Nucleophilic Attacks on Carbon–Carbon Double Bonds. Part XXI.[1] Substitution of (*E*)-α-Chloro-β-nitrostyrene by Anilines in Acetonitrile

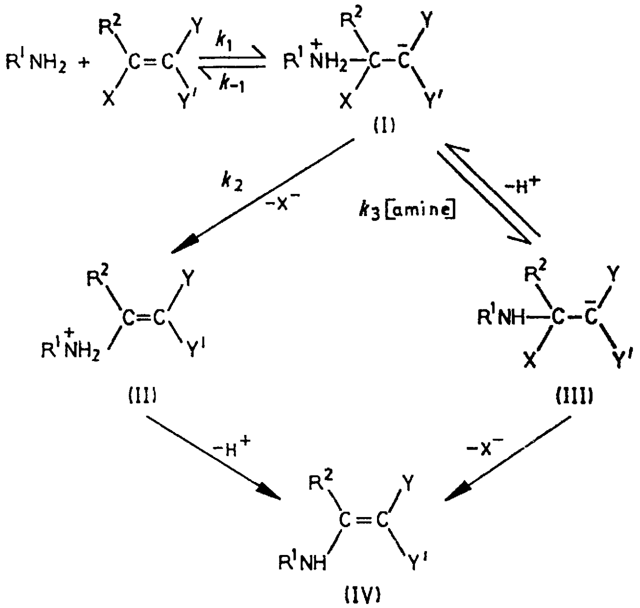
By **Zvi Rappoport** * and **Shmaryahu Hoz**, Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel

The replacement of the chloro-substituent of (*E*)-α-chloro-β-nitrostyrene (VI) by substituted anilines in acetonitrile, which gives the corresponding nitro-enamines (VII), is first-order in the amine, giving $\Delta H^\ddagger$ = 3·7—5·7 kcal mol^{-1}, $\Delta S^\ddagger$ = −50 to −58 cal mol^{-1} K^{-1} and a Hammett ρ value of 3. Replacing the vinylic hydrogen atom of (VI) by deuterium resulted in an isotope effect of *ca.* 1 with several anilines, and in the reaction of aniline with (VI) in MeCN–D$_2$O no deuterium is incorporated into the product (VII). A multi-step mechanism, in which the nucleophilic attack step (k_1) to form the zwitterion (I) is followed by its reversal (k_{-1}) or by expulsion of chloride ion from (I) (k_2), with $k_{obs} = k_1k_2/k_{-1}$, is suggested. The absence of catalysis in the reactions of (VI) and the activating effect of the nitro-group in nucleophilic vinylic substitution are discussed.

SUBSTITUTION of electrophilic olefins which carry a 'sluggish' leaving group (X = F,[2-4] CN,[4,5] OEt,[5] or O·CH$_2$·CF$_3$ [6]) by amines shows both a first-order and a second-order dependence on amine [equation (1); k_{obs}

$$k_{obs} = k_2' + k_3'[\text{amine}] \qquad (1)$$

is a second-order constant]. The amine catalysis, *i.e.* the second-order term in amine, is taken as evidence for the multi-step Scheme 1, which involves competition between leaving group expulsion (k_2) from, and base-catalysed (k_3[amine]) deprotonation of, the ammonium ion residue of the zwitterion (I). Steady-state treatment of Scheme 1 gives equation (2), which fits



SCHEME 1 Y and Y′ are activating groups

$$k_{obs} = k_1(k_2 + k_3[\text{amine}])/(k_{-1} + k_2 + k_3[\text{amine}]) \qquad (2)$$

the observed kinetics when $k_{-1} \gg (k_2 + k_3[\text{amine}])$. However, overall second-order kinetics in reactions with amines does not necessarily mean that k_1 is rate determining,[7] since this behaviour may also be observed when $k_{-1} > k_2 > k_3$[amine], and the rate constant is composite [equation (3)].

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

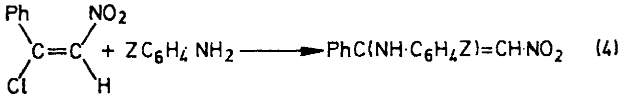
An extensive search for amine catalysis in reactions of systems carrying good leaving groups (X = Cl, Br, OTs, OBs, or OMs) [2,3,8] revealed only one such case, the reaction of 2-chloro-1,1-dicyano-2-*p*-dimethylaminophenylethylene (V) with ring-substituted anilines in acetonitrile [2a] or in tetrahydrofuran.[8b] The values of

$$p\text{-Me}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CCl}{=}\text{C(CN)}_2$$

(V)

k_3'/k_2' for this system were low, and although there is little doubt that base catalysis is involved, it was of interest to search for amine catalysis in another system.

