Nucleophilic Substitution in the Side Chain of Five-membered Hetero-cycles. Part 4.[1] Reaction Kinetics of Selenophen Compounds

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The polarity σ^* constant of the selenophen ring has been obtained from the rates of acid- and base-catalysed hydrolysis of ethyl selenophen-2-carboxylate, following the Taft procedure. Kinetics of the reaction of selenophen-2-sulphonyl chloride and 2-chloromethylselenophen with aniline, and of selenophen-2-carbaldehyde with aniline and with a phosphorus ylide have been investigated. Comparison between the reactivities of selenophen and thiophen compounds confirms the similarity of the electrical effects of both heterocycles. The results, together with previous data for furan, thiophen, pyrrole, and benzene derivatives, are rationalized by correlation analysis with polar or electrophilic constants of heterocycles, depending on the side-chain electron demand.

WE are interested in the side-chain nucleophilic substitution of five-membered heterocyclic compounds, with regard to structure–reactivity relationships and details of the reaction mechanisms.[1-3] Correlation analysis of the kinetic results may be performed satisfactorily in terms of the polarity (σ^*)[4] and electrophilicity (σ^+)[5] constants of the ring systems, but the different molecular geometry of the heterocycles † sometimes can involve additional steric effects, so that the data treatment becomes more complex.[1]

We have previously investigated the nucleophilic substitution reactions of choromethyl compounds,[3] arenesulphonyl chlorides,[2] and aroyl chlorides[6] with aniline, the condensations of aromatic aldehydes with aniline and phosphorus ylides,[1] the acidic[7] and alkaline hydrolysis[8] of aromatic carboxanilides, and the reaction of chloroacetyl chlorides with triethyl phosphite.[9] Other workers, have studied the acidic and alkaline hydrolysis of ethyl esters[4] and the reduction of aryl methyl ketones with sodium borohydride.[10]

Most studies on five-membered heterocycles have reported the kinetics of phenyl, 2- and 3-furyl, and 2- and 3-thienyl derivatives, and some have also included pyrrole derivatives; however, up to now there are no data for the corresponding selenophen derivatives.

Accordingly, we now report new kinetic results for side-chain nucleophilic reactions of selenophen derivatives (Scheme 1): the acidic and alkaline hydrolyses of ethyl selenophen-2-carboxylate in aqueous acetone, the reaction of selenophen-2-sulphonyl chloride with aniline in methanol and of 2-chloromethylselenophen with aniline in acetonitrile, and the condensations of selenophen-2-carbaldehyde with aniline in acetonitrile and with benzoylmethylenetriphenylphosphorane (BMTPP) in methanol.

Selenophen compounds are more reactive than the corresponding thiophen derivatives in electrophilic substitutions[5] and solvolyses,[5,11] the reactivity order for the aromatic ring systems being: pyrrole ≫ furan > tellurophen > selenophen > thiophen > benzene, as indicated by the σ^+ electrophilic constants of the hetero-atoms. Selenophen compounds also react faster than the corresponding thiophen in aromatic nucleophilic

† (a) For bond lengths and angles in the furan, thiophen, and pyrrole rings see ref. 5, p. 237; (b) for selenophen see N. Magdesieva, *Adv. Heterocyclic Chem.,* 1970, **12**, 3.

substitutions, as Spinelli and his co-workers have pointed out.[12]

The ability of selenophen to delocalize both positive and negative charges can be ascribed to the larger and more polarizable selenium atom, which can release its p electrons and accept electrons into its free d orbitals more readily than sulphur in thiophen.†
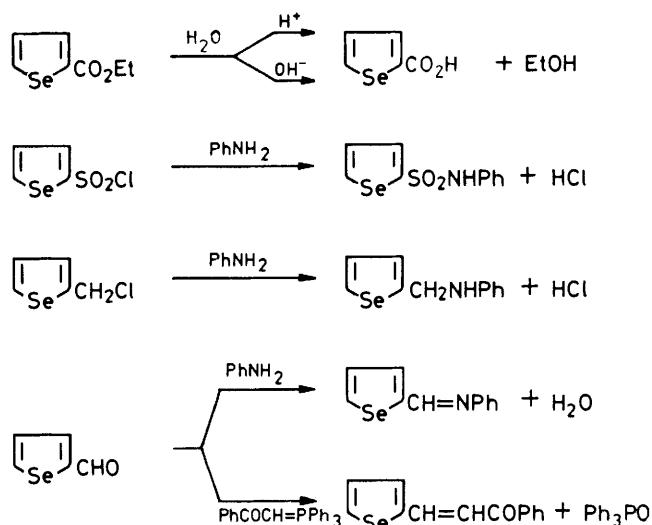
SCHEME 1

