Nucleophilic Attacks on Carbon–Carbon Double Bonds. Part XXII.¹ Base Catalysis, Leaving Group Effects, and Solvent Effects in Several Nucleophilic Vinylic Substitutions by Amines

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Displacements of the leaving groups X from 1-X-2,2-bisethoxycarbonyl-1-p-nitrophenylethylenes [6; X = CI, $OSO_2Me(OMs)$, $OSO_2C_6H_4Me-p(OTs)$, $OSO_2C_6H_4Br-p(OBs)$] by piperidine and morpholine in MeCN, tetrahydrofuran (THF), and EtOH and by benzenethiolate ions in EtOH are of the second order (rate constant kobs). Reactions of anilines with 1-chloro- (and 1-bromo-)2.2-dicyano-1-p-nitrophenylethylenes (7) show very mild catalysis by the amine, while the reactions of 1-chloro- (and 1-bromo-)2-cyano-2-methoxycarbonylethylenes (9) with p-cyanoaniline, and of other electrophilic olefins with piperidine and morpholine show no catalysis. The reactivity ratios of the leaving groups in system (6) are: $k_{\rm OMs}/k_{\rm Cl} = 10.4-59.7$; $k_{\rm OTs}/k_{\rm Cl} = 10.6-29.9$; $k_{\rm OBs}/k_{\rm OTs} = 1.56-2.85$, and for systems (7) and (9) $k_{\rm Br}/k_{\rm Cl} = 0.67-1.32$. For most systems the solvent effect on the reactivity is MeCN > THF > EtOH. It is suggested that a zwitterion is formed by the nucleophilic attack (k_1) of the amine on the electrophilic olefin. This is followed either by a reversal of this step (k_{-1}) , or by expulsion of X⁻ (k_2), or by deprotonation of the zwitterion by another amine molecule (k_3). In the catalysed reaction of system (7) $k_3/k_2 = 0.69-6.55$, for system (9) k_1 is rate determining, while for system (6) $k_{obs} = k_1k_2k_{-1}$. The leaving group effect is mainly attributed to k_2 and an early transition state is suggested for this step. The solvent effect is due to the change of the dielectric constant and to the formation of intra- and inter-molecular hydrogen bonds

IN nucleophilic vinylic substitution of the additionelimination type $(Ad_N-E)^{2,3}$ the nucleophilic attack is usually rate determining, and the observed second-order kinetics cannot distinguish between concerted one-

¹ Part XXI, Z. Rappoport and S. Hoz, J.C.S. Perkin II, 1975, 272.

 Z. Rappoport, Adv. Phys. Org. Chem., 1969, 7, 1.
 G. Modena, Accounts Chem. Res., 1971, 4, 73.
 (a) L. Maioli, G. Modena, and P. E. Todesco, Bull. sci. Fac. (a) E. Malon, G. Modena, and F. E. Housso, Built St. Pat. Chim. ind. Bologna, 1960, **18**, 66; (b) A. Campagni, G. Modena, and P. E. Todesco, Gazzetta, 1960, **90**, 694; (c) G. Modena, F. Taddei, and P. E. Todesco, Ricerca sci., 1960, **30**, 894; (d) P. Beltrame and G. Cortili, Rend. Acad. naz. Lincei, **1965**, **39**, 475; (e) P. Beltrame, P. L. Beltrame, O. Sighinolfi, and M. Simonetta,

and multi-step mechanisms. Comparison of systems carrying chloride and bromide 2-6 (and sometimes iodide) ⁶⁶ leaving groups showed that they usually have similar reactivities, arguing strongly for the multi-step

J. Chem. Soc. (B), 1967, 1103; (f) G. Marchese, F. Naso, and G. Modena, *ibid.*, 1968, 958; (g) P. Beltrame, P. L. Beltrame, and L. Bellotti, *ibid.*, 1969, 932; (h) P. Beltrame, P. L. Beltrame, G. Carboni, and M. L. Cereda, *ibid.*, 1970, 730; (i) L. I. Kostenko, A. F. Popov, L. M. Litvinenko, and I. I. Tormosin, *Zhur. Org. Within*, 1972, Khim., 1974, 10, 774.

⁵ Z. Rappoport and A. Topol, J.C.S. Perhin II, 1972, 1823.
 ⁶ (a) J. Biongne, F. Théron, and R. Vessière, Bull. Soc. chim.
 France, 1972, 2882; (b) J.-C. Chalchat, F. Théron, and R. Vessière, *ibid.*, 1973, 2501; (c) J.-C. Chalchat and F. Théron, *ibid.*, p. 3361.

nature of the reaction. Consequently, changes in the leaving group X give in most cases information concerning the effect of X on the electrophilicity of the C=C bond, rather than on the relative ' leaving ' ability.

We recently found that the reaction of amines with electrophilic olefins carrying sluggish leaving groups, such as F,^{7,8} CN,^{9,10} EtO,⁹ and CF₃CH₂O¹¹ involves both a first-order and a second-order term in the amine. The appearance of this 'amine catalysis,' *i.e.*, the secondorder term in the amine, was taken as evidence for the Scheme, where the initially formed zwitterion (1) is involved in two competing routes: (i) expulsion of $X^{-}(k_{2})$ via (2), and (ii) deprotonation of the ammonium ion



residue $(k_3[Amine])$ via (3). The second-order rate coefficient for formation of product (4) $k_{obs} = (d[(4)]/dt)/dt$ [Substrate][Amine], is given by equation (1), according to the Scheme. If the $k_2/(k_3[\text{Amine}])$ ratio is very high (or very low) the reaction is first order (or second order)

$$k_{\text{obs}} = k_1(k_2 + k_3[\text{Amine}])/(k_{-1} + k_2 + k_3[\text{Amine}])$$
 (1)

in the amine, as observed.⁷⁻¹¹ If the ratio is neither too high, nor too low, both first- and second-order terms in the amine are observed.^{7,9-11} Thus, a deviation from overall second-order kinetics indicates that expulsion of X from (1) is slow in comparison with the deprotonation of (1).

Amine catalysis with a good leaving group was found only for the substitution of 2-chloro-1,1-dicyano-2-pdimethylaminophenylethylene (5) by aromatic amines in acetonitrile.^{7a} In our opinion, this is a strong indication



for a multi-step mechanism for 'good' leaving groups. However, neither the literature on other vinylic substitutions by amines,^{2,3} nor our previous search for other

- ⁷ Z. Rappoport and R. Ta-Shma, J. Chem. Soc. (B), 1971 (a), 871; (b) 1461. ⁸ Z. Rappoport and N. Ronen, J.C.S. Perkin II, 1972, 955.

J.C.S. Perkin II

examples,¹ showed evidence for catalysis in reactions of structurally related compounds.

We now extend our work to systems related to (5) by changing the α - and β -substituents, the nucleophile, the leaving group, and the solvent. Our aim is two-fold: (i) to try to find another example(s) of amine (base)catalysis in order to understand what made compound (5) unique in this respect and (ii) following previous work,⁵ to see whether such changes which affect k_{-1} , k_2 , and k_3 may distinguish between the two variants of the Scheme which give second-order kinetics, *i.e.*, that when $k_2 + k_3$ [Amine] $\gg k_{-1}$, and k_{obs} is given by equation (2), and that when $k_{-1} \gg k_2 + k_3$ [Amine], and k_{obs} is given by equation (3).

$$k_{\rm obs} = k_1 \tag{2}$$

$$k_{\rm obs} = k_1 k_2 / k_{-1} \tag{3}$$

RESULTS

Reaction of Nucleophiles with Electrophilic Ethylenes.—The reactions of morpholine and piperidine with 1-chloro-2,2bisethoxycarbonyl-1-p-nitrophenylethylene (6; X = Cl) and its 1-mesylate (6; X = OMs), 1-tosylate (6; X = OTs) and 1-p-bromobenzenesulphonate [brosylate (6; X = OBs)] analogues in acetonitrile, tetrahydrofuran (THF), and ethanol [equation (4)] and the reactions of p-chloro- and pmethylbenzenethiolate ions with the same substrates in EtOH were followed spectrophotometrically at the $\lambda_{max.}$ of the products. The reactions of aniline and p-chloroaniline with 1-chloro-2,2-dicyano-1-p-nitrophenylethylene (7; X = Cl) and its 1-bromo-analogue (7; X = Br) in acetonitrile and in THF [equation (5)], and the reactions of piperidine

$$\begin{array}{c} \rho - O_2 N C_6 H_4 \\ X \\ C O_2 E t \\ (6) \end{array} + N u \xrightarrow{\rho - O_2 N C_6 H_4} C = C \\ N u \\ C O_2 E t \\ N u \\ C O_2 E t \end{array} + X^{-(4)}$$

Nu = piperidine, morpholine, $p - ClC_6H_2S^2$, $p - MeC_6H_2S^2$ X = CI. OMs. OTs. OBs

$$x = CI. Br; Y = H, CI$$

$$p = O_2 NC_6 H_4 C = C + p = YC_6 H_4 NH_2 \xrightarrow{p = O_2 NC_6 H_4} C = C + HX (5)$$

$$x = CI. Br; Y = H, CI$$

$$Ph = NO_2 + D NU = D + C = C + HX (5)$$

$$\begin{array}{c} \text{FI} \\ \text{Cl} \\ \text{Cl} \\ \text{(8)} \end{array} + R_2 \text{NH} \longrightarrow \begin{array}{c} \text{Cl} \\ \text{R}_2 \text{N} \end{array} + HC1 \quad (6)$$

R₂NH = piperidine, morpholine

in methanol and of morpholine in acetonitrile with (E)-1chloro-2-nitro-1,2-diphenylethylene [equation (6)] were followed similarly. The nucleophile concentrations were sufficiently high to ensure pseudo-first-order kinetics, and they were usually changed 3-20 fold, using 3-8 different concentrations. The reproducibility was high, except for

- ⁹ Z. Rappoport and P. Peled, J.C.S. Perkin II, 1973, 616. ¹⁰ Z. Rappoport and D. Ladkani, J.C.S. Perkin II, 1973, 1045.
- ¹¹ Z. Rappoport and P. Peled, unpublished results.