We chose the reaction of (*E*)-α-chloro-β-nitrostyrene with ring-substituted anilines in acetonitrile [equation (4)] for several reasons, as follows. (*a*) An obvious way to increase the likelihood of observing catalysis is to reduce k_2 relative to k_3[amine]. Increase in the negative charge dispersal ability of the groups Y and Y′ will reduce the availability of the electron pair on the carbon atom adjacent to that carrying X, and consequently will reduce the rate of internal displacement (k_2). The correlation between log k for the addition of amines to the CH$_2$=CHX system and the pK_a values of MeX,[9] coupled with the relatively high acidity of MeNO$_2$,[10]



$$\text{PhClC}{=}\text{CH·NO}_2 + \text{ZC}_6\text{H}_4\text{NH}_2 \longrightarrow \text{PhC(NH·C}_6\text{H}_4\text{Z)}{=}\text{CH·NO}_2 \qquad (4)$$

(VI) (VII)

---

[1] Part XX, Z. Rappoport and D. Ladkani, *J.C.S. Perkin I*, 1974, 2595.

[2] Z. Rappoport and R. Ta-Shma, *J. Chem. Soc.* (*B*), 1971, (*a*) p. 871; (*b*) p. 1461.

[3] Z. Rappoport and N. Ronen, *J.C.S. Perkin II*, 1972, 955.

[4] Z. Rappoport and P. Peled, *J.C.S. Perkin II*, 1973, 616.

[5] Z. Rappoport and D. Ladkani, *J.C.S. Perkin II*, 1973, 1045.

[6] Z. Rappoport and P. Peled, unpublished results.

[7] (*a*) G. Modena, P. E. Todesco, and S. Tonti, *Gazzetta*, 1959, **89**, 878; (*b*) G. Modena, F. Taddei, and P. E. Todesco, *Ricerca. Sci.*, 1960, **30**, 894; (*c*) L. Maioli, G. Modena, and P. E. Todesco, *Boll. sci. Fac. Chim. ind. Bologna*, 1960, **18**, 66; (*d*) A. Campagni, G. Modena, and P. E. Todesco, *Gazzetta*, 1960, **90**, 694; (*e*) P. Beltrame, G. Favini, M. G. Cattania, and F. Guella, *ibid.*, 1968, **98**, 380.

[8] Z. Rappoport and A. Topol, *J.C.S. Perkin II*, (*a*) 1972, 1823; (*b*) in the press.

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

[10] R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, 1953, **75**, 2439.

suggests that a nitro-group will disperse the negative charge effectively. (*b*) Although the nitro-group has been placed at the top of the list of single activating groups in nucleophilic vinylic reactions [9] in the light of indirect evidence based on the rates of addition to [11] and cleavage of [12] nitro-olefins, data for direct comparison with those for other activating groups are lacking. For reaction with anilines, the Hammett ρ value may be compared with those for related reactions.[2,5] (*c*) Substitution of compound (VI) may also occur *via* the elimination–addition route.[13] The competition between this route and the addition–elimination route had been studied previously for several substrates,[13] and it was of interest to discover whether the course of substitution would be governed by the enhanced acidity of an α-hydrogen atom or by the simultaneous enhanced electrophilicity of a β-carbon atom caused by an α-nitro-group.

RESULTS

(*E*)-α-Chloro-β-nitrostyrene (VI) was prepared by the addition of an excess of nitrosyl chloride to phenylacetylene.[14] Reference 14 reports the formation of both (*E*)- and (*Z*)-isomers in 33·5 and 5·9% yield, respectively, but in our hands only the *E*-isomer was obtained. Assuming that the excess of nitrosyl chloride oxidises the initially formed α-chloro-β-nitrosostyrene to (VI), we tried using a dilute solution of hydrogen peroxide instead of the excess amount of reagent. Under these conditions the yield of (VI) was reduced and the *Z*-isomer was not formed. Attempts to convert the *E*- into the *Z*-isomer by photoisomerisation failed.

