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 = Cl, 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 k_{obs}). 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_{OMs}/k_{Cl} = 10·4—59·7; k_{OTs}/k_{Cl} = 10·6—29·9; k_{OBs}/k_{OTs} = 1·56—2·85, and for systems (7) and (9) k_{Br}/k_{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) $k_{obs} = k_1k_2\,k_{-1}$. 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 addition–elimination type (Ad_N–E),[2,3] the nucleophilic attack is usually rate determining, and the observed second-order kinetics cannot distinguish between concerted one- and multi-step mechanisms. Comparison of systems carrying chloride and bromide[2-6] (and sometimes iodide)[6b] leaving groups showed that they usually have similar reactivities, arguing strongly for the multi-step

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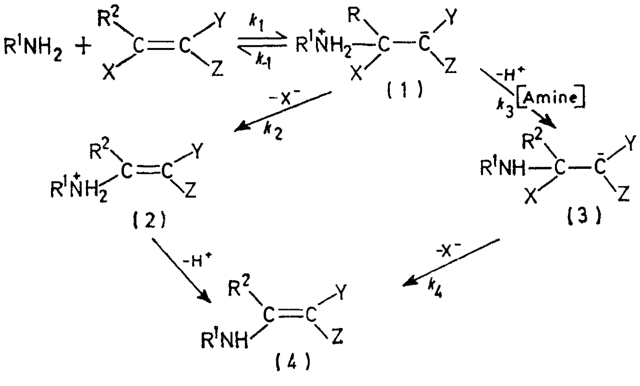
nature of the reaction. Consequently, changes in the leaving group X give in most cases information concerning the effect of X on the electrophilicity of the C=C bond, rather than on the relative ' leaving ' ability.

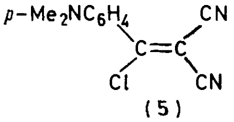
We recently found that the reaction of amines with electrophilic olefins carrying sluggish leaving groups, such as F,[7,8] CN,[9,10] EtO,[9] and CF_3CH_2O [11] involves both a first-order and a second-order term in the amine. The appearance of this ' amine catalysis,' *i.e.*, the second-order term in 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) $k_{obs} = (d[(4)]/dt)/$[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) 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).



SCHEME

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

Amine catalysis with a good leaving group was found only for the substitution of 2-chloro-1,1-dicyano-2-*p*-dimethylaminophenylethylene (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 examples,[1] showed evidence for catalysis in reactions of structurally related compounds.



(5)

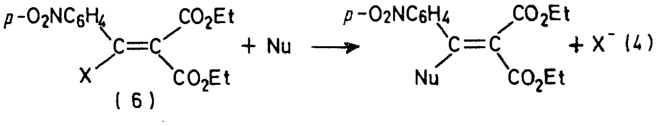
We now extend our work to systems related to (5) by changing the α- and β-substituents, the nucleophile, the leaving group, and the solvent. Our aim is two-fold: (i) to try to find another example(s) of amine (base)-catalysis in order to understand what made compound (5) unique in this respect and (ii) 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 $k_2 + k_3[\text{Amine}] \gg k_{-1}$, and k_{obs} is given by equation (2), and that when $k_{-1} \gg k_2 + k_3[\text{Amine}]$, and k_{obs} is given by equation (3).

$$k_{obs} = k_1 \quad (2)$$

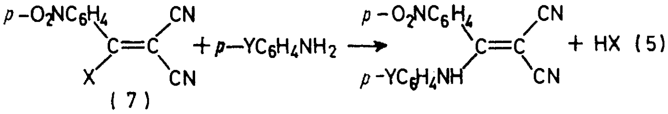
$$k_{obs} = k_1k_2/k_{-1} \quad (3)$$

RESULTS

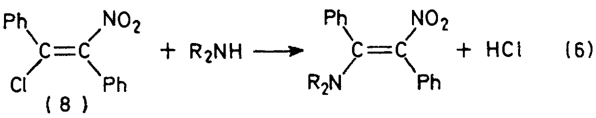
Reaction of Nucleophiles with Electrophilic Ethylenes.—The reactions of morpholine and piperidine with 1-chloro-2,2-bisethoxycarbonyl-1-*p*-nitrophenylethylene (6; X = Cl) and its 1-mesylate (6; X = OMs), 1-tosylate (6; X = OTs) and 1-*p*-bromobenzenesulphonate [brosylate (6; X = OBs)] analogues in acetonitrile, tetrahydrofuran (THF), and ethanol [equation (4)] and the reactions of *p*-chloro- and *p*-methylbenzenethiolate 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 in methanol and of morpholine in acetonitrile with (*E*)-1-chloro-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



Nu = piperidine, morpholine, $p\text{-}ClC_6H_4S^-$, $p\text{-}MeC_6H_4S^-$
X = Cl, OMs, OTs, OBs