TABLE 1 Second-order rate coefficients for the reaction of p-O₂NC₆H₄CX:CY₂ with nucleophiles

						-				A Ct
										(303 K)
				o			$10^{2}k_{2}/l \text{ mol}^{-1} \text{ s}^{-1}$		$\Delta H^{\ddagger}/$	cal
x۰	Y	Solvent	Nucleophile	Concentration/ M	n ^b	22°		40°	mol ⁻¹	Mol 1 K-1 d
OMs	CO.Et	MeCN	Morpholine	0.04 - 0.32	8		1.36 + 0.02	1.98 ± 0.06	6·4	-45.8
01110	002201		Piperidine	0.0038 - 0.024	7		$21{\cdot}0 \stackrel{-}{\pm} 0{\cdot}3$	$27 \cdot 1 \stackrel{-}{\pm} 0 \cdot 1$	4.1	-48.0
		$\mathbf{T}\mathbf{H}\mathbf{F}$	Morpholine	0.047 - 0.48	5		0.517 ± 0.009	0.787 ± 0.017	7.3	-45.0
			Piperidine	0.007 - 0.064	5		$4.56 \stackrel{-}{\pm} 0.09$	$6 \cdot 39 \stackrel{-}{\pm} 0 \cdot 21$	5.8	- 45.8
		EtOH	Morpholine	0.076 - 0.69	5		0.385 ± 0.011	0.715 ± 0.032	11-1	$-33 \cdot 2$
			Piperidine	0.025 - 0.074	6		8.6 ± 0.5	$17\cdot 3 \stackrel{-}{\pm} 0\cdot 07$	12.6	-22.0
			p-ClC _s H _s S−	0.0003 - 0.003	4	65 ± 3	144.0 ± 12		17.01	-1·8 J
OTs	CO.Et	THF	Morpholine	0.047 - 0.48	5		0.543 ± 0.005	0.737 ± 0.025	$5 \cdot 2$	-51.0
	-		Piperidine	0.007 - 0.064	5		4.94 ± 0.17	6.56 ± 0.16	4.7	-49.0
		EtOH	Morpholine	0.16 - 0.48	5		0.487 ± 0.012	0.774 ± 0.030	8.1	-42.3
			Piperidine	0.01 - 0.09	6		$2 \cdot 69 \pm 0 \cdot 011$	4.73 ± 0.07	10.0	-32.8
			<i>p</i> -MeC _s H₄S [−]	0.001 - 0.004	5	132 ± 10	195 ± 7		8.11	- 30.7 1
			p-ClC ₆ H ₄ S−	0.001 - 0.0036	5	99 ± 17	136 ± 15		6·4 1	-36.71
OBs	CO_2Et	\mathbf{THF}	Morpholine	0.042 - 0.483	7		$1 \cdot 22 \pm 0 \cdot 04$	1.70 ± 0.02	5.6	-48.7
	-		Piperidine	0.0042 - 0.084	8		10.8 ± 0.2	14.9 ± 0.4	5.4	-45.0
		EtOH	Morpholine	0.08 - 0.54	7		0.881 ± 0.014	1.38 ± 0.3	7.8	-42.2
			Piperidine	0.01 - 0.076	6		5.94 ± 0.09	9.65 ± 0.20	8.5	-36.0
			p-MeC ₆ H ₄ S−	0.0005 - 0.003	3	317 ± 12	438 ± 3		6.6	34.0
			p-ClC ₆ H₄S−	0.001 - 0.003	3	283 ± 33	379 ± 5		5.9	-36.6
Cl	CO ₂ Et	MeCN	Morpholine	0.15 - 1.19	7		0.0711 ± 0.0014	0.114 ± 0.002	$8 \cdot 3$	-45.6
			Piperidine	0.027 - 0.29	8		1.19 ± 0.03	1.76 ± 0.05	6.8	-45.0
		\mathbf{THF}	Morpholine	0.26 - 1.12	5		0.0422	0.0683	8.5	46 • 1
							± 0.0010	± 0.0006		
			Piperidine	0.03 - 1.10	6		0.420 ± 0.010	0.617 ± 0.023	6.6	-47.6
		EtOH	Morpholine	0.18 - 1.02	5		0.0199	0.0259	4.4	-61.0
							$\pm0{\cdot}0008$ °	± 0.0006		
			Piperidine	0.08 - 0.70	7		0.155 ± 0.003	0.290 ± 0.013	11.2	-34.5
			p-MeC ₆ H ₄ S	0.001 - 0.005	5	98 ± 5	141 ± 7		7.5	33-3
			p-ClC ₆ H ₄ S ⁻	0.0011 - 0.0054	5	$46\cdot2\pm1\cdot5$	$89\cdot7\pm1\cdot5$		14.1	-12.9
Cl	CN	MeCN	$C_6H_5NH_2$	0.0036 - 0.054	7		$11\cdot3\pm0\cdot4$	14.5 ± 0.1	4.1	-49.4
			p-ClC ₆ H ₄ NH ₂	0.010 - 0.18	8		1.56 ± 0.06	$2{\cdot}03\pm0{\cdot}07$	4.4	-52.5
		THF	$C_6H_5NH_2$	0.006 - 0.049	5		$18\cdot3\pm0\cdot02$	20.6 ± 0.3	1.6	-56.6
			p-ClC ₆ H ₄ NH ₂	0.006 - 0.12	6		$2 \cdot 10 \pm 0 \cdot 04$	$2\cdot57\pm0\cdot20$	$3 \cdot 2$	-55.7
\mathbf{Br}	CN	MeCN	$C_6H_5NH_2$	0.0053 - 0.033	7		11.7 ± 0.2	15.6 ± 0.2	4.8	-47.0
			p-ClC ₆ H ₄ NH ₂	0.024 - 0.19	8		1.81 ± 0.05	$2\cdot48\pm0\cdot05$	5.3	-49.0
		\mathbf{THF}	$C_6H_5NH_2$	0.0068 - 0.0545	7		9.89 ± 0.12	$13\cdot4\pm0\cdot3$	$5 \cdot 1$	-46.3
			p-ClC ₆ H ₄ NH ₂	0.024 - 0.10	3		1.56 ± 0.06	1.97 ± 0.02	3.8	-54.4

• Substrate concentrations $(1.8-9.0) \times 10^{-4}$ M. • Number of kinetic runs at 30°. • Estimated ± 1 kcal mol⁻¹. • Estimated ± 3 cal mol⁻¹ K⁻¹. • k_{obs} Increases by 12% on a six-fold increase in [Morpholine]. • The error is higher than for the other compounds (see text).

TABLE 2

Reaction of several vinylic substrates with amines

(a) p -O ₂ NC ₆ H ₄ C(OMs)=	C(CO ₂ Et	$)_2 + morp$	pholine ir	n MeCN a							
10 ² [Morpholine]/м	$2 \cdot 02$	4.04	8.08	$12 \cdot 1$	16.2	20.2	$24 \cdot 2$	32.3			
$10^{2}k_{obs}/1 \text{ mol}^{-1} \text{ s}^{-1} \text{ at } 30^{\circ}$		1.38	1.35	1.38	1.35	1.34	1.37	1.34	1.36 ± 0	0.02 0	
$10^{2}k_{\rm obs}/{\rm l}~{\rm mol}^{-1}~{\rm s}^{-1}$ at 40°	$2 \cdot 05$	2.03	2.04	$1 \cdot 92$	1.95	1.88			1.98 ± 0	0.06 8	
(b) (Z) -PhC(Cl)=C(Ph)S	$O_2C_6H_4N$	Ie-p + pi	peridine	in MeOH	c						
10[Piperidine]/м	3.06	3.96	6.12	7.92	12.0	15.8					
$10^{6}k_{obs}/1 \text{ mol}^{-1} \text{ s}^{-1} \text{ at } 30^{\circ}$	5.59		5.94		5.65		5.73 \pm	0·14 ^{b,d}			
$10^{6}k_{\rm obs}/{\rm l}~{ m mol}^{-1}~{ m s}^{-1}$ at 45°		15.7		17.5	15.8	16.4	16·35 \pm	0.6 0			
(c) (E) -PhC(Cl)=C(NO ₂)	Ph + pi	peridine i	n MeOH	e							
10[Piperidine]/м	0.5	1.0	1.5	$2 \cdot 0$	4 ·0	4.6	6.0	9.0			
$10^{4}k_{\rm obs}/l \ {\rm mol^{-1} \ s^{-1}} \ {\rm at} \ 30^{\circ}$		4.21		4.30	4.37		4.33	4.36	4.31 ± 0	0.05 3,1	
$10^{4}k_{\rm obs}/{\rm l}~{ m mol^{-1}~s^{-1}}$ at 45°	9.95		10.6			10.5			10.35 ± 0	0-27 ه	
(d) (E) -PhC(Cl)=C(NO ₂)	Ph + m	orpholine	in MeCN	Ţ 9							
10[Morpholine]/M	0.64	0.69	1.28	1.38	2.56	2.75	3.84	5.50	5.76	16.9	
$10^{4}k_{obs}/\bar{1} \text{ mol}^{-1} \text{ s}^{-1} \text{ at } 30^{\circ}$		6.48		6.34		6.10		6.33		6.90	6·43 ± 0·21 ».»
$10^{4}k_{\rm obs}/l \ {\rm mol^{-1} \ s^{-1}}$ at 45°	11.4		11.8		13.5		$13 \cdot 2$		12.8		12·5 ± 0·8 °
(e) (E)-PhC(Cl)=CHNO	$_2 + morp$	pholine in	MeCN '								
10 ³ [Morpholine]/м	2.83	5.66	6.04	10.3	12.1	17.0	18.1	25.5	$27 \cdot 2$		
$10k_{obs}/1 \text{ mol}^{-1} \text{ s}^{-1} \text{ at } 30^{\circ}$	1.07	1.07		1.18		1.09		1.11		1.10 ± 0.00	03 0
10k _{obs} /l mol ⁻¹ s ⁻¹ at 30° j			1.08		1.02		1.03		1.04	1.04 ± 0.01	2 8

 $\overset{\bullet}{} [\text{ROMs}] = 2 - 4 \times 10^{-4} \text{M}. \quad \overset{\bullet}{} \text{Average value.} \quad \overset{\bullet}{} [\text{RCI}] = 7 \cdot 8 - 8 \cdot 3 \times 10^{-4} \text{M}. \quad \text{Measured at 331 nm}. \quad \overset{\bullet}{} \Delta H^{\ddagger} = 12 \cdot 8 \text{ kcal mol}^{-1}, \\ \Delta S^{\ddagger} = -40 \cdot 4 \text{ cal mol}^{-1} \text{ K}^{-1}. \quad \overset{\bullet}{} [\text{RCI}] = 2 \cdot 2 - 2 \cdot 4 \times 10^{-4} \text{M}. \quad \text{Measured at 408 nm}. \quad \overset{f}{} \Delta H^{\ddagger} = 10 \cdot 6 \text{ kcal mol}^{-1}, \\ \Delta S^{\ddagger} = -40 \cdot 4 \text{ cal mol}^{-1} \text{ K}^{-1}. \quad \overset{\bullet}{} [\text{RCI}] = 2 \cdot 2 - 2 \cdot 4 \times 10^{-4} \text{M}. \quad \text{Measured at 408 nm}. \quad \overset{f}{} \Delta H^{\ddagger} = 10 \cdot 6 \text{ kcal mol}^{-1}, \\ \Delta S^{\ddagger} = -39 \text{ cal mol}^{-1} \text{K}^{-1}. \quad \overset{f}{} [\text{RCI}] = 1 \cdot 1 \times 10^{-4} \text{M}. \quad \text{Measured at 405 nm}. \quad \overset{h}{} \Delta H^{\ddagger} = 7 \cdot 9 \text{ kcal mol}^{-1}, \\ \Delta S^{\ddagger} = -47 \text{ cal mol}^{-1} \text{ K}^{-1}. \quad \overset{f}{} [\text{RCI}] = 1 \cdot 1 \times 10^{-4} \text{M}. \\ \text{Measured at 356 nm}. \quad \overset{f}{} \text{Reaction of } (E) - \text{PhC}(\text{CI}) = \text{CDNO}_2.$

the fast reactions of the thiolate anions, although even in these cases a reproducibility of $\pm 5\%$ was obtained for each set of reactions, using the same stock solution of the nucleophile and the same batch of solvent. This may result from competing reaction with traces of ethoxide ion, since the solution of the thiolate anion was prepared from the thiol and ethoxide ions. The reactions were always of the second order, first order in both the substrate and the nucleophile, with no evidence for catalysis by the amine. The average rate coefficients for ca. 400 kinetic runs for systems (6) and (7), and the derived activation parameters are summarised in Table 1. The data for the reaction of p-MeC₆H₄S⁻ with

