Transmission of Substituent Effects in Systems with Bonds of Different Order. Kinetics of the Reactions of 3-Bromo-2-nitro-4-X-thiophens and 3-Bromo-4-nitro-2-X-thiophens with Sodium Benzenethiolate in Methanol †

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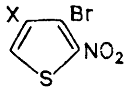
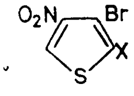
The rates of the reactions of some 3-bromo-2-nitro-4-X-thiophens (I) and of some 3-bromo-4-nitro-2-X-thiophens (II) with sodium benzenethiolate in methanol have been measured with the aim of obtaining information on the transmission of substituent effects through the C(2)–C(3) and C(3)–C(4) bonds of the thiophen ring, which are known to have different bond orders. The correlation of the log *k* values of these reactions with σ_p constants in series (I) and with σ_p^- constants in series (II) together with the ρ-values obtained ($\rho_{\rm I} = +3{\cdot}95$, $\rho_{\rm II} = +8{\cdot}18$) suggest that a low conjugative effect and an extra conjugative one are exerted from position 4 and position 2 respectively upon position 3 of the thiophen ring.

The $\rho_{\rm I}$-value compared with those reported for the same reaction of 3-bromo-2-nitro-5-X-thiophens (series III) and 1-halogeno-2-nitro-5- and -6-X-benzenes indicate a $\rho_{ortho}:\rho_{meta}$ ratio for thiophen derivatives (0·88) greater than that observed for similar reactions of benzene derivatives (0·67). These results suggest that *ortho*-substituents can exert their polar effect on the reaction centre more effectively in the thiophen than in the benzene series owing to the lower steric effects between neighbouring substituents in 5-membered heterocyclic rings. The different features of the u.v. spectra of the products obtained by benzenethiolate debromination of compounds of series (I) and (II) are consistent with the kinetic results.

CONTINUING our study of five-membered heterocycles,[1] we now report work to obtain information on the transmission of substituent effects through the C(2)–C(3) and C(3)–C(4) bonds of the thiophen ring, which have different bond orders.[2] 3-Bromo-2-nitro-4-X-thiophens (Ia—h) and 3-bromo-4-nitro-2-X-thiophens (IIb—f) were prepared and the kinetics of their reactions with sodium benzenethiolate in methanol at various temperatures were studied. The results were compared with those reported for the same reaction of 3-bromo-2-nitro-5-X-thiophens (III) [1a] and 1-halogeno-2-nitro-6-X-benzenes.[3]



(I)



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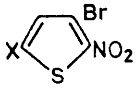
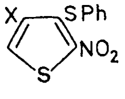
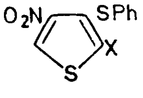


(III)



(IV)



(V)

a; X = H
b; X = CO_2Me
c; X = Ac
d; X = $CONH_2$
e; X = NO_2
f; X = SO_2Me
g; X = Br
h; X = CN

It was also our purpose to verify the *ortho*-Hammett relationship in the thiophen system. The question of substituent effects close to the reaction centre (*ortho*-effect or proximity effect) has been examined [4] and discussed in connection with nucleophilic aromatic substitutions,[5] but never in 5-membered heteroaromatic compounds, although the different geometry of these rings from benzene and the different values of π-bonds [2] in them are of interest.

RESULTS AND DISCUSSION

Products.—The 2-nitro-4-X-3-thienyl phenyl sulphides (IVa—h) and 4-nitro-2-X-3-thienyl phenyl sulphides (Vb—f) were obtained almost quantitatively by benzenethiolate debromination of compounds (Ia—h) and (IIb—f) (see Table 1).

Kinetic Data.—Table 2 gives rate constants and activation parameters for benzenethiolate debromination of 3-bromo-2-nitro-4-X-thiophens (Ia—h) and 3-bromo-4-nitro-2-X-thiophens (IIb—f). In both series the rate of nucleophilic substitution is increased upon introduction of electron-withdrawing groups. Generally such reactions are enthalpy-controlled. However, a variation of enthalpy as well as of entropy of activation can be observed on going from one derivative to another.

