same solvent (15 cm^3), and the mixture was kept at room temperature. After the appropriate reaction time, the solution was cooled in acetone–CO_2 and most unchanged substrate recovered by filtration. The filtered solution was evaporated at room temperature. The residue was taken up with CH_2Cl_2, the insoluble $NaNO_2$ filtered off, and the solution chromatographed on a silica gel column with CH_2Cl_2–light petroleum (b.p. 40—70 °C) (1:2.5) as eluant. For compound (**1b**) separation from by-products was more troublesome; toluene–CH_2Cl_2–ethyl acetate (30:5:1) and light petroleum (b.p. 40—70 °C)–ethyl acetate (3:1) were used successively. For crystallisation of the crude products light petroleum (b.p. 80—100 °C) was employed. Reaction time, yield, and physical and spectroscopic characteristics of each compound are reported (the ^1H n.m.r. chemical-shift assignment to 2-H and 3-H is tentative[3,4]).

The *2,3-bis-(4-methoxyphenylthio)dihydrothiophene* (**1b**): 1 h; 17% non-distillable oil* (Found: C, 53.3; H, 4.3; N, 3.6. $C_{18}H_{17}NO_4S_3$ requires C, 53.1; H, 4.2; N, 3.4%); $\lambda_{max.}$ 354 nm (ε 6 500 dm^3 mol^{-1} cm^{-1}); δ_H 3.80 (6 H, s, 2 × MeO), 4.70 (1 H, d, *J* 0.9 Hz, 3-H), 4.85 (1 H, dd, *J* 0.9 and 1.2 Hz, 2-H), 6.67—7.33 (8 H, m, 2 × 4-MeOC$_6H_4$S), and 7.70 (1 H, d, *J* 1.2 Hz, 5-H).

The *2,3-bis-(4-methylphenylthio)dihydrothiophene* (**1c**): 40 min; 33%; m.p. 94.5—95.5 °C (Found: C, 57.7; H, 4.6; N, 3.8. $C_{18}H_{17}NO_2S_3$ requires C, 57.6; H, 4.6; N, 3.7%); $\lambda_{max.}$ 354 nm (ε 7 800 dm^3 mol^{-1} cm^{-1}); δ_H 2.34 (6 H, s, 2 × Me), 4.78 (1 H, d, *J* 0.85 Hz, 3-H), 4.92 (1 H, dd, *J* 0.85 and 1.2 Hz, 2-H), 6.96—7.29 (8 H, m, 2 × 4-MeC$_6H_4$S), and 7.72 (1 H, d, *J* 1.2 Hz, 5-H).

[2,3,5-$^2H_3$]-(**1c**): 45 min; 40%; m.p. 95—96 °C; deuteriation at δ 4.78 was 84% (^1H n.m.r.).

The *2,3-bisphenylthiodihydrothiophene* (**1d**): 40 min; 40%; m.p. 67.5—69 °C (Found: C, 55.2; H, 3.8; N, 4.3. $C_{16}H_{13}NO_2S_3$ requires C, 55.3; H, 3.8; N, 4.0%); $\lambda_{max.}$ 352 nm (ε 7 700 dm^3 mol^{-1} cm^{-1}); δ_H 4.85 (1 H, d, *J* 0.8 Hz, 3-H), 4.98 (1 H, dd, *J* 0.8 and 1.2 Hz, 2-H), 7.23—7.32 (10 H, m, 2 × C_6H_5S), and 7.76 (1 H, d, *J* 1.2 Hz, 5-H).

The *2,3-bis-(4-chlorophenylthio)dihydrothiophene* (**1e**): 30 min; 42%; m.p. 114—115.5 °C (Found: C, 46.3; H, 2.7; N, 3.5. $C_{16}H_{11}Cl_2NO_2S_3$ requires C, 46.2; H, 2.7; N, 3.4%); $\lambda_{max.}$ 349 nm (ε 7 900 dm^3 mol^{-1} cm^{-1}); δ_H 4.70 (1 H, d, *J* 0.8 Hz, 3-H), 4.88 (1 H, dd, *J* 0.8 and 1.3 Hz, 2-H), 7.21—7.25 (8 H, m, 2 × 4-ClC$_6H_4$S), and 7.81 (1 H, d, *J* 1.3 Hz, 5-H).