X = Cl, Br ; Y = H, Cl



R_2NH = piperidine, morpholine

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TABLE 1

Second-order rate coefficients for the reaction of *p*-$O_2NC_6H_4CX{:}CY_2$ with nucleophiles

X [a]	Y	Solvent	Nucleophile	Concentration/M	*n* [b]	10^2k_2/l mol^{-1} s^{-1}			$\Delta H^‡$/kcal mol^{-1} [c]	$\Delta S^‡$ (303 K)/cal mol^{-1} K^{-1} [d]
						22°	30°	40°		
OMs	CO_2Et	MeCN	Morpholine	0·04—0·32	8		1·36 ± 0·02	1·98 ± 0·06	6·4	−45·8
			Piperidine	0·0038—0·024	7		21·0 ± 0·3	27·1 ± 0·1	4·1	−48·0
		THF	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 ± 0·09	6·39 ± 0·21	5·8	−45·8
		EtOH	Morpholine	0·076—0·69	5		0·385 ± 0·011	0·715 ± 0·032	11·1	−33·2
			Piperidine	0·025—0·074	6		8·6 ± 0·5	17·3 ± 0·07	12·6	−22·0
			p-$ClC_6H_4S^-$	0·0003—0·003	4	65 ± 3	144·0 ± 12		17·0 [f]	−1·8 [f]
OTs	CO_2Et	THF	Morpholine	0·047—0·48	5		0·543 ± 0·005	0·737 ± 0·025	5·2	−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		2·69 ± 0·011	4·73 ± 0·07	10·0	−32·8
			p-$MeC_6H_4S^-$	0·001—0·004	5	132 ± 10	195 ± 7		8·1 [f]	−30·7 [f]
			p-$ClC_6H_4S^-$	0·001—0·0036	5	99 ± 17	136 ± 15		6·4 [f]	−36·7 [f]
OBs	CO_2Et	THF	Morpholine	0·042—0·483	7		1·22 ± 0·04	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-$MeC_6H_4S^-$	0·0005—0·003	3	317 ± 12	438 ± 3		6·6	−34·0
			p-$ClC_6H_4S^-$	0·001—0·003	3	283 ± 33	379 ± 5		5·9	−36·6
Cl	CO_2Et	MeCN	Morpholine	0·15—1·19	7		0·0711 ± 0·0014	0·114 ± 0·002	8·3	−45·6
			Piperidine	0·027—0·29	8		1·19 ± 0·03	1·76 ± 0·05	6·8	−45·0
		THF	Morpholine	0·26—1·17	5		0·0422 ±0·0010	0·0683 ±0·0006	8·5	−46·1
			Piperidine	0·03—1·10	6		0·420 ± 0·010	0·617 ± 0·023	6·6	−47·6
		EtOH	Morpholine	0·18—1·07	5		0·0199 ±0·0008 [e]	0·0259 ±0·0006	4·4	−61·0
			Piperidine	0·08—0·70	7		0·155 ± 0·003	0·290 ± 0·013	11·2	−34·5
			p-$MeC_6H_4S^-$	0·001—0·005	5	98 ± 5	141 ± 7		7·5	−33·3
			p-$ClC_6H_4S^-$	0·0011—0·0054	5	46·2 ± 1·5	89·7 ± 1·5		14·1	−12·9
Cl	CN	MeCN	$C_6H_5NH_2$	0·0036—0·054	7		11·3 ± 0·4	14·5 ± 0·1	4·1	−49·4
			p-$ClC_6H_4NH_2$	0·010—0·18	8		1·56 ± 0·06	2·03 ± 0·07	4·4	−52·5
		THF	$C_6H_5NH_2$	0·006—0·049	5		18·3 ± 0·02	20·6 ± 0·3	1·6	−56·6
			p-$ClC_6H_4NH_2$	0·006—0·12	6		2·10 ± 0·04	2·57 ± 0·20	3·2	−55·7
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-$ClC_6H_4NH_2$	0·024—0·19	8		1·81 ± 0·05	2·48 ± 0·05	5·3	−49·0
		THF	$C_6H_5NH_2$	0·0068—0·0545	7		9·89 ± 0·12	13·4 ± 0·3	5·1	−46·3
			p-$ClC_6H_4NH_2$	0·024—0·10	3		1·56 ± 0·06	1·97 ± 0·02	3·8	−54·4

[a] Substrate concentrations (1·8—9·0) × 10^{-4}M. [b] Number of kinetic runs at 30°. [c] Estimated ±1 kcal mol^{-1}. [d] Estimated ±3 cal mol^{-1} K^{-1}. [e] k_{obs} Increases by 12% on a six-fold increase in [Morpholine]. [f] The error is higher than for the other compounds (see text).