RESULTS AND DISCUSSION

Acidic and Alkaline Hydrolysis of Ethyl Selenophen-2-carboxylate.—The hydrolysis of esters is the usual standard reaction for studies of the electrical effects of a substrate. However, for five-membered heterocyclic esters, additional effects obscure the kinetic data. Ten Thije and Janssen attempted, by the Taft approach,[13] using alkaline and acidic hydrolysis measurements, to deduce the polarity constants (σ^*) of five-membered heterocycles.[4] Following this work we have measured the rates of alkaline and acidic hydrolysis of ethyl selenophen-2-carboxylate at 25 °C in aqueous acetone (62% w/w). Since the acidic hydrolysis proceeds very slowly at 25 °C, experimental values for k_2 were determined at 125, 100, and 75 °C, and the rate constant at 25 °C was evaluated by extrapolation.

The results (Table 1) were used to calculate the polar constant of the selenophen ring system, in the way indi-

cated by Taft, using the alkaline and acidic hydrolysis rate constants of ethyl acetate (k_0) as references [equation (1)].[14]

$$\sigma^* = (1/2.48)[\log \ (k/k_0)_{\text{B}} - \log \ (k/k_0)_{\text{A}}] \qquad (1)$$

As we would expect, alkaline hydrolysis is faster than acidic hydrolysis by a factor of $>10^5$. Comparison of the rates for heterocyclic and benzoic esters (Table 2) shows the strong resemblance between selenophen and thiophen derivatives, as indicated by the σ^* values for selenophen (0.85) and thiophen (0.93).

Although the σ^* values correlate well the dissociation

TABLE 1

Second-order rate constants for the acidic (k_A) and alkaline (k_B) hydrolysis of ethyl selenophen-2-carboxylate in aqueous acetone (62% w/w), and parameters of the Taft equation

$T/°C$	$\dfrac{k_\text{A} \times 10^4}{\text{l mol}^{-1}\ \text{min}^{-1}}$	$\dfrac{k_\text{B}}{\text{l mol}^{-1}\ \text{min}^{-1}}$	$\dfrac{\Delta H^\ddagger}{\text{kcal mol}^{-1}}$	$\dfrac{\Delta S^\ddagger}{\text{cal mol}^{-1}\ \text{K}^{-1}}$
125	125			
100	15.1		20.2	−17.2
75	2.72		(± 2.0)	(± 5.7)
25	0.0149 [a]	0.172		
25	$\log(k/k_0)_\text{A}$ −3.26 [b]			
25	$\log(k/k_0)_\text{B}$ −1.15 [b]	σ^* 0.85		

[a] Extrapolated value from the activation parameters. [b] The values of $(k_0)_\text{A}$ and $(k_0)_\text{B}$ were taken from ref. 14.

constants for the arenecarboxylic acids (Figure 1), satisfactory correlations are not found for acidic and alkaline hydrolyses of the corresponding ethyl esters. This finding confirms the consistency of the σ^* value found for selenophen with those of other heterocycles, but suggests that other effects need to be considered for a comprehensive rationalization of the kinetic results.

Reaction of Selenophen-2-sulphonyl Chloride with Aniline.—Arenesulphonyl chlorides and anilines in

TABLE 2

Second-order rate constants (1 mol^{-1} min^{-1}) for the acidic (k_A) and alkaline hydrolysis (k_B) of the ethyl esters (ArCO$_2$Et) of aromatic carboxylic acids at 25 °C in aqueous acetone (62% w/w)

No.	Ar	$k_\text{A} \times 10^6$	k_B	σ^*	pK_a of ArCO$_2$H
(1)	2-Furyl [a]	1.89	0.791	1.08	3.16 [b]
(2)	3-Furyl [a]	5.27	0.190	0.65	3.95 [b]
(3)	2-Thienyl [a]	1.11	0.196	0.93	3.53 [b]
(4)	3-Thienyl [a]	4.99	0.180	0.65	4.10 [b]
(5)	Selenophen-2-yl [c]	1.49	0.172	0.85	3.60 [d]
(6)	Ph [e]	7.74	0.228	0.60	4.21 [b]

