Nucleophilic Attacks on Carbon–Carbon Double Bonds. Part XVI.[1] Some Relative Reactivities of the Leaving Groups (k_{Br}/k_{Cl}, k_{OMs}/k_{Cl}, and k_{OBs}/k_{OTs}) in Vinylic Substitutions

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Displacement of the halogen of 1-chloro- and 1-bromo-2,2-dimethoxycarbonylethylenes (II) and (III) by several substituted anilines in acetonitrile is of the second order; Hammett's ρ values are between $-2{\cdot}24$ and $-2{\cdot}40$ and k_{II}/k_{III} is *ca.* 1. Reaction of *p*-cyanoaniline with 1-chloro- and 1-mesyloxy-2,2-dicyanoethylenes gives $k_{OMs}/k_{Cl} = 1$. Substitution of 1-*p*-nitrophenyl-1-tosyloxy-(and 1-brosyloxy-)2,2-diethoxycarbonylethylenes by piperidine and morpholine gives $k_{OBs}/k_{OTs} = 1{\cdot}63$—$1{\cdot}90$, and k_{pip}/k_{morp} of 13·7—16·2. Two α-cyano-groups are 100-fold more activating than two α-ethoxycarbonyl groups in nucleophilic vinylic substitution. A rate-determining nucleophilic addition of amines is suggested for these reactions. The relative reactivities concerning the first step in nucleophilic vinylic substitutions of the addition–elimination type (Ad_N–E) are discussed, as well as criteria for distinguishing between the Ad_N–E and the vinylic S_N1 mechanisms.

AMONG the variety of nucleophilic vinylic substitution routes[2] the addition–elimination (Ad_N–E)[2,3] and the S_N1 mechanisms[4] are the most widely studied. We recently suggested and used several criteria for distinguishing between these two routes in the reactions of nucleophiles with 9-(α-halogenoarylidene)fluorenes.[5] One criterion was the 'element effect' k_{Br}/k_{Cl}, *i.e.*, the relative mobility of the chloride and bromide leaving groups.[6] The brosylate–tosylate (k_{OBs}/k_{OTs})[7-9] and the tosylate–bromide (k_{OTs}/k_{Br})[9b-11] reactivity ratios were used for distinguishing between the S_N1 and competing

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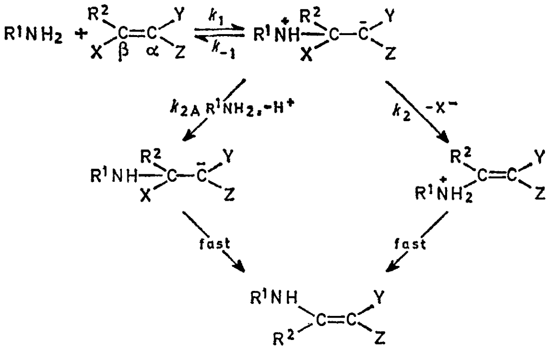
routes in both saturated and vinylic systems. Such ratios should also be useful in deciding whether bond-formation or bond-cleavage is important in the transition state of the rate-determining step of a vinylic substitution.

The Ad_N–E route is a multi-step reaction.[2] Usually, the initial nucleophilic attack is rate-determining, but with a sluggish leaving group subsequent steps also appear in the rate equation. With amines, the initial attack may be reversible.[12] The intermediate zwitterion can lose HX in a slow amine-assisted expulsion of a proton (step k_{2A}), or the C–X bond cleavage may be rate-determining (step k_2). The observed third-order coefficient for the catalysed reaction [equation (2)] or the second-order coefficient for the uncatalysed reaction [equation (3)] are both composite.[13] Both types of behaviour were recently observed in the reactions of 1,1-dicyano-2-p-dimethylaminophenyl-2-halogenoethylenes (I) with amines.[13] In acetonitrile when X = F equation (2) applies, and when X = Cl the main reaction is *via* the k_2 route with small contribution from the k_{2A} route.[13a] For such systems the activation parameters, the Hammett ρ values, and the Brønsted α values for the amine all have contributions from the various steps. Opposing substituent effects on the various steps may lead to unusual reactivity ratios for the nucleophiles and to very low and even negative activation enthalpies. The analysis of the behaviour of such systems would be helped by separate study of the substituent effects in the substrate and in the nucleophile when the nucleophilic attack is rate-determining, *i.e.*, in systems with good leaving groups.



(1)

$$k_{obs} = k_1 k_{2A}/k_{-1} \qquad (2)$$

$$k_{obs} = k_1 k_2/k_{-1} \qquad (3)$$

p-$Me_2N{\cdot}C_6H_4{\cdot}C(X)=C(CN)_2$
(I), X = F, Cl

In order to get information on these questions we studied three reactions: (*a*) The reaction of several anilines with 1-chloro- and 1-bromo-2,2-dimethoxycarbonylethylenes (II) and (III) [equation (4)]; (*b*) the reaction of 1-chloro- and 1-mesyloxy-2,2-dicyanoethylenes (IV) and (V) with p-cyanoaniline [equation (5)]; and (*c*) the reactions of 1-brosyloxy- and 1-tosyloxy-1-p-nitrophenyl-2,2-diethoxycarbonylethylenes (VI) and (VII) with piperidine and morpholine [equation (6)].

$$XCH{:}C(CO_2Me)_2 + RC_6H_4{\cdot}NH_2 \longrightarrow RC_6H_4NHCH{:}C(CO_2Me)_2 + HX \qquad (4)$$

(II) X = Cl
(III) X = Br

$$XCH{:}C(CN)_2 + p\text{-}NC{\cdot}C_6H_4{\cdot}NH_2 \longrightarrow p\text{-}NCC_6H_4{\cdot}NHCH{:}C(CN)_2 + HX \qquad (5)$$

(IV) X = Cl
(V) X = OSO_2Me (OMs)


(6)

$$p\text{-}O_2NC_6H_4{\cdot}CX{:}C(CO_2Et)_2 + Z(CH_2{\cdot}CH_2)_2NH \longrightarrow p\text{-}O_2NC_6H_4{\cdot}C[N(CH_2{\cdot}CH_2)_2Z]{:}C(CO_2Et)_2 + HX \qquad (6)$$

(VI) X = $OSO_2{\cdot}C_6H_4Me$-p (OTs)
(VII) X = $OSO_2{\cdot}C_6H_4Br$-p (OBs)
Z = O, CH_2

RESULTS

Reaction of Anilines with the Halogenoethylenes (II) *and* (III).—The chloro- and bromo-compounds (II) and (III) were prepared from the phosphorus pentahalides and the enolate of dimethyl hydroxymethylenemalonate according to equation (7). The displacement of the vinylic halogen by six anilines was followed spectrophotometrically in acetonitrile by observing the absorptions of the product enamines. The reactions were overall of the second order (with rate coefficients k_{obs}), first order each in the vinyl halide and the amine, with no apparent trend of increase in k_{obs} with the increase in the amine concentration (Table 1). The derived Hammett ρ values (Table 2) are −2·24 to −2·40 and the differences between the ρ's of compounds (II) and (III) are within the experimental error. The ρ values decrease slightly on increasing the temperature. Brønsted plots of log k_{obs} against the pK_a(H_2O) of the *para*- and the *meta*-substituted anilines are approximately linear with slopes of 0·75—0·80 (Table 2). The points for 2,6-dimethylaniline are 0·57—0·67 log unit below the Brønsted lines, *i.e.*, the amine is 3·7—4·7 times less reactive than expected by electronic effects alone. The k_{Br}/k_{Cl} ratios for all the amines are near unity with the values for 2,6-dimethylaniline being the lowest (Table 3). The

$$HC(OEt)_3 + CH_2(CO_2Me)_2 \xrightarrow{NaOMe} {}^-OCH{:}C(CO_2Me)_2 \xrightarrow{PX_5} XCH{:}C(CO_2Me)_2 \qquad (7)$$

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activation enthalpies are low and the activation entropies highly negative (Table 4). Tables 3 and 4 also summarise data derived from the k_{obs} values for the reactions described by equations (5) and (6).