TABLE 2

Reaction of several vinylic substrates with amines

(*a*) *p*-$O_2NC_6H_4C(OMs){=}C(CO_2Et)_2$ + morpholine in MeCN [a]

10^2[Morpholine]/M	2·02	4·04	8·08	12·1	16·2	20·2	24·2	32·3	
10^2k_{obs}/l mol^{-1} s^{-1} at 30°		1·38	1·35	1·38	1·35	1·34	1·37	1·34	1·36 ± 0·02 [b]
10^2k_{obs}/l mol^{-1} s^{-1} at 40°	2·05	2·03	2·04	1·92	1·95	1·88			1·98 ± 0·06 [b]

(*b*) (*Z*)-$PhC(Cl){=}C(Ph)SO_2C_6H_4Me$-*p* + piperidine in MeOH [c]

10[Piperidine]/M	3·06	3·96	6·12	7·92	12·0	15·8	
10^6k_{obs}/l mol^{-1} s^{-1} at 30°	5·59		5·94		5·65		5·73 ± 0·14 [b,d]
10^6k_{obs}/l mol^{-1} s^{-1} at 45°		15·7		17·5	15·8	16·4	16·35 ± 0·6 [b]

(*c*) (*E*)-$PhC(Cl){=}C(NO_2)Ph$ + piperidine in MeOH [e]

10[Piperidine]/M	0·5	1·0	1·5	2·0	4·0	4·6	6·0	9·0	
10^4k_{obs}/l mol^{-1} s^{-1} at 30°		4·21		4·30	4·37		4·33	4·36	4·31 ± 0·05 [b,f]
10^4k_{obs}/l mol^{-1} s^{-1} at 45°	9·95		10·6			10·5			10·35 ± 0·27 [b]

(*d*) (*E*)-$PhC(Cl){=}C(NO_2)Ph$ + morpholine in MeCN [g]

10[Morpholine]/M	0·64	0·69	1·28	1·38	2·56	2·75	3·84	5·50	5·76	16·9	
10^4k_{obs}/l mol^{-1} s^{-1} at 30°		6·48		6·34		6·10		6·33		6·90	6·43 ± 0·21 [b,h]
10^4k_{obs}/l mol^{-1} s^{-1} at 45°	11·4		11·8		13·5		13·2		12·8		12·5 ± 0·8 [b]

(*e*) (*E*)-$PhC(Cl){=}CHNO_2$ + morpholine in MeCN [i]

10^3[Morpholine]/M	2·83	5·66	6·04	10·3	12·1	17·0	18·1	25·5	27·2	
$10k_{obs}$/l mol^{-1} s^{-1} at 30°	1·07	1·07		1·18		1·09		1·11		1·10 ± 0·03 [b]
$10k_{obs}$/l mol^{-1} s^{-1} at 30° [j]			1·08		1·02		1·03		1·04	1·04 ± 0·2 [b]

[a] [ROMs] = 2—4 × 10^{-4}M. [b] Average value. [c] [RCl] = 7·8—8·3 × 10^{-4}M. Measured at 331 nm. [d] $\Delta H^‡$ = 12·8 kcal mol^{-1}, $\Delta S^‡$ = −40·4 cal mol^{-1} K^{-1}. [e] [RCl] = 2·2—2·4 × 10^{-4}M. Measured at 408 nm. [f] $\Delta H^‡$ = 10·6 kcal mol^{-1}, $\Delta S^‡$ = −39 cal mol^{-1} K^{-1}. [g] [RCl] = 1·1 × 10^{-4}M. Measured at 405 nm. [h] $\Delta H^‡$ = 7·9 kcal mol^{-1}, $\Delta S^‡$ = −47 cal mol^{-1} K^{-1}. [i] [RCl] = 1·1 × 10^{-4}M. Measured at 356 nm. [j] Reaction of (*E*)-$PhC(Cl){=}CDNO_2$.

the fast reactions of the thiolate anions, although even in these cases a reproducibility of ±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-MeC$_6$H$_4$S$^-$ with 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*)-α-chloro-β-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_H/k_D of 1·06.

TABLE 3

Reaction of *p*-cyanoaniline with HCX=C(CN)CO$_2$Me [a]

X	Solvent	10^3[Amine]/M	n [b]	10^4k_{obs}/l mol^{-1} s^{-1} 30°	40°	$\Delta H^‡$/ kcal mol^{-1}	$\Delta S^‡$ (303 K)/ cal mol^{-1} K^{-1}
Cl	THF	2·0—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	THF	2·0—18	5	1·12 ± 0·09	1·60 ± 0·11	6·1	−43
Br	MeCN	1·0—8·0	5	1·66 ± 0·03	2·42 ± 0·04	6·5	−41

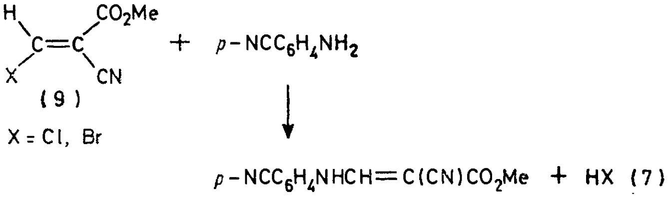
[a] [RX] = (5·6—6·1) × 10^{-5}M. [b] Number of amine concentrations studied.

