Nucleophilic Attacks on Carbon–Carbon Double Bonds. Part XXIII.[1] Substitution of β-Chloro-α-phenylacrylonitriles

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Substitutions of (*E*)- and (*Z*)-β-chloro-α-phenylacrylonitriles by arenethiolate, azide, and ethoxide ions proceed with retention of configuration, while reactions with piperidine or morpholine give the same enamino-nitrile from the two isomeric chlorides. The second-order rate constants give the nucleophilicity order $ArS^- > EtO^- >$ piperidine $> PhO^- >$ morpholine $> N_3^-$. These results are discussed in terms of the addition–elimination route of nucleophilic vinylic substitution, and the data are compared with those found for related reactions.

SOME questions connected with the details of the nucleophilic vinylic substitution *via* addition–elimination[2,3] are the dependence of the stereochemistry of the reaction on the activating group and the nucleophile,[2,3] the possibility of base catalysis in the reaction with amines,[4] the *cis–trans*-reactivity differences as a function of the nucleophile,[2,3,5] the nucleophilicity order towards a vinylic carbon,[2] and the activating order of various α-activating groups.[2] We have investigated these questions for the β-chloro-α-phenylacrylonitrile system.

RESULTS

(*E*)- and (*Z*)-β-chloro-α-phenylacrylonitriles (*E*)- and (*Z*)-RCl were prepared according to Cariou,[6] who assigned the *cis*-configuration to the liquid isomer and the *trans* to the

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[1] Part XXII, Z. Rappoport and A. Topol, *J.C.S. Perkin II*, 1975, 863.

[2] Z. Rappoport, *Adv. Phys. Org. Chem.*, 1969, **7**, 1.

[3] G. Modena, *Accounts Chem. Res.*, 1971, **4**, 73.

[4] (*a*) Z. Rappoport and R. Ta-Shma, *J. Chem. Soc.* (*B*), 1971, 871, 1461; (*b*) Z. Rappoport and N. Ronen, *J.C.S. Perkin II*, 1972, 955; (*c*) Z. Rappoport and P. Peled, *ibid.*, 1973, 616; (*d*) Z. Rappoport and D. Ladkani, *ibid.*, p. 1045.

[5] (*a*) P. Beltrame, P. L. Beltrame, and L. Belloti, *J. Chem. Soc.* (*B*), 1969, 932; (*b*) P. Beltrame, P. L. Beltrame, G. Carboni, and M. L. Cereda, *ibid.*, 1970, 730; (*c*) G. Marchese, G. Modena, and F. Naso, *Tetrahedron*, 1968, **24**, 663; *J. Chem. Soc.* (*B*), 1968, 958; (*d*) D. Landini, F. Montanari, G. Modena, and F. Naso, *ibid.*, 1969, 243.

[6] M. Cariou, *Bull. Soc. chim. France*, 1969, 217.

TABLE 1

Kinetic data for the reactions of (*E*)- and (*Z*)-HCCl=C(CN)Ph with nucleophiles [a]

Nucleophile	Isomer	Solvent	10^4 Concentration (M)	n [b]	10^2k_2/l mol^{-1} s^{-1}			$\Delta H^{\ddagger}$ [c]/ kcal mol^{-1}	$\Delta S^{\ddagger}$ [d]/ cal mol^{-1} K^{-1}	λ/ nm [e]
					22°	30°	45°			
Morpholine	*Z*	EtOH	41—320	4		4.04 ± 0.07	7.64 ± 0.27	7.5	−40.3	310
Piperidine	*Z*	EtOH	11—91	5		25.9 ± 1.7	47.6 ± 1.8	7.1	−37.8	310
Piperidine	*Z*	MeOH	20—80	4		21.5 ± 0.8	42.0 ± 2.0	7.8	−36.0	310
p-$ClC_6H_4S^-$	*Z*	EtOH	2.4—3.9	3	$1\,690 \pm 90$	$2\,850 \pm 13$		11.0 [f]	−15.6 [g]	319
p-$ClC_6H_4S^-$	*Z*	MeOH	1.8—5.4	3	432 ± 8	597 ± 28		6.6 [f]	−29.2 [g]	319
p-$MeC_6H_4S^-$	*Z*	EtOH	0.7—2.8	3	$3\,410 \pm 200$	$4\,950 \pm 150$		7.7 [f]	−25.3 [g]	319
EtO^-	*Z*	EtOH	25—304	4		25.6 ± 2.0	90.0 ± 5.6	15.5	−9.8	290
PhO^-	*Z*	EtOH	6.4—32	4		4.97 ± 0.3	17.7 ± 1.5	15.5	−13.1	310
N_3^-	*Z*	EtOH	60—268	4	0.503 ± 0.003	1.05 ± 0.02		15.7	−16.1	315
N_3^-	*Z*	MeOH	113—2 220	4	0.216 ± 0.008	0.39 ± 0.02		12.5	−28.1	315
Morpholine	*E*	EtOH	41—378	4		4.75 ± 0.05	8.86 ± 0.09	7.3	−40.5	310
Piperidine	*E*	EtOH	11—90	4		33.5 ± 1.9	51.1 ± 1.0	4.7	−45.5	310
p-$ClC_6H_4S^-$	*E*	EtOH	0.33—1.95	3	$3\,060 \pm 130$	$7\,020 \pm 350$		17.8 [f]	8.7 [g]	319
p-$MeC_6H_4S^-$	*E*	EtOH	0.31—0.91	3	$6\,750 \pm 170$	$11\,230 \pm 1\,020$		10.6 [f]	−14.1 [g]	319
EtO^-	*E*	EtOH	19.5—78	6		239 ± 13	537 ± 33	9.7	−29.1	290
N_3^-	*E*	MeOH	112—896	4	0.209 ± 0.01	0.391 ± 0.008		13.0	−26.4	315

[a] [RCl] = 1.61—28×10^{-5}M. [b] Number of nucleophile concentrations used. [c] ±1 kcal mol^{-1}. [d] ±3 cal mol^{-1} K^{-1}. [e] Wavelength of kinetic measurement. [f] ±2 kcal mol^{-1}. [g] ±6 cal mol^{-1} K^{-1}.