TABLE 1

Reaction of anilines with XCH:C$(CO_2Me)_2$ in acetonitrile

	At 30 °C						At 40 °C			
(II), X = Cl										
p-Toluidine										
10^{3}[Amine]/M	4·0	6·0	6·0	8·0	12·0		1·0	2·0	4·0	
10^{2}[(II)]/M	1·4	0·7	1·4	1·4	1·4		1·4	1·4	1·4	
$10^{2}k_{\text{obs}}$/l mol^{-1} s^{-1}	21·3	18·5	21·5	22·8	18·8	20·5 ± 0·13 [a]	27·6	28·0	28·3	28·4 ± 0·6 [b]
m-Toluidine										
10^{3}[Amine]/M	3·75	7·5	15·0	22·5			2·5	5·0	10·0	
10^{5}[(II)]/M	7·5	7·5	3·75	7·5			6·5	4·6	6·5	
$10^{2}k_{\text{obs}}$/l mol^{-1} s^{-1}	8·90	9·22	9·15	9·90		9·27 ± 0·32 [a]	12·9	13·0	13·1	13·0 ± 0·1 [b]
Aniline										
10^{4}[Amine]/M	0·5	1·0	1·5	2·5			0·25	0·5	1·0	
10^{5}[(II)]/M	10·0	7·5	10·0	10·0			8·0	8·0	8·0	
$10^{2}k_{\text{obs}}$/l mol^{-1} s^{-1}	7·00	6·69	7·00	6·85		6·84 ± 0·17 [a]	10·6	10·5	10·4	10·4 ± 0·1 [b]
m-Anisidine										
10^{4}[Amine]/M	1·0	3·0	4·0	4·5			0·5	1·0	2·0	
10^{5}[(II)]/M	7·5	7·5	5·6	7·5			7·5	7·5	7·5	
$10^{2}k_{\text{obs}}$/l mol^{-1} s^{-1}	4·68	4·70	5·04	4·80		4·87 ± 0·20 [a]	7·45	7·39	7·45	7·41 ± 0·04 [b]
p-Bromoaniline										
10^{4}[Amine]/M	2·0	6·0	10·0				1·0	3·0	5·0	
10^{5}[(II)]/M	12·0	6·0	12·0				7·0	10·0	10·0	
$10^{2}k_{\text{obs}}$/l mol^{-1} s^{-1}	1·84	1·80	1·90			1·84 ± 0·03 [a]	2·92	2·72	2·84	2·85 ± 0·07 [b]
2,6-Dimethylaniline										
10^{3}[Amine]/M	0·5	2·0	3·0				0·4	0·8	1·6	
10^{5}[(II)]/M	5·0	2·5	5·0				4·0	2·8	4·0	
$10^{2}k_{\text{obs}}$/l mol^{-1} s^{-1}	0·650	0·605	0·647			0·631 ± 0·021 [a]	0·948	0·935	0·895	0·931 ± 0·018 [b]
(III) X = Br										
p-Toluidine										
10^{3}[Amine]/M	4·0	10·0	14·0				1·0	3·0	6·0	
10^{4}[(III)]/M	1·4	1·4	0·7				1·2	0·8	1·2	
$10^{2}k_{\text{obs}}$/l mol^{-1} s^{-1}	18·4	19·0	18·1			18·7 ± 0·4 [a]	28·4	29·6	30·2	29·4 ± 0·5 [b]
m-Toluidine										
10^{3}[Amine]/M	3·2	6·5	13·0	19·5			2·5	5·0	10·0	
10^{5}[(III)]/M	6·5	6·5	6·5	6·5			6·5	6·5	6·5	
$10^{2}k_{\text{obs}}$/l mol^{-1} s^{-1}	9·30	9·24	9·09	9·18		9·11 ± 0·11 [a]	13·9	13·5	13·5	13·4 ± 0·3 [b]
Aniline										
10^{3}[Amine]/M	5·0	10·0	25·0	30·0			2·5	5·0	10·0	
10^{5}[(III)]/M	10·0	10·0	10·0	10·0			8·0	5·0	8·0	
$10^{2}k_{\text{obs}}$/l mol^{-1} s^{-1}	7·42	7·30	7·25	7·56		7·25 ± 0·22 [a]	11·0	10·6	10·8	10·8 ± 0·2 [b]
m-Anisidine										
10^{4}[Amine]/M	1·0	2·0	4·0	4·5			0·5	1·0	2·0	
10^{5}[(III)]/M	6·0	6·0	4·2	6·0			7·8	5·2	7·8	
$10^{2}k_{\text{obs}}$/l mol^{-1} s^{-1}	4·80	4·92	4·96	4·96		4·94 ± 0·08 [a]	7·50	7·73	7·55	7·60 ± 0·07 [b]
p-Bromoaniline										
10^{4}[Amine]/M	2·0	4·0	7·0	10·0			1·0	3·0	3·0	
10^{5}[(III)]/M	10·0	7·5	10·0	10·0			10·0	7·0	10·0	
$10^{2}k_{\text{obs}}$/l mol^{-1} s^{-1}	1·89	1·92	1·96	1·92		1·93 ± 0·03 [a]	3·06	3·04	3·00	3·04 ± 0·02 [b]
2,6-Dimethylaniline										
10^{4}[Amine]/M	5·0	10·0	20·0	30·0			4·0	8·0	16·0	
10^{4}[(III)]/M	5·0	5·0	5·0	3·8			4·0	3·0	4·0	
$10^{2}k_{\text{obs}}$/l mol^{-1} s^{-1}	0·572	0·521	0·525	0·530		0·535 ± 0·013 [a]	0·865	0·842	0·838	0·849 ± 0·009 [b]

[a] Average value of 5—10 experiments. [b] Average value of 4 experiments.