These reactions are considered to proceed through a two-step mechanism. The decomposition of the intermediate complex is the fast step as indicated by the

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[1] (*a*) G. Guanti, C. Dell'Erba, and D. Spinelli, *J. Heterocyclic Chem.*, 1970, **7**, 1333; (*b*) C. Dell'Erba and D. Spinelli, *Tetrahedron*, 1965, **21**, 1061; C. Dell'Erba, A. Guareschi, and D. Spinelli, *J. Heterocyclic Chem.*, 1967, **4**, 438.

[2] A. J. H. Wachters and D. W. Davies, *Tetrahedron*, 1964, **20**, 2841; M. Nardelli, F. Fava, and G. Giraldi, *Acta Cryst.*, 1962, **15**, 737 and references therein.

[3] A. M. Porto, L. Altieri, A. J. Castro, and J. A. Brieux, *J. Chem. Soc.* (*B*), 1966, 963.

[4] G. E. K. Branch and M. Calvin, 'The Theory of Organic Chemistry,' Prentice Hall, New York, 2nd edn., p. 257; R. W. Taft, 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, ch. 13; B. Capon, *Quart. Rev.*, 1964, **18**, 45; J. F. J. Dippy and R. H. Lewis, *J. Chem. Soc.*, 1937, 1426; L. P. Hammett, 'Physical Organic Chemistry,' McGraw-Hill, New York, pp. 204 *et seq.*

[5] E. Berliner, M. Quinn, and P. Edgerton, *J. Amer. Chem. Soc.*, 1950, **72**, 5305; O. L. Brady and F. R. Cropper, *J. Chem. Soc.*, 1950, 507; J. F. Bunnett, *J. Amer. Chem. Soc.*, 1962, **84**, 3284; J. Miller, 'Aromatic Nucleophilic Substitution,' Elsevier, Amsterdam, 1968, p. 95 and references therein; N. E. Sbarbati, *J. Org. Chem.*, 1965, **30**, 3365.

absence of element effect from the benzenethiolate dehalogenation of 3-halogeno-2-nitrothiophens.[6]

The rate constants of series (I) and (II) (Table 2) show that for the same substituent the reactivity of compounds (I) is always greater than that of compounds (II). The difference of reactivity decreases with increasing electron-withdrawing power of the substituent until the rate constants converge to the same value for X = NO_2 (Ie and IIe). This demonstrates that the sensitivity to the substituent effect in series (I) is considerably different (lower) from that in series (II). The lack of a linear correlation between the logarithms of the rate constants of series (I) and those of series (II) also supports the assumption that the substituent effect must be different in these two series.

TABLE 1

Analytical and spectroscopic data of sulphides (IVa—h) and (Vb—f) [a]

Sulphides	Crystallization solvent	M.p. (°C)	Found (%)		Molecular formula	Required (%)		$\lambda_{max.}$ [b]	log ε [b]
			N	S		N	S		
(IVa) [d]	Methanol	92						372	4·02
(IVb)	Methanol	81	4·8	21·6	$C_{12}H_9NO_4S_2$	4·75	21·69	394	3·75
(IVc)	Light petroleum (b.p. 80—100°)	127	5·1	22·5	$C_{12}H_9NO_3S_2$	5·02	22·94	394	3·69
(IVd)	Benzene	173	10·1	22·7	$C_{11}H_8N_2O_3S_2$	10·00	22·86	392	3·70
(IVe)	Ethanol	122	10·1	22·8	$C_{10}H_6N_2O_4S_2$	9·93	22·70	390	3·70
(IVf)	Methanol–dioxan	148	4·5	30·4	$C_{11}H_9NO_4S_3$	4·44	30·48	390	3·36
(IVg)	Light petroleum (b.p. 80—100°)	81	4·5	20·5	$C_{10}H_6BrNO_2S_2$	4·43	20·25	390	3·50
(IVh)	Light petroleum (b.p. 80—100°)	125	10·8	24·3	$C_{11}H_6N_2O_2S_2$	10·69	24·43	374	3·80
(Vb)	Methanol	132	4·8	21·6	$C_{12}H_9NO_4S_2$	4·75	21·69	328	3·61
(Vc)	Light petroleum (b.p. 80—100°)	94	5·1	22·6	$C_{12}H_9NO_3S_2$	5·02	22·94	332	3·48
(Vd)	Methanol	147	10·1	22·9	$C_{11}H_8N_2O_3S_2$	10·00	22·86	326 [c]	3·31
(Vf)	Methanol	141	4·5	31·1	$C_{11}H_9NO_4S_3$	4·44	30·48	304	3·57

[a] The sulphides are yellow. [b] In methanol. [c] Shoulder. [d] Data from ref. 14.