CO2Me group (since Tobey gives no definite value for CO₂Me¹²) for calculating the positions of the vinylic protons. The following values were obtained for each pair of isomers: (E)-(9; X = Cl), $\delta 8.00$; (Z)-(9; X = Cl), $\delta 7.63$; (E)-(9; X = Br), δ 7.97; (Z)-(9; X = Br), δ 7.60. Hence, (9; X = Cl and Br) are probably the *E*-isomers. The appearance of two methoxy signals (in the ratio 5:6) for the product p-cyanoaniline enamine (cf. Table 10) suggests that it consists of approximately equal amounts of the E- and Zisomers. The data are given in Table 3, which shows that the activation enthalpies are relatively low and the activation entropies are highly negative.

	TABLE 3									
Reaction	of p-c	vanoaniline	with	HCX=C	(CN)CO.	Mea				

x				$10^4 k_{\rm obs} / 1$	mol ⁻¹ s ⁻¹	A HIII	A St (202 K)/
	Solvent	10 ³ [Amine]/м	n ^b	<u>30°</u>	40°	kcal mol ^{-1}	cal mol ⁻¹ K^{-1}
Cl	THF	$2 \cdot 0 - 18$	5	1.00 + 0.02	1.45 ± 0.09	6.4	-42
Cl	MeCN	0.5 - 7.9	8	1.38 ± 0.05	1.83 + 0.02	4.7	-47
Br	$\mathbf{T}\mathbf{H}\mathbf{F}$	$2 \cdot 0 - 18$	5	1.12 ± 0.09	1.60 + 0.11	6.1	-43
Br	MeCN	1.0 - 8.0	5	1.66 ± 0.03	$2 \cdot 42 \stackrel{\frown}{\pm} 0 \cdot 04$	6.2	-41

" $[RX] = (5.6-6.1) \times 10^{-5}$ M. ^b Number of amine concentrations studied.

TABLE 4

Relative reactivities	of the	$p - O_{g}$	$_{2}NC_{6}H_{4}$	CX=C($(CO_2Et)_2$	system
-----------------------	--------	-------------	-------------------	-------	--------------	--------

	In	MeCN	In l	EtOH	In J	THF	In EtOH		
x	Morpholin	e Piperidine	Morpholine	Piperidine	Morpholine	Piperidine	p-CIC,HAS-	p-MeC,H,S-	
Cl OTs	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccc} 1 \cdot 0 & 1 \cdot 0 \\ 1 & 15 \cdot 5 & 12 \cdot 8 \end{array}$	$\begin{array}{ccc} 1{\cdot}0 & 1{\cdot}0 \\ 24{\cdot}5 & 29{\cdot}9 \end{array}$	$\begin{array}{ccc} 1.0 & 1.0 \\ 17.4 & 16.3 \end{array}$	$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	
OMs OBs	$ \begin{array}{ccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccc} 19{\cdot}3 & 27{\cdot}6 \\ 44{\cdot}3 & 53{\cdot}3 \end{array}$	$55 \cdot 5 59 \cdot 7$ $38 \cdot 3 33 \cdot 3$	$\begin{array}{cccc} 12 \cdot 3 & 11 \cdot 5 \\ 28 \cdot 9 & 24 \cdot 9 \end{array}$	$\begin{array}{cccc} 10{\cdot}9 & 10{\cdot}4 \\ 25{\cdot}7 & 24{\cdot}1 \end{array}$	$ \begin{array}{rrrr} 1 \cdot 41 & 1 \cdot 61 \\ 6 \cdot 10 & 4 \cdot 20 \end{array} $	3·23 3·11	

compound (6; X = OMs), which showed higher irreproducibility, were not included. An example for the reaction of morpholine with (6; X = OMs) is given in Table 2. Table 2 also contains data for the reactions of compound (8) and of additional two activated vinyl halides [(Z)-1-chloro-2-p-methylsulphonyl-1,2-diphenylethylene and $(E)-\alpha$ chloro-\beta-nitrostyrene] with amine and anionic nucleophiles, where we searched for amine catalysis and found none. An elimination-addition mechanism^{2,3} may operate for the latter compound, and the deuterio-compound was also investigated, giving an isotope effect $k_{\rm H}/k_{\rm D}$ of 1.06.

The reactions of p-cyanoaniline with 1-bromo- and 1chloro-2-cyano-2-methoxycarbonylethylenes (9) [equation (7)] were also first order in the amine. Only one isomer of



(9) was formed from the reactions of sodium methyl hydroxymethylenecyanoacetate and phosphorus pentachloride and -bromide. The signals for the vinylic protons of (9; X = Cl and Br) are at δ 7.97 and 8.27, respectively. We applied Tobey's additivity parameters for the CN and the Br substituents,12 and that of Pascual et al.13 for the

The derived relative reactivities for system (6) are given in Table 4. An appreciable reactivity difference was observed between the sulphonate-substituted compounds on

TABLE 5

$k_{\rm Br}/k_{\rm Cl}$ Ratios for the reactions of systems (7) and (9) with anilines

			k _{Br}	$ k_{\rm Cl} $
Substrate	Solvent	Nucleophile	3 0°	40°
$p - O_2 NC_6 H_4 CX = C(CN)_2$	$\mathbf{T}\mathbf{H}\mathbf{F}$	PhNH ₂	0.74	0.77
· · · · · · ·	\mathbf{THF}	p-ClC ₆ H₄NH ₂	0.67	0.71
	MeCN	PhNH,	1.04	1.08
	MeCN	p-ClC,H ₄ NH ₂	1.16	1.22
HCX=C(CN)CO ₂ Me	\mathbf{THF}	p-NCC, H ₄ NH ₂	1.12	1.10
	MeCN	p-NCC HANH	1.20	1.32

the one hand, and the chloro-compound on the other, with two amines in three solvents. Much smaller differences are observed with the reactions of the thio-nucleophiles.

The $k_{\rm Br}/k_{\rm Cl}$ ratios for systems (7) and (9) are given in Table 5. Those for compound (7) in THF are based on extrapolated values. The ratios are close to unity for ρ -NCC₆H₄NHCH=C(CN)CO₂Me + HX (7) different substrates, solvents, nucleophiles, and temperatures. The ratios for system (6) are not available since attempts to prepare (6; X = Br) from diethyl p-nitrobenzoylmalonate and phosphorus penta- or tri-bromide failed.

 S. W. Tobey, J. Org. Chem., 1969, 34, 1281.
 C. Pascual, J. Meier, and W. Simon, Helv. Chim. Acta, 1966, 49, 164.

Table 6 summarises the solvent effect on the various reactions. In spite of the differences in the dielectric constants and the comparison of protic and aprotic solvents, the relative reactivities are only moderately sensitive to a change of solvent. The Hammett ρ values, -3.5 to -4.1, for the reaction of anilines with system (7) (which are based only

tion, although the difference in the stereochemistry of the compounds compared should be taken into account.

The reaction of (5) with amines, which previously showed catalysis in MeCN and in several alcohols 7 was studied now in THF. Table 8 shows the regular increase of k_{obs} values with the increase in the amine concentrations. When k_{obs}

TABLE 6

Solvent effect on the reactivities of morpholine (Morp) and piperidine (Pip) with the p-NO₂C₆H₄CX=C(CO₂Et)₂ (RX)

system

	ROBs				ROTs			ROMs				RCl				
	Mo	orp	Р	ip	Mo	orp	P	ip	Mo	orp	Р	ip	Mo	orp	P	ip
Solvent	30°	40°	30°	40°	30°	40°	30°	40°	30°	40°	30°	40°	3 0°	40°	30°	40°
EtOH MeCN THF	$1 \\ 2 \cdot 24 \\ 1 \cdot 38$	$1 \\ 2.07 \\ 1.23$	$1 \\ 5.39 \\ 1.82$	1 4·41 1·54	$1 \\ 2 \cdot 48 \\ 1 \cdot 11$	$1 \\ 2 \cdot 12 \\ 0 \cdot 95$	$1 \\ 6.88 \\ 1.84$	1 4∙74 1∙39	1 3∙53 1∙34	$1 \\ 2.76 \\ 1.10$	1 2∙44 0∙57	1 1∙57 0∙37	1 3∙57 2∙12	1 4∙40 2∙63	1 7·68 2·70	1 6∙07 2∙12

TABLE 7

Relative activation by α -activating groups

		entranne groupe	Relati	ve k _{obs}
Substrate	Nucleophile	Solvent	30°	45°
HCCl:C(CO ₂ Me) ₂	p-NCC ₆ H ₄ NH ₃	MeCN	1 *	
HCCl:C(CN)CO ₂ Me			77.5	
$HCCl:C(CN)_2$			983	
Z-PhCCl:C(SO ₂ C ₆ H ₄ Me- p)Ph	Piperidine	MeOH	1	1
E-PhCCl:C(NO ₂)Ph			75	63
E-PhCCl:C(NO ₂)Ph	Morpholine	MeCN	1	
E-PhCCl:CHNO ₂			171	

" Calculated by using the op relationship.