Reaction of p-*Cyanoaniline with the Dicyanoethylenes* (IV) *and* (V).—Attempts to prepare mesylate or tosylate analogues of (II) from dimethyl hydroxymethylenemalonate with mesylic or tosylic anhydride or from (II) with silver tosylate or mesylate failed. However, 1-mesyloxy-2,2-dicyanoethylene (V) was prepared from 1-chloro-2,2-dicyanoethylene (IV) with silver mesylate. Amines (anilines, diethylamine, morpholine) replaced readily the chlorine of (IV) (Tables 7—8) but the reactions with most of the *meta*- and the *para*-substituted anilines were too fast to measure by the conventional spectrophotometric method. With *p*-nitroaniline the absorptions of the free amine and the product enamine were too close. However, the reaction of *p*-cyanoaniline with the dicyanoethylenes (IV) and

(V) could be followed and was found to be of the second order (Table 5). The activation parameters are in Table 4, and the mesylate–chloride reactivity ratio in Table 3.

Reaction of Piperidine and Morpholine with the Nitrophenylethylenes (VI) *and* (VII).—*p*-Bromobenzenesulphonyl chloride and toluene-*p*-sulphonic anhydride with diethyl *p*-nitrobenzoylmalonate in basic solution gave (VI) and

TABLE 2

Hammett ρ and Brønsted α values for the reaction of anilines with $XCH{:}C(CO_2Me)_2$ in acetonitrile

X	t/°C	ρ [a]	r [b]	α [a,c]	r [b]
Cl	**30**	−2·40 ± 0·2	0·987	0·80 ± 0·05	0·984
	40	−2·30 ± 0·2	0·984	0·76 ± 0·05	0·983
Br	**30**	−2·29 ± 0·2	0·985	0·76 ± 0·05	0·986
	40	−2·24 ± 0·2	0·981	0·75 ± 0·05	0·985

[a] The error quoted is the standard deviation of the slope. [b] Correlation coefficient. [c] Using the pK_a values in water.

TABLE 3

k_{Br}/k_{Cl}, k_{OBs}/k_{OTs}, and k_{OMs}/k_{Cl} ratios in vinylic substitutions of X in $RCX{:}CY_2$ by amines in acetonitrile

			Reactivity ratio at	
Amine	R	Y	30 °C	40 °C
			k_{Br}/k_{Cl}	
p-$MeC_6H_4{\cdot}NH_2$	H	CO_2Me	0·91	1·04
m-$MeC_6H_4{\cdot}NH_2$	H	CO_2Me	0·98	1·03
$PhNH_2$	H	CO_2Me	1·06	1·04
m-$MeOC_6H_4{\cdot}NH_2$	H	CO_2Me	1·01	1·02
p-$BrC_6H_4{\cdot}NH_2$	H	CO_2Me	1·05	1·07
2,6-$Me_2C_6H_4{\cdot}NH_2$	H	CO_2Me	0·85	0·91
			k_{OBs}/k_{OTs}	
Piperidine	p-$O_2N{\cdot}C_6H_4$	CO_2Et	1·73	1·90
Morpholine	p-$O_2N{\cdot}C_6H_4$	CO_2Et	1·63	1·75
			k_{OMs}/k_{Cl}	
p-$NCC_6H_4{\cdot}NH_2$	H	CN	1·00	

TABLE 4

Activation parameters for the reaction of amines with $XCR{:}CY_2$ in acetonitrile

				$\Delta H^{\ddagger}$ [a]	$\Delta S^{\ddagger}$ [b]		$\Delta H^{\ddagger}$ [a]	$\Delta S^{\ddagger}$ [b]
Amine	R	Y	X	kcal mol^{-1}	cal mol^{-1} K^{-1}	X	kcal mol^{-1}	cal mol^{-1} K^{-1}
p-$MeC_6H_4{\cdot}NH_2$	H	CO_2Me	Cl	6·0	−42	Br	7·9	−36
m-$MeC_6H_4{\cdot}NH_2$	H	CO_2Me	Cl	5·9	−44	Br	6·8	−41
$PhNH_2$	H	CO_2Me	Cl	7·3	−40	Br	6·7	−42
m-$MeOC_6H_4{\cdot}NH_2$	H	CO_2Me	Cl	7·8	−39	Br	7·4	−40
p-$BrC_6H_4{\cdot}NH_2$	H	CO_2Me	Cl	7·6	−41	Br	7·5	−42
2,6-$Me_2C_6H_3{\cdot}NH_2$	H	CO_2Me	Cl	7·0	−45	Br	8·5	−43
p-$NCC_6H_4{\cdot}NH_2$	H	CN	Cl	4·9	−41			
Morpholine	p-$O_2N{\cdot}C_6H_4$	CO_2Et	OTs	5·1	−50	OBs	6·4	−47
Piperidine	p-$O_2N{\cdot}C_6H_4$	CO_2Et	OTs	3·1	−54	OBs	4·9	−47

[a] Estimated ±0·5 kcal mol^{-1}. [b] Estimated ±2 cal mol^{-1} K^{-1}.

TABLE 5

Reaction of $XCH{:}C(CN)_2$ with p-cyanoaniline

	At 15 °C				At 30 °C				
(IV), X = Cl									
10^4[Amine]/M	4·5	9·0	18·0		4·5	9·0	22·5		
10^5[(IV)]/M	4·5	4·5	4·5		4·5	4·5	4·5		
k_{obs}/l mol^{-1} s^{-1}	1·03	1·08	1·09	1·10 ± 0·04 [a]	1·73	1·84	1·83	1·75 ± 0·06 [a]	
(V), X = OMs									
10^4[Amine]/M					4·0	8·0	8·0	14·0	
10^5[(V)]/M					4·0	2·1	4·1	4·0	
k_{obs}/l mol^{-1} s^{-1}					1·64	1·74	1·71	1·84	1·76 ± 0·09 [a]

[a] Average value of 5—7 experiments.

TABLE 6

Reaction of amines with p-$O_2NC_6H_4{\cdot}C(OSO_2{\cdot}C_6H_4{\cdot}X$-$p){:}C(CO_2Et)_2$ (VI and VII) in acetonitrile

	At 30 °C					At 40 °C			
(VI), X = Me									
10^3[Piperidine]/M	3·2	6·4	11·2			3·2	6·4	9·6	
10^4[(VI)]/M	4·0	5·6	4·0			4·0	2·8	4·0	
$10k_{obs}$/l mol^{-1} s^{-1}	1·87	2·00	1·78	1·85 ± 0·06 [a]		2·25	2·27	2·22	2·24 ± 0·02 [b]
10^2[Morpholine]/M	1·4	4·2	6·3	8·4		2·2	4·4	8·8	
10^4[(VI)]/M	3·8	3·8	2·3	3·8		4·0	4·0	4·0	
10^2k_{obs}/l mol^{-1} s^{-1}	1·16	1·28	1·20	1·09	1·21 ± 0·06 [a]	1·58	1·57	1·76	1·64 ± 0·07 [b]
(VII), X = Br									
10^3[Piperidine]/M	3·2	4·8	8·0			3·2	4·8	6·4	
10^4[(VII)]/M	4·0	2·4	4·0			4·0	2·8	4·0	
$10k_{obs}$/l mol^{-1} s^{-1}	3·06	3·12	3·19	3·20 ± 0·08 [a]		4·50	4·06	4·25	4·26 ± 0·12 [b]
10^3[Morpholine]/M	1·4	2·8	5·5	8·2		2·0	8·0	8·0	
10^4[(VII)]/M	3·3	3·3	4·4	3·3		4·0	2·8	4·0	
10^2k_{obs}/l mol^{-1} s^{-1}	1·94	1·90	1·94	2·01	1·97 ± 0·04 [a]	2·84	2·87	2·86	2·86 ± 0·02 [b]

[a] Average value of 6 experiments. [b] Average value of 4 experiments.