TABLE 2

Rate constants at various temperatures and thermodynamic parameters for benzenethiolate debrominations of 3-bromo-2-nitro-4-X-thiophens (Ia—h), 3-bromo-4-nitro-2-X-thiophens (IIb—f), and 3-bromo-2-nitro-5-X-thiophens (IIIb, c, d, g, and h)

Substrate	k/l mol^{-1} s^{-1} at various temperatures (°C) [a]					$\Delta H^‡$ [b]	$-\Delta S^‡$ [b]	σ [c]
	0·00	10·00	20·02	30·00	40·00	kcal mol^{-1}	cal mol^{-1} K^{-1}	
(Ia) [d]			0·234			13·6	14·9	0·000
(Ib)	1·76	3·80	7·73			11·1	16·3	0·385
(Ic)	2·91	6·26	12·0			10·7	17·1	0·502
(Id)	9·35	20·3	41·8			11·3	12·5	0·550
(Ie)	68·4	135	253			9·8	14·0	0·778 [f]
(If)	2·60	5·93	12·8			12·1	12·1	0·720
(Ig)	1·13	2·43	5·06			11·3	16·7	0·232
(Ih)	28·0	56·2	109			10·2	14·5	0·660
(IIb)			$1·06 \times 10^{-3}$	$3·00 \times 10^{-3}$	$7·97 \times 10^{-3}$	17·8	11·2	0·636
(IIc)		$6·57 \times 10^{-2}$	$1·45 \times 10^{-1}$	$3·01 \times 10^{-1}$		12·4	20·0	0·874
(IId)			$2·15 \times 10^{-3}$	$5·63 \times 10^{-3}$	$1·38 \times 10^{-2}$	16·4	14·7	0·627
(IIf)			$8·38 \times 10^{-4}$	$2·39 \times 10^{-3}$	$6·39 \times 10^{-3}$	18·0	11·2	1·049
(IIIb) [e]			8·01			11·3	15·7	0·370
(IIIc) [e]			9·29			12·5	11·2	0·376
(IIId) [e]			3·00			11·7	16·2	0·280
(IIIg) [e]			19·3			10·8	15·7	0·391
(IIIh) [e]			75·7			11·8	9·4	0·560

[a] The rate constants are accurate to ±3%. [b] At 20 °C. The values of $\Delta H^‡$ are accurate to ±0·5 kcal mol^{-1} and of $\Delta S^‡$ to ±1·5 cal mol^{-1} K^{-1}. [c] J. Hine, 'Physical Organic Chemistry,' McGraw-Hill, New York, 1962, 2nd edn., p. 87. [d] Data from ref. 14. [e] Data from ref. 1*a*. [f] This is the σ-value for the nitro-group in series (I); $\sigma^-_p = 1·27$ is the used value for the nitro-group in series (II) (*cf.* Figure 1).

In order to clarify the nature of the effect exercised by a substituent in position 4 on the reaction centre [(position 3, series (I)] we can compare the benzenethiolate debromination rates of compounds of series (I) with those of series (III)[1a] (Table 2). In the case of (Ib) and (IIIb) the reactivity is similar in the two series; (Ic), (Id), and (Ih), however are more reactive than (IIIc), (IIId), and (IIIh), while the reactivity of (Ig) is lower than (IIIg). Since the effect arising at position 5 is *meta*-like with respect to position 3, the above comparison indicates that the substituent at position 4 must also exert a conjugative effect at the reaction centre under consideration. Consequently, in series (I) a correlation can confidently be sought between the measured log k and σ-values. A good linear correlation is obtained by use of σ_p-values (Figure 1, $\rho_{I} = +3·95$; $r = 0·993$). When a similar treatment is applied to series (II), the σ^-_p-values are required (Figure 1, $\rho_{II} = +8·18$, $r = 0·998$) to obtain a meaningful correlation. The points corresponding to (If), (Ig), and (IIf) fall away from the straight line and have not been considered in calculating the ρ-values. The reactivity of $MeSO_2$ derivatives [(If) and (IIf)], lower than that predicted on the basis of the

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[6] G. Guanti, C. Dell'Erba, and P. Macera, *J. Heterocyclic Chem.*, 1971, **8**, 537.