TABLE 4

Relative reactivities of the *p*-O$_2$NC$_6$H$_4$CX=C(CO$_2$Et)$_2$ system

	In MeCN				In EtOH				In THF				In EtOH			
X	Morpholine		Piperidine		Morpholine		Piperidine		Morpholine		Piperidine		*p*-ClC$_6$H$_4$S$^-$		*p*-MeC$_6$H$_4$S$^-$	
Cl	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0
OTs	17·0	14·4	15·5	12·8	24·5	29·9	17·4	16·3	12·9	10·8	11·8	10·6	2·14	1·51	1·35	1·38
OMs	19·1	17·4	17·6	15·4	19·3	27·6	55·5	59·7	12·3	11·5	10·9	10·4	1·41	1·61		
OBs	27·7	25·1	26·9	24·2	44·3	53·3	38·3	33·3	28·9	24·9	25·7	24·1	6·10	4·20	3·23	3·11

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



(7)

(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 CO$_2$Me group (since Tobey gives no definite value for CO$_2$Me [12]) for calculating the positions of the vinylic protons. The following values were obtained for each pair of isomers: (*E*)-(9; X = Cl), δ 8·00; (*Z*)-(9; X = Cl), δ 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 *Z*-isomers. The data are given in Table 3, which shows that the activation enthalpies are relatively low and the activation entropies are highly negative.

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

TABLE 5

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

Substrate	Solvent	Nucleophile	k_{Br}/k_{Cl} 30°	40°
p-O$_2$NC$_6$H$_4$CX=C(CN)$_2$	THF	PhNH$_2$	0·74	0·77
	THF	*p*-ClC$_6$H$_4$NH$_2$	0·67	0·71
	MeCN	PhNH$_2$	1·04	1·08
	MeCN	*p*-ClC$_6$H$_4$NH$_2$	1·16	1·22
HCX=C(CN)CO$_2$Me	THF	*p*-NCC$_6$H$_4$NH$_2$	1·12	1·10
	MeCN	*p*-NCC$_6$H$_4$NH$_2$	1·20	1·32

The k_{Br}/k_{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 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.

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[12] S. W. Tobey, *J. Org. Chem.*, 1969, **34**, 1281.

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

TABLE 6

Solvent effect on the reactivities of morpholine (Morp) and piperidine (Pip) with the *p*-$NO_2C_6H_4CX{=}C(CO_2Et)_2$ (RX) system

	ROBs				ROTs				ROMs				RCl			
	Morp		Pip		Morp		Pip		Morp		Pip		Morp		Pip	
Solvent	30°	40°	30°	40°	30°	40°	30°	40°	30°	40°	30°	40°	30°	40°	30°	40°
EtOH	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
MeCN	2·24	2·07	5·39	4·41	2·48	2·12	6·88	4·74	3·53	2·76	2·44	1·57	3·57	4·40	7·68	6·07
THF	1·38	1·23	1·82	1·54	1·11	0·95	1·84	1·39	1·34	1·10	0·57	0·37	2·12	2·63	2·70	2·12

TABLE 7

Relative activation by α-activating groups

Substrate	Nucleophile	Solvent	Relative k_{obs} 30°	45°
$HCCl{:}C(CO_2Me)_2$	*p*-$NCC_6H_4NH_2$	MeCN	1 [a]	
$HCCl{:}C(CN)CO_2Me$			77·5	
$HCCl{:}C(CN)_2$			983	
Z-$PhCCl{:}C(SO_2C_6H_4Me$-*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	

[a] Calculated by using the σρ relationship.