TABLE 1

Reaction of (*E*)-α-chloro-β-nitrostyrene (VI) with *m*-toluidine in acetonitrile

10^3 [(VI)]/mol l^{-1}	0·5	1·0	1·0	1·0	1·0	1·0	1·5	3·3	
10^3 [$ArNH_2$]/mol l^{-1}	6·8	1·3	4·0	6·7	12·0	16·3	6·7	6·7	
10^4k_2/l mol^{-1} s^{-1} at 30°		24·3	22·2	23·2	25·2		23·5	21·8	23·4 ± 1·2 [a]
10^4k_2/l mol^{-1} s^{-1} at 45°	31·8	34·6		31·8		31·7	34·4		32·8 ± 1·3 [a]

[a] Average value.

Campbell and Schultz [15] report that chlorination of 2-nitroacetophenone with phosphorus pentachloride gives α-chloro-β-benzoyl-β-nitrostyrene. We tried treating 2-nitroacetophenone with the milder chlorination reagents oxalyl chloride and thionyl chloride, but neither the *E*- nor the *Z*-isomer of (VI) was formed under various experimental conditions.

The replacement of the chlorine atom of (VI) by seven ring-substituted anilines was followed spectrophotometrically in dry acetonitrile at 30 and at 45° by observing the change in absorption at 365—370 nm [$\lambda_{max.}$ of the product nitro-enamines (VII)]. Six or more runs at various amine and substrate concentrations were conducted at each temperature; at least four different amine concentrations covering a 5- to 10-fold change were studied. An excess of amine was used, and division of the first-order rate constants thus obtained by the amine concentrations gave the second-order constants, k_{obs}. These were reasonably constant, although at high amine or substrate concentrations they were sometimes slightly lower than the average values. No apparent increase of k_{obs} with [amine] was observed, and the overall second-order behaviour is demonstrated for *m*-toluidine in Table 1. The concentration range of the amines studied, the average rate constants, and the derived activation parameters are given in Table 2. The activation enthalpies are very low (3·7—5·7 kcal mol^{-1}) and the activation entropies are highly negative (−50 to −58 cal mol^{-1} K^{-1}).

Hammett plots, constructed using Jaffe's σ values,[16] give ρ values of −2·99 ± 0·35 and −3·01 ± 0·34 at 30 and 45°, respectively, with correlation coefficients of 0·967 and 0·969.

The reactions of β-deuteriated (VI) {[^{2}H](VI)} with *p*-anisidine and with *p*-chloroaniline were compared with those of the unlabelled (VI) in order to evaluate the extent, if any, of elimination–addition. Exchange of the deuterium of [^{2}H](VI) with traces of adventitious water, which, if it happens, may reduce the isotope effect, was avoided by comparing the reaction rates of [^{2}H](VI) in acetonitrile containing added D_2O (50 µl) with those of (VI) in acetonitrile containing added H_2O (50 µl). The assumption that the low water concentrations result in no appreciable solvent isotope effect is supported by the similarity of k_{obs} values for reactions with and without the added water. The data in Table 3 show that the isotope effect {*k*(VI)/*k*[^{2}H](VI)} for three anilines is unity within experimental error.

TABLE 2

Rate data for the substitution of (*E*)-α-chloro-β-nitrostyrene by anilines ($ZC_6H_4{\cdot}NH_2$) in acetonitrile

Z	Amine concn. (10^4 mol l^{-1})	10^4k_2/l mol^{-1} s^{-1} at 30°	10^4k_2/l mol^{-1} s^{-1} at 45°	$\Delta H^‡$/ [a] kcal mol^{-1}	$\Delta S^‡$ (30°)/ [b] cal mol^{-1} K^{-1}
p-Cl	96—1455	4·2 ± 0·3	6·4 ± 0·3	4·8	−58
m-MeO	11—128	12·5 ± 0·4	18·8 ± 0·3	4·6	−57
H	33—223	16·3 ± 1·0	25·1 ± 0·9	4·9	−55
p-F	15—148	18·3 ± 2·0	26·4 ± 0·7	4·1	−58
m-Me	13—163	23·4 ± 1·2	32·8 ± 1·3	3·7	−58
p-Me	6—500	51·3 ± 5·3	83·9 ± 6·7	5·7	−50
p-MeO	3·3—23	197 ± 5	296 ± 12	4·6	−51

[a] Estimated ±1 kcal mol^{-2}. [b] Estimated ±3 cal mol^{-1} K^{-1}.