Hammett relationship, is consistent with the bulkiness of this group producing a steric effect which seriously distorts the activation parameters. The greater reactivity than expected of the bromo-derivative (Ig) seems to depend on the peculiar effect exerted by the bromine atom *ortho* to a reaction centre undergoing attack by a benzenethiolate ion, as pointed out by Reinheimer and Bunnett.[7]

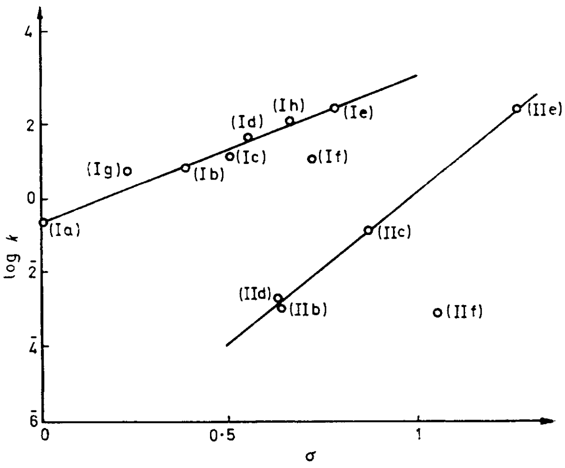

FIGURE 1 Hammett plot for the benzenethiolate debromination of (Ia—h) and (IIb—f) in methanol at 20 °C; $\rho_{\rm I} = 3{\cdot}96$, $r = 0{\cdot}993$, $\rho_{\rm II} = 8{\cdot}18$, $r = 0{\cdot}998$. Data for (If), (Ig), and (IIf) have been excluded from ρ-calculation

The clear difference in the substituent effects characterizing series (I) and (II), influencing as it does the type of substituent constant (σ_p and σ_p^-) and the ρ-values, is consistent with the different bond order between carbon atoms C(2) and C(3) and C(3) and C(4) in the thiophen ring.* The modest double-bond character between the β-positions obviously determines the low contribution of the conjugative effect of the substituent exercised from position 4 on position 3 [series (I)]. In contrast the large double-bond character between positions 2 and 3 of the thiophen ring is the factor allowing the extra conjugative effect to be exerted by a substituent in position 2 on position 3 [series (II)]. Accordingly the σ_p-values are required in the first case whereas σ^-_p are successfully applied in the latter. Moreover the ρ-value observed for series (II) is higher than those found for series (I) and for 1-halogeno-2-nitro-6-X-benzenes.†

The good correlations observed in both cases agree with the tetrahedral, or nearly so, geometry at the reaction centre in the transition state of the nucleophilic aromatic substitutions.[3,5,8] The $\rho_{ortho} : \rho_{meta}$ ratio, greater in thiophen derivatives ($\rho_{\rm I} : \rho_{\rm III} = 0{\cdot}88$) than in benzene derivatives ($\rho_{ortho} : \rho_{meta} = 0{\cdot}67$) [3] undergoing similar reactions, suggests that in the thiophen ring the electric *ortho*-effect is more active than in the benzene ring. The lack of steric interaction generally noted here between neighbouring substituents in a 5-membered heterocyclic ring agrees with the results we obtained [9] by studying the secondary steric effect in nucleophilic substitutions of the thiophen derivatives.