TABLE 8

Amine-catalysed reactions

(A) *p*-$Me_2NC_6H_4CCl{=}C(CN)_2$ + $PhNH_2$ in THF [a]							
10[Amine]/M	3·0	6·0	12·04	18·06	27·27		
10^4k_{obs}/l mol^{-1} s^{-1} at 30°	3·11	3·22	4·83	5·70	7·11		
(B) *p*-$O_2NC_6H_4CBr{=}C(CN)_2$ + *p*-$ClC_6H_4NH_2$ in THF [b]							
10^2[Amine]/M	6·14	9·21	12·30	15·40	18·40	24·60	
10^2k_{obs}/l mol^{-1} s^{-1} at 30°	1·44	1·47	1·53	1·58 [c]	1·65	1·67	
(C) *p*-$O_2NC_6H_4CCl{=}C(CN)_2$ + *p*-$ClC_6H_4NH_2$ in THF [d]							
10^2[Amine]/M	4·04	6·10	9·10				
10^2k_{obs}/l mol^{-1} s^{-1} at 30°	2·58	2·78	2·99				
(D) *p*-$O_2NC_6H_4CBr{=}C(CN)_2$ + *p*-$NCC_6H_4NH_2$ in MeCN [b]							
10^2[Amine]/M	5·45	8·18	10·9	21·8	28·0	42·0	43·6
10^5k_{obs}/l mol^{-1} s^{-1} at 30°	5·05	5·10	5·95	6·75			12·8
10^5k_{obs}/l mol^{-1} s^{-1} at 45°					18·1	20·9	
(E) *p*-$O_2NC_6H_4CCl{=}C(CN)_2$ + *p*-$NCC_6H_4NH_2$ in MeCN [e]							
10^2[Amine]/M	1·62	3·24	6·48	13·0	41·6		
10^5k_{obs}/l mol^{-1} s^{-1} at 30°	6·4	7·2	9·9	11·0	12·3		

[a] [RCl] = 4·5 × 10^{-5}M. [b] [RBr] = 1·8—2·9 × 10^{-4}M. [c] Average of two experiments at different RBr concentrations. [d] [RCl] = 3·08 × 10^{-4}M. [e] [RCl] = 2·7—4·7 × 10^{-4}M.

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 reaction, 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} 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

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[14] S. Patai and Z. Rappoport, *J. Chem. Soc.*, 1962, 392.

[15] H. Shenhav, Z. Rappoport, and S. Patai, *J. Chem. Soc.* (*B*), 1970, 469.

dependence, and the slopes, intercepts, and slope : intercept ratios ($= k_3/k_2$, see Discussion section) for these 'amine-catalysed' 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 $\lambda_{max.}$ and ε values of the enamines reflect their dipolar nature. An interesting 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]

TABLE 9

Kinetic data for the amine-catalysed reactions at 30 °C

Substrate	X in $XC_6H_4NH_2$	Solvent	10^4(Slope)/ l^2 mol^{-2} s^{-1} [a]	10^4(Intercept)/ l mol^{-1} s^{-1} [a]	$k_3k_2^{-1}$/ l mol^{-1} [b]	r [c]
(5)	H	THF	1·72	2·5	0·69	0·992
(7; X = Br)	*p*-Cl	THF	172 [d]	132 [d]	1·30	0·992
(7; X = Cl)	*p*-Cl	THF	802	227	3·53	0·996
(7; X = Br)	*p*-CN	MeCN	2·03	0·35	5·80	0·977
(7; X = Cl)	*p*-CN	MeCN	4·06 [d]	0·62 [d]	6·55	0·939

[a] Parameters of the k_{obs} against [Amine] plot. [b] Slope/intercept. See text. [c] Correlation coefficient of the linear regression line. [d] Last point (of Table 8) was not used in the correlation.

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 $k_{-1} > k_3[\text{Amine}] + k_2$, and k_{obs} is given by equation (8),[7] and especially when $k_2 < k_3[\text{Amine}]$. Starting with system (5) which shows catalysis,[7,8] we predict that

$$k_{obs} = k_1k_2/k_{-1} + (k_1k_3/k_{-1})[\text{Amine}] \qquad (8)$$

catalysis will be observed on using better negative charge-dispersing 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 $C-\overset{+}{N}R_3$ 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

$PhC(CN)_2-\overset{-}{C}(CN)_2$ (10) $PhC(CN)-\overset{-}{C}(NO_2)_2$ (11)

better leaving group with higher σ_I and σ_R [18] will reduce the possibility of observing catalysis, since k_2 will increase 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_NAr 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_3X and the rates of nucleophilic reactions at $R^1R^2C{=}CHX$ [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 10^2—10^3 more activating than two α-CO_2Et 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

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[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_N1 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 rate-determining 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_{Br}/k_{Cl} ratios of Table 5.

k_{OMs}/k_{Cl} *and* k_{OTs}/k_{Cl} *Ratios*.—Significant leaving group effects were found for system (6). The k_{OTs}/k_{Cl} ratios of 10·6—29·9 and the k_{OMs}/k_{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* values [$\sigma^*_{CH_2Cl}$ 1·05;[25] $\sigma^*_{CH_2Br}$ 1·00;[25] $\sigma^*_{CH_2OTs}$ ($\sim\sigma^*_{CH_2OMs}$) 1·31 [26]], and analysis of *E*lcB reactions [27] 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_{OTs}/k_{Br} ratios (and consequently k_{OMs}/k_{Cl} ratios) for S_N1 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_N2-like mechanism, since the k_{OTs}/k_{Br} ratios for S_N2 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)–π(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_{OTs}/k_{Br} ratios observed for vinylic S_N1 solvolyses,[30] and it was concluded that if they are not negligible, they will reduce, rather than increase, the k_{OTs}/k_{Br} ratios.

$$XCH{=}C(CN)_2$$

(12)

The remaining alternative is that $k_{-1} > k_2 \gg k_3[\text{Amine}]$. 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 approximations are our two k_{OMs}/k_{Cl} ratios of 1·41 and 1·61 (and the k_{OTs}/k_{Cl} ratios of 1·35—2·14) for the reaction of *p*-chloro- 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

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

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[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.