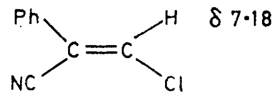
TABLE 2

Reaction of RCl [a] with morpholine in EtOH

	30°								45°							
10^3[Morpholine]/M	4.1	4.7	8.1	9.5	16.0	18.9	32.0	37.8	4.0	4.4	8.0	8.9	16.0	17.8	24.0	35.5
10^2k_2/l mol^{-1} s^{-1} for (*Z*)-RCl	4.10		4.13		4.01		3.94		7.86		7.95		7.45		7.29	
10^2k_2/l mol^{-1} s^{-1} for (*E*)-RCl		4.67		4.77		4.80		4.78		8.84		9.03		8.80		8.77

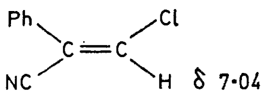
[a] [RCl] = 1.1×10^{-4}M

solid on the basis of the slightly higher $\lambda_{max.}$ and ε values for the latter. These assignments are corroborated by calculating the positions of the vinylic protons in the n.m.r. spectra according to Tobey's additivity rule:[7] the calculated δ(:CH) values of 7.01 [(*E*)-RCl] and 7.24 [(*Z*)-RCl] fit the observed values.



(Z)-RCl (*trans*)

λ max. (EtOH) 267.5nm (ε 11,600)



(E)-RCl (*cis*)

λ max. (EtOH) 261nm (ε 10,200)

The reactions of the vinyl chlorides with six nucleophiles in ethanol, and of (*Z*)-RCl with piperidine, azide ion, and *p*-chlorobenzenethiolate ion in methanol were followed spectrophotometrically either at the $\lambda_{max.}$ of the product or at a wavelength where the difference between the absorptions of the product and the starting material is appreciable. A large excess of the nucleophile was usually used in order to ensure pseudo-first-order conditions. The nucleophile concentrations were changed several fold in order to obtain the second-order rate coefficient. The higher reactivity of the arenethiolate ions required the use of low concentrations of the nucleophiles and work under second-order conditions. Consequently, the errors in the rate coefficients and the derived activation parameters are higher than for the other nucleophiles. No evidence for amine catalysis was found in the reactions of the two amines. The high correlation coefficients for the first order plots ($r > 0.999$ for all these plots) indicate the absence of an (*E*)-RCl $\rightleftharpoons$ (*Z*)-RCl isomerization during any of these reactions. We found no appropriate wavelength to follow the reaction of phenoxide ion with (*E*)-RCl.

TABLE 3

Relative nucleophilicities towards HC(Cl)=C(CN)Ph in EtOH

Nucleophile	Relative k_2 [a] for (*E*)-RCl at 30°	Relative k_2 [b] for (*Z*)-RCl at 30°	k[(*E*)-RCl)]/ k[(*Z*)-RCl]		
			22°	30°	35°
p-$MeC_6H_4S^-$	2 364	1 225	1.98	2.27	
p-$ClC_6H_4S^-$	1 478	705	1.81	2.46	
EtO^-	50.3	6.34		9.34	5.97
Piperidine	7.1	6.4		1.29	1.07
PhO^-		1.23			
Morpholine	1.0	1.0		1.18	1.16
N_3^-		0.26	0.97 [c]	1.00 [c]	

[a] Relative rates in MeOH : piperidine (1.0) > N_3^- (0.012). [b] Relative rates in MeOH : *p*-$ClC_6H_4S^-$ (27.8) > piperidine (1.0) > N_3^- (0.015). [c] In MeOH.

TABLE 4

Stereochemistry of the substitution of RCl by nucleophiles in EtOH

Substrate	Nucleophile	Reaction [a] time/h	Product [b]
E	*p*-$ClC_6H_4S^-$	1	>90% (*E*)-RSC_6H_4Cl-*p*
E	*p*-$MeC_6H_4S^-$	1	>92% (*E*)-RSC_6H_4Me-*p*
E	EtO^-	3	>88% (*E*)-ROEt
E	N_3^- [c]	12	>87% (*E*)-RN_3
Z	*p*-$ClC_6H_4S^-$	1	>91% (*Z*)-RSC_6H_4Cl-*p*
Z	*p*-$MeC_6H_4S^-$	1	>93% (*Z*)-RSC_6H_4Me-*p*
Z	EtO^-	3	>95% (*Z*)-ROEt
Z	N_3^- [c]	12	>95% (*Z*)-RN_3
Z	PhO^-	3	>89% (*Z*)-ROPh
E	Morpholine	3	>92% (*E*)-RNC_4H_8O
E	Piperidine	3	>92% (*E*)-RNC_5H_{10}
Z	Morpholine	3	>96% (*E*)-RNC_4H_8O
Z	Piperidine	3	>94% (*E*)-RNC_5H_{10}

[a] At room temperature. [b] Yield of crude product before recrystallisation or distillation. The m.p. is ⩽2° lower than that of the recrystallised product. No trace of the geometrical isomer was observed, and the value given is therefore a lower limit for the stereochemical purity. [c] In MeOH at 0 °C.