(VII). Surprisingly, the analogous reactions with dimethyl *p*-nitrobenzoylmalonate failed. The reactions of these esters with piperidine and morpholine in acetonitrile were of the second order (Table 6), and the derived activation parameters and the k_{OBs}/k_{OTs} ratios are in Tables 3 and 4.

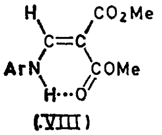
TABLE 7

Spectral data for the enamines $R^1C(NR^2R^3){:}CY_2$

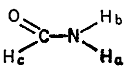
R^1	R^2	R^3	Y	$\lambda_{max.}^{MeCN}(\epsilon)$/nm	$\nu_{max.}$/cm^{-1} [a]	N.m.r. (τ values) [b] Ar	Me	CO_2R^4	:CH	NH
H [c]	*m*-$MeOC_6H_4$ [c]	H [c]	CO_2Me [c]	317 (33,400)	3200w, 1728m, 1690s, 1645s, 1610s	2·47—2·90	6·01	6·05; 6·08	1·15 [d]	[e]
H	*m*-MeC_6H_4	H	CO_2Me	315 (22,400)	3200—3260w, 1730m, 1695s, 1650s, 1615s	2·73—3·15	7·63	6·15; 6·22	1·47 [d]	[e]
H	Ph	H	CO_2Me	315 (23,900)	3240w, 1720s, 1680s, 1650s, 1610s	2·68—2·97 [f] 2·40—2·77 [g]		6·25; 6·30 [f] 6·22; 6·27 [g]	1·55 [d, f] 1·46 [g]	−1·22 [d,f] −0·81 [d, g]
H [h]	2,6-$Me_2C_6H_3$ [h]	H [h]	CO_2Me	289 (21,600)	3200w, 1725m, 1683s, 1650s, 1615m	2·95 [i] 2·82 [g]	7·72 [i] 7·65 [g]	6·13; 6·27 6·24; 6·37 [g]	1·94 [d] 2·08 [g]	−0·1 [j] −0·22 [j]
H	*p*-BrC_6H_4	H	CO_2Me	318·5 (26,600)	3200w, 1725m, 1685s, 1645s, 1610m	2·43—3·05		6·15; 6·23	1·59 [d]	−1·0 [j]
H [k]	*p*-MeC_6H_4 [k]	H [k]	CO_2Me [k]	330 (25,300)	3260w, 1710s, 1660s, 1610m	2·87—3·19	7·72	6·22; 6·29	1·63 [d]	[e]
H	*p*-$O_2NC_6H_4$	H	CN	344·5 (32,500)	3310, 3200w, 2220s,[j] 1650s, 1590s	1·70—2·40			1·30 [i]	−1·45 [i,j]
H [l]	*p*-$MeOC_6H_4$ [l]	H [l]	CN [l]	318 (22,000)	3290, 3210w, 2220s,[j] 1650s, 1590s	2·60—3·25	6·25		1·87 [i, j]	−0·78 [i, j]
H	*p*-NCC_6H_4	H	CN	320 (42,000)	3190w, 2220s,[j] 1740m, 1660s, 1600m	2·03—2·45			1·33 [d]	−1·35 [d,j]
H	*p*-ClC_6H_4	H	CN	317 (27,300)	3280, 3200w, 2220, 2200s, 1650s	2·45—2·78			1·54 [d]	−0·69 [d, j]
H [m]	*p*-MeC_6H_4 [m]	H [m]	CN [m]	288·5sh (14,000) 313 (23,600)	3300, 3230w, 2225, 2205s, 1675s	2·55—2·73	7·70		1·56 [d]	−0·05 [d,j]
H	Et	Et	CN	279·5 (20,600)	2210, 2197s, 1620v [n]		8·67 [o]		2·94 [i, o]	
H	R^2R^3 = morpholino		CN	281 (24,200)	2220s, 1630s				2·25 [i, p]	
p-$O_2NC_6H_4$	R^2R^3 = morpholino		CO_2Et	277 (20,300) 353·5 (4,300)	1740s, 1600s	1·55—2·35	8·91 [q]			
p-$O_2NC_6H_4$	R^2R^3 = piperidino		CO_2Et	282 (20,000) 366·5 (4450)	1760s, 1605w [n]	1·95—2·63	8·89 [r]			

[a] In Nujol, unless otherwise stated. [b] In $CDCl_3$ for the enaminodiesters, in $(CD_3)_2SO$ for the enaminodinitriles. Integration and multiplicity are in agreement with the assignments. [c] Mass spectrum: *m/e* 265 (83%, *M*), 233 (26, *M* − OMe − H), 232 (base peak, *M* − MeO − 2H), 205 (46, *M* − HCO_2Me), 202 (23), 174 (75, *M* − MeO − HCO_2Me), 160 (20), 146 (22), 132 (20), 107 (26), 77 (34). [d] Doublet, *J* 14 Hz. The internal line of the doublet is slightly higher than the external line. [e] Not observed. [f] In CCl_4. [g] In $(CD_3)_2SO$. [h] Mass spectrum: *m/e* 263 (57%, *M*), 233 (base peak, *M* − 2Me), 199 (23), 172 (62, *M* − MeO − HCO_2Me), 160 (23), 158 (28), 144 (61, *M* − $Me_2C_6H_3NH$), 143 (32), 142 (21), 132 (59), 131 (38), 130 (27), 117 (28), 91 (28), 77 (55). [i] Singlet. [j] Broad signal. [k] Mass spectrum: *m/e*: 249 (75%, *M*), 218 (95, *M* − MeO), 218 (base peak, *M* − MeO − H), 189 (34, *M* − HCO_2Me), 186 (23), 158 (67, *M* − HCO_2Me − MeO), 144 (23), 130 (25), 91 (36). [l] Mass spectrum: *m/e* 199 (base peak, *M*), 184 (86, *M* − Me), 158 (37), 157 (23), 134 [9, *M* − $CH(CN)_2$], 129 (17), 102 (11), 92 (7), 77 (11). [m] Mass spectrum: *m/e* 183 (base peak, *M*), 182 (38%, *M* − H), 155 (15, *M* − H − HCN), 156 (5, *M* − HCN), 119 [15, *M* − $C(CN)_2$], 107 (33), 106 (50, Me-azatropylium), 91 (22, tropylium). [n] In KBr. [o] Centres of the two methylene quartets τ 6·27 and 6·52. [p] Centre of the methylene absorption τ 6·23. [q] Centre of the methylene quartet τ 5·87; the morpholino-protons appear as two multiplets of 4H each, at τ 6·07—6·27; 6·63—6·93. [r] Centre of the methylene protons τ 5·98; the piperidino-protons appear at τ 8·32br (4H) and 6·95br (6H).