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[31] O. Exner in 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum Press, London, 1972, 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_{OTs}/k_{Br} ratios (*ca.* 10^3—10^4) for S_N1 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(OMs)/k_2(Cl) and k_2(OTs)/k_2(Cl) ratios would be much lower than those in the S_N1 reaction. The k_2(OMs)/k_2(Cl) and k_2(OTs)/k_2(Cl) ratios are thus predicted to be appreciable, and to be by far the most important contributors to the k_{obs}(OMs)/k_{obs}(Cl) and k_{obs}(OTs)/k_{obs}(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_{OTs}/k_{Cl} ratio of 23·3 was found for the analogous S_NAr substitution of 2,4-dinitro-1-X-benzenes by piperidine in MeOH.[34] A similar composite k_{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 rate-determining 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 π(Ar)–π(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_{Br}/k_{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 α-arylsulphonyl-β-halogenoethylenes,[4a–c,f] α,α-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,[2,3,6b] or to synchronous substitution routes.[6b] 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_{obs}(Cl) ratios by equation (10).

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

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_{OMs}/k_{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_{Br}/k_{Cl} ratios, the k_2(Br)/k_2(Cl) ratio will be near unity, since the k_{Br}/k_{Cl} ratios in S_N1 reactions are below 100.[28,36] This analysis suggests that our k_{obs}(Br)/k_{obs}(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_{OBs}/k_{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 (ρ 0·89—1·14) found for rate-determining nucleophilic attack by the thio-nucleophiles (Table 4).

The k_{OTs}/k_{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

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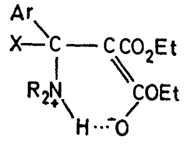
amines,[1,5,7,40] were used previously as a support for a rate constant according to equation (3). Although the $\Delta H^{\ddagger}$ values for systems (7) (Table 1) are indeed lower than those for the more activated system (9) (Table 3), the differences are too small to serve as a useful mechanistic criterion. The low $\Delta H^{\ddagger}$ values are expected for the combination of reactive nucleophiles and substrates, and the highly negative $\Delta S^{\ddagger}$ values are due to the formation of a dipolar transition state from neutral precursors. There is a trend for a lower $\Delta H^{\ddagger}$ 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 α-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-CO_2R > α-CO_2R, α-CO_2R finds precedents in other nucleophilic vinylic reactions.[14,42] The replacement of the first CO_2R 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 β-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 π(C=C)–π(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_1k_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 $\Delta H^{\ddagger}$ and the less negative $\Delta S^{\ddagger}$ 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.



(13)

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 *p*-toluidine where the relative k_{obs} are: MeCN (1·0), Bu^{t}OH (7·8), Pr^{i}OH (16), MeOH (56),[7] and by interpolation, EtOH (*ca.* 30). The inability of the linear cyano-groups 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_{obs}(MeCN)/k_{obs}(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

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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 $CaCl_2$, 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.