Ultraviolet Spectra of Products.—The relative resonance stabilization of the products obtained by benzenethiolate debromination of compounds of series (I) and (II) can be estimated by examination of the u.v. spectra reported in Figure 2. The u.v. spectra considered are those of (IVa—f) and (Vb—f). They show that the two series of compounds fall into two classes. The sulphides (IV) related to series (I) share the common characteristic of having a band in the 350—420 nm region. In contrast, the sulphides (V) derived from series (II) present a shoulder or a maximum, which is not very pronounced, in the 300—330 nm region. The absorption band observed in the 350—450 nm region for the sulphides (IV) should be assigned to the [$^-{}^+S{=}C(3) \longrightarrow C(2){=}NO_2{}^-$] electronic transition. The decrease of absorption intensity observed on going from (IVa) to (IVb—e) ($\Delta \log \varepsilon \approx 0{\cdot}3$) can be considered as arising from steric inhibition of resonance determined by the 4-X-groups. Steric inhibition of resonance affects u.v. spectra of sulphides but not benzenethiolate debromination rates of corresponding bromo-derivatives, to which the Hammett relation can readily be applied. Further, the comparison of the u.v. spectra of the compounds (IVa) and (IVf) reveals a higher steric effect for the 4-SO_2Me group ($\Delta \log \varepsilon = 0{\cdot}65$). Therefore the spectroscopic result appears to be in good agreement with the kinetic data. The manifest differences in the features of the u.v. spectra of the sulphides (Vb—f) (shoulder on maximum at 300—330 nm) compared with the sulphides (IVb—f) are also consistent with the kinetic results. Together they substantiate the fact that the lower double-bond character between C(3) and C(4) than C(2) and C(3) in the thiophen

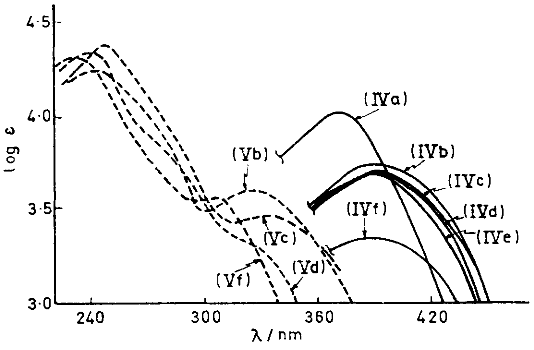

FIGURE 2 U.v. absorption spectra of sulphides (IVa—f) (solid curves) and (Vb—f) (broken curves)

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* The calculated [2] values of π-bond order in thiophen are C(2)–C(3) = 0·863 and C(3)–C(4) = 0·467.

† In the benzene series the log *k* of the rate constants for analogous reaction on *ortho*-substituted *ortho*-halogenitrobenzenes have been correlated with σ^-_p.[3,5]

[7] J. D. Reinheimer and J. F. Bunnett, *J. Amer. Chem. Soc.*, 1959, **81**, 315.

[8] F. Pietra, D. Vitali, F. Del Cima, and G. Cardinali, *J. Chem. Soc.* (*B*), 1970, 1659 and previous papers; C. W. L. Bevan, A. J. Foley, J. Hirst, and W. O. Uwamu, *ibid.*, p. 794.

[9] D. Spinelli, G. Guanti, and C. Dell'Erba, *J. Heterocyclic Chem.*, 1968, **5**, 323.

ring results in a very low conjugation between the nitro-group and the sulphur of the sulphide [$-^{+}S{=}C(3) \longrightarrow C(4){=}NO_2^{-}$].

EXPERIMENTAL

3-Bromo-2-nitrothiophen (Ia),[10] methyl 4-bromo-5-nitrothiophen-3-carboxylate (Ib),[11] 4-bromo-5-nitrothiophen-3-carboxamide (Id),[12] 3-bromo-2,4-dinitrothiophen (Ie),[10] 3,4-dibromo-2-nitrothiophen (Ig),[10] and methyl 3-bromo-4-nitrothiophen-2-carboxylate (IIb) [13] were prepared and purified by the methods reported.

2-Nitro-4-X-3-thienyl phenyl sulphides (IVa—h) and 4-nitro-2-X-3-thienyl phenyl sulphides (Vb—f) were prepared in high yield from the corresponding 3-bromo-2-nitro-4-X-thiophens (Ia—h) or 3-bromo-4-nitro-2-X-thiophens (IIb—f) and sodium benzenethiolate as described for 2-nitro-3-thienyl phenyl sulphide (IVa) [14] (see Table 1). The other compounds were prepared as reported below.