TABLE 8

Amine-catalysed reactions

	(A) p -Me ₂ NC ₆ H ₄ CCl=C(CN) ₂ + F	hNH ₂ in TH	HF •					
	10[Amine]/м	3.0	6.0	12.04	18.06	27.27		
	$10^{4}k_{\rm obs}/l \ {\rm mol^{-1} \ s^{-1}} \ {\rm at} \ 30^{\circ}$	3.11	3.22	4.83	5.70	7.11		
4	(B) p -O ₂ NC ₆ H ₄ CBr=C(CN) ₂ + p -	CIC ₆ H ₄ NH ₂	in THF ^b					
	10 ² [Amine]/м	6·14	9.21	12.30	15.40	18.40	24.60	
	$10^{2}k_{obs}/1 \text{ mol}^{-1} \text{ s}^{-1} \text{ at } 30^{\circ}$	1.44	1.47	1.53	ء 1.58	1.65	1.67	
1	(C) p -O ₂ NC ₆ H ₄ CCl=C(CN) ₂ + p -C	CIC ₆ H ₄ NH ₂ i	in THF ^d					
	10²[Amine]/м	4.04	6.10	9.10				
	$10^{2}k_{\rm obs}/l \ {\rm mol^{-1} \ s^{-1} \ at \ } 30^{\circ}$	2.58	2.78	2.99				
((D) p -O ₂ NC ₆ H ₄ CBr=C(CN) ₂ + p -	NCC ₆ H₄NH	2 in MeCN	6				
	10²[Amine]/м	5.45	8·18	10.9	21.8	28.0	42 ·0	43.6
	$10^{5}k_{\rm obs}/l \ {\rm mol^{-1} \ s^{-1}} \ {\rm at} \ 30^{\circ}$	5.05	5.10	5.95	6.75			12.8
	$10^{5}k_{\rm obs}/{ m l}~{ m mol^{-1}}~{ m s^{-1}}$ at 45°					18.1	20.9	
($E) p - O_2 NC_6 H_4 CCl = C(CN)_2 + p - 1$	NCC ₆ H ₄ NH ₂	in MeCN	•				
	10²[Amine]/м	1.62	3.24	6.48	13.0	41 ·6		
	$10^{5}k_{obs}/1 \text{ mol}^{-1} \text{ s}^{-1} \text{ at } 30^{\circ}$	6.4	7.2	9.9	11.0	12.3		

^a [RCl] = 4.5×10^{-5} M. ^b [RBr] = $1.8 - 2.9 \times 10^{-4}$ M. ^c Average of two experiments at different RBr concentrations. ^d [RCl] = 3.08×10^{-4} M. ^c [RCl] = $2.7 - 4.7 \times 10^{-4}$ M.

on the two points for aniline and p-chloroaniline), are only slightly solvent sensitive.

Table 7 summarises the data from this and the earlier paper ⁵ on the relative activation by the α -substituents in our reactions. The reactivity of (9) is between those of the α, α -dicyano- and the α, α -bismethoxycarbonyl analogues, as expected from data on nucleophilic cleavage of similarly substituted electrophilic olefins.¹⁴ As observed for other systems 1, 15 where the nitro-group is the most powerful single activating substituent in nucleophilic vinylic reactions, it is much more activating than p-methylsulphonyl in our reac-

was divided by [Amine], the third-order coefficients decreased, and hence the reaction shows both first- and second-order terms in the amine. The faster reactions of (7; X = Cl and Br) with p-chloro- and p-cyano-aniline in THF and acetonitrile show similar kinetic behaviour, although the use of lower amine concentrations resulted in a relatively smaller change in k_{obs} (Table 8).

A plot of k_{obs} against [Amine] gave approximate linear

 ¹⁴ S. Patai and Z. Rappoport, J. Chem. Soc., 1962, 392.
 ¹⁵ H. Shenhav, Z. Rappoport, and S. Patai, J. Chem. Soc. (B), 19 (1997) 1970, 469.

dependence, and the slopes, intercepts, and slope : intercept ratios (= k_3/k_2 , see Discussion section) for these 'aminecatalysed ' reactions are given in Table 9.

In an attempt to observe amine catalysis in our reactions by addition of excess of triethylamine, it was found that the amine reacts rather rapidly with (7; X = Br). The second-order k_{obs} values (2-20 l mol⁻¹ s⁻¹) decreased on increasing the amine concentrations, and these reactions were not investigated further.

Spectral Properties of the Products .-- The spectral data are summarised in Table 10. The high λ_{max} and ε values of the enamines reflect their dipolar nature. An interesting bond cleavage, as exemplified by the >500-times faster expulsion of CN^- from the dicyano-carbanion (10) than from the dinitro-carbanion (11); 17 k_3 will be less affected since Y and Z exert only inductive effects on this step and the reaction centre is more remote. A change to a

PhC(CN)₂—
$$\bar{C}$$
(CN)₂ Ph₂C(CN)— \bar{C} (NO₂)₂
(10) (11)

better leaving group with higher σ_I and σ_R ¹⁸ will reduce the possibility of observing catalysis, since k_2 will increase

	Kine	etic data for t	he amine-catalys	ed reactions at 30	°C	
Substrate	X in XC ₆ H ₄ NH ₂	Solvent	$10^4({ m Slope})/{ m l^2\ mol^{-2}\ s^{-1}}$ a	$\frac{10^4(\text{Intercept})}{1 \text{ mol}^{-1} \text{ s}^{-1} \text{ a}}$	$k_3 k_2^{-1} / l \mod^{-1} b$	r c
(5)	H	\mathbf{THF}	1.72	2.5	0.69	0.992
$(7; \mathbf{X} = \mathbf{Br})$	<i>p</i> -Cl	THF	172 ª	132 d	1.30	0.992
(7; $X = Cl$)	- <i>p</i> -C1	THF	802	227	3.53	0.996
(7: $X = Br$)	¢-CN	MeCN	2.03	0.35	5.80	0.977
(7; X = Cl)'	\hat{p} -CN	MeCN	4 ⋅06 ^{<i>d</i>}	0.62 d	6.55	0.939

TABLE 9

• Parameters of the k_{obs} against [Amine] plot.	^b Slope/intercept.	See text.	• Correlation coefficient of th	e linear regression line
^d Last point (of Table 8) was not used in the con	rrelation.			

feature of the mass spectra of the dicyanoenamines is the appearance of fragments corresponding to the loss of the HC(CN)₂ unit, as found in the spectra of related compounds.5,16

DISCUSSION

The multi-step nature of the vinylic substitution reaction can be inferred from the appearance of amine catalysis in the reaction with amines [equation (1)].⁷ In the more complicated case, when amine catalysis is absent, the kinetic order neither distinguishes between the concerted one-step mechanism, nor between the two variants of the multi-step mechanism, that when k_1 is rate determining [equation (2)] and that when k_2 is rate determining [equation (3)]. However, the rate data can sometimes distinguish between these alternatives, and we will discuss our results both in relation to this question, and the effects of structural and medium parameters on the reaction.

The Search for Base Catalysis.-Base catalysis in the reaction of amines with electrophilic olefins carrying a leaving group will be observed when in the Scheme $k_{-1} > k_3$ [Amine] + k_2 , and k_{obs} is given by equation (8),⁷ and especially when $k_2 < k_3$ [Amine]. Starting with system (5) which shows catalysis,^{7,8} we predict that

$$k_{\rm obs} = k_1 k_2 / k_{-1} + (k_1 k_3 / k_{-1}) [Amine]$$
 (8)

catalysis will be observed on using better negative chargedispersing α -substituents Y and Z or β -substituents. This change will reduce the charge on the α -carbon, and

consequently reduce k_2 and k_{-1} for the C-X and C-NR₃

more than k_3 for similar reasons. The extensive catalysis observed for sluggish leaving groups 7-11 was indeed ascribed to a low k_2 . In the present work two related questions are whether the catalysis observed for system (5) is genuine, and if so, why did we not observe catalysis for most of our other substrates.

The extent of catalysis is measured by the slope : intercept ratios of the k_{obs} against [Amine] plots which according to equation (8) are identical to the k_3/k_2 ratio of the Scheme. Ratios as low as those observed for the reaction of anilines with (5) $(k_3/k_2 = 0.08 - 0.28$ in acetonitrile) are usually not regarded as strong argument for catalysis in the analogous S_N Ar reaction.¹⁹ Our new result that the reaction of aniline with (5) in THF also shows amine catalysis with $k_3/k_2 = 0.69$, indicates that catalysis for the reactions of (5) in aprotic solvents is genuine. However, the low ratios suggest that catalysis will not be observed for electrophilic olefins which carry α - and β -substituents less electron-attracting than those in (5), even using appreciable amine concentrations.

The correlation between the pK_a values of the carbon acids CH_aX and the rates of nucleophilic reactions at R¹R²C=CHX ¹⁵ indicates that catalysis will not be observed for (Z)-1-chloro-1-p-methylsulphonyl-1,2-diphenylethylene. Comparison of systems (5) and (6) is made in the following way: judged by the data of Table 7 and that for the OH⁻-catalysed cleavage of ArCH=CYZ substrates,¹⁴ two α-CN groups are 10²-10³ more activating than two α -CO₂Et groups. From the observed and the extrapolated data for the reactions of p-cyanoaniline with compounds (5) and (7), $\rho = 1.08$ for changes in the aryl

¹⁶ Z. Rappoport and E. Shohamy, Israel J. Chem., 1968, **6**, 865. ¹⁷ S. Hoz, M. Albeck, and Z. Rappoport, *Tetrahedron Letters*, 1972, 3511; M. Albeck, S. Hoz, and Z. Rappoport, *J.C.S.* Perkin II, 1975, 628.

¹⁸ R. W. Taft and I. C. Lewis, J. Amer. Chem. Soc., 1959, **81**,

^{5343.} ¹⁹ J. F. Bunnett and R. H. Garst, J. Amer. Chem. Soc., 1965, 87, 3875.

group of $ArC(Cl)=C(CN)_2$. The combined effect of the α and the β -substituents leads therefore to a lower negative charge-dispersal ability in the reaction of (6; X = Cl) compared with (5). Even in cases of higher ρ values, as observed for the reactions of other β -aryl- α , α -dicyanoethylenes,²⁰ catalysis is not observed. Since the cleavage of the C-X bond in S_N reactions is faster when X = OTs, OBs, or OMs than when $X = Cl^{21}$ the k_3/k_2 values will be lower for (6; X = OBs, OTs or OMs) than for (6; X = Cl, resulting in the absence of catalysis for system (6). These considerations are borne out by the results of Tables 1 and 2.

The same arguments call for base catalysis in the reactions of systems (7) and (9) with amines. The reasons for its absence for system (9) are discussed below. System (7) indeed showed catalysis (Table 8), and the k_3/k_2 ratios at 30° (Table 9) are higher than those for system (5). However, compounds (7) react faster than (5) even on using lower concentrations of a less reactive amine, and k_{obs} changes less than for system (5) at the amine concentrations studied. Consequently, the scatter in the k_{obs} against [Amine] plot (cf. the r values, Table 9) is higher than for system (5) and the trend in the less accurate derived k_3/k_2 ratios as a function of the solvent and the substituent will not be discussed. Nevertheless, it should be emphasised that amine catalysis (albeit low) was demonstrated for the first time for bromide as leaving group, and again for chloride as leaving group. This should be regarded as strong evidence for the multi-step route of nucleophilic vinylic substitution by neutral nucleophiles (Scheme) even for systems which carry good leaving groups.