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

The rate coefficients and the activation parameters are given in Table 1, and Table 2 demonstrates the absence of amine catalysis in the reaction of both isomers with morpholine. The relative nucleophilicity order of our nucleophiles, and the relative reactivities of the *E*- and *Z*-isomers towards different nucleophiles are given in Table 3.

The stereochemical results are collected in Table 4. Except for the reactions with the amines, the reactions of (*E*)- and (*Z*)-RCl gave a different isomeric product R-Nu with each of the anionic nucleophiles (Nu). The pure (*E*)- and (*Z*)-R-Nu isomers are available for each of the four nucleophiles, and each has a characteristic absorption in the i.r. which is absent in its isomer. A search (by i.r.) for the copresence of the isomers gave negative results in all the cases investigated. Moreover, the crude products had m.p.s almost identical with those of the pure compounds, and the stereospecificity of the reaction should be appreciably higher than that deduced from the values of Table 4 which are based on the *isolated* yields from the reactions of few hundreds mg of the compounds. We attempted to obtain a higher limit for the stereospecificity by analysing the crude mixtures by g.l.c. or by t.l.c. However, extensive (*E*)-R-Nu $\rightleftharpoons$ (*Z*)-R-Nu isomerization, leading to *ca.* 1 : 1 mixture of (*E*)- and (*Z*)-R-Nu took place with different g.l.c. columns or t.l.c. plates. Although the isomers could be purified by g.l.c. or t.l.c., the isomerization prevented the determination of the kinetically controlled product distributions by these methods.

TABLE 5

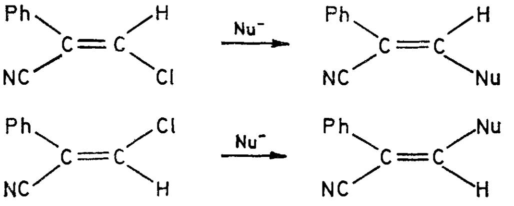
Spectral properties of the substitution products HCX=C(CN)Ph

X	Configuration	$\lambda_{max.}$(EtOH)/nm (ε)	$\nu_{max.}$(KBr)/cm^{-1}	δ ($CDCl_3$)	*m/e* (Relative abundance, assignment)
OC_4H_8N [a]	*Z*	225 (9 100), 252 (5 900), 294sh (15 200), 310 (16 600)	2 195s, 1 610s, 1 595s	3.95 (8H, s, CH_2), 7.00 (1H, s, =CH), 7.42—7.55 (5H, m, Ar)	214 (100, *M*), 178 (31), 155 (49), 128 (15, *M* − morpholine)
$C_5H_{10}N$ [b]	*Z*	225 (8 900), 252 (6 200), 295sh (15 500), 312 (17 700)	2 180s, 1 615s, 1 595s	1.65 (6H, m, CH_2), 3.58 (4H, m, CH_2), 6.82 (1H, s, =CH), 7.17 (5H, m, Ar)	212 (100, *M*), 178 (44), 155 (39), 128 (13, *M* − piperidine)
p-ClC_6H_4S	*Z*	224 (20 700), 266 (8 300), 319 (23 900)	2 240s, 1 620s	7.25—7.53 (m, Ar + =CH)	273, 271 (37, 100, *M*), 270 (30, *M* − H), 236 (28, *M* − Cl), 203 (44, *M* − Cl − SH), 159 (31, *M* − PhCl), 155 (25), 139 (36), 108 (27, C_6H_4S)
p-ClC_6H_4S	*E*	218 (20 700), 305 (23 900)	2 210m, 1 630w, 865m [c]	7.22—7.61 (m, Ar + =CH)	273, 271 (36, 100, *M*), 270 (29, *M* − H), 236 (40, *M* − Cl), 203 (58, *M* − Cl − SH), 159 (24, *M* − PhCl), 143 (29, SC_6H_4Cl), 108 (29, C_6H_4S)
p-MeC_6H_4S	*Z*	224 (20 400), 261 (8 600), 319 (25 500)	2 215s, 1 625s	2.40 (3H, s, Me), 7.17—7.57 (10H, m, Ar + =CH)	251 (6, *M*), 178 (22), 173 (61, *M* − C_6H_6), 145 (100, *M* − HCN − Ph), 117 (87)
p-MeC_6H_4S	*E*	218 (16 000), 257 (6 300), 307 (16 000)	2 210s, 1 650w, 865m [c]	2.32 (3H, s, Me), 7.10—7.77 (10H, m, Ar + =CH)	251 (24, *M*), 173 (13, *M* − C_6H_6), 161 (71), 159 (100, *M* − PhMe), 145 (21), 132 (33), 125 (56), 117 (37)
PhO	*Z*	267 (15 000)	2 230s, 1 630s, 1 590s	7.07 (1H, s, =CH), 7.25 (10H, s, Ar)	221 (1, *M*), 164 (100), 128 (55, *M* − OPh), 101 (18)
EtO	*Z*	266 (15 400)	2 225s, 1 600s [d]	1.40 (3H, t, Me), 4.25 (2H, q, CH_2), 7.07 (1H, s, =CH), 7.33—7.85 (5H, m, Ar)	173 (60, *M*), 151 (17, *M* − CH_2), 155 (100, *M* − C_2H_4), 144 (14, *M* − OEt), 119 (28), 117 (99, *M* − HCN − OEt)
EtO	*E*	266.5 (6 500) [e]	2 215s, 1 600s [d]	1.40 (3H, t, Me), 4.20 (2H, q, CH_2), 7.22 (1H, s, =CH), 7.30 (5H, s, Ar)	173 (96, *M*), 145 (96, *M* − C_2H_4), 144 (26, *M* − OEt), 118 (18), 117 (100, *M* − HCN − Et), 116 (49)
N_3	*Z*	224.5 (12 500), 293 (18 000)	2 230w, 2 220w, 2 130s, 1 610s	7.50 (m, Ar + =CH)	170 (5, *M*), 142 (63, *M* − N_2), 115 (100, *M* − N_2 − HCN), 88 (26)
N_3	*E*	224 (5 300), 286 (6 100)	2 220w, 2 125s, 1 600s, 1 265s	7.15—7.88 (m, Ar + =CH)	170 (8, *M*), 143 (21, *M* − HCN), 142 (99, *M* − N_2), 116 (41, *M* − N_2 − CN), 115 (100, *M* − N_2 − HCN), 114 (49), 88 (45)