[a] Ref. 4. [b] Ref. 5, p. 242. [c] This work. [d] D. Spinelli, G. Guanti, and C. Dell'Erba, *Ricerca Sci.*, 1968, **38**, 104. [e] W. S. G. Newling and C. N. Hinshelwood, *J. Chem. Soc.*, 1956, 1357.

methanol solution react quantitatively yielding arenesulphonanilides. The more important factors affecting the kinetics of this reaction have been widely studied, including the effect of substituents in the substrate and in the nucleophile,[15,16] leaving groups,[17] and the solvent.[2,18] Second-order rate constants have been obtained by potentiometric titration of the acid produced during the reaction.

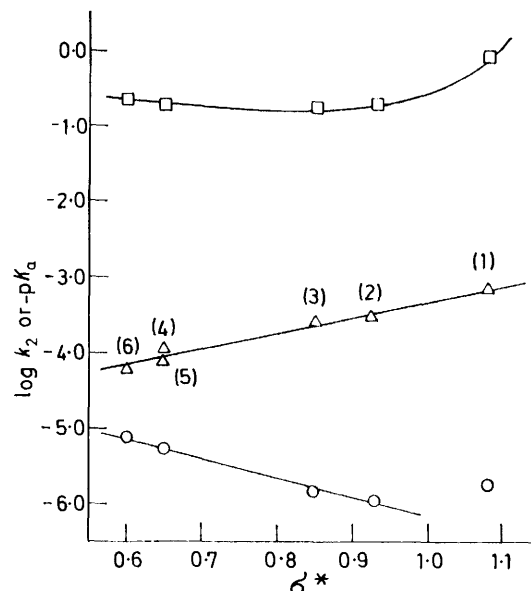Selenophen-2-sulphonyl chloride also gives the cor-

FIGURE 1 Correlations of log k_2 for the alkaline (□) and acidic (○) hydrolysis of aromatic ethyl carboxylates (ArCO$_2$Et) and of pK_a of the aromatic carboxylic acids (△) against σ^* constants. For numbering system, see Table 2

responding anilide almost quantitatively (yield $>90\%$), and the kinetic experiments carried out in a large excess of aniline provide pseudo-first-order rate constants (k_1) to at least 75—80% completion.

Table 3 reports k_1 values at different aniline concentrations measured at various temperatures, together with k_2 constants calculated from the slopes of the plots of k_1 against aniline concentrations.

Rate constants for selenophen-2-sulphonyl chloride are similar to those for the 2-thienyl and 2-furyl derivatives,[16] and are lower than that for benzenesulphonyl chloride.[15]

The good correlation between log k_2 and σ^+ mesomeric constants for heteroarene sulphonyl and substituted benzenesulphonyl chlorides (Figure 2) confirms an $S_\text{A}N$ mechanism involving intermediate complex formation, in which the rate-determining step is the nucleophile addition to the sulphonyl sulphur atom.[19]

Reaction of 2-Chloromethylselenophen with Aniline.—The kinetics of the reaction of 2-chloromethylselenophen and aniline in acetonitrile were studied as for the reactions

TABLE 3

Kinetic data for the reaction of selenophen-2-sulphonyl chloride with aniline in methanol [a]

$T/°C$	[Aniline] mol l^{-1}	$k_1 \times 10^4$ s^{-1}	$k_2 \times 10^3$ l mol^{-1} s^{-1}
25	0.0499	3.60	
25	0.100	7.18	7.41
25	0.150	11.0	
35	0.0251	4.22	
35	0.050	7.93	13.4
35	0.101	14.4	
45	0.0251	7.74	
45	0.0502	13.0	21.6
45	0.0750	18.5	