Effect of the Leaving Group.—The absence of catalysis for most of our systems may indicate either a ratedetermining nucleophilic attack $\{k_2 + k_3[\text{Amine}] > k_{-1};$ equation (2)}, or a very low k_3/k_2 ratio and a composite k_{obs} [equation (3)]. The second-order kinetics also fit the highly unlikely 2,22 one step (concerted) substitution.23 The change of the leaving group may distinguish these alternatives, and reactivity ratios for different halide leaving groups are frequently used for this purpose.^{4,5} However, only two cases of sulphonate leaving groups were investigated,^{5,24} and our work gives the most extensive list of the available sulphonate-halide and sulphonate-sulphonate leaving group effects (Table 4). We will discuss separately these ratios and the $k_{\rm Br}/k_{\rm Cl}$ ratios of Table 5.

²⁰ (a) S. Patai and Z. Rappoport, J. Chem. Soc., 1962, 383;
 (b) R. B. Pritchard, C. E. Lough, J. B. Reesor, H. L. Holmes, and D. J. Currie, Canad. J. Chem., 1967,45, 775; (c) E. Lord, M. P. Naan, and C. D. Hall, J. Chem. Soc. (B), 1971, 213; (d) Z. Rappoport and D. Ladkani, Chemica Scripta, 1974, 5, 124.
 ²¹ H. M. R. Hoffmann, J. Chem. Soc., 1965, (a) 6753; (b) 6762.
 ²² D. R. Kelsey and R. G. Bergman, J. Amer. Chem. Soc., 1971, 032 1953.

93, 1953.

J. Klein and R. Levene, J. Amer. Chem. Soc., 1972, 94, 2520. ²⁴ D. Cepocasale, L. Di Nunno, S. Florio, and F. Naso, J.C.S. Perkin II, 1973, 2078.

 ²⁵ R. W. Taft, jun., (a) J. Amer. Chem. Soc., 1952, 74, 2729;
 ⁵ Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, ch. 13.

J. Hine and O. B. Ramsay, J. Amer. Chem. Soc., 1962, 84, 973.

koms/kci and kots/kci Ratios.-Significant leaving group effects were found for system (6). The $k_{\text{OTs}}/k_{\text{OI}}$ ratios of 10.6–29.9 and the $k_{\rm OMs}/k_{\rm Cl}$ ratios of 10.4–59.7 are in sharp contrast to the k_{OMs}/k_{Cl} value of unity found for the substitution of 2-X-1, 1-dicyanoethylenes (12) by *p*-cyanoaniline in acetonitrile. The similarity of the σ^*

$$XCH = C(CN)_2$$

values $[\sigma^*_{CH_2Cl} \ 1.05; ^{25} \ \sigma^*_{CH_2Br} \ 1.00; ^{25}$ $\sigma^*_{\rm CH_2OTs}$ $(\sim \sigma^*_{CH_2OMs})$ 1.31²⁶], and analysis of ElcB reactions²⁷ suggest only a small difference in the electrophilicities of the β -carbons of (12; X = Cl and OMs), and the k_{OMs}/k_{Cl} ratio was therefore ascribed to a pure rate-determining bond-forming process.⁵ On the other hand, $k_{\text{OTs}}/k_{\text{Br}}$ ratios (and consequently $k_{\rm OMs}/k_{\rm Cl}$ ratios) for $S_{\rm N}1$ reactions of saturated substrates are high.^{21b, 28} Table 4 indicates therefore that k_1 is not rate determining for system (6), and that C-X bond cleavage is involved in the rate-determining step. The data also excludes an $S_{\rm N}2$ -like mechanism, since the $k_{\rm OTs}/k_{\rm Br}$ ratios for $S_{\rm N}2$ reactions at a saturated centre for the soft thio-nucleophiles are below unity, while for the amines they will be close to unity.^{21a.29} A possible stabilising $n(Br) - \pi(C=C)$ interaction which is higher than the analogous n(OTs)- π (C=C) interaction may increase this value in vinylic systems. Such interactions were considered in relation to the low $k_{\text{OTs}}/k_{\text{Br}}$ ratios observed for vinylic S_{N} solvolyses,³⁰ and it was concluded that if they are not negligible, they will reduce, rather than increase, the $k_{\rm OTs}/k_{\rm Br}$ ratios.

The remaining alternative is that $k_{-1} > k_2 \gg k_3$ [Amine]. Analysis of equation (3) gives the observed $k_{obs}(OMs)/$ $k_{obs}(Cl)$ and $k_{obs}(OTs)/k_{obs}(Cl)$ ratios for this case as the products of three ratios [equation (9)]. One approximation for the first term is unity, the value for the reaction of p-cyanoaniline with (12) (see below). Other approxim-

$$k_{\rm obs}(\rm OMs)/k_{\rm obs}(\rm Cl) = [k_1(\rm OMs)/k_1(\rm Cl)] - [k_2(\rm OMs)/k_2(\rm Cl)][k_{-1}(\rm Cl)/k_{-1} (\rm OMs)]$$
(9)

ations are our two $k_{\rm OMs}/k_{\rm Cl}$ ratios of 1.41 and 1.61 (and the $k_{\text{OTs}}/k_{\text{Cl}}$ ratios of 1.35–2.14) for the reaction of pchloro- and p-methyl-benzenethiolate ions with compounds (6), where it is unlikely that $k_{-1} > k_2$. The third term should be close to unity in the absence of steric effects, since the σ_I values of Cl (0.51) ³¹ and OMs (0.41) ³² are similar. The second term which relates to the C-X

²⁷ A. F. Cockerill, Tetrahedron Letters, 1969, 4913; J. Banger, A. F. Cockerill, and G. L. O. Davies, J. Chem. Soc. (B), 1971, 498.
 ²⁸ R. C. Bingham and P. v. R. Schleyer, J. Amer. Chem. Soc.,

1971, **93**, 3189.

²⁹ R. G. Pearson and J. Songstad, J. Org. Chem., 1967, **32**, 2899; L. B. Engemyr and J. Songstad, Acta Chem. Scand., 1972, 26,

²¹ D. E. B. B. C. B

ch. 1, p. 37. ³² Z. Rappoport and Y. Apeloig, J. Amer. Chem. Soc., 1975, 97, 825.

bond cleavage should be high as judged by the high $k_{\rm OTs}/k_{\rm Br}$ ratios (ca. 10³—10⁴) for $S_{\rm N}1$ solvolysis of neutral substrates.^{21b,28} However, while the S_N1 reaction is endothermic and Hammond's postulate 33 suggests a 'late' transition state, the C-X bond cleavage in the zwitterion (I) is probably exothermic with an 'early' transition state. Consequently, the $k_2(\text{OMs})/k_2(\text{Cl})$ and $k_2(\text{OTs})/k_2(\text{Cl})$ ratios would be much lower than those in the $S_{\rm N}l$ reaction. The $k_2({\rm OMs})/k_2({\rm Cl})$ and $k_2({\rm OTs})/k_2({\rm Cl})$ ratios are thus predicted to be appreciable, and to be by far the most important contributors to the $k_{obs}(OMs)/$ $k_{\rm obs}(\rm Cl)$ and $k_{\rm obs}(\rm OTs)/k_{\rm obs}(\rm Cl)$ ratios. The fit of the observed ratios with the prediction according to equation (3) argues strongly for the multi-step nature of the substitution reaction.

It is noteworthy that a $k_{\text{OTs}}/k_{\text{Cl}}$ ratio of 23.3 was found for the analogous S_NAr substitution of 2,4-dinitro-1-Xbenzenes by piperidine in MeOH.³⁴ A similar composite $k_{\rm obs}$ is plausible also in this case.

The 4400-fold higher reactivity of system (12; X =Cl) compared with (7; X = Cl), and the different ratedetermining step for the two systems are due to their markedly different steric and electronic effects. k_1 [system (12)] is greater than k_1 [system (7)] since steric hindrance to the approach of the nucleophile by a bulky β-substituent is well known in nucleophilic vinylic reactions.³⁵ Ground state $\pi(Ar)-\pi(C=C)$ interaction in (7) also contributes to this order. On the other hand, k_{-1}/k_2 [system (7)] will be much higher than k_2 [system (12)]. Combination of these effects gives the conditions $k_{-1} > k_2$ for system (7) and $k_2 > k_{-1}$ for system (12). Catalysis was not observed for system (12) since (i) k_{-1} is lower than in the other systems, and (ii) the high reactivity required reaction with low amine concentrations, and the condition $k_3[Amine] > k_2$ could not be achieved experimentally.

k_{Br}/k_{Cl} Ratios.—The most widely studied 'element effects '³⁴ are $k_{\rm Br}/k_{\rm Cl}$ ratios. Our twelve values for six different reactions are 0.67-1.32, reminiscent of the ratios of near unity observed for the reactions of anilines with 2-halogeno-1,1-bismethoxycarbonylethylenes 5 and for substitutions in *a*-arylsulphonyl-*β*-halogenoethylenes, $4a-c, f \alpha, \alpha$ -diaryl- β -halogenoethylenes, 4d, e, g and ethyl β -halogenoacrylates 6a and crotonates. 6b,c Since σ_I and σ_R of the halogens are similar,³¹ these element effects are cited as strong evidence for rate-determining bond formation,²⁻⁶ and ratios higher than unity are ascribed to elimination-addition,^{2,3,66} or to synchronous substitution routes.⁶⁰ This explanation which certainly applies to

reactions with nucleophiles where $k_{-1} < k_2$ (e.g., RO⁻, RS⁻, and N_3^-), probably holds also for system (9) where k_1 is assumed to be rate determining. However, the evidence for a composite k_{obs} for system (6) and for catalysis for system (7) calls for analysis of the $k_{obs}(Br)/$ $k_{\rm obs}$ (Cl) ratios by equation (10).

$$k_{\rm obs}({\rm Br})/k_{\rm obs}({\rm Cl}) = [k_1({\rm Br})/k_1({\rm Cl})] - [k_2({\rm Br})/k_2({\rm Cl})][k_{-1}({\rm Cl})/k_{-1}({\rm Br})] \quad (10)$$

From the above data the first term is *ca*. unity, so that the product of the other two terms should also be near unity. One possibility is that a $k_2(Br)/k_2(Cl)$ ratio >1 is fortuitously balanced by $k_{-1}(Cl)/k_{-1}(Br) > 1$ due to steric acceleration of $k_{-1}(Br)$. A more likely alternative is that both terms are near unity, the third term since steric effects are negligible and the electronic effects on k_{-1} are similar, and the second term since the transition state for C-X bond cleavage is early. This is expected since a low energy barrier for C-X bond cleavage in a short lived carbanion is indicated by the retention of stereochemistry in vinylic substitutions of vinyl chlorides and bromides.^{2,3} The data above for the $k_{\rm OMs}/k_{\rm Cl}$ ratios suggest that they decrease by 10^2 — 10^3 -fold when the substrate is changed from a saturated one to a zwitterion such as (1). If a similar factor applies for the $k_{\rm Br}/k_{\rm OI}$ ratios, the $k_2(Br)/k_2(Cl)$ ratio will be near unity, since the $k_{\rm Br}/k_{\rm Cl}$ ratios in $S_{\rm N}1$ reactions are below 100.^{28,36} This analysis suggests that our $k_{\rm obs}({\rm Br})/k_{\rm obs}({\rm Cl})$ ratios do not contradict a composite k_{obs} . However, it raises the question of the scope and of the usefulness of these ratios as mechanistic criteria.³⁷

 k_{OBs}/k_{OTs} and k_{OTs}/k_{OMs} Ratios.—The k_{OBs}/k_{OTs} values for the two amines (1.56-2.3) correspond to Hammett ρ values of 0.53—0.90 for arenesulphonate leaving groups, and are appreciably lower than the ratios of ca. 3 for solvolysis of saturated and vinylic systems.³⁸ We commented earlier that low $k_{\rm OBs}/k_{\rm OTs}$ ratios fit a rate determining nucleophilic attack.⁵ For reasons similar to those discussed above, $k_2(OBs)/k_2(OTs)$ is ca. 1, and the ratios cannot distinguish between equations (2) and (3) That the $k_1(OBs)/k_1(OTs)$ ratios are the main contributors to the observed values is shown by the ratios of 2.25-2.85 (p 0.89-1.14) found for rate-determining nucleophilic attack by the thio-nucleophiles (Table 4).