The *2,3-bis-(3-chlorophenylthio)dihydrothiophene* (**1f**): 30 min; 25%; m.p. 97—98.5 °C (Found: C, 46.1; H, 2.7; N, 3.6. $C_{16}H_{11}Cl_2NO_2S_3$ requires C, 46.2; H, 2.7; N, 3.4%); $\lambda_{max.}$ 349 nm (ε 8 000 dm^3 mol^{-1} cm^{-1}); δ_H 4.77 (1 H, d, *J* 0.75 Hz, 3-H), 4.92 (1 H, dd, *J* 0.75 and 0.9 Hz, 2-H), 7.09—7.37 (8 H, m, 2 × 3-ClC$_6H_4$S), and 7.83 (1 H, d, *J* 0.9 Hz, 5-H).

[2,3,5-$^2H_3$]-(**1f**): 50 min; 28%; m.p. 96.5—98 °C; deuteriation at δ 4.77 was 86% (^1H n.m.r.).

2-(Arylthio)-4-nitrothiophenes (**2b**—**f**).—A solution of sodium arenethiolate (2 mmol) and arenethiol (2.2 mmol) in CH_3OH (7 cm^3) was added to a solution of 3,4-dinitrothiophene (2 mmol) in the same solvent (5 cm^3) and the mixture was kept at reflux. After the appropriate reaction time the solution was evaporated. The residue was taken up with CH_2Cl_2, the insoluble $NaNO_2$ filtered off, and the solution chromatographed on a silica gel column with CH_2Cl_2–light petroleum (b.p. 40—70 °C) (1:2.5) as eluant. Reactions time, yield, and physical and spectroscopic characteristics of each compound are reported.

The *4-methoxyphenyl sulphide* (**2b**):† 12%; m.p. 35.5—36.5 °C [from light petroleum (b.p. 80—100 °C)] (Found: C, 47.3; H, 3.6; N, 5.4. $C_{11}H_9NO_3S_2$ requires C, 49.4; H, 3.4; N, 5.2%); δ_H 3.80 (3 H, s, MeO), 6.82—7.47 (4 H, m, 4-MeOC$_6H_4$S), 7.59 (1 H, d, *J* 1.5 Hz, 3-H), and 8.18 (1 H, d, *J* 1.5 Hz, 5-H).

The 4-methylphenyl sulphide (**2c**): 2 h; 31%; m.p. 54—55 °C [from light petroleum (b.p. 40—70 °C); lit.,[16] 58 °C].

The phenyl sulphide (**2d**): 1 h; 55%; m.p. 61—62.5 °C [from petroleum (b.p. 80—100 °C); lit.,[16] 56 °C].

The 4-chlorophenyl sulphide (**2e**): 1 h; 40%; m.p. 50—51 °C [from light petroleum (b.p. 40—70 °C): lit.,[17] 59 °C].

The 3-chlorophenyl sulphide (**2f**): 40 min; 61%; viscous oil characterised as sulphone;[17] δ_H 7.17—7.28 (4 H, m, 3-ClC$_6H_4$S), 7.79 (1 H, d, *J* 1.6 Hz, 3-H), and 8.36 (1 H, d, *J* 1.6 Hz, 5-H).

Kinetics.—Kinetic runs were performed as previously reported.[3] The reaction was followed by recording the absorbance decrease at 340 nm (reference air). The u.v. spectrum of the final mixture was always identical, within experimental error, with that expected for a 100% conversion into (**2**). Each value reported in Tables 1 and 3 is the mean of at least two independent runs, reproducibility always being within ±5%.

Deuterium-exchange Experiment.—The experiment was performed at 25 °C with [$^2H_3$]-(**1c**) (9.02×10^{-3}M), [$Bu^n{}_3N$] 8.16×10^{-1}M, and [$Bu^n{}_3NH^+Cl^-$] 1.89×10^{-2}M. The reaction was quenched after *ca.* 28% of the overall absorbance variation with 10% HCl. The organic layer was washed with water, dried (Na_2SO_4), and evaporated at room temperature, and the residue was chromatographed on a silica gel column with CH_2Cl_2–light petroleum (b.p. 40—70 °C) (1:2.5) as eluant. The recovered substrate showed (^1H n.m.r.) the same deuteriation as the starting material.

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* The purity of the sample used for the kinetic experiments was checked by h.p.l.c. [0.39 × 30 cm μPorasil column, CH_2Cl_2–hexane (4:1) as eluant].

† Obtained in sufficient amounts by chromatography directly from the preparation of (**1b**).

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