The possibility of incorporation of deuterium from the medium into the product in the reaction of (VI) with aniline in 10 : 1 MeCN–D_2O was investigated by comparing the i.r. spectrum of the isolated material with that of authentic β-deuteriated enamine. No deuterium incorporation was observed. Study of the reaction of [^{2}H](VI)

---

[11] A. N. Nesmeyanov, L. V. Rybin, and M. I. Rybinskaya, *Zhur. org. Khim.*, 1966, **2**, 991.

[12] T. I. Crowell and A. W. Francis, jun., *J. Amer. Chem. Soc.*, 1961, **83**, 591; see also S. Patai and Z. Rappoport, in 'The Chemistry of Alkenes,' ed. S. Patai, Wiley–Interscience, New York, 1964, ch. 8.

[13] (*a*) Z. Rappoport, *Adv. Phys. Org. Chem.*, 1969, **7**, 1; (*b*) G. Modena, *Accounts Chem. Res.*, 1971, **4**, 73.

[14] I. Iwai, K. Tomita, and J. Ide, *Chem. and Pharm. Bull.* (*Japan*), 1965, **13** (2), 118.

[15] R. D. Campbell and F. J. Schultz, *J. Org. Chem.*, 1960, **25**, 1877.

[16] H. H. Jaffe, *Chem. Rev.*, 1953, **53**, 206.

with aniline in dry acetonitrile did not show any decrease in the C–^{2}H peak at 2320 cm^{-1}, while mass spectra showed the formation of β-deuteriated (VII; Z = H). Undeuteriated (VII; Z = *p*-MeO) does not incorporate deuterium from MeCN–D_2O either in the presence or in the absence of added *p*-anisidine.

TABLE 3

Isotope effects in the reactions of compounds (VI) and [^{2}H](VI) with anilines in acetonitrile

Compound	Concn. (10^3M)	Aniline	Concn. (10^2M)	Additive	T/°C	10^3k_{obs}/ l mol^{-1} s^{-1}	k(VI)/ k[^{2}H](VI)
(VI)	0·5—3·0	*p*-H	1·2—2·2		30	1·63 ± 0·1 [a]	
(VI)	1·98	*p*-H	1·2		30	1·52	
[^{2}H] (VI)	2·04	*p*-H	1·3	50 μl D_2O	30	1·72	
[^{2}H] (VI)	2·04	*p*-H	1·3	50 μl H_2O	30	1·65	0·98
[^{2}H] (VI)	2·55	*p*-H	1·7		30	1·60	
(VI)	0·77	*p*-Cl	2·6		45	0·69	0·96
[^{2}H] (VI)	0·75	*p*-Cl	2·6		45	0·72	
[^{2}H] (VI)	1·24	*p*-Cl	2·6		45	0·72	
(VI)	0·77	*p*-MeO	0·033		45	31·3	
[^{2}H] (VI)	0·75	*p*-MeO	0·033		45	32·5	0·96

[a] Average value of several experiments (*cf.* Table 2).

Hydrogen–deuterium exchange does not take place even with a tertiary amine (triethylamine) in acetonitrile–deuterium oxide mixtures. On mixing triethylamine with (VI) a red colour which may be due to a complex slowly develops but was not investigated further. At reaction times when the substitution of (VI) by *p*-anisidine was complete, the recovered (VI) from the reaction with triethylamine did not show any deuterium incorporation.

DISCUSSION

Exclusion of the Elimination–Addition Route.—There is a fine balance between the addition–elimination and elimination–addition mechanisms at activated vinylic carbon,[13] and both should be considered for systems containing a vinylic hydrogen atom. The elimination–addition route has been observed with vinyl halides activated by arylsulphonyl,[17] aroyl,[18] and aryl [19] groups with alkoxide nucleophiles, and for arylsulphonylvinyl [20] and cyanovinyl [21] halides with amines. The *cis*-disposition of H and the Cl in (VI) will hinder the $E2$ reaction, but an elimination–addition with an initial E1cB step should be considered. The 'irreversible' [22] E1cB variant calls for an appreciable isotope effect $\{k(\mathrm{VI})/k[^2\mathrm{H}](\mathrm{VI})\}$ and for little or no deuterium incorporation from the solvent into both (VI) and the products. The 'reversible' E1cB [22] calls for deuterium incorporation into (VI) and into the products (VII).