Spectral Data of the Enamines.—The high $\lambda_{max.}$ and ε values of the enamines reflect their highly dipolar nature. The blue shift observed for the 2,6-dimethylanilinoenamine is noteworthy since $\lambda_{max.}$ changes much less between the 2,6-diethyl and the 4-methyl derivatives in the *p*-$Me_2N{\cdot}C_6H_4{\cdot}C(ArNH){:}C(CN)_2$ system.[13a] There is an i.r. band for hydrogen-bonded N–H, and in most of the cyano-enamines the C≡N stretching appears as a strong doublet of bands of equal intensity 10—20 cm^{-1} apart. Splitting of the C≡N band occurs with many αα-dicyano-compounds which are substituted by electron-donating groups.[14] The band for the ethoxycarbonyl group is also a doublet (it being assumed that the band at *ca.* 1690 cm^{-1} is not a C–N bending, which appears at a lower wavelength in the cyanoenamines). The n.m.r. spectrum shows the vinylic hydrogen as a doublet in most of the systems. In the dicyanoenamines, this is clearly due to a coupling to the N–H proton which appears as a broad doublet with the same *J* value (14 Hz) at a lower field. In the *p*-nitro- and the *p*-methoxy-dicyanoenamines both the N–H and the :CH signals appear as a broad singlet. When a solution of the *p*-cyanodicyanoenamine is shaken with excess of D_2O and the spectrum is taken after 1 min, the N–H absorption at τ −1·35 disappears and the doublet for the :CH collapses to a singlet at τ 1·44. When the anilino-dimethoxycarbonylenamine in dimethyl sulphoxide is shaken with D_2O, the N–H doublet at τ −1·46 disappears and the :CH doublet at τ 0·81 changes to a broad singlet at τ 1·52. The low-field position of the N–H proton is ascribed to hydrogen bonding between the N–H proton and the α-electron-attracting group. Indeed, in the 2,6-dimethyl-anilinoenamine, where steric effects interfere with hydrogen-bond formation, the N–H proton is at a higher field. The value of *J* suggests the predominance of the conformer (VIII) in which the two hydrogens are **at** ***anti***-positions, in analogy with the coupling observed for formamide (IX) where J_{bc} = 13 Hz and J_{ac} = 2·1 Hz.[15]



(VIII)



(IX)

In the mass spectra of the dicyanoenamines the molecular peak is the base peak and fragments corresponding to the loss of Me, HCN, $CH(CN)_2$, and $C(CN)_2$ units as well as those for tropylium and substituted tropylium ions were observed. In the dimethoxycarbonylenamines the base peak usually corresponds to the fragment found after the loss of methyl or methoxyl radicals. The spectral data are in Table 7.

DISCUSSION

All three sets of reactions are of the first order in the amine. The absence of a second-order term for the amine [as found for (I) and related systems] [13,16] shows that expulsion of the leaving group is faster than the amine-catalysed proton expulsion from the zwitterionic intermediate. In terms of equation (1), $k_2 \gg k_{2A}$.

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[14] For references see Z. Rappoport and S. Gertler, *J. Chem. Soc.*, 1964, 1360.

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Since anilinium ions can be good leaving groups, in the two limiting cases $k_2 \gg k_{-1}$ and $k_{obs} = k_1$ or $k_{-1} \gg k_2$ and $k_{obs} = k_1k_2/k_{-1}$. Which case prevails, and the use of k_{Br}/k_{Cl}, k_{OMs}/k_{Cl}, and k_{OBs}/k_{OTs} as mechanistic probes is discussed separately for each system.

Reaction Series (*a*). *Bromide–Chloride Reactivity Ratios*.—The k_{Br}/k_{Cl} ratios near unity (Table 3) are similar to those observed for the vinylic substitutions of α-arylsulphonyl-β-halogenoethylenes by several nucleophiles[17,18] including amines. The element effect expected for a one-step substitution would be much higher than unity. It is therefore likely that bond formation between the nucleophile and the β-carbon precedes the carbon–halogen bond breaking and k_1 is rate-determining in the formation of the zwitterionic intermediate. The similar reactivities are due to the similar inductive and resonance effects of the two halogens which affect similarly the electrophilicity of the β-carbon.

The other limiting possibility is that $k_{-1} \gg k_2$ and $k_{obs} = k_1k_2/k_{-1}$. Since the bond-breaking step should show a high k_2(Br)/k_2(Cl) element effect, the observed element effects require that the carbon basicity (k_1/k_{-1})(Cl) of the vinyl chlorides towards the anilines must be much higher than the (k_1/k_{-1})(Br) values of the vinyl bromide and that $(k_1/k_{-1})(\text{Cl})/(k_1/k_{-1})(\text{Br}) \simeq k_2(\text{Br})/k_2(\text{Cl})$ for the whole series of amines. Since k_1(Br)/k_1(Cl) for other nucleophilic vinylic reactions is not far from unity[2] it follows that $k_{-1}(\text{Br})/k_{-1}(\text{Cl}) \sim k_2(\text{Br})/k_2(\text{Cl})$. For steric reasons it is possible that $k_{-1}(\text{Br})/k_{-1}(\text{Cl}) > 1$ for the *m*- and the *p*-anilino-zwitterions. However, the very similar element effect for the reaction of the bulky 2,6-dimethylaniline would require a very unlikely cancelling effect of the rate coefficients above for all the amines. It is much more likely that k_1 is rate-determining. The fact that 2,6-dimethylaniline reacts 33 times more slowly than *p*-toluidine then reflects the steric hindrance of two methyl groups to attack on the double bond. Similarly, 2,4,6-trimethylaniline reacts 110 times more slowly than *p*-toluidine with (I; X = F).[13a]

Tables 2 and 4 give values for the activation parameters and for the Hammett ρ value for the k_1 step, and these can be used as approximations for these values in systems of related structure [such as (I)] for which the rate coefficient is composite. When these values are applied for the reaction of (I; X = Cl) with anilines in acetonitrile (where $k_{obs} = k_1k_2/k_{-1}$, $\Delta H^{\ddagger} = 6{\cdot}7$—$10{\cdot}9$ kcal mol^{-1}, $\Delta S^{\ddagger} = -43$ to -52 cal mol^{-1} K^{-1})[13a] it is found that the $(\Delta H_2^{\ddagger} - \Delta H_{-1}^{\ddagger})$ and the $(\Delta S_2^{\ddagger} - \Delta S_{-1}^{\ddagger})$ terms are low as expected for the k_2 and the k_{-1} steps. Further, since $\rho\ (= \rho_1 + \rho_2 - \rho_{-1}) = -3{\cdot}88$ (at 30 °C) for this reaction,[13a] $\rho_2 - \rho_{-1}$ should be negative or close to zero.