The $k_{\text{OTs}}/k_{\text{OMs}}$ ratios (excluding that with piperidine in EtOH) are similar to those found for saturated solvolyses.39

Activation Parameters.—The very low activation energies in several nucleophilic vinylic substitutions by

³⁸ S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, J. Amer. Chem. Soc., 1956, **78**, 328; Z. Rappoport and J. Kaspi, *ibid.*, 1970, **92**, 3220; J.C.S. Perkin II, 1972, 1102.

³³ G. S. Hammond, J. Amer. Chem. Soc., 1955, 77, 334.
³⁴ J. F. Bunnett, E. W. Garbisch, jun., and K. M. Pruitt, J. Amer. Chem. Soc., 1957, 79, 385.
³⁵ S. Patai and Z. Rappoport in 'The Chemistry of Alkenes,' ed. S. Patai, Wiley, New York, 1964, ch. 8.
³⁶ (a) E. D. Hughes and U. G. Shapiro, J. Chem. Soc., 1937, 1177; K. A. Copper and E. D. Hughes, *ibid.*, p. 1183; (b) A. H. Fainberg and S. Winstein, J. Amer. Chem. Soc., 1957, 79, 1608; (c) P. v. R. Schleyer and R. D. Nicholas, *ibid.*, 1961, 83, 2700; (d) Z. Rappoport and A. Gal, *ibid.*, 1969, 91, 5246; J. Org. Chem., 1972, 37, 1174. 1972, **37,** 1174.

³⁷ B. Lamm and J. Lammert, Acta Chem. Scand., 1973, 27, 191.

 ³⁹ (a) D. S. Noyce, B. E. Johnston, and B. Weinstein, J. Org. Chem., 1969, 34, 463; (b) F. J. Choupek and G. Zweifel, *ibid.*, 1964, 29, 2092; (c) R. M. deSousa and R. M. Moriarty, *ibid.*, 1965, 30, 1509; J. F. Biellman and G. Ourisson, Bull. Soc. chim. France, 1962, 341; (d) K. T. Leffek, R. E. Heppolette, and R. E.
 Robertson, Canad. J. Chem., 1966, 44, 677; R. E. Robertson,
 Progr. Phys. Org. Chem., 1967, 4, 213; (e) R. S. Bly and R.
 Veazey, J. Amer. Chem. Soc., 1969, 91, 4221; (f) R. S. Bly, R. C.
 Strickland, R. T. Swindell, and R. L. Veazey, *ibid.*, 1970, 92, 3722

amines,^{1,5,7,40} were used previously as a support for a rate constant according to equation (3). Although the ΔH^{\ddagger} values for systems (7) (Table 1) are indeed lower than those for the more activated system (9) (Table 3), the differences are too small to serve as a useful mechanistic criterion. The low ΔH^{\ddagger} values are expected for the combination of reactive nucleophiles and substrates, and the highly negative ΔS^{\ddagger} values are due to the formation of a dipolar transition state from neutral precursors. There is a trend for a lower ΔH^{\ddagger} and higher $-\Delta S^{\ddagger}$ for system (7) compared with (6). The trend in the solvent effect on these parameters is discussed below. The relatively high error in the activation parameters for the thio-nucleophiles prevents comparison with the values for the reactions of the amines.

Effect of the Nucleophile and the a-Activating Group.-The relative reactivities of piperidine and morpholine which differ in basicity but not in their steric requirements, are nearly constant for systems (6) in a given solvent. The decrease of the k(piperidine)/k(morpholine) ratio from 15 ± 2 in MeCN, to 9 ± 1 in THF and to 7 ± 2 (6; X = OMs excluded) in EtOH probably reflects a differential solvent effect on the ground states and the transition states as discussed below. These values, and the ' ρ ' values of -3.5 to -4.1 for the two anilines indicate the formation of a substantial charge on the nitrogen in the transition state. If we disregard the different rate-determining step, the selectivity-reactivity principle predicts a lower ρ value for the highly reactive thiolates, as indeed observed. These ' ρ ' values for the two thiolate ions are much lower than those observed for other nucleophilic vinylic reactions of benzenethiolate ions,⁴¹ and the transition state in this reaction is achieved very early.

Table 7 contains information on the activation by one or two α -substituents in the substitution reaction. The reactivity order α -CN, α -CN > α -CN, α -CO₂R > α -CO₂R, α -CO₂R finds precedents in other nucleophilic vinylic reactions.^{14,42} The replacement of the first CO₂R group by cyano is more effective than the replacement of the second, which shows some 'saturation' effect. The correlation expected between $pK_a(CH_2YZ)$ and the activation of the $\beta\text{-carbon}$ by Y and Z suggest that the approximate pK_a value reported for ethyl cyanoacetate (<9)⁴³ is too low, and that the value should be between those of malononitrile and diethyl malonate, i.e., ca. 12.2

Bearing in mind that k_{obs} may be given by equation (3), α -nitro was found to be a highly activating group, as expected.¹⁵ The 171-fold rate reduction caused by replacing α -H by α -Ph in the nitro-activated systems showed that the lower ground state energy due to the $\pi(C=C)-\pi(Ph)$ conjugation and the steric hindrance to the nucleophilic attack are more important than the relief of cis-interactions which accompany the $sp^2 \longrightarrow sp^3$ reaction, and the negative charge dispersal by α -Ph.

Solvent Effects.—The solvent effects in the reaction of the amines are moderate: a change from EtOH to THF results mostly in a 2-fold rate increase, and the change from THF to MeCN results in a 1.6-4.3-fold rate increase (Table 6). These small effects cannot distinguish between k_1 and $k_1 k_2 / k_{-1}$, since both k_1 and k_2 should increase with the increase in the dielectric constant ε . The small change from THF to MeCN is in the expected direction, but the low relative rate in EtOH, which has precedents [e.g., in the reaction of piperidine with p- $ClC_6H_4NO_2$, k(MeCN)/k(EtOH) = 10],⁴⁴ cannot be due to a change in ε alone and is explained by hydrogen bond formation. Intermolecular ethanol-amine hydrogen bonds reduce the ground state energy in comparison to that in the aprotic solvents. On the other hand, the transition state is strongly solvated by intramolecular hydrogen bonds [cf. (13)] as found for enamino-malonates.^{5,45} Consequently, the reaction in ethanol is the slowest. The higher ΔH^{\ddagger} and the less negative ΔS^{\ddagger}



values in EtOH compared with those in THF and MeCN support this explanation, since the energy-consuming rupture of the intermolecular hydrogen bond is accompanied by an entropy increase due to the 'defreezing' of a solvent molecule in forming the transition state.

When the geometry of the system makes intramolecular hydrogen bonding less favourable, the polar transition state would be stabilised by intermolecular hydrogen bonds, and probably more so with the less polar amine. An example is the reaction of compound (5) with ptoluidine where the relative k_{obs} are: MeCN (1.0), Bu^tOH (7.8), $Pr^{i}OH$ (16), MeOH (56),⁷ and by interpolation, EtOH (ca. 30). The inability of the linear cyanogroups in (5) to participate effectively in intramolecular hydrogen bonding increases the k(EtOH)/k(MeCN) ratio ca. 100-fold over the value for system (6). The smaller $k_{\rm obs}({\rm MeCN})/k_{\rm obs}({\rm THF})$ ratio for system (9) than for system (7) may indicate the contribution of the solvent change on the charge-separation step k_2 .

EXPERIMENTAL

M.p.s are uncorrected. U.v. spectra were measured with a Perkin-Elmer 450 spectrophotometer, i.r. spectra with a Perkin-Elmer 337 spectrophotometer, mass spectra with a MAT 311 instrument, and n.m.r. spectra with Varian T-60

- 75, 2439.
 ⁴⁴ H. Suhr, Chem. Ber., 1964, 97, 3277; N. B. Chapman, R. E.
 ⁴⁵ H. Suhr, Chem. Soc. 1954, 2109. Parker, and P. W. Soanes, J. Chem. Soc., 1954, 2109.
 ⁴⁵ Y. Shvo and I. Belsky, Tetrahedron, 1969, 25, 4649.

⁴⁰ Z. Rappoport, P. Greenzaid, and A. Horowitz, J. Chem. Soc., 1964, 1334.

 ⁴¹ (a) P. De Maria and A. Fini, J. Chem. Soc. (B), 1971, 2335;
 (b) D. Semenow-Garwood, J. Org. Chem., 1972, 37, 3797.
 ⁴² C. E. Lough, D. J. Currie, and H. L. Holmes, Canad. J.

Chem., 1968, 46, 771.

⁴³ R. G. Pearson and R. L. Dillon, J. Amer. Chem. Soc., 1953,

instrument; signal positions are given in δ units downfield from tetramethylsilane.

Solvents .--- Acetonitrile (Baker Analysed) was dried for one day over $CaCl_2$ and then refluxed for 5 h over P_2O_5 , distilled through a fractionating column, and the middle fraction, b.p. 78.5° , was used. THF (Frutarom) was kept for 24 h over CaCl₂, then chromatographed over alumina, refluxed for 3 h over a dispersion of sodium, then 2 h over lithium aluminum hydride, distilled, and the fraction with b.p. 67° was used. Ethanol (Frutarom), b.p. 78°, and methanol (Frutarom), b.p. 65°, were dried according to ref. 46.