Table 3 and the experiments performed in the presence of low concentrations of added D_2O or H_2O show the absence of deuterium isotope effect for the reactions of three anilines which cover the whole reactivity spectrum investigated. The reactions of anilines with (VI) in MeCN–D_2O and with [^{2}H](VI) in MeCN–H_2O showed no incorporation of the corresponding hydrogen isotope from the solvent into the product (VII; X = *p*-MeO), which does not exchange its vinylic deuterium under the reaction conditions. Both experiments exclude the elimination–addition *via* E1cB, and the absence of isotope effect excludes the $E2$ route as well; we therefore discuss our reaction in terms of the addition–elimination route (Scheme 1). The absence of the elimination–addition route is in accord with the behaviour observed with other systems,[17-21] in that attack of amines occurs preferentially at the electrophilic carbon atom rather than at the vinylic hydrogen atom, and when the elimination–addition route is observed with amines in alcohols, it is a consequence of the formation of another basic species, the alkoxide ion.[20,21]

The Addition–Elimination Route. Absence of Catalysis.—The second-order kinetics fit either (*a*) a rate-determining nucleophilic attack such that $(k_2 + k_3[\mathrm{amine}]) \gg k_{-1}$ (either $k_2 \gg k_3[\mathrm{amine}], k_{-1}$ or $k_3[\mathrm{amine}] \gg k_2, k_{-1}$) and $k_{obs} = k_1$; or (*b*) a reversible nucleophilic addition followed by a non-catalysed halide ion expulsion which is faster than the catalysed route, *i.e.* $k_{-1} \gg k_2 \gg k_3[\mathrm{amine}]$, and k_{obs} is given by equation (3). As suggested previously,[2b,4,5] k_3 is not necessarily rate-determining in the catalysed route. The reaction may proceed *via* a pre-equilibrium deprotonation of (I) to (III), followed by a rate-determining ammonium-ion-assisted expulsion of X^-, which will show the same kinetics. However, in the absence of data we prefer to discuss our results in terms of the simpler scheme where k_3 is rate-determining.

Reactions of electrophilic olefins have usually been treated in terms of (*a*) above both for anionic nucleophiles and for amines;[13] variant (*b*) is usually considered for sluggish leaving groups. However, although the evidence is not conclusive, two analogies suggest that variant (*b*) and equation (3) may apply for our system. First, the catalysis for system (V) [2,3] showed the feasibility of route (*b*) for the reaction of amines with the similarly reactive (VI). Secondly, the activation enthalpies are much lower than those (11·5—15 kcal mol^{-1}) found for reactions of amines with various electrophilic olefins,[13a] while the activation entropies are much more negative. Similar activation parameters have been found earlier for the reactions of anilines with (V) in acetonitrile ($\Delta H^\ddagger$ = 6·7—10·9 kcal mol^{-1}; $\Delta S^\ddagger$ = −43 to −52 cal mol^{-1} K^{-1}),[20] for the reaction of tricyanovinyl chloride with *NN*-dialkylanilines ($\Delta H^\ddagger$ = 0·8—2·0 kcal mol^{-1}; $\Delta S^\ddagger$ = −52 to −56 cal mol^{-1} K^{-1}),[23] and for the reactions of piperidine and morpholine with 2,2-bisethoxycarbonyl-1-*p*-nitrophenylvinyl toluene-*p*-sulphonate ($\Delta H^\ddagger$ = 3·1—5·1 kcal mol^{-1}; $\Delta S^\ddagger$ = −50 to −54 cal mol^{-1} K^{-1}),[8a] and were ascribed to a composite rate constant [according to equation (3)]. The $\Delta H^\ddagger$ values (3·7—5·7 kcal mol^{-1}) of Table 2 are only few kcal higher than those for diffusion-controlled processes. Only the compensating extremely high negative activation entropies (−50 to −58 cal mol^{-1} K^{-1}) reduce the rate constants to easily measured

---

[17] L. DiNunno, G. Modena, and G. Scorrano, *J. Chem. Soc.* (*B*), 1966, 1186.

[18] D. Landini, F. Montanari, G. Modena, and F. Naso, *J. Chem. Soc.* (*B*), 1969, 243.