[a] Morpholino. [b] Piperidino. [c] This absorption alone distinguishes the i.r. spectra of the *E*- and *Z*-isomers; it is absent in the spectrum of the *Z*-isomer. [d] Spectra of neat compounds. [e] Reported: $\lambda_{max.}$(EtOH) 267.5 nm (ε 15 000) for a mixture of the two isomers.[8]

We suggest that the stereochemical outcome is retention of configuration, on the basis of the higher $\lambda_{max.}$ of the (*Z*)-vinyl sulphide and azide compared with the *E*-isomers, in line with the assignments for the vinyl chlorides.[6] Since the $\lambda_{max.}$ of the two vinyl ethers is the same, we assigned the *Z*-configuration to the ethyl vinyl ether formed from (*Z*)-RCl on the basis of its higher ε, in line with the corresponding assignments of the methyl vinyl ethers [(*E*)-ROMe $\lambda_{max.}$ 268.5 nm (ε 12 600); (*Z*)-ROMe $\lambda_{max.}$ 266 nm (ε 16 000)].[8] These determinations are supported by the lower $\nu_{max.}$ for the C≡N absorption of the *E*-isomers as expected for a *trans*-disposition of the electron-donor (Nu) and the electron-attracting cyano-substituents (Table 5). (*E*)- and (*Z*)-RCl behave similarly. Due to overlap of signals, the n.m.r. spectra could be used only in the case of the ethyl vinyl ethers for distinguishing between the isomers. In this case the vinyl proton of the *E*-isomer was at lower field than that of the *Z*-isomer, in contrast with the expectation based on Tobey's additivity rule.[7] Appropriate data for comparison are not available, since the n.m.r. spectra of the methyl ethers were not reported.[8] Extensive conjugation between the ethoxy- and cyano-groups may be responsible for the failure of Tobey's rule. The retention of configuration [equation (1)] is reminiscent of the behaviour of many other nucleophilic vinylic substitutions.[2,3,9]

The reactions of piperidine and morpholine gave the same enamine from either (*E*)- or (*Z*)-RCl with $>94\%$ yield, without even traces of an isomeric enamine. In the absence of the second isomer, and in view of the n.m.r. data for the ethoxy-compounds, assignment of configuration is difficult. Tentatively, we suggest the *E*-configuration in analogy with the reported stereochemistry of the corresponding piperidino-enamine formed in the analogous reaction of β-chloroacrylonitrile.[10]

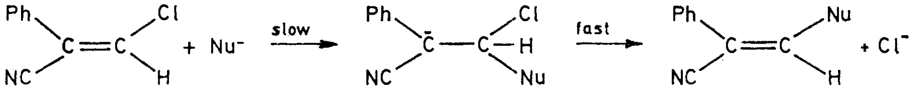


(1)

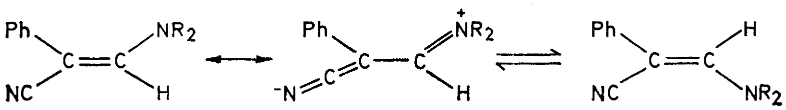
Spectral Properties of the Products.—The spectral data are partially discussed above. In addition, the u.v. spectra (Table 5) show the expected conjugation effects of 'complimentary' α-CN and β-SR, β-NR, and β-OR substituents. This effect is also manifested by the very low $\nu_{\text{max.}}$ for the absorption of the cyano-group in the i.r. as found for other cyano-enamines.[11] The C=C absorptions in the i.r. have high intensities as found for structurally analogous systems.[10] An interesting feature of the n.m.r. spectrum of (*E*)-ROEt is the appearance of the phenyl resonance as a singlet, while it is a multiplet in all the other cases. The mass spectra, especially of the enamines, contains some expected fragments, but several abundant fragments are apparently not formed by a simple fragmentation, *e.g.* those at *m*/*e* 178 in the spectra of the cyano-enamines (Table 5).

DISCUSSION

Stereochemistry of the Substitution.—The two main stereochemical features of our reactions are the almost exclusive retention of configuration in the substitution by four anionic nucleophiles which cover an appreciable reactivity difference, and the formation of an identical product from (*E*)- and (*Z*)-RCl in the reactions with the amines. Both features represent the normal outcome of substitution at a vinylic carbon *via* addition–elimination,[2,3,9,10,12] and fit a rate-determining nucleophilic attack on the β-carbon to form a carbanionic intermediate, which expels the leaving group faster than it gives internal rotation [equation (2)]. The higher stereospecificity compared with that obtained in the reactions of EtO^- and p-$MeC_6H_4S^-$ with β-chloroacrylonitriles (where $<5\%$ of the 'inverted' isomer was formed)[10] is probably due to the higher structural stability of the products in our system.