[a] [Selenophen-2-sulphonyl chloride] *ca.* 2×10^{-3} mol l^{-1}. Activation parameters: $\Delta H^\ddagger$ 9.5 $\pm$ 0.4 kcal mol^{-1}; $\Delta S^\ddagger$ −36.5 $\pm$ 1.5 cal mol^{-1} K^{-1}.
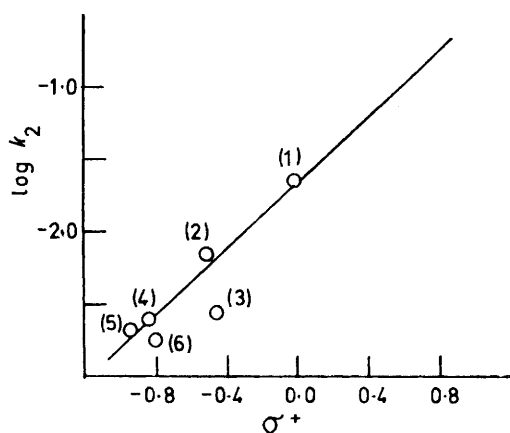
Figure 2 Correlation between log k_2 and σ^+ mesomeric constants for the reaction of heteroarene sulphonyl chlorides (ArSO$_2$Cl) with aniline in methanol at 25 °C. (1), Ar = Ph; (2), 3-thienyl; (3), 3-furyl; (4), selenophen-2-yl; (5), 2-furyl; (6). 2-thienyl. The straight line is that drawn for reactions of benzenoid compounds

of furfuryl, 2-thienyl, and benzyl chlorides, by potentiometric titration of the acid produced.[1] In agreement with previous results, the formation of N-(selenophen-2-ylmethyl)aniline follows a third-order kinetic law, first-order with respect to the substrate and second-order with respect to the nucleophile. Pseudo-first-order rate constants, in fact, correlate well the square of the aniline concentrations (Table 4). The contribution of a second molecule of aniline has been ascribed to base catalysis in the rate-determining step.[3]

The observed reactivity order for chloromethyl aromatic compounds (2-furyl > 2-thienyl > selenophen-2-yl > phenyl) may clearly be correlated with the σ^* polarity constants. The availability of the data for chloromethylselenophen in this correlation was important to discriminate between the dependence of the reactivity on σ^* and or σ^+ constants.

Reactions of Selenophen-2-carbaldehyde with Aniline and with BMTPP.—The Schiff reaction of selenophen-2-carbaldehyde with aniline in acetonitrile was followed by monitoring the u.v. absorbance of the N-(selenophen-

2-ylmethylene)aniline formed at an appropriate wavelength, as already described for the reactions of other aromatic aldehydes.[1] The average value of the second-order rate constant at 25 °C, obtained from four kinetic runs carried out at different concentration of the reagents, is 6.28×10^{-6} ($\pm 0.25 \times 10^{-6}$) l mol^{-1} s^{-1}.

The reactivity order of the heterocyclic aldehydes is clearly correlated with the i.r. stretching frequencies of the carbonyl group (Table 5), measured in acetonitrile for comparison with a homogeneous system. Benzaldehyde deviates from linearity, being less reactive than that indicated by its CO frequency. Thus, the kinetic results appear to be associated with the partial positive charges on the carbonyl carbon atom in the ground state of the aldehyde. Moreover, the linear correlation with σ^+ electrophilic constants confirms that resonance effects of the heteroatoms prevail in the nucleophilic attack on the substrate.

Kinetic data for the Wittig reaction of selenophen-2-carbaldehyde and BMTPP were obtained in methanol solution at various temperatures by titration of the ylide remaining unchanged during the reaction, as previously described.[1] Second-order rate constants and activation parameters were: 2.03×10^4 l mol^{-1} s^{-1} at 35 °C, 4.06×10^4 at 45 °C, and 9.11×10^4 at 60 °C, $\Delta H^{\ddagger} = 11.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -37.8$ cal mol^{-1} K^{-1}.

Good linear correspondence was found between the reactivity and the i.r. carbonyl stretching frequencies in methanol (Table 5), apart from the benzaldehyde reaction, as in the Schiff reaction. However, an unsatisfactory correlation with σ^+ constants, owing to the apparently anomalous reactivities of 2-furaldehyde and benzaldehyde, was found.

TABLE 4

Kinetic data for the reaction of 2-chloromethylselenophene with aniline in acetonitrile [a]

$T/°C$	[Aniline] mol l^{-1}	$k_1 \times 10^5$ s^{-1}	$k_3 \times 10^4$ l^2 mol^{-2} s^{-1}
30	0.404	0.660	
30	0.755	2.38	0.409
30	1.06	4.58	
40	0.500	2.29	
40	0.751	5.18	0.902
40	0.999	9.04	
50	0.251	1.80	
50	0.500	3.70	1.51
50	0.755	8.82	
50	1.03	16.6	
60	0.252	1.57	
60	0.502	6.12	2.38
60	0.748	13.4	

[a] [2-Chloromethylselenophen] *ca.* 2×10^{-3} mol l^{-1}. Activation parameters: $\Delta H^{\ddagger}$ 11.1 ± 0.9 kcal mol^{-1}; $\Delta S^{\ddagger}$ -41.9 ± 2.6 cal mol^{-1} K^{-1}.