Materials.— (*Z*)-1-Chloro-2-*p*-methylsulphonyl-1,2-diphenylethylene, m.p. 153—154° (lit.,[47] 153·5—154·5°), δ ($CDCl_3$) 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°, 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*-1-*olate*.—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 (NO_2) cm^{-1}, δ ($CDCl_3$) 2·11 (9H, t, Me), 3·95 (6H, q, CH_2), 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, 16·2 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 × 50 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 (ε 7600) and 289 nm (14,200), $\nu_{max.}$ (KBr) 2240s (C≡N), 1605w (C=C), and 1525s (NO_2) cm^{-1}, δ ($CDCl_3$) 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* − 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, 24·2 mmol) were added to the above enolate (7·5 g, 24·2 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 × 50 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. $C_{10}H_4Br_3N_3O_2$ requires C, 43·15; H, 1·45; N, 15·1; Br, 28·8%), $\lambda_{max.}$ (MeCN) 289 nm (ε 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*-1,1-*dicarboxylate*.—This compound was prepared by a modification of the method of Fleming and Owen.[50] Diethyl *p*-nitrobenzoylmalonate (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. $C_{15}H_{17}NO_9S$ requires C, 46·5; H, 4·4; N, 3·6; S, 8·3%), $\lambda_{max.}$ (MeCN) 280·5 nm (ε 18,100), $\nu_{max.}$ (KBr) 1720s (CO_2Et), 1635m (C=C), 1595w, and 1620s (NO_2) cm^{-1}, δ ($CDCl_3$) 1·17 and 1·35 (6H, 2t, *J* 7·0 Hz, 2 Me), 3·20 (3H, s, Me), 4·10 and 4·31 (4H, 2 centres of q, *J* 7·0 Hz, CH_2), and 7·90 [4H, AA′BB′ q (δ H_A 7·58, δ H_B 8·15) *J* 8·5 Hz, Ar], *m/e* 387 (*M*, 21%), 342 (*M* − OEt, 26), 314 (*M* − CO_2Et, 15), 264 (*M*H − SO_2Me − OEt, 70), 263 (*M* − OEt − SO_2Me, 59), 241 (*M* − $2CO_2Et$, 13), 219 (60), 191 (47), 151 (50), 150 ($p\text{-}O_2NC_6H_4CO^+$, 100), and 120 ($OC_6H_4CO^+$, 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 ($MgSO_4$), 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. $C_{14}H_{14}ClNO_6$ requires C, 51·4; H, 4·3; N, 4·3; Cl, 10·8%), $\lambda_{max.}$ (MeCN) 272 nm (ε 11,550), $\nu_{max.}$ (KBr) 1725s (CO_2Et), 1610w (C=C), and 1515s (NO_2) cm^{-1}, δ ($CDCl_3$) 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, CH_2), and 7·45 and 8·06 (2 × 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* − CO_2Et, 45), 236 (30), 210 (60), and 174 (*M* − Cl − OEt − CO_2Et, 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. $C_5H_4NNaO_3$ requires C, 40·25; H, 2·7; N, 9·4%) δ [$(CD_3)_2SO$] 3·46 and 3·50 (3H, 2s, 2 CO_2Me) 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

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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. $C_5H_4ClNO_2$ requires C, 41·3; H, 2·75; N, 9·62; Cl, 24·4%), $\lambda_{max.}$ (MeCN) 232 nm (ε 11·600), $\nu_{max.}$ (KBr) 2240s (C≡N), 1735s (CO_2Me), and 1590s (C=C) cm^{-1}, δ ($CDCl_3$ or C_6D_6) 3·85 (3H, s, Me) and 7·97 (1H, s, :CH). G.l.c. on a 6 ft × ¼ 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).

TABLE 10

Spectral properties of substitution products

Compound	$\lambda_{max.}$(MeCN)/nm (log ε)	$\nu_{max.}$(KBr)/cm^{-1}	δ($CDCl_3$) [a]	*m/e* (% Relative intensity, assignment)
(6; X = *p*-MeC_6H_4S)	273·5 (21,400) [b]	1725s, 1590w [c]	0·93; 1·37 (2t, Me), 2·17 (s, Me), 4·34 (2q, CH_2), 6·87; 7·00; 7·27; 7·93 (2q, Ar)	415 (8, *M*), 367 (12), 341 (9, *M* − H − CO_2Et), 246 (100, *M* − NO_2 − MeC_6H_4S), 124 (35, ArSH), 123 (99, *p*-$MeC_6H_4S^+$), 91 (42, tropylium⁺)
(6; X = *p*-ClC_6H_4S)	272·5 (21,500),[b] 272·5 (25,000)	1695s, 1605w, 1515s [c]	0·95; 1·33 (2t, Me), 3·83; 4·25 (2q, CH_2), 6·87, 7·00, 7·75 (overlapping 2q, Ar)	437, 435 (14, 35, *M*), 390 (28, *M* − EtO), 362 (85, *M* − CO_2Et), 344 (31), 318 (56), 316 (100, *M* − NO_2 − CO_2Et), 292 (14, *M* − SC_6H_4Cl), 192 (70), 174 (60), 168 (68), 150 (63), 143 (63, $SC_6H_4Cl^+$), 128 (59), 108 (58)
(7; X = PhNH)	280 (15,900), 338 (5500)	3320s, 2220, 2205s (C≡N), 1620s, 1600s, 1555, 1355s	6·42 (s, Ph),[d] 7·17—7·39 (q, Ar) [d]	290 (100, *M*), 244 (4, *M* − NO_2), 243 (23, *M* − HNO_2), 225 [13, *M* − $HC(CN)_2$], 179 [15, *M* − $CH(CN)_2$ − NO_2], 149 (45, $O_2NC_6H_4NH^+$), 142 (40, *M* − CN − $C_6H_4NO_2$)
(7; X = *p*-ClC_6H_4NH)	278 (20,400), 331 (7500)	3300s, 2220, 2210s (C≡N), 1630, 1600s, 1555, 1355s (NO_2)	6·53 (q, ArCl),[d] 7·31—7·63 (m, Ar) [d]	326, 324 (75, 28, *M*), 259 [26, *M* − $CH(CN)_2$], 213 [21, *M* − $CH(CN)_2$ − NO_2], 176 (37, *M* − $C_6H_4NO_2$ − CN), 149 (100, $O_2NC_6H_4NH^+$), 111 (21, Ar)
(7; X = *p*-NCC_6H_4NH)	274 (28,800), 337 (13,700)	3440, 3250s, 2220s (C≡N), 1605s	7·00—7·80 (m, Ar) [d]	315 (100, *M*), 269 (12, *M* − NO_2), 250 [25, *M* − $CH(CN)_2$], 204 [17, *M* − $CH(CN)_2$ − NO_2], 104 (17)
(9; X = *p*-NCC_6H_4NH)	323 (34,800)	3290s, 3320, 3300s, 2225s (C≡N), 1725s, 1645s, 1610s	2·75 (b, NH), 3·08, 3·13,[d,e] (2s, OMe,) 6·73—7·12 (m, Ar), 7·85 (d, *J* 6 Hz, CH), 7·55 (d, *J* 6 Hz, CH)	227 (60, *M*), 196 (42, *M* − MeO), 195 (100, *M* − MeOH), 168 (17, *M* − CO_2Me), 132 (18), 130 [97, *M* − $C(CO_2Me)CN$], 102 [39, *M* − $C(CN)CO_2Me$ − HCN]
$C_5H_{10}N(Ph)C{=}C(Ph)SO_2C_6H_4Me$-*p* [f]	331 (11,200) [g]	3050w, 1550s	1·32 (6H, m, β, γ-CH_2 of piperidine), 2·27 (s, Me), 2·53 (4H, m, α-CH_2 of piperidino), 6·75—7·32 (m, Ar)	417 (21, *M*), 262 (100, *M* − $SO_2C_6H_4Me$), 178 (72, PhC≡CPh⁺), 91 (23, tropylium⁺)