The reactions of α-chloro-β-nitrostyrene with the same anilines in acetonitrile[19] are one order of magnitude slower. This is due to a 10 cal mol^{-1} K^{-1} lower $\Delta S^{\ddagger}$, although $\Delta H^{\ddagger}$ is also 2 kcal mol^{-1} lower. Our ρ value (Table 2) is lower than the value of $\rho = -3{\cdot}4$ for α-chloro-β-nitrostyrenes,[19] in line with the reactivity–selectivity principle. This cautions against using a single nucleophile (*e.g.*, aniline) for establishing a quantitative scale for the activation by various α-groups.[20] The knowledge of ρ values for the series of nucleophiles (*e.g.*, anilines) with each of the electrophilic olefins is also required.

Reaction Series (*b*). *Mesylate–Chloride Reactivity Ratio*.—In saturated systems the k_{OTs}/k_{Bs} ratios are used as a probe for distinguishing between the S_N1 and the S_N2 routes, and for estimation of the charge separation in the transition state.[10] Our k_{OMs}/k_{Cl} ratio of unity should be comparable with the (unavailable) k_{OTs}/k_{Br} ratio in our system since k_{Br}/k_{Cl} ratios are close to unity (see above) and saturated tosylates and mesylates solvolyse with very similar rates.[21]

The mesylate should react much more rapidly if k_2 is rate-determining and arguments similar to those used above point to k_1 as being rate-determining. The mesylate–chloride reactivity ratio measures the relative activation of the β-carbon in a pure bond-forming process. When the k_{OTs}/k_{Br} ratio reflect only bond breaking, as in the solvolyses of tertiary systems[11] or the adamantan-2-yl system[22] the k_{OTs}/k_{Br} ratios are of the order 10^2—10^3. Cockerill pointed out in discussing $E1cB$ eliminations[23] that k_{OTs}/k_{Br} ratios do not necessarily increase monotonically with the amount of the carbon–leaving group bond breaking. He suggested that the ratios are slightly higher than unity for the extreme case (which according to him is unachievable) where no bond-breaking occurs, since the tosylate group ($\sigma^* = 1{\cdot}31$) is slightly more electron-attracting than bromide ($\sigma^* = 1{\cdot}00$). The ratios decrease and then increase when first the higher polarisability of the bromide and then the higher delocalisation ability of the tosylate gain in importance.[23] Our k_{OMs}/k_{Cl} ratio of unity fits this picture since σ^*_{OMs} should be only slightly lower than σ^*_{OTs}, thus giving the experimental information for the ' unachievable ' case when the two leaving groups exert their inductive effects with no bond-cleavage. The use of data from nucleophilic vinylic reactions to $E1cB$ eliminations is allowed, since the latter is the reversal of the nucleophilic vinylic addition.

The alternative explanation is that the low k_{OMs}/k_{Cl}

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ratios are due to a one-step S_N2 reaction with a small degree of C–X bond cleavage in the transition state. It is much less plausible since a one-step vinylic S_N2 reaction was not yet observed.[2]

The k_{OTs}/k_{Br} and the k_{OMs}/k_{Cl} ratios may serve as a tool for distinguishing between the vinylic S_N1 and the Ad_N–E routes. We found recently values of k_{OTs}/k_{Br} ratios of 20—87,[9b,24] k_{OTs}/k_{OMs} ratio of 2 [9b] and k_{Br}/k_{Cl} ratios of 10—75 [5,25] for several vinylic S_N1 solvolyses. The expected k_{OMs}/k_{Cl} ratios for S_N1 reactions are therefore several hundreds as compared with unity in the Ad_N–E route. These ratios are sensitive enough even to detect a few percent of the S_N1 route in competition with the main Ad_N–E route.

Reaction Series (*c*). *Brosylate–Tosylate Reactivity Ratios.*—Our k_{OBs}/k_{OTs} reactivity ratios of 1·63—1·90 (Table 3) correspond to Hammett ρ values of 0·53—0·69 and they are the lowest observed for nucleophilic displacement of these leaving groups. The values of k_{OBs}/k_{OTs} in solvolyses are 3 or higher for S_N1 reactions (ρ = 1·2),[26] while the low values observed for primary arylsulphonates [27] were ascribed to solvent participation in the transition state.[8] Our values fit a rate-determining bond-formation, when the differences between the two groups reflect the higher electron-withdrawing ability of the brosylate group, and correspondingly the higher electrophilicity of C_β of (VII) than of (VI).

However, the activation enthalpies (Table 4) are very low. Indeed, if the activation entropies would not be so strongly negative owing to the formation of the zwitterionic transition state, the reaction rates would be enormously high. We ascribed [12,13,28] such low activation enthalpies in nucleophilic vinylic reactions to composite rate coefficients, which in our case would amount to $k_{obs} = k_1k_2/k_{-1}$. Moreover, the aryl group on the β-carbon seems to accelerate more the k_{-1} than the k_2 step as shown by the base-catalysis observed for (I; X = Cl) [13a] but not for our β-halogeno-αα-dicyanoethylenes. An argument against a composite rate coefficient is that in the decarboxylative elimination from $Ar^1C(OSO_2Ar^2){:}C(CO_2^-)_2$ in which the arylsulphonate group and the carbon dioxide are lost simultaneously, the ρ value (1·16) is still higher than in our case.[8] Since k_1/k_{-1} is probably somewhat higher for (VII) than for (VI), a higher k_{OBs}/k_{OTs} ratio is expected for the case when $k_2 \ll k_{-1}$.

The differences between the k_{OBs}/k_{OTs} ratios in the Ad_N–E route and the ratios observed for the vinylic S_N1 route (2·3—5·0) [7b,9] allow the use of such ratios for distinguishing between the two routes. It is more important that k_{OBs}/k_{OTs} ratios of 0·3 were found [7a] for vinylic substitutions *via* electrophilic addition–elimination (Ad_E–E) where protonation of the double bond is rate-determining [equation (8)].[7a,29] The k_{OBs}/k_{OTs} ratios can be therefore used to distinguish between the electrophilic and the nucleophilic addition–elimination routes, which are both possible with substrates such as 9-[α-(arylsulphonyloxy)arylidene]fluorene in AcOH–NaOAc mixture.

$$R^1R^2C{=}CR^3X \xrightarrow{+H^+} R^1R^2CH{-}\overset{+}{C}R^3X \xrightarrow{+Nu^-}$$
$$R^1R^2CH{-}CR^3(Nu)X \xrightarrow{-HX} R^1R^2C{=}C(Nu)R^3 \quad (8)$$

Piperidine–Morpholine Reactivity Ratio.—Piperidine and morpholine were chosen as nucleophiles towards the nitrophenylethylenes (VI) and (VII) since they differ appreciably in their basicity but not in their steric effects. The k_{pip}/k_{morp} reactivity ratios of 13·7—16·2 correspond to Brønsted α's of *ca.* 0·5 when the pK_a's of the amines in acetonitrile are used.[30] Ratios of 7—30 were found for the addition of these two amines to *p*-tolyl vinyl sulphone,[31] for their reactions with n-butyl and *p*-nitrobenzyl bromides,[32a] and for the reaction with *p*-nitrophenyl acetate,[32b] but the ratio is only 2·7 in the reaction with methyl iodide in water.[32b] A k_{pip}/k_{morp} value lower than unity was observed for the displacement of the vinylic ethoxy-group of (I; X = OEt) in acetonitrile.[16a] Our present value can be taken as an approximation for the ratio expected for the initial addition step to (I; X = OEt) in this multi-step reaction.