TABLE 5

Reactivity of aromatic aldehydes (ArCHO) with aniline (Schiff reaction) and with BMTPP (Wittig reaction) and i.r. stretching frequencies of the aldehyde carbonyl group

	Schiff reaction		Wittig reaction	
Ar	$k_2 \times 10^6$ l mol^{-1} s^{-1} (MeCN; 25 °C)	$\nu_{C=O}$ cm^{-1}	$k_2 \times 10^4$ l mol^{-1} s^{-1} (MeOH; 35 °C)	$\nu_{C=O}$ cm^{-1}
Ph	720	1 703	10.4	1 706
2-Furyl		1 678— 1 692	29.0	1 674—1 694
2-Thienyl	26.4	1 675	5.40	1 662—1 679
Selenophen-2-yl	6.28	1 668	2.03	1 660—1 673
Pyrrol-2-yl	0.452	1 661	0.230	1 650

CONCLUSIONS

The side-chain reactivities of selenophen compounds are similar to those of thiophen derivatives; the greatest difference is obtained in the reaction of aldehydes with aniline, where the reactivity ratio of both substrates is *ca.* 4.2. Table 6 shows the relative reactivities for the six reactions studied.

In the acidic hydrolyses and in the reactions of arenesulphonyl chlorides and aromatic aldehydes with aniline, the phenyl derivative reacts faster than the heterocyclic

TABLE 6

Relative reactivities of aromatic compounds with respect to selenophen derivatives in some side-chain nucleophilic substitutions

		Ar					
Reaction	Ph	2-Furyl	3-Furyl	2-Thienyl	3-Thienyl	Pyrrol-2-yl	Selenophen-2-yl
(I) Acid hydr. $ArCO_2Et$ (aq. Me_2CO; 25 °C)	5.19	1.27	3.54	0.74	3.35		1.00
(II) Base hydr. $ArCO_2Et$ (aq. Me_2CO; 25 °C)	1.33	4.60	1.10	1.14	1.05		1.00
(III) $ArSO_2Cl + PhNH_2$ (MeOH; 25 °C)	9.26	0.82	1.15	0.76	2.81		1.00
(IV) $ArCH_2Cl + PhNH_2$ (MeCN; 40 °C)	0.30	1.37		1.10			1.00
(V) ArCHO + $PhNH_2$ (MeCN; 25 °C)	115			4.20		0.072	1.00
(VI) ArCHO + BMTPP (MeOH; 35 °C)	5.12	14.3		2.66		0.113	1.00

TABLE 7

Statistical analysis of the free-energy relationships

Reaction [a]	N [b]	V [c]	F.d. [d]	R [e]	E.v. [f]	F-test	$\log k_0$ [g]	ρ [h]	S [i]
(I)	1—6	σ^+	4	0.888	78.8	14.8 [j]	−5.01	0.874	0.227
(III)	1—6	σ^+	4	0.903	81.5	17.6 [j]	−1.27	1.09	0.26
(IV)	1, 3, 5, 6	σ^*	2	0.991	98.3	113 [k]	−3.13	2.11	0.20
(V)	3, 5—7	σ^+	2	0.987	97.4	75 [j]	−5.73	1.50	0.17
(VI)	1 3, 5, 7 [l]	σ^*	2	0.979	95.9	46.6 [j]	−6.23	3.25	0.48

[a] The numbers correspond to the reactions in Table 6. [b] Aryl groups to which the correlations apply, numbered as in Table 2; no. 7 corresponds to the pyrrol-2-yl group. [c] Variable employed in the regression. [d] No. of degrees of freedom. [e] Correlation coefficient. [f] % of explained variation. [g] Constant term of the regression. [h] Coefficient of the variable. [i] Standard error of the coefficient. [j] Significant above 95% confidence level. [k] Significant above 99% confidence level. [l] The polarity constant for the pyrrole ring (0.46) was obtained by extrapolation of the plot of the pK_a of the aromatic carboxylic acids against σ^* values for five-membered heterocycles (ref. 1).

compounds. This trend can be ascribed to the greater ability of the heterocycles to provide resonance stabilization of the substrate, compared with the transition state; in fact, on increasing the electron-releasing ability, the reaction rate decreases owing to the diminished positive charge available in the side chain for the nucleophilic attack.