[19] *E.g.* G. Marchese, G. Modena, F. Naso, and N. Tangari, *Boll. sci. Fac. Chim. ind. Bologna*, 1968, **26**, 209; *J. Chem. Soc.* (*B*), 1970, 1196.

[20] S. Ghersetti, G. Lugli, G. Melloni, G. Modena, P. E. Todesco, and P. Vivarelli, *J. Chem. Soc.*, 1965, 2227.

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

[22] D. J. McLennan, *Quart. Rev.*, 1967, **21**, 490.

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

values. Other reactions of amines with electrophilic olefins, having low $\Delta H^\ddagger$ and high negative $\Delta S^\ddagger$ values,[24] could be interpreted similarly.

In terms of equation (3) one can write $\Delta H^\ddagger = \Delta H^0 + \Delta H_2^\ddagger$ and $\Delta S^\ddagger = \Delta S^0 + \Delta S_2^\ddagger$, where ΔH^0 and ΔS^0 are the enthalpy and the entropy changes for the equilibrium (5), and $\Delta H_2^\ddagger$ and $\Delta S_2^\ddagger$ are the activation parameters for the k_2 step. The ΔH^0 and the ΔS^0 values

$$\text{(VI)} + \text{amine} \rightleftharpoons \text{(I)} \qquad (5)$$

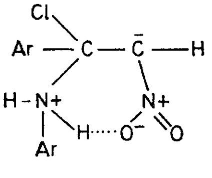
should be similar to those ($\Delta H^0 = -13·4$ to $-21·4$ kcal mol^{-1}; $\Delta S^0 = -27·4$ to -50 cal mol^{-1} K^{-1}) measured for the equilibrium (6).[25] The k_2 value should be very high, with a low $\Delta H_2^\ddagger$ value, since the reaction

$$\text{Bu}_3\text{P} + \text{ArCH}{=}\text{C(CN)}_2 \rightleftharpoons \text{ArCH}(\overset{+}{\text{P}}\text{Bu}_3)\text{-}\overset{-}{\text{C}}\text{(CN)}_2 \qquad (6)$$

is faster than the amine-catalysed deprotonation of (I). Moreover, k_2 values for good leaving groups should be very high in order to explain the retention of stereochemistry associated with nucleophilic vinylic substitutions.[13a] The $\Delta H^\ddagger$ values for analogous processes, *i.e.* the expulsion of nitro,[26] methoxy,[27] or cyano[28] as anions from carbanions, are 20—25 kcal mol^{-1}, but the values for the much faster expulsion of Cl^-, which has an earlier transition state,[29] may be lower, resulting in an overall low $\Delta H^\ddagger$.

Evaluating $\Delta S_2^\ddagger$ is difficult since the difference in the extents of charge dispersal between the ground and the transition states are unknown; however for an earlier transition state the $\Delta S_2^\ddagger$ term should be low. Even in cases where the transition states are relatively late, as in the expulsion of NO_2^- [26] or MeO^- [27] from a carbanion, the $\Delta S_2^\ddagger$ values are close to zero.

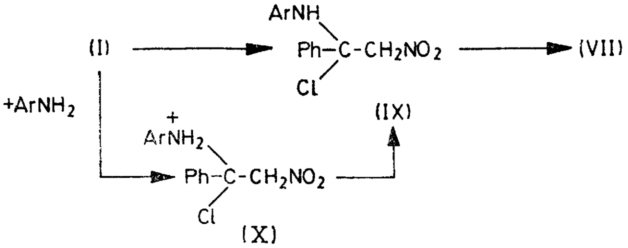
In addition to the usual high negative ΔS^0 and negative ΔH^0 values associated with zwitterion formation, internal hydrogen bonding between the strong donor (ammonium ion) and the strong acceptor (NO_2 group) in the six-membered transition state (VIII) will further lower both ΔH^0 and ΔS^0, with a compensating effect on k_{obs}. Similar stabilising hydrogen bonds have been suggested for the zwitterion formation in the addition of amines to β-nitrostyrenes.



(VIII)

The absence of catalysis shows that at our amine concentrations first-order expulsions of either chloride ion or the aniline (as anilinium ion), which are both good leaving groups, are faster than the deprotonation of the ammonium ion of (I). That the second-order deprotonation is not competitive with k_{-1} or k_2 may be due to the k_3[amine] term in our reaction being lower than the same term in the reaction of (V), since for reactivity reasons the amine concentrations studied with (VI) are lower than those studied with (V). However, the difference between the α- and the β-substituents in the two systems should be also taken into account. Catalysis at much higher amine concentrations than those used in the present work is not excluded.