(Z)-1-Chloro-2-p-methylsulphonyl-1,2-di-Materials. phenylethylene, m.p. 153-154° (lit.,47 153.5-154.5°), δ (CDCl₃) 2·40 (3H, s, Me), 6·99-7·97 (10H, m, Ph), and 7·18, 7.26, 7.66, and 7.74 (4H, AA'BB' q, Ar) was prepared according to Amiel,⁴⁷ and (E)- α -chloro- β -nitrostyrene, m.p. $50-52^{\circ}$, and (E)-1-chloro-2-nitro-1,2-diphenylethylene, m.p. 144°, were prepared according to Iwai et al.48

Triethylammonium 2,2-Dicyano-1-p-nitrophenylethen-1olate .- This compound was prepared by the alleged Libis' method for preparing '2,2-dicyano-1-p-nitrophenylethen-1-ol.' 49 Malononitrile (33 g, 0.5 mol) and p-nitrobenzoyl chloride (93 g, 0.5 mol) were dissolved in dry benzene (1000 ml), and triethylamine (101 g, 1 mol) was added with cooling. The triethylamine hydrochloride formed was filtered off. The filtrate contained an upper benzene layer and an oily red layer. The latter was crystallised twice from n-butanol-light petroleum, giving the enolate (142 g 90%), m.p. 126° (lit. for the 'enol,' 49 124°) (Found: C, 60.7; H, 6·4; N, 17·55. $C_{16}H_{20}N_4O_3$ requires C, 60·7; H, 6·4; N, 17·75%), $\lambda_{max.}$ (MeCN) 261·4 nm (ϵ 14,100), $\nu_{max.}$ (KBr) 3600s, 3450, 2205, 2190s (C=N), 1640m (C=C), 1610m, 1523, and 1515s (NO₂) cm⁻¹, δ (CDCl₃) 2·11 (9H, t, Me), 3·95 (6H, q, CH₂), and 8.46 and 8.65 (4H, AA'BB' q, J 8 Hz, Ar).

1-Chloro-2,2-dicyano-1-p-nitrophenylethylene.-Phosphorus pentachloride (3.4 g, 16.2 mmol) was added slowly to a stirred solution of the above enolate (5 g, $16 \cdot 2 \text{ mmol}$) in dry methylene chloride (150 ml). The mixture was refluxed with stirring for 5 h, the solvent was removed in vacuo, and the dark residue was extracted with ether $(4 \times 50 \text{ ml})$ and dried (Na_2SO_4) . The ether was removed in vacuo, and the crude solid was recrystallised from chloroform-carbon tetrachloride to give pale yellow crystals of the *chloride* (4.1 g, 68%), m.p. 117° (decomp.) (Found: C, 51·45; H, 2·05; N, 17·95; Cl, 15·4. $C_{10}H_4ClN_3O_2$ requires C, 51·45; H, 1·7; N, 18.0; Cl, 15.2%), $\lambda_{max.}$ (MeCN) 244.5 (z 7600) and 289 nm (14,200), ν_{max} (KBr) 2240s (C=N), 1605w (C=C), and 1525s (NO₂) cm⁻¹, δ (CDCl₃) δ 7.85 and 8.26 (AA'BB' q, J 8 Hz), m/e 235, 233 (M, 35, 100%), 205, 203 (M - NO, 5, 18), 198 (M - Cl, 2.3), 189, 187 $(M - \text{NO}_2, 20, 63)$, 177, 175 (42, 14), 160 (14), 152 ($M - Cl - NO_2$, 95), 125 (25), and 124 (25).

1-Bromo-2,2-dicyano-1-p-nitrophenylethylene.-Phosphorus tribromide (6.55 g, 24.2 mmol) and bromine (3.9 g, $24 \cdot 2 \text{ mmol}$) were added to the above enolate (7.5 g, $24 \cdot 2$ mmol) in methylene chloride (100 ml). The mixture was refluxed for 8 h, filtered, the solvent was evaporated, and the remaining oil was extracted with ether $(3 \times 50 \text{ ml})$, and dried (Na_2SO_4) . The ether was evaporated, and the oil obtained was crystallised from carbon tetrachloride, giving pale yellow crystals of the bromide, m.p. 141 °C (decomp.) (Found: C, 42.8; H, 1.6; N, 15.0; Br, 28.8. C₁₀H₄Br₃N₃O₂ requires C, 43·15; H, 1·45; N, 15·1; Br, 28·8%), λ_{max}

⁴⁶ A. I. Vogel, 'Practical Organic Chemistry,' Longman, Green and Co., London, 1948, p. 164. ⁴⁷ Y. Amiel, J. Org. Chem., 1971, **36**, 3691.

(MeCN) 289 nm (z 14,900), $\nu_{max.}$ (KBr) 2240m (C=N), 1605w (C=C), and 1525s (NO_2) cm^{-1}, δ (CDCl_3) δ 7.47 and 8.28 (AA'BB' q, J 8 Hz), m/e 279, 277 (M, 35, 36%), 249, 247 $(M - NO, 8, 8), 233, 231 (M - NO_2, 16, 16), 221, 219 (14)$ 14), 198 (M - Br, 3), 152 $(M - Br - NO_2, 100)$ and 125 $(M - Br - NO_2 - HCN, 17).$

Diethyl 2-Methylsulphonyloxy-2-p-nitrophenylethylene-1,1dicarboxylate.—This compound was prepared by a modification of the method of Fleming and Owen.⁵⁰ Diethyl pnitrobenzoylmalonate (7.73 g, 25 mmol) was added to a stirred solution of sodium (0.58 g, 25 mmol) in ethanol (150 ml). The yellow sodium salt was filtered off and dried. To a suspension of the salt (5.5 g, 16.6 mmol) in acetonitrile (100 ml), methanesulphonic anhydride (5.5 g, 31.6 mmol) was added. The mixture was refluxed for 2 h, filtered, the solvent was evaporated, and the remaining oil was extracted with ether (100 ml), washed twice with aqueous 5% sodium hydroxide solution (100 ml) and with water (100 ml), and dried (Na_2SO_4) . The ether was evaporated and the oil was crystallised from ethanol, giving crystals (2.6 g, 40%) of the diester, m.p. 90-91° (Found: C, 46.35; H, 4.2; N, 3.9; S, 8.5. C₁₅H₁₇NO₉S requires C, 46.5; H, 4.4; N, 3.6; S, $8\cdot3\%),\,\lambda_{\rm max.}$ (MeCN) 280.5 nm (z 18,100), $\nu_{\rm max.}$ (KBr) 1720s (CO₂Et), 1635m (C=C), 1595w, and 1620s (NO₂) cm⁻¹, δ (CDCl₃) 1.17 and 1.35 (6H, 2t, J 7.0 Hz, 2 Me), 3.20 (3H, s, Me), $4 \cdot 10$ and $4 \cdot 31$ (4H, 2 centres of q, J $7 \cdot 0$ Hz, CH₂), and 7.90 [4H, AA'BB' q (8 HA 7.58, 8 HB 8.15) J 8.5 Hz, Ar], m/e 387 (M, 21%), 342 (M - OEt, 26), 314 (M - CO₂Et, 15), 264 ($MH - SO_2Me - OEt$, 70), 263 (M - OEt -SO₂Me, 59), 241 (M = 2CO₂Et, 13), 219 (60), 191 (47), 151 (50), 150 (p-O₂NC₆H₄CO⁺, 100), and 120 (OC₆H₄CO⁺, 38).

Diethyl 2-Chloro-2-p-nitrophenylethylene-1,1-dicarboxylate. -Diethyl 2-p-bromophenylsulphenyloxy-2-p-nitrophenylethylene-1,1-dicarboxylate (2.5 g, 4.5 mmol) and dry lithium chloride (0.25 g, 13.5 mmol) in t-butanol (100 ml) were refluxed for 24 h. The mixture was filtered, the solvent was evaporated, the remainder was extracted with ether (100 ml), washed with aqueous 5% NaOH solution (100 ml), dried (MgSO₄), the ether was evaporated, and the remaining liquid was chromatographed using silica gel (50 g) as absorbant and benzene as eluant. The chloride (1.32 g, 95%) was obtained as crystals, m.p. 45° (Found: C, 51.65; H, 4.6; N, 6.1; Cl, 10.8. C₁₄H₁₄ClNO₆ requires C, 51.4; H, 4·3; N, 4·3; Cl, 10·8%), λ_{max} (MeCN) 272 nm (ε 11,550), ν_{max} (KBr) 1725s (CO₂Et), 1610w (C=C), and 1515s (NO₂) cm⁻¹, δ (CDCl₃) 1·07 and 1·35 (6H, 2 t, J 7 Hz, 2 Me), 4·03 and 4·30 (4H, centres of 2 q, J 7 Hz, CH₂), and 7.45 and 8.06 (2 \times 2H, AA'BB' q, J 8.5 Hz, Ar), m/e 329, 327 (M, 12, 35%), 292 (M - Cl, 60), 284 (M - OEt, 100, 32), 282, 254 (M - CL) CO_2Et , 45), 236 (30), 210 (60), and 174 (M - Cl - OEt -CO2Et, 56).

Methyl 3-Chloro-2-cyanoacrylate.—Sodium methyl hydroxymethylenecyanoacetate was prepared in quantitative yield from the reaction of ethyl formate (75 g, 1.05 mol) and methyl cyanoacetate (49.5 g, 0.5 mol) in methanol (400 ml) containing 0.5M-NaOMe (Found: C, 40.8; H, 2.9; N, 9.25. $C_{5}H_{4}NNaO_{3}$ requires C, 40.25; H, 2.7; N, 9.4%) $\delta[(CD_{3})_{2}SO]$ 3.46 and 3.50 (3H, 2s, 2 CO₂Me) and 9.28 (1H, CH). To a suspension of the salt (20 g, 140 mmol) in methylene chloride (250 ml), phosphorus pentachloride (28.4 g, 140 mmol) was added slowly, and the mixture was refluxed for

48 J. Iwai, K. Tomita, and J. Ide, Chem. Pharm. Bull. (Japan), 1965, **13**(2), 118.

- 49 F. Libis, Compt. Rend., 1963, 256, 2419.
- ⁵⁰ I. Fleming and C. R. Owen, J. Chem. Soc. (C), 1971, 2013.

2.5 h, cooled, filtered, the solvent was evaporated, and the remainder was distilled. The fraction boiling at 80° and 5 mmHg was collected (13.8 g, 70%) and was identified as the desired ester (Found: C, 41.2; H, 2.85; N, 9.85; Cl, 24.05. C₅H₄ClNO₂ requires C, 41.3; H, 2.75; N, 9.62; Cl, 24.4%), λ_{max} . (MeCN) 232 nm (ϵ 11.600), ν_{max} . (KBr)

Methyl 3-Bromo-2-cyanoacrylate.—To a suspension of sodium methyl hydroxymethylenecyanoacetate (41 g, 280 mmol) in methylene chloride (300 ml), phosphorus tribromide (74·5 g, 280 mmol) and bromine (44 g, 280 mmol) in methylene chloride (100 ml) were added slowly. The mixture was refluxed for 2 h, cooled, and poured on ice (500 g).