4-Acetyl-3-bromo-2-nitrothiophen (Ic).—4-Acetyl-3-bromothiophen (8 g, 0·04 mol) was slowly added with stirring, at −15 to −20 °C, to the nitrating mixture (nitric acid, *d* 1·42, 20 ml; concentrated sulphuric acid 20 ml). After being kept at −20 °C for 30 min, the mixture was poured onto crushed ice. The precipitated solid was filtered off and purified by column chromatography on silica gel with benzene as eluant. The *crystals* had m.p. 127—128°, from light petroleum (b.p. 80—120°) (Found: Br, 32·1; N, 5·7; S, 12·9. $C_6H_4BrNO_3S$ requires Br, 32·0; N, 5·6; S, 12·8%). The assigned structure was confirmed by oxidation of the benzenethiolate debromination product of (Ic) with sodium hypochlorite to 5-nitro-4-phenylthiothiophen-3-carboxylic acid which by esterification with methanol and sulphuric acid yields an ester identical to (IVb).

4-Acetyl-3-bromothiophen.—To a solution of 3-bromo-4-thienyl-lithium prepared at −70 °C from n-butyl-lithium (128 ml of a 1·4N solution) and 3,4-dibromothiophen [15] (36·8 g, 0·15 mol) was added dropwise acetaldehyde (8·5 g, 0·19 mol) dissolved in ether (40 ml). 30 Minutes after the addition the cooling bath was removed and after 1 h the solution was hydrolysed. The ether phase was washed with water, dried, and fractioned. 1-(*4-Bromo-3-thienyl)ethanol* (18·9 g), b.p. 140—142° at 12 mmHg, was obtained (correct analysis for Br and S). To this alcohol (16·2 g, 0·08 mol) dissolved in acetic acid (75 ml), was added a solution of CrO_3 (5·3 g, 0·05 mol) in water (30 ml) and acetic acid (70 ml) during 1 h. The mixture was stirred for an additional h at room temperature, after which the dark violet solution was poured into 1 l of water. The aqueous phase was extracted with ether and the ether layer was washed with sodium carbonate solution until the extract was alkaline, then with water and was dried and distilled. *4-Acetyl-3-bromothiophen* (10 g, 0·049 mol), b.p. 135—136° at 12 mmHg was obtained (Found: Br, 39·2; S, 15·7. C_6H_5BrOS requires Br, 39·0; S, 15·6%).

Methyl 4-Bromo-5-nitro-3-thienyl Sulphone (If).—*4-Bromo-3-thienyl methyl sulphone* (6 g, 0·025 mol), obtained by refluxing a solution in acetic acid of 4-bromo-3-thienyl methyl sulphide [15] with a large excess of hydrogen peroxide, gave crystals from benzene–light petroleum (b.p. 80—120°), m.p. 106° (correct analysis for Br and S). It was slowly added with stirring at 0 °C to nitric acid (*d* 1·52, 40 ml). After being kept at 0 °C for 30 min the mixture was poured onto crushed ice. The precipitated *solid* was filtered off and crystallized from light petroleum (b.p. 80—120°), m.p. 190° (Found: Br, 28·1; N, 5·0; S, 22·2. $C_5H_4BrNO_4S_2$ requires Br, 28·0; N, 4·9; S, 22·4%).

4-Bromo-5-nitrothiophen-3-carbonitrile (Ih).—Nitric acid (*d* 1·52, 3 ml) was slowly added with stirring, at room temperature, to a solution of *4-bromothiophen-3-carbonitrile* (6 g, 0·032 mol) {[obtained by treatment with acetic anhydride of the corresponding *aldoxime* * as crystals, m.p. 64—65° [from light petroleum (b.p. 80—120°] (correct analysis for N and S)} in acetic anhydride (40 ml). After being kept at 50 °C for 2 h the mixture was poured onto crushed ice. The precipitated *solid* was filtered off and crystallized from methanol, and had m.p. 178° (Found: Br, 33·9; N, 12·1; S, 13·7. $C_5HBrN_2O_2S$ requires Br, 34·3; N, 12·0; S, 13·7%).