[a] The integrations fit the assignment. [b] In EtOH. [c] In Nujol. [d] In $(CD_3)_2CO$. [e] 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. [g] In methanol.

TABLE 11

Analytical data for substitution products

			Found (%)						Requires (%)				
Substrate	Yield	M.p. (°C)	C	H	N	S	Hal	Formula	C	H	N	S	Hal
Ar(SC_6H_4Cl-*p*)C=C$(CO_2Et)_2$ [a,b]	73	104—105	55·2	4·2	3·0	7·55	8·1	$C_{20}H_{18}ClNO_6S$	55·1	4·2	3·2	7·2	8·15
Ar(SC_6H_4Me-*p*)C=C$(CO_2Et)_2$ [a,b]	85	58—60	61·0	5·1	3·1	7·7		$C_{21}H_{21}NO_6S$	60·7	5·1	3·4	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		
Ar(NHC_6H_4Cl-*p*)C=C$(CN)_2$ [a,c]	91	230—231	58·9	3·0	17·1		11·1	$C_{16}H_9ClN_4O_2$	59·2	2·7	17·2		10·9
p-NCC_6H_4NHCH=C(CN)CO_2Me [c]	98	209—211	63·1	4·1	18·8			$C_{12}H_9N_3O_2$	63·4	4·0	18·5		
Ar(NHC_6H_4CN-*p*)C=C$(CN)_2$ [c]	91	244—245	64·6	3·1	22·0			$C_{17}H_9N_5O_2$	64·75	2·9	22·2		
Ph(NC_5H_{10})C=C(Ph)$SO_2C_6H_4Me$-*p* [c,d]	68	155—156	75·2	6·7	3·7	7·85		$C_{26}H_{27}NO_2S$	75·0	6·5	3·35	7·7	

[a] Ar = *p*-$NO_2C_6H_4$. [b] From the reaction of the corresponding brosylate with RS^-–EtOH. [c] From the reaction of the corresponding chloride with the amine in MeCN. [d] NC_5H_{10} = Piperidino.

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). The organic layer was rapidly decanted, washed with sodium thiosulphate (3 × 50 ml), dried (Na_2SO_4), 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. $C_5H_4BrNO_2$ requires C, 31·6; H, 2·1; N, 7·35; Br, 42·1%), $\lambda_{max.}$ (MeCN) 244·6 nm (ε 13,500), $\nu_{max.}$ ($CHCl_3$) 2215vw (C≡N), 1735s (CO_2Me), and 1580s (C=C), δ ($CDCl_3$) 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 (*M*H − CO_2Me, 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 1·1 mol. equiv. of the thiol and sodium ethoxide, and 1·0 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 $\lambda_{max.}$ 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_{obs} Values were obtained by dividing the first-order coefficients by the concentration of the nucleophile. k_{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 >0·99.

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