Another mechanistic variant (Scheme 2) involves the saturated adduct(s) (IX) and/or (X), formed from (I) either by an internal proton transfer or by proton transfer from another amine molecule. In analogy with the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values observed for nucleophilic vinylic addition of amines to electrophilic olefins,[9] reaction *via* Scheme 2 would also show low $\Delta H^\ddagger$ and high negative $\Delta S^\ddagger$ values. However, Scheme 2 is excluded since it requires that in the deuteriated media (IX) and (X) will be partially deuteriated, and some of the label should be retained in the products (VII), contrary to observation. Moreover, an amine catalysis is likely for Scheme 2 in the (*E*1cB) step (IX) ⟶ (VII).



Scheme 2

Activation by Electron-attracting Substituents.—The ratio of the second-order rate constants, *k*(VI) : *k*(V), for the reaction with aniline is 3·9 : 1 in acetonitrile at 30°. ρ Values for changes of the aryl group of (V) are not available, but data on nucleophilic vinylic reactions[30] of the systems $ArCX{=}C(CN)_2$ with water,[31] cyanide ion,[32] di-isobutylamine,[32] and cyclopentadienylidenetriphenylphosphorane[33] give ρ *ca.* 1·5, and addition of aniline to $ArCH{=}CHNO_2$ gives ρ 2·08;[34] lower ρ values have been found for more reactive amines.[34] Taking ρ as 1·5 for our reaction, we calculate $k(PhCCl{=}CH\text{-}NO_2)/k\{PhCCl{=}C(CN)_2\} = 0·22$ for the reaction with aniline. There is a linear relationship between log *k* for the addition of amines to mono-X-activated olefins in MeOH and the $-pK_a$ value of MeX in water,[9] with a slope of 0·46. Although systems

---

[24] D. Capocasale, L. Di Nunno, S. Florio, and F. Naso, *J.C.S. Perkin II*, 1973, 2078.

[25] Z. Rappoport and S. Gertler, *J. Chem. Soc.*, 1964, 1360.

[26] A. Berndt, *Angew. Chem. Internat. Edn.*, 1969, **8**, 613.

[27] F. G. Bordwell, M. M. Vestling, and K. C. Yee, *J. Amer. Chem. Soc.*, 1970, **92**, 5950.

[28] (*a*) Z. Rappoport and E. Shohamy, *J. Chem. Soc.* (*B*), 1971, 2060; (*b*) M. Albeck, S. Hoz, and Z. Rappoport, *J.C.S. Perkin II*, 1972, 1248.

[29] G. S. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.

[30] Z. Rappoport and D. Ladkani, *Chemica Scripta*, 1974, **5**, 124.

[31] S. Patai and Z. Rappoport, *J. Chem. Soc.*, 1962, 383.

[32] R. B. Pritchard, C. E. Lough, J. B. Ressor, H. L. Holmes, and D. J. Currie, *Canad. J. Chem.*, 1967, **45**, 775.

[33] E. Lord, M. P. Naan, and C. D. Hall, *J. Chem. Soc.* (*B*), 1971, 213.

[34] C. E. Lough and D. J. Currie, *Canad. J. Chem.*, 1966, **44**, 1563.

activated by two substituents Y and Y′ do not follow this relationship quantitatively,[35] it is interesting that for (VI) and for (V; X = H), the 'slope' of such a relationship will be negative since $\Delta \log k = -0{\cdot}66$ and $\mathrm{p}K_a\{\mathrm{CH_2(CN_a)_2}\} - \mathrm{p}K_a(\mathrm{MeNO_2}) = 1{\cdot}02$ in water.[10] This behaviour may be due to the measurement of log k in acetonitrile and of the pK_a values in water. Indeed, malonitrile in dimethyl sulphoxide is a stronger acid (pK_a 11·0) [36] than nitromethane (pK_a 15·9) [37] and if this applies also to acetonitrile, for which pK_a data are not available, a positive 'slope' will be obtained for (V; X = H) and (VI).