2-Acetyl-3-bromo-4-nitrothiophen (IIc).— 2-Acetyl-3-bromothiophen [10] (10 g, 0·05 mol) dissolved in concentrated sulphuric acid (48·5 ml) was slowly added with stirring at −20 °C to the nitrating mixture (nitric acid, *d* 1·42, 15·1 ml; concentrated sulphuric acid, 51·5 ml). After being kept at −20 °C for 30 min the mixture was poured onto crushed ice. The precipitated solid was filtered off and chromatographed on silica gel with benzene as eluant. In order the eluate gave 3-bromo-2,5-dinitrothiophen (0·5 g),[10] 3-bromo-2,4-dinitrothiophen [10] (3·5 g), and *2-acetyl-3-bromo-4-nitrothiophen* (5·8 g) which was crystallized from light petroleum (b.p. 80—110°) and had m.p. 108—109° (Found: Br, 32·1; N, 5·6; S, 13·0. $C_6H_4BrNO_3S$ requires Br, 32·0; N, 5·6; S, 12·8%).

3-Bromo-4-nitrothiophen-2-carboxamide (IId).—3-Bromo-4-nitrothiophen-2-carboxylic acid [12] was converted into the acid chloride (by thionyl chloride) and then into the *amide* by treatment with aqueous ammonia; pale yellow crystals, m.p. 204—205°, from ethanol–dioxan (Found: Br, 31·8; N, 11·3; S, 12·6. $C_5H_3BrN_2O_3S$ requires Br, 31·8; N, 11·2; S, 12·8%).

3-Bromo-4-nitro-2-thienyl Methyl Sulphone (IIf).—*3-Bromo-2-thienyl methyl sulphone* (7·8 g, 0·03 mol) [obtained by refluxing a solution in acetic acid of 3-bromo-2-thienyl methyl sulphide [15] with a large excess of hydrogen peroxide as crystals from benzene–light petroleum (b.p. 80—120°), m.p. 83° (correct analysis for Br and S)] was added with stirring at 0—5° to the nitrating mixture (nitric acid, *d* 1·52, 18·2 ml; concentrated sulphuric acid, 14·9 ml). After being kept at 0—5° for 10 min the mixture was poured onto crushed ice. The precipitated solid was filtered off and chromatographed on silica gel with benzene–chloroform (2 : 1) as eluant. The successive fractions of eluate gave a trace of 3-bromo-2,5-dinitrothiophen,[10] 3-bromo-2,4-dinitrothiophen [10] (0·7 g), *3-bromo-5-nitro-2-thienyl methyl sulphone* (2·13 g), crystals from ethanol, m.p. 142° (correct analysis for Br, N, and S), and *3-bromo-4-nitro-2-thienyl methyl sul-*

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* Obtained from 4-bromothiophen-3-carbaldehyde [15] by the action of hydroxylamine chloride and pyridine (crystals from water–ethanol, m.p. 107°).

[10] W. Steinkopf, H. Jacob, and H. Penz, *Annalen*, 1934, **512**, 136.

[11] S. Gronowitz and P. Gustavson, *Arkiv Kemi*, 1962, **20**, 289.

[12] S. O. Lawesson, *Arkiv Kemi*, 1957, **11**, 325.

[13] S. Gronowitz and K. Dahlgren, *Arkiv Kemi*, 1963, **21**, 201.

[14] D. Spinelli, G. Guantì, and C. Dell'Erba, *Ricerca sci.*, 1968, **38**, 1051.

[15] S. Gronowitz, P. Moses, and R. Hokansson, *Arkiv Kemi*, 1960, **16**, 267.

phone (3·75 g). The last was recrystallized from methanol and had m.p. 168—170° (Found: Br, 28·4; N, 5·0; S, 22·3. $C_5H_4BrNO_4S_2$ requires Br, 28·0; N, 4·9; S, 22·4%).

Kinetics.—The kinetics were followed as described [16] by measuring the increase in absorbance at the wavelengths indicated in Table 1; the absorptions of sulphides at such wavelengths are also in Table 1. The infinity optical densities registered in the range 200—450 nm indicate that formation of the sulphides (IIIa—h) and (IVb—f) from 3-bromo-2-nitro-4-X-thiophens (Ia—h) and 3-bromo-4-nitro-2-X-thiophens (IIb—f) by action of sodium benzenethiolate is the only reaction occurring appreciably. T.l.c. of reaction mixtures confirms the photometric data. The concentrations employed were $2·5 \times 10^{-4}$M for nitrobromothiophens and sodium methoxide, 1×10^{-3}M for benzenethiol. In the case of the reaction with 3-bromo-2,4-dinitrothiophen the concentrations employed were respectively 1×10^{-4}M and 4×10^{-4}M.

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