The Effects of α- *and* β-*Substituents.*—The present work enables us to make some indirect comparisons regarding the activation by α- and β-substituents. By using the Hammett relationship the extrapolated k_{obs} for the reaction of (II) with *p*-cyanoaniline is $1{\cdot}77 \times 10^{-3}$ l mol^{-1} s^{-1} at 30 °C. Two α-cyano-groups are therefore 100 times more activating than two α-methoxycarbonyl groups. This fits the fact that the hydroxide-catalysed cleavage of $p\text{-}MeOC_6H_4{\cdot}CH{:}CXY$ is 8·3 times faster when X = Y = CN than when X = CN, Y = CO_2Et.[33]

The reaction of *p*-cyanoaniline with (IV) is $1{\cdot}7 \times 10^6$ times faster than that with (I; X = Cl), whereby the Hammett relationship $k_{obs} = 10^{-6}$ l mol^{-1} s^{-1}.[13a] Large reduction in the reactivity in nucleophilic vinylic addition was observed previously [20] when a vinylic β-hydrogen was replaced by a β-aryl group. This is probably due to increased ground-state stabilisation by aryl–double bond conjugation, and also to the reversibility of the first step in the case of the aryl derivatives.

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EXPERIMENTAL

Solvent.—Acetonitrile (Baker Analysed) was dried for one day and then refluxed for 5 h over P_2O_5, distilled through a fractionating column, and the middle fraction, b.p. 78·5 °C, was used.

Materials.— 1-Chloro-2,2-dimethoxycarbonylethylene (II), b.p. 109 °C/20 mmHg (Found: C, 40·5; H, 4·1. Calc. for $C_6H_7ClO_4$: C, 40·3; H, 3·9%), $\nu_{max.}$ (KBr) 3085 (w, C–H), 1740 (s, CO_2R), and 1612 cm^{-1} (m, C:C), was prepared in 70% yield from dimethyl hydroxymethylenemalonate (formed in 95% yield from ethyl formate and dimethyl malonate) and phosphorus pentachloride according to Shvo and Osman.[34] 1-Chloro-2,2-dicyanoethylene (IV) was prepared according to Josey and his co-workers.[35] 2,2-Diethoxycarbonyl-*p*-nitrophenylvinyl *p*-bromobenzenesulphonate (VII), m.p. 125—128 °C (lit.,[36] 125—126 °C) was prepared in 60% yield from diethyl *p*-nitrobenzoylmalonate according to Brown and Harley-Mason;[36] $\lambda_{max.}$ (MeCN): 241·5 nm (ϵ 25,400); $\nu_{max.}$ (Nujol) 1725 (CO_2Et), 1630 (C:C), 1580 and 1560 (NO_2) cm^{-1}, τ ($CDCl_3$) 8·50—9·03 (6H, 2t, 2Me), 5·60—5·97 (4H, 2q, $2CH_2$), and 1·60—2·60 (8H, 2q, 2Ar).

1-*Bromo*-2,2-*dimethoxycarbonylethylene* (III).—The sodium salt of dimethyl hydroxymethylenemalonate was prepared by analogy to the preparation of sodium alkoxymethylenemalononitrile[35] in 95% yield. To a suspension of the salt (10 g, 55 mmol) in carbon tetrachloride (50 ml), a mixture of phosphorus tribromide (14·9 g, 55 mmol) and bromine (8·8 g, 55 mmol) in dry carbon tetrachloride (50 ml) was added. The mixture was refluxed with stirring for 2 h and poured into ice–water (100 ml). The organic layer was separated, washed with dilute sodium thiosulphate solution, dried ($CaCl_2$), and distilled. The fraction boiling at 112—118 °C/6 mmHg was purified by chromatography over silica, with light petroleum and benzene as eluants, giving 1·4 g (10%) of (III) as a colourless liquid (Found: C, 32·6; H, 2·8; Br, 36·1. Calc. for $C_6H_7BrO_4$: C, 32·35; H, 3·1; Br, 35·8%); $\lambda_{max.}$ (MeCN) 231 nm (ϵ 10,000), $\nu_{max.}$ (Nujol) 3070 (H–C:), 1745, 1725 (CO_2Me), 1610 (C:C), and strong bands at 1435, 1325, 1255, and 1068 cm^{-1}, τ (CCl_4) 6·13 and 6·20 (6H, 2s, 2Me) and 2·22 (1H, s, H–C:).

2,2-*Dicyanovinyl Methanesulphonate* (V).—A solution of silver methanesulphonate (1 g, 9·6 mmol) in dry acetonitrile (40 ml) was added to a solution of 1-chloro-2,2-dicyanoethylene (2 g, 17·8 mmol) in acetonitrile (20 ml). After 1 h, the silver chloride was filtered off, the solvent was evaporated, the residue dissolved in chloroform, the remaining silver salts were filtered off, and on cooling 0·5 g (31%) of white *plates* of (V), m.p. 85—87 °C were obtained (Found: C, 34·7; H, 2·5; N, 16·0; S, 18·4. $C_5H_4N_2O_3S$ requires C, 34·9; H, 2·3; N, 16·3; S, 18·6%); $\lambda_{max.}$ (MeCN) 233 nm (ϵ 14,000), $\nu_{max.}$ (KBr) 2230 (s, C≡N), 2195 (s, C≡N), and 1630 (s, C:C) cm^{-1}, τ [$(CD_3)_2SO$] 6·41 (3H, s, Me) and 1·35 (1H, s, H–C:).

2,2-*Diethoxycarbonyl*-1-p-*nitrophenylvinyl Toluene*-p-*sulphonate* (VI).—This compound was prepared by a modification of the method of Fleming and Owen.[37] 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 precipitated quantitatively, filtered off, and dried. To a suspension of the salt in dry acetonitrile (100 ml), toluene-*p*-sulphonic anhydride (9 g, 27·5 mmol) was added and the mixture was refluxed for 2 h. The solvent was removed *in vacuo* and the residue was shaken with ether (100 ml) and dilute sodium hydroxide solution (100 ml). The organic layer was separated, washed with water, dried (Na_2SO_4), and evaporated, and the residue was crystallised from ethanol, giving 11·5 g (70%) of pale yellow *crystals* of (VI), m.p. 92—93° (Found: C, 54·7; H, 4·8; N, 3·1; S, 7·3. $C_{21}H_{21}NO_9S$ requires C, 54·8; H, 4·5; N, 3·0; S, 6·9%); $\lambda_{max.}$ (MeCN) 230 (ϵ 20,000) and 276 nm (ϵ 12,300), $\nu_{max.}$ (Nujol) 3110 (w, C–H), 1740, 1700 (s, CO_2Et), 1625 (C:C), and 1595 (NO_2) cm^{-1}, τ ($CDCl_3$) 8·95 (3H, t, Me), 8·67 (3H, t, Me), 7·60 (3H, s, Me), 5·50—6·02 (4H, 2 merging q, $2CH_2$), and 1·89—2·90 (8H, 2 merging AA′BB′ q, Ar).