(2)



(3)

The same initial step presumably takes place with the amines, with the formation of a zwitterionic intermediate. However, the enamino-nitriles are configurationally unstable, and the barrier for internal rotation around the Cα–Cβ bond [equation (3)] is sufficiently low[13] (*cf.* the contributing zwitterionic structure to the ground state) at room temperature to ensure a rapid equilibration of the *E*- and *Z*-enamines. The appearance of only one isomer indicates its predominance in equilibrium (3).

There is reason to believe and some preliminary evidence,[14] that as the carbanionic intermediate will become more stable by using a highly activating α-substituent, the rate of the internal rotation will exceed the rate of C–X bond cleavage, and the stereochemistry would be changed from retention to 'racemisation', *i.e.*, the formation of the same mixture of *E*- and *Z*-isomers from either the *E*- or the *Z*-vinyl chloride. Our results indicate that this situation is not achieved with the combination of α-CN and α-Ph as the activating groups.

Absence of Base Catalysis.—Considerations based on the appearance of base catalysis in the reaction of amines with α,α-dicyano-β-halogenoethylenes[1,4] and its absence in less activated vinyl halides,[1] suggest that such catalysis will be observed for highly activating α-substituents.[1] The absence of catalysis in our system is therefore due to the lower stabilisation of the inter-

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[8] M. Cariou, *Bull. Soc. chim. France*, 1969, 198.

[9] *E.g.* (*a*) F. Montanari, *Gazzeta*, 1957, **87**, 149; (*b*) G. Modena, *Ricerca sci.*, 1958, **28**, 341; (*c*) L. Maioli and G. Modena, *Gazzetta*, 1959, **89**, 854; (*d*) G. Modena and P. E. Todesco, *ibid.*, p. 866; (*e*) G. Modena, P. E. Todesco, and S. Tonti, *ibid.*, 1960, **90**, 878; (*f*) D. Landini and F. Montanari, *Chem. Comm.*, 1967, 180; (*g*) B. Cavalchi, D. Landini, and F. Montanari, *J. Chem. Soc.* (*C*), 1969, 1204; (*h*) A. N. Nesmeyanov, M. I. Rybinskaya, and T. G. Kelekhsaeva, *Zhur. Org. Khim.*, 1968, **4**, 921; (*i*) S. I. Miller and P. K. Yonan, *J. Amer. Chem. Soc.*, 1957, **79**, 5931; (*j*) A. M. Aguiar and D. Daigle, *ibid.*, 1964, **86**, 2299, *J. Org. Chem.*, 1965, **30**, 2826, 3527; (*k*) J. S. Meek and J. S. Fowler, *ibid.*, 1968, **33**, 985; (*l*) P. Beltrame and P. L. Beltrame, *Gazzetta*, 1968, **98**, 367.

[10] F. Scotti and E. J. Frazza, *J. Org. Chem.*, 1964, **29**, 1800.

[11] S. Baldwin, *J. Org. Chem.*, 1961, **26**, 3288; Z. Rappoport and E. Shohamy, *Israel J. Chem.*, 1968, **6**, 865.

[12] (*a*) W. E. Truce, J. E. Parr, and M. L. Gorbaty, *Chem. and Ind.*, 1967, 660; (*b*) W. E. Truce and M. L. Gorbaty, *J. Org. Chem.*, 1970, **35**, 2113; (*c*) J. S. Pizey and W. E. Truce, *J. Org. Chem.*, 1965, **30**, 4355; (*d*) S. Ghersetti, G. Lugli, G. Melloni, G. Modena, P. E. Todesco, and P. Vivarelli, *J. Chem. Soc.*, 1965, 2227.

[13] Y. Shvo, E. C. Taylor, and J. Bartulin, *Tetrahedron Letters*, 1967, 3259; Y. Shvo and H. Shanan-Atidi, *J. Amer. Chem. Soc.*, 1969, **91**, 6683, 6689; R. Osman, Ph.D. Thesis, University of Tel-Aviv, 1974.

[14] Z. Rappoport and A. Topol, unpublished results.

mediate carbanion by an α-Ph group compared with an α-CN group.

Relative Reactivities.—Table 3 summarises the relative reactivities of several nucleophiles in our system. Since severe steric interactions are not expected in the planar ground states of (*E*)- and (*Z*)-RCl, and the steric interactions in the tetrahedral transition states would be probably lower, large differences between the reactivities of (*E*)- and (*Z*)-RCl are not expected. This is borne out by the $k[(E)\text{-RCl}]/k[(Z)\text{-RCl}]$ ratios of 0.97—2.46 for all the nucleophiles, excluding EtO^-. This is reminiscent of the behaviour of many other systems where the change of configuration has a minor effect on the reactivity.[2,3,9] An exception is the reaction with EtO^- where the $k[(E)\text{-RCl}]/k[(Z)\text{-RCl}]$ ratios are 6.0—9.3. While ratios higher than unity were observed for systems where coplanarity between the activating group and the ethylene system is sterically hindered in one of the isomers,[5] this is not an important factor for our system, as judged by the other $k[(E)\text{-RCl}]/k[(Z)\text{-RCl}]$ ratios of Table 3. It is difficult to assess whether (*E*)-RCl reacts faster, or whether (*Z*)-RCl reacts slower than expected. Most of the reactions of ethoxide ion with other systems are either known or suspected to belong to the elimination–addition category,[2,3,15,16] and comparison of the scarce data for addition–elimination of EtO^-, ArS^-, and piperidine nucleophiles to various systems [2] does not give a definite answer to this question.