To verify this hypothesis we tested the correlation between $\log k_2$ and mesomeric σ^+ endocyclic constants.[5] The results (Table 7) appear to be statistically meaningful, confirming the foregoing hypothesis.

Effective delocalization of positive charge from the side chain to the heteroatom is possible for those three reactions in which nucleophilic attack on the substrate is the rate determining step [Scheme 2, (a)—(c)].

It is noteworthy that the acidic hydrolysis rate appears to be dependent on the resonance effects of the hetero-atom, despite the fact that this is the standard reaction for the measurement of steric effects. Therefore the $\log (k/k_0)_A$ value (E_s) in the Taft equation must be used with great caution for reactions of heteroaromatic ring systems.

A different order of reactivity is obtained in the reactions of chloromethyl derivatives with aniline, in which the phenyl derivative reacts slower than the hetero-cyclic compounds. The correlation with polar constants is statistically very good (Table 7) and is clearly consistent with the reaction mechanism.

In this case the reaction centre may be represented by a saturated carbon atom [Scheme 2, (d)] on to which electron release from the heterocycle is not possible. The

reaction in acetonitrile has no S_N1 character and proceeds by synchronous bond making and bond breaking.[3] Consequently, only inductive effects of the heterocycles, represented well by σ^* constants, influence the reactivities.

A third reactivity sequence is observed in the alkaline

SCHEME 2   X = O, S, Se, CH=CH
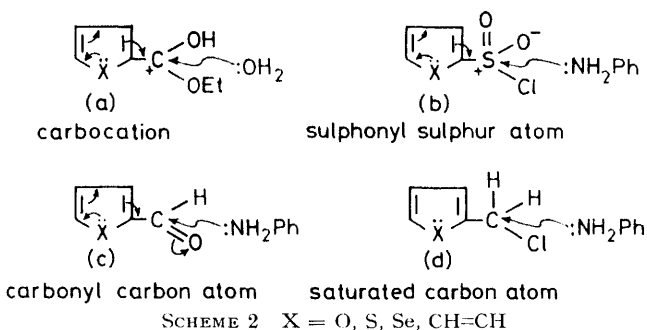
hydrolysis and in the Wittig reaction: 2-furyl > phenyl > 2-thienyl > selenophen-2-yl > pyrrol-2-yl. For both reactions we examined the applicability of free-energy relationships using one or two variables; application of the Taft–Pavelich equation [$\log k_2 = f(\sigma^*, E_s)$†] and the Yukawa–Tsuno equation [$\log k_2 = f(\sigma^*, \sigma^+)$] did not furnish statistically meaningful parameters.

In the Wittig reaction the failure of possible free-energy relationships suggests a more complex dependence of the

† The application of the Taft–Pavelich equation to the alkaline hydrolysis of esters is uncorrected, since it is the standard reaction from which σ^* and E_s are deduced: the tested regression is an obvious identity.

reactivity on the structural effects of the substrates. Nevertheless, a good linear plot is obtained for the reactions of only the heterocyclic compounds. This may be criticised, however, since two analogous nucleophilic reactions of aldehydes (Schiff and Wittig reactions) are correlated by different variables (σ^+ and σ^* respectively). This apparent anomaly arises from the different reaction mechanisms. In the former reaction, with aldehydes bearing an electron-donating group, the rate-determining step is the nucleophilic attack on the carbonyl carbon atom,[1,20] whilst in the latter reaction this is not the case. The rate-determining step has been shown to be the decomposition of a tetra-atomic intermediate.[21] Thus, since the reaction centre is a saturated carbon atom, the inductive effects of the heterocycles (σ^*) become predominant, as for the reaction of chloromethyl derivatives.