Dimethyl p-*Nitrobenzoylmalonate.*—(*a*) Dimethyl methoxymagnesiummalonate was prepared by Bowman's method[38] for the preparation of the ethoxy-analogue.

(*b*) To the above ester which was prepared from magnesium (9·2 g, 0·38 mol) and dimethyl malonate (50·2 g, 0·38 mol) in benzene (40 ml), *p*-nitrobenzoyl chloride (35·2 g, 0·19 mol) in dry benzene (20 ml) was added during 10 min, and the mixture was refluxed for 1 h. The cooled solution was decomposed by addition of ice and dilute sulphuric acid, the organic layer washed with a solution of dilute sulphuric acid, dried (Na_2SO_4), and the solvent was evaporated *in vacuo* at room temperature, and the excess of dimethyl malonate was recovered by distillation at 0·5 mmHg (bath-temp. 100 °C). The crude solid fraction was recrystallised from methanol, giving dimethyl *p*-nitrobenzoylmalonate (3 g) as yellow *crystals*, m.p. 95—97 °C (Found: C, 51·4; H, 3·9; N, 5·3. $C_{12}H_{11}NO_7$ requires C, 51·3; H, 3·9; N, 5·0%).

Attempted Brosylation of Dimethyl p-*Nitrobenzoylmalonate.*—Sodium (0·16 g, 7·1 mmol) in methanol (10 ml) was added to dimethyl *p*-nitrobenzoylmalonate (2 g, 7·1 mmol) in methanol (15 ml). The cooled solution was treated with *p*-bromobenzenesulphonyl chloride (1·8 g, 7·1 mmol) in methanol (15 ml), the reaction mixture was allowed to stand for 2 days at room temperature, the solvent was evaporated, the residue shaken with ether (50 ml) and very dilute sodium hydroxide solution, and the ether layer was dried and evaporated. Attempts at crystallisation gave no vinyl brosylate, and only *p*-bromobenzenesulphonic acid was isolated.

Preparation of the Enamines.—Two equiv. of the amine were added to one equiv. of compounds (II), (IV), or (VII) in dry acetonitrile until a homogeneous solution was formed. The alkyl- or aryl-ammonium salt was filtered off after 1 h, the solvent was evaporated, the residue was dissolved in dry ether, the remaining salts were filtered off, the ether was evaporated, and the oil obtained was recrystallised or purified by chromatography. Analytical and physical properties of the enamines are in Table 8. The isolated yields of the enamines were 85—90% of the dicyanoenamines, 20—50% of the more soluble dimethoxycarbonylenamines, and 50—60% of the morpholino- and the piperidino-*p*-nitrophenylenamines. The u.v. spectra of the reaction mixtures showed however that the enamines were formed in quantitative yield.

Kinetic Procedure.—Stock solutions of the reactants were prepared daily, the samples were mixed at the reaction

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Table 8

Enamines $R^1C(NR^2R^3){:}CX_2$

R^1	R^2	R^3	X	M.p./°C	Colour [a]	Crystal-lisation solvent [b]	Analysis								
							Found %					Required %			
							C	H	N	Hal	Formula	C	H	N	Hal
H	*p*-MeC_6H_4	H	CO_2Me	108—110		A	62·5	6·1	5·7		$C_{13}H_{15}NO_4$	62·6	6·1	5·6	
H	*p*-BrC_6H_4	H	CO_2Me	116—117	Brown	A	45·6	3·9	4·3	25·7	$C_{12}H_{12}BrNO_4$	45·9	3·8	4·45	25·9
H	*m*-MeC_6H_4	H	CO_2Me	90—92		A	62·6	6·1	5·8		$C_{13}H_{15}NO_4$	62·6	6·1	5·6	
H	*m*-$MeOC_6H_4$	H	CO_2Me	75—76		A	59·1	5·8	5·3		$C_{13}H_{15}NO_5$	58·9	5·7	5·3	
H	Ph	H	CO_2Me	47		A	61·2	5·7	6·1		$C_{12}H_{12}NO_4$	61·3	5·6	5·95	
H	2,6-$Me_2C_6H_3$	H	CO_2Me	103—104		A	63·7	6·4	5·35		$C_{14}H_{17}NO_4$	63·9	6·5	5·3	
H	*p*-NCC_6H_4	H	CN	288		B	67·7	3·3	29·0		$C_{11}H_6N_4$	68·0	3·5	28·9	
H	*p*-$O_2NC_6H_4$	H	CN	235	Yellow	B	56·0	3·0	26·2		$C_{10}H_6N_4O_2$	56·1	2·8	26·2	
H	*p*-MeC_6H_4	H	CN	297		B	72·1	4·95	22·9		$C_{11}H_9N_3$	72·3	5·25	22·6	
H	*p*-ClC_6H_4	H	CN	240		B	58·9	3·0	20·4	17·3	$C_{10}H_6ClN_3$	59·0	2·9	20·6	17·5
H	*p*-$MeOC_6H_4$	H	CN	245	Yellow	B	66·6	4·8	21·0		$C_{11}H_9N_3O$	66·3	4·55	21·1	
H	Et	Et	CN	72—74		A	64·2	7·2	28·3		$C_8H_{11}N_3$	64·4	7·4	28·2	
H	R^2R^3 = morpholino		CN	150—151		C	58·6	5·6	25·9		$C_8H_9N_3O$	58·9	5·6	25·8	
p-$O_2NC_6H_4$	R^2R^3 = morpholino		CO_2Et	144—145	Yellow [c]	D	57·15	5·8	7·45		$C_{18}H_{22}N_2O_7$	57·1	5·9	7·4	
p-$O_2NC_6H_4$	R^2R^3 = piperidino		CO_2Et	156—157	Yellow [c]	A	60·6	6·6	7·5		$C_{19}H_{24}N_2O_6$	60·6	6·4	7·4	

Colourless crystals unless otherwise stated. [b] A, Chloroform–light petroleum; B, acetonitrile; C, acetone–chloroform; D, from chromatography. [c] Needles.

temperature, and the reaction was followed in the thermostatically-controlled chamber of a Beckman DU spectrophotometer. Measurements were usually conducted at a longer wavelength than the $\lambda_{max.}$ of the product enamines, thus avoiding corrections for the absorption of the free amine. Measurements for the dimethoxycarbonylenamines were conducted at *m*-Me, 320; *m*-MeO, 330; H, 324; *p*-Me, 344; *p*-Br, 343; and 2,6-Me_2, 335 nm; for the diethoxycarbonylenamines at 360, and for the dicyanoenamine at 320 nm. The spectra of the mixtures after several half-lives corresponded to those of the enamines.

The pseudo-first-order rate coefficients in the presence of excess of amine were calculated with the aid of the KINDAT programme.[39] The correlation coefficients were >0·999. k_{obs} Values were obtained by dividing the first-order coefficients by the amine concentration.

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