The higher reactivity of the *E*-isomer could be ascribed to an α-elimination–addition with the formation of the vinylic carbene Ph(CN)C=C**:**. Formation of this carbene in the reaction of the enol Ph(CN)C=CHOH and PCl_5 was inferred from the formation of 3,7-dicyano-1,2,5,6-dibenzocyclo-octatetraene (which is the dimer of the carbene) in this reaction.[8] However, attempts to form the dimer by reaction of (*E*)- and (*Z*)-RCl with potassium t-butoxide in several solvents resulted in the formation of β-t-butoxy-α-phenylacrylonitrile, but neither the geometry nor any other property of this ether was given.[8] In our opinion this is not evidence against an α-elimination–addition since formation of vinyl ethers from alkoxide ions and vinylic carbenes which were formed in an α-elimination–addition process was previously observed.[17] However, there is no reason why (*E*)-RCl will be more reactive since the base approaches the hydrogen atom from the less hindered side of the vinylic system. Moreover, a mixture of (*E*)- and (*Z*)-ROEt is expected for this route, as observed in the analogous reactions of vinyl trifluoromethanesulphonates,[17] contrary to the retention observed in our system. In order to exclude finally this mechanism we conducted the reaction with EtO^- in EtOD. Complete deuterium incorporation at the vinylic position will be the outcome of a reaction *via* vinylic carbene, but the i.r. of the product in EtOD showed no C–D absorption, and the n.m.r. suggested that if incorporation took place, its extent is low.

The nucleophilicity order of Table 3 differs in some details from that found [2] for the reaction of *trans*-β-chloro-α-*p*-tolylsulphonylethylene, where the relative reactivity order in MeOH at 0° is $p\text{-MeC}_6H_4S^-$ (290) > piperidine (260) > PhS^- (174) > MeO^- (28) > N_3^- (0.63). As in many other nucleophilic vinylic reactions [2] the soft arenethiolates are the most reactive nucleophiles, but the soft azide ion is the least reactive in our series, and the hard nucleophiles (EtO^-, PhO^-, amines) show moderate reactivities. The β-carbon of β-chloro-α-phenylacrylonitriles is neither too hard (as a carbonyl carbon) nor too soft (as a saturated carbon) and both basicity and polarisability contribute to the nucleophilic order. Symbiotic effects on the rates [18] may also be important and since chlorine is not too soft this effect may slightly favour the hard nucleophiles. Consequently, the balance between the basicity and the polarisability factors will strongly depend on the system studied, as shown by the $k(N_3^-)/k(\text{piperidine})$ ratios found for β-chloro-α,β-unsaturated ketones.[19] Caution is required when the rate constants for the amines are compared with those for the other nucleophiles, since when the reversal of the nucleophilic attack is faster than C–Cl bond cleavage the reaction will be second order but the rate coefficient will be composite and different from that for the nucleophilic attack step. While we have no evidence for this in our case, such behaviour was suggested for some vinylic substitutions by amines in closely related systems,[1] and in this case k_2 for piperidine and morpholine would be lower than the rate constant for the nucleophilic attack, and comparison with the anionic nucleophiles is unjustified.

The $k(p\text{-MeC}_6H_4S^-)/k(p\text{-ClC}_6H_4S^-)$ ratios lead to low Hammett's ρ values of −0.52 to −0.60. Other low Hammett ρ values were obtained in the substitution in the $p\text{-O}_2NC_6H_4CX{=}C(CO_2Et)_2$ system ($X = Cl$, $OSO_2C_6H_4Me\text{-}p$, or $OSO_2C_6H_4Br\text{-}p$; $\rho = -0.15$ to -0.5) [1] and for the reactions of (*E*)-PhC(Cl)=C(NO_2)Ph ($\rho = -0.9$),[14] but the values are lower than −1.22, −0.83, −0.95, and −1.9 for the nucleophilic additions of arenethiolate ions to phenyl vinyl sulphone,[20a] ethyl arylpropiolates,[20b] and *N*-methylmaleimide,[20c] respectively. Our values indicate that a large fraction of the negative charge still resides on the nucleophile in the transition state, and consequently, the transition state is early. The $k(EtO^-)/k(PhO^-)$ ratio of 5.1 with (*Z*)-RCl leads to a similar conclusion since the pK_a values of phenol and ethanol differ by several pK_a units. The $k(\text{piperidine})/k(\text{morpholine})$ ratios of 6.4—7.1 are of the order of magnitude found

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[15] (*a*) L. DiNunno, G. Modena, and G. Scorrano, *J. Chem. Soc.* (*B*), 1966, 1186; (*b*) J. Biougne, F. Théron, and R. Vessière, *Bull. Soc. chim. France*, 1972, 2882.

[16] J. C. Chalchat, F. Théron, and R. Vessière, *Bull. Soc. chim. France*, 1973, 2501.

[17] P. J. Stang, M. G. Mangum, D. P. Fox, and P. Haak, *J. Amer. Chem. Soc.*, 1974, **96**, 4562.

[18] C. K. Jorgensen, *Inorg. Chem.*, 1964, **3**, 1201; R. G. Pearson in 'Advances in Linear Free Energy Relationships, eds. N. B. Chapman and J. Shorter, Plenum Press, London, 1972, ch. 6.