The greater reactivity observed for benzaldehyde in comparison with that predicted by the σ^* value for Ph can be ascribed to an additional secondary steric effect of the phenyl ring in the tetra-atomic intermediate which favours its decomposition to products. Steric effects in phenyl ring-containing systems are in fact more important than in five-membered heterocyclic compounds, as indicated well by some recent studies.[22,23]

EXPERIMENTAL

Materials.—Selenophen was synthesized by heating selenium in a current of acetylene at 450—480 °C, following the procedure of Chierici and Pappalardo,[24] b.p. 110 °C. 2-Chloromethylselenophen was obtained by action of hydrogen chloride on a solution of selenophen and formaldehyde in dichloroethane,[25] b.p. 40—42 °C at 0.15 mmHg. The product must be stored at 0 °C since it is prone to autocondensation with formation of hydrogen chloride; δ (CDCl$_3$): 4.7 (s, CH$_2$), 7.1 (m, 3- and 4-H), and 7.85 (q, 5-H).

Selenophen-2-sulphonyl chloride was prepared by the method used for the preparation of thiophen-2-sulphonyl chloride:[26] selenophen (0.1 mol) was added dropwise to a stirred solution of chlorosulphonic acid (0.25 mol) and phosphorus pentachloride (0.1 mol) at -15 °C. The mixture was poured, with caution, into crushed ice, and the organic layer was extracted with carbon tetrachloride. After dehydration and evaporation, the residue was recrystallized from light petroleum (b.p. 30—50 °C), m.p. 31 °C,[27] δ (CDCl$_3$): 7.55 (q, 4-H), 8.3 (d, 3-H), and 8.85 (d, 5-H).

Selenophen-2-carbaldehyde, selenophen-2-carboxylic acid, and ethyl selenophen-2-carboxylate were prepared by standard methods.[24] Their purity and identity were checked by g.l.c. and n.m.r. spectroscopy.

Benzoylmethylenetriphenylphosphorane (BMTPP) was synthesized according by the literature method,[28] m.p. 178—180 °C. Aniline and solvents for kinetic studies were commercially available samples, and distilled before use.

Kinetic Measurements.—The procedures for the determination of the rate constants for 2-chloromethylselenophen, selenophen-2-sulphonyl chloride, and selenophen-2-carbaldehyde were as described in our previous papers.[1-3] The acidic and alkaline hydrolyses of the ester were followed by using the methods of Timm and Hinshelwood[29] and Price and Oae,[30] respectively.

Reaction Products.—*Selenophen-2-sulphonanilide.* Sele-

nophen-2-sulphonyl chloride (1.5 g) and aniline (1.3 g) in methanol (50 ml) were kept for 4 h at room temperature. The methanol was evaporated off, and the residue was made alkaline with 40% aqueous sodium hydroxide and extracted twice with ether. The aqueous layer was acidified and the precipitate of crude selenophen-2-sulphonanilide filtered off, washed, and recrystallized from aqueous ethanol, yield 94%, m.p. 109 °C (Found: C, 41.9; H, 3.1; N, 4.9. C$_{10}$H$_9$NO$_2$SSe requires C, 42.0; H, 3.2; N, 4.9%).

N-(*Selenophen-2-ylmethyl)aniline.* 2-Chloromethylselenophen (2.4 g) and aniline (2.6 g) in acetronitrile (30 ml) were kept for 7 h at room temperature. The mixture was treated with 0.1M sodium hydroxide and extracted with ether. The extract was dried and evaporated, and the residue crystallized from light petroleum; yield 85%, m.p. 49 °C (Found: C, 55.7; H, 4.1; N, 5.8. C$_{11}$H$_{11}$NSe requires C, 55.9; H, 4.7, N, 5.9%).

N-(*Selenophen-2-ylmethylene)aniline.* This was prepared from selenophen-2-carbaldehyde and aniline in acetonitrile solution. After 72 h at room temperature the solvent was evaporated off and the residue distilled, yield 85%, b.p. 135 °C at 0.13 mmHg.[31]

1-*Benzoyl-2-(selenophen-2-yl)ethylene.* This was obtained by the reaction of selenophen-2-carbaldehyde and BMTPP in methanol at 50 °C for 24 h. Methanol was evaporated off and the residue crystallized from light petroleum, yield 75%, m.p. 56 °C.[32]

Method Calculation.—The statistical parameters which measure the 'goodness' of the correlations used (F-test, standard errors, correlation coefficient) were calculated using a CDC 7600 computer. A stepwise regression procedure was used to find the best equation.[33]

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