TABLE 10

Spectral properties of substitution products

	$\lambda_{\rm max}$ (MeCN)/nr	n		
Compo	und $(\log \varepsilon)$	$\nu_{\rm max.}({\rm KBr})/{\rm cm}^{-1}$	δ(CDCl ₃) «	m/e (% Relative intensity, assignment)
(6; $X = p$ -MeC	$2_{6}H_{4}S) = 273.5(21,400)$	^b 1725s, 1590w ^c	0.93; 1.37 (2t, Me),	415 (8, M), 367 (12), 341 (9, M - H -
			2.17 (s, Me), 4.34 (2q,	$CO_2 Et$), 246 (100, $\dot{M} - NO_2 - MeC_6H_4S$),
			CH ₂), 6·87; 7·00;	124 (35, ArSH), 123 (99, p-MeC ₆ H ₄ S ⁺), 91
		_	7·27; 7·93 (2q, Ar)	(42, tropylium ⁺)
(6; $X = p$ -ClC ₆	H_4S) 272.5 (21,500),	^b 1695s, 1605w,	0.95; 1.33 (2t, Me),	437, 435 (14, 35, M), 390 (28, M - EtO),
	$272 \cdot 5 (25,000)$	1515s ¢	$3.83; 4.25 (2q, CH_2),$	$362 (85, M - CO_2Et), 344 (31), 318 (56),$
			6.87, 7.00, 7.75 (over-	$316 (100, M - NO_2 - CO_2Et), 292 (14, 100) = 100 (100) = 100 (100)$
			lapping 2q, Ar)	$M = SC_6H_4Cl$, 192 (70), 174 (60), 168 (68),
				$100(03), 143(03, SU_6\Pi_4U^{+}), 128(09),$
7. V DENIE	() 980 (15 000)	22200 2220 22050	6.49 (c. Db) 47.17	100(100 M) 944(4 M NO) 949(99)
$(I, \mathbf{A} = \operatorname{Fund})$	338 (5500)	(C=N) 1620s 1600s	$7.39 (a Ar)^{d}$	M = HNO) 225 [13 $M = HC(CN)$]
	558 (5500)	1555 13559	, 1 00 (q, m)	179[15 M - CH(CN) - NO 1 149(45)]
		1000, 10000		$O_NC_H NH^+$ 142 (40 $M - CN -$
				C-H-NO ₃)
(7: $X = p$ -ClC _e	(H_ANH) 278 (20,400),	3300s, 2220, 2210s	6.53 (q, ArCl), ^d 7.31—	326, 324 (75, 28, M), 259 [26, M –
., 1 0	331 (7500)	(C=N), 1630, 1600s,	7.63 (m, Ar) d	$CH(CN)_{2}$, 213 [21, $M - CH(CN)_{2} - NO_{2}$],
		$1555, 1355s (NO_2)$		$176(37, M - C_6H_4NO_2 - CN), 149(100, 100)$
				$O_2NC_6H_4NH^+$), 111 (21, Ar)
(7; $X = p$ -NCC	C_6H_4NH) 274 (28,800),	3440, 3250s, 2220s	$7.00 - 7.80 \text{ (m, Ar)}^{d}$	$315 (100, M)$, 269 (12, $M - NO_2$), 250
	337 (13,700)	$(C \equiv N), 1605s$		$[25, M - CH(CN)_2], 204 [17, M - CH(CN)_2]$
		8888 8888 8800		$-NO_2$, 104 (17)
(9; $X = p$ -NCC	L_6H_4NH 323 (34,800)	32908, 3320, 33008,	2.75 (b, NH), 3.08 ,	227 (60, M), 196 (42, M - MeO), 195 (100, M) 100 (100, M)
		2220s (C=N), 1720s, 1645a 1610a	3.13, 4.6 (2S, OMe,)	$M = MeOH$, 168 (17, $M = CO_2Me$), 132 (19) 120 [07 $M = C(CO M_2)CNI$ 102 [20
		10405, 10105	7.85 (3 I 6 Hg CH)	$(18), 130[97, M - C(CO_2Me)CN], 102[39, M - C(CN)CO M_2 - HCN]$
			7.55 (d, J, 6 Hz, CH),	$M = C(CN)CO_2Me = HCN$
$C_H H_N(Ph)C=$	331 (11 200) #	3050w 1550s	1.32 (6H m B v-CH	417(21 M) 262(100 M - SO C H Me)
C(Ph)SO ₂ C ₂ H	Me-p1	50501, 10005	of piperidine) 2.27 (s	178 (72 PhC=CPh+) 91 (23 tronvlium+)
-\	41		Me). 2.53 (4H, m.	
			α -CH, of piperidino).	
			6.75 - 7.32 (m, Ar)	

• The integrations fit the assignment. ^b In EtOH. • In Nujol. ^d In $(CD_3)_2CO$. • In $(CD_3)_2SO$. The δ 3.08/3.13 ratio is 5:6. On addition of D_2O to the solvent, the δ 2.75 disappears, the CH signals give broad signal at δ 7.90, and the MeO signals are at a δ 3.20/3.17 ratio of 6:5. ^f $C_5H_{10}N =$ Piperidino. • In methanol.

TABLE 11

Analytical data for substitution products

		M p Found (%)						Requires (%)					
Substrate	Yield	(°C)	C	Н	N	S	Hal	Formula	C	н	N	S	Hal
$\operatorname{Ar}(\operatorname{SC}_{6}\operatorname{H}_{4}\operatorname{Cl}_{p})C = C(\operatorname{CO}_{2}\operatorname{Et})_{2}^{a,b}$	73	104-105	$55 \cdot 2$	$4 \cdot 2$	$3 \cdot 0$	7.55	8.1	C ₂₀ H ₁₈ ClNO ₆ S	$55 \cdot 1$	$4 \cdot 2$	$3 \cdot 2$	$7 \cdot 2$	8.15
$\operatorname{Ar}(\operatorname{SC}_{6}\operatorname{H}_{4}\operatorname{Me}_{-}p)C = C(\operatorname{CO}_{2}\operatorname{Et})_{2}^{a,b}$	85	58 - 60	61 ·0	$5 \cdot 1$	$3 \cdot 1$	7.7		C ₂₁ H ₂₁ NO ₆ S	60.7	$5 \cdot 1$	$3 \cdot 4$	7.7	
Ar(NHPh)C=C(CN) ₂ ^{a,c}	73	219 - 221	66.5	3.7	19.2			$C_{16}H_{10}N_4O_2$	66.2	3.5	19.3		
$\operatorname{Ar}(\operatorname{NHC}_{6}\operatorname{H}_{4}\operatorname{Cl}_{-}p)C=C(\operatorname{CN})_{2}^{a,c}$	91	230 - 231	58.9	$3 \cdot 0$	17.1		$11 \cdot 1$	C ₁₆ H ₉ ClN ₄ O ₂	59.2	2.7	17.2		10.9
p-NCC ₆ H ₄ NHCH=C(CN)CO ₂ Me ^c	98	209 - 211	63.1	4.1	18.8			$C_{12}H_9N_3O_2$	63.4	$4 \cdot 0$	18.5		
$Ar(NHC_6H_4CN-p)C=C(CN)_2^{\circ}$	91	244 - 245	64.6	$3 \cdot 1$	$22 \cdot 0$			$C_{17}H_9N_5O_2$	64.75	$2 \cdot 9$	$22 \cdot 2$		
$Ph(NC_5H_{10})C=C(Ph)SO_2C_6H_4Me-p^{\circ,\circ}$	² 68	155 - 156	75.2	6.7	3.7	7.85		$C_{26}H_{27}NO_2S$	75.0	6.5	3.32	7.7	

 $^{\bullet}$ Ar = p-NO₂C₆H₄. $^{\bullet}$ From the reaction of the corresponding brosylate with RS⁻-EtOH. $^{\circ}$ From the reaction of the corresponding chloride with the amine in MeCN. $^{\bullet}$ NC₅H₁₀ = Piperidino.

2240s (C=N), 1735s (CO₂Me), and 1590s (C=C) cm⁻¹, δ (CDCl₃ or C₆D₆) 3.85 (3H, s, Me) and 7.97 (1H, s, :CH). G.l.c. on a 6 ft \times $\frac{1}{4}$ in 15% SE 30 column on Chromosorb W 60–80 (injector at 220°, column at 180°, detector at 200°) gave only a single peak, m/e 147, 145 (M, 35, 100%), 132 (M – Me, 3), 117 (M – CN, 18), 114 (M – MeO, 50), and 110 (M – Cl, 17). The organic layer was rapidly decanted, washed with sodium thiosulphate (3 \times 50 ml), dried (Na₂SO₄), evaporated, and the residue was distilled. The fraction boiling at 80° and 2 mmHg (34.5 g, 65%) solidified to the desired *ester*, m.p. 41° (Found: C, 31.7; H, 2.2; N, 7.3; Br, 42.3. C₅H₄BrNO₂ requires C, 31.6; H, 2.1; N, 7.35; Br, 42.1%), $\lambda_{\text{max.}}$ (MeCN) 244.6 nm (ε 13,500), $\nu_{\text{max.}}$ (CHCl₃) 2215vw (C \equiv N),

1735s (CO₂Me), and 1580s (C=C), δ (CDCl₃) 3.80 (3H, s, MeO) and 8.27 (1H, s, CH), m/e 191, 189 (M, 44, 44%), 160, 158 (M — MeO, 100, 99), 133, 131 (MH — CO₂Me, 68, 68), 110 (M — Br, 100), and 82 (69).

Preparation of the Enamines and the Vinyl Sulphides.— Two equivalents of the amine were added to one equivalent of the vinylic substrate in dry acetonitrile until a homogeneous solution was formed, and the ammonium salt formed was filtered off after 1-2 h. The residue was either crystallised directly, or the solvent was evaporated, the remainder was dissolved in dry ether, filtered, the ether was evaporated, and the oil obtained was recrystallised from chloroform-petroleum or ethanol. Analytical and physical properties of the enamines are given in Tables 10 and 11.

The vinyl sulphides were prepared from the reaction of $1 \cdot 1$ mol. equiv. of the thiol and sodium ethoxide, and $1 \cdot 0$ mol. equiv. of (6; X = OBs) in ethanol. The solvent was evaporated, and work-up as described above for the enamines gave the solid vinyl sulphides which were crystallised from petroleum. The analytical data are also given in Tables 10 and 11. The u.v. spectra of the reaction mixtures showed that both the enamines and the vinyl sulphides were formed in quantitative yields.

Kinetic Procedure .- Stock solutions of the reactants were

prepared daily, the samples were mixed at the reaction temperature and the reaction was followed in the thermostatically-controlled chamber of a Gilford 2400S spectrophotometer. Measurements were conducted either at the $\lambda_{\max x}$ of the product or at a longer wavelength in order to avoid corrections for the absorption of the free amine.

The pseudo-first-order coefficients in the presence of excess of the amine were calculated with the aid of the KINDAT program.⁵¹ The correlation coefficients r were >0.9999. $k_{\rm obs}$ Values were obtained by dividing the first-order coefficients by the concentration of the nucleophile. $k_{\rm obs}$ Values with the thiolate ions, where the [RS⁻]/[Substrate] ratios were 2—5, were calculated by an appropriate program for a second-order rate equation. The r values were >0.999.

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⁵¹ R. C. Williams and J. W. Taylor, J. Chem. Educ., 1970, 47, 129.