[19] P. Beltrame, G. Favini, M. G. Cattania, and F. Guella, *Gazzetta*, 1968, **98**, 380.

[20] (*a*) P. de Maria and A. Fini, *J. Chem. Soc.* (*B*), 1971, 2335; (*b*) G. S. Krishnamurthy and S. I. Miller, *J. Amer. Chem. Soc.*, 1961, **83**, 3961; (*c*) D. Semenow-Garwood, *J. Org. Chem.* 1972, **37**, 3797.

by us for vinylic substitutions,[21] and by McDowell and Stirling for addition to *p*-tolyl vinyl sulphone in benzene,[22] and also fit an early transition state.

The relative reactivities in ethanol and in methanol $k(\text{EtOH})/k(\text{MeOH})$ are 2.5 ± 0.2 for N_3^- and 4.3 ± 0.4 for $p\text{-ClC}_6H_4S^-$. A faster rate for the ion–molecule reaction is expected in ethanol which has a low dielectric constant due to charge dispersal over the bulkier transition state,[23] and a $k(\text{EtOH})/k(\text{MeOH})$ ratio of 6.3 was found in the reaction of $p\text{-MeC}_6H_4S^-$ with *trans*-β-chloro-α-*p*-tolylsulphonylethylene.[9d] The $k(\text{EtOH})/k(\text{MeOH})$ ratio of 1.17 ± 0.03 for the reaction with piperidine suggests that stronger hydrogen bonds between the amine and methanol balance the expected increase in rate due to the higher polarity of the zwitterionic transition state.

The Effect of the α-Activating Group.—The effectivity of α-CN and α-Ph as activating groups is compared with that for the α-COPh and α-Ph groups by using the data of Beltrame and his co-workers [19] for the reaction of Ph(COPh)C=CHCl with piperidine in ethanol and with N_3^- in 98% EtOH. The $k[\text{Ph(CN)C=CHCl}]/k[\text{Ph(COPh)C=CHCl}]$ ratios at 30° are 182 for piperidine and 246 for N_3^- (neglecting the difference between 98 and 100% EtOH). These values are in sharp contrast with the $k(CH_2\text{=CHCOPh})/k(CH_2\text{=CHCN})$ ratio of 713 for the nucleophilic addition of morpholine in MeOH,[24] and with the lower activation by an α-CN compared with an α-COR in other nucleophilic vinylic reactions.[25] We believe that the relatively high reactivity of our system reflects an increase in the transition state energy in the reaction of PhC(COPh)=CHCl due to distortion of the benzoyl group from planarity. That the α-Ph group slightly activates the system for a nucleophilic attack is shown by the 1.73-fold higher reactivity of (*E*)-RCl compared with (*E*)-CHCl=CHCN,[10] in their reaction with piperidine in MeOH at 0°. Indeed, activation by two α-Ph groups is sufficient for the occurrence of the addition–elimination mechanism in the reaction of $p\text{-MeC}_6H_4S^-$ with 1-chloro-2,2-diphenylethylene.[26]

Comparison with the reactions of (*E*)- and (*Z*)-β-chlorocrotononitriles with EtO^- in EtOH,[16] shows that the *E*-isomer is 20.8-times slower, and the *Z*-isomer is 2.7-times faster than (*E*)- and (*Z*)-RCl, respectively. The reactions of the crotononitriles were ascribed to the elimination–addition route, and the preference of this route over the addition–elimination route probably reflects the deactivation by the β-methyl group of the latter route.

Activation Parameters.—Low activation enthalpies and compensating high negative activation entropies characterise the reactions with piperidine and morpholine. The formation of a dipolar transition state accounts for these observations, although a composite rate coefficient is also a plausible explanation.[21,27] The necessary desolvation of the anionic nucleophiles and charge dispersal over the anionic transition state, results in higher $\Delta H^\ddagger$ and more positive $\Delta S^\ddagger$ values for the anionic nucleophiles.

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 a Varian T-60 instrument, and the signal positions are given in δ units downfield from tetramethylsilane. The kinetic measurements were followed in the thermostatically controlled chamber of a Gilford 2400-S spectrophotometer.

Solvents and Materials.—Ethanol (Frutarom), b.p. 78°, and methanol (Frutarom), b.p. 65°, were purified according to Vogel.[28] (*E*)- and (*Z*)-β-chloro-α-phenylacrylonitriles were prepared according to Cariou.[6] The *E*-isomer has b.p. 125° at 10 mmHg, $\lambda_{\text{max.}}$ (EtOH) 261.5 nm (ε 10 000), $\nu_{\text{max.}}$ (neat) 2 235 and 1 685 cm^{-1}, $\delta(\text{CDCl}_3)$ 7.04 (1H, s, :CH), and 7.35—7.86 (5H, m, Ph), *m/e* 165 (35%, 100%, *M*), 128 (89, *M* – Cl), and 101 (35, *M* – HCl – CN). The *Z*-isomer has m.p. 53°, $\lambda_{\text{max.}}$ (EtOH) 221 (ε 11 400) and 267.5 nm (11 600), $\nu_{\text{max.}}$ (CHCl_3) 2 240 and 1 680 cm^{-1}, $\delta(\text{CDCl}_3)$ 7.18 (1H, s, :CH) and 7.42—7.54 (5H, m, Ph), *m/e* 165, 163 (35%, 100%, *M*), 128 (93, *M* – Cl), 101 (33, *M* – HCl – CN).

Preparation of the Substitution Products.—(a) *Enamines*. Two equiv. of morpholine or piperidine were added to one equiv. of the vinyl chloride in dry acetonitrile. The solvent was evaporated after 3 h, the remainder was dissolved in dry ether, the ammonium hydrochloride salt was filtered, the ether was evaporated, and the solid was crystallised from methanol.

(b) *Vinyl sulphides*. 1.1 Equiv. of the thiol and of sodium ethoxide and one equiv. of the vinyl chloride were reacted in ethanol. After 5 min, 20% of the vinyl sulphide had already precipitated and was filtered after 1 h. The solvent was evaporated, the remainder was dissolved in ether, washed with 5% HCl and water, dried (MgSO_4), and the ether was evaporated. The combined solids were crystallised from ethanol or chromatographed.

(c) *Vinyl ethers*. The ethyl ethers were obtained from reaction of a 2 : 1 mixture of sodium ethoxide and the vinyl chloride in ethanol. Work-up similar to that described for the vinyl sulphides gave the ethyl vinyl ethers as liquids which were purified by distillation. The phenyl ether was prepared from reaction of a 1 : 1 : 1 mixture of phenol, triethylamine, and (*Z*)-RCl in acetonitrile, following the work-up described above. The *Z*-phenoxide was distilled *in vacuo* and then recrystallised.

(d) *Vinyl azides*. A 5 : 1 mixture of sodium azide and the vinyl chloride was kept in methanol at 0° for 12 h, and then the solvent was evaporated at 20°. The remainder was

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[21] Z. Rappoport and A. Topol, *J.C.S. Perkin II*, 1972, 1823.

[22] S. T. McDowell and C. J. M. Stirling, *J. Chem. Soc.* (*B*), 1967, 342.

[23] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' Wiley, New York, 1963, p. 147; E. S. Amis, 'Solvent Effects on Reaction Rates and Mechanisms,' Academic Press, New York, 1966.

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

[25] R. N. Ring, G. C. Tesoro, and D. R. Moore, *J. Org. Chem.*, 1967, **32**, 1091; M. Friedman and J. Wall, *ibid.*, 1966, **31**, 2888.

[26] P. Beltrame, D. Pitea, and M. Simonetta, *J. Chem. Soc.* (*B*), 1967, 1108.

[27] Z. Rappoport, P. Greenzaid, and A. Horowitz, *J. Chem. Soc.*, 1964, 1334.

[28] A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, 1956, 3rd edn., pp. 166—169.

dissolved in dry ether, filtered, and evaporated, leaving a solid or an oil, which was crystallised and recrystallised from ether and light petroleum at 20°.

The analyses and the physical properties of the products are given in Table 6. and their spectral properties in Table 5.

The m.p.s of the crude products were always identical, or at most 2° lower, than those of the recrystallised samples, and i.r. of the crude products did not show any evidence for the presence of geometrical isomers. G.l.c. of the crude material using Carbowax SE-30 columns, or t.l.c. using silica or alumina columns always resulted in $E \rightleftharpoons Z$ isomerisation.

TABLE 6

Analytical data for HCX=C(Ph)CN

X	Con-figuration	Yield (%)	M.p. (°C)	Cryst. solvent	Found (%)					Formula	Required (%)				
					C	H	N	Hal	S		C	H	N	Hal	S
OC_4H_8N [a]	*Z*	82	114—116	MeOH	73.0	6.9	13.15			$C_{13}H_{14}N_2O$	72.85	6.6	13.05		
$C_5H_{10}N$ [b]	*Z*	85	105—108	MeOH	78.95	7.5	12.95			$C_{14}H_{16}N_2$	79.2	7.6	13.2		
p-ClC_6H_4S	*Z*	74	140—141	EtOH	66.5	3.65	5.2	12.9	1115	$C_{15}H_{10}ClNS$	66.45	3.7	5.15	13.0	11.7
p-ClC_6H_4S	*E*	76	105—107	EtOH	66.15	3.7	5.1	12.8	11.8	$C_{15}H_{10}ClNS$	66.45	3.7	5.15	13.0	11.7
p-MeC_6H_4S	*Z*	78	75—76	EtOH	76.15	5.15	5.3		12.5	$C_{16}H_{13}NS$	76.5	5.2	5.55		12.75
p-MeC_6H_4S	*E*	65	70—72	*c*	76.15	5.45	5.2		13.15	$C_{16}H_{13}NS$	76.5	5.2	5.55		12.75
OPh	*Z*	65	33 [d]		81.25	5.15	6.4			$C_{15}H_{11}NO$	81.45	5.0	6.35		
OEt	*Z*	90	*e*		76.1	6.6	8.35			$C_{11}H_{11}NO$	76.3	6.4	8.1		
OEt	*E*	52	*f*		76.0	6.65	8.5			$C_{11}H_{11}NO$	76.3	6.4	8.1		
N_3	*Z*	95	64—66	*g*	63.4	3.25	32.65			$C_9H_6N_4$	63.5	3.55	32.9		
N_3	*E*	87	18—20	*h*	63.4	3.7	33.05			$C_9H_6N_4$	63.5	3.55	32.9		

[a] Morpholino. [b] Piperidino. [c] Purified by t.l.c. [d] B.p. 190° at 4 mmHg. [e] B.p. 170° at 4 mmHg. [f] B.p. 170° at 5 mmHg. [g] Ether–light petroleum. [h] Light petroleum.

Kinetic Procedure.—The kinetic procedure and the calculation method of the rate coefficients are identical with those described earlier.[1]

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