The fact that the reactivity of our nitro-activated compound is lower than expected in comparison with other activating groups finds precedent in a nucleophilic vinylic addition [11] and in E1cB eliminations.[38] Common to these reactions is a rate-determining formation of an α-nitro-carbanion, and the lower reactivity may be explained in terms similar to those used for explaining the slow formation of α-nitrocarbanions from the corresponding carbon acids.[39]

TABLE 4

Analytical and spectral data for α-arylamino-β-nitrostyrenes [PhC(ZC$_6$H$_4$·NH)=CH·NO$_2$]

Z	M.p. (°C)	Found (%) C	Found (%) H	Found (%) N	Found (%) Hal	Formula	Required (%) C	Required (%) H	Required (%) N	Required (%) Hal	λ$_{\max.}$ (MeCN)/nm (ε)
p-Me	95	70·8	5·75	11·05		$C_{15}H_{14}N_2O_2$	70·85	5·55	11·0		234 (11,800), 295 (5400), 369 (19 000)
H [a]	124	70·0	4·9	11·6		$C_{14}H_{12}N_2O_2$	70·0	5·05	11·65		234 (10,900), 293 (5000), 368 (19,500)
p-MeO	70	67·05	5·2	10·3		$C_{15}H_{14}N_2O_3$	66·65	5·2	10·35		234 (14,700), 302 (7100), 369 (17,000)
m-Me	125	71·0	5·35	11·05		$C_{15}H_{14}N_2O_2$	70·85	5·55	11·0		234 (10,000), 295 (4900) 369 (19,300)
p-Cl	135	61·35	3·9	10·1	13·25	$C_{14}H_{11}ClN_2O_2$	61·3	4·0	10·2	12·95	239 (13,200), 293 (5900) 369 (21,600)
p-F	142	65·2	4·15	10·85	7·25	$C_{14}H_{11}FN_2O_2$	65·0	4·25	10·85	7·35	231 (10,400), 285 (5300), 365 (18,800)
m-MeO	112	66·8	5·15	10·35		$C_{15}H_{14}N_2O_3$	66·65	5·2	10·35		258 (7100), 292 (5500), 370 (18,900)

[a] Lit.,[15] m.p. 123—124°; λ$_{\max.}$ (95% EtOH) 233 (ε 13,700) and 299 nm (16,700).

The high negative ρ value for the reaction of (VI) with substituted anilines (*ca.* −3·0), fits the suggested mechanism. Both the nucleophilic attack and the deprotonation step (k_1 and k_3) are enhanced by electron donation from the ring to the nitrogen atom. Unfortunately, data for hydrogen and carbon basicities of the anilines in acetonitrile are not available for comparison.

EXPERIMENTAL

U.v. spectra were taken with a Perkin-Elmer 450 spectrophotometer, and n.m.r. spectra with a Varian H-100 instrument.

Materials.—All the anilines were commercial products. The solid anilines were crystallised from aqueous ethanol and dried, and the liquid anilines were distilled at reduced pressure. Their m.p.s and b.p.s agreed with literature values.[40] Commercial acetonitrile was refluxed for 12 h over phosphorus pentoxide and distilled through a fractionating column; the middle fraction, b.p. 78·5°, was used for the kinetic runs. 2-Nitroacetophenone was prepared as described by Long and Troutman.[41]

(E)-α-*Chloro*-β-*nitrostyrene* (VI). This compound, m.p. 50—52°; δ (CCl$_4$) 7·38 (1H, s, ⁚CH) and 7·39 (5H, s, Ar); δ (C$_6$D$_6$) 7·51 (1H, s, ⁚CH) and 7·76 (5H, s, Ar), was prepared from phenylacetylene and nitrosyl chloride (2 mol. equiv.) in carbon tetrachloride.[14] In spite of the claim [14] that both (VI) and its Z-isomer are formed, in two experiments under identical conditions we obtained only (VI), in 35% yield, and in a third experiment only traces (<1%) of the Z-isomer were formed. When the reaction was conducted with only 1 mol. equiv. of nitrosyl chloride, and aqueous hydrogen peroxide was then added, only (VI) and none of the Z-isomer was formed.

Numerous attempts to prepare the two isomers from 2-nitroacetophenone and thionyl chloride or oxalyl chloride showed no evidence (u.v.) for the formation of either (VI) or its Z-isomer.

(E)-α-*Chloro*-β-*nitro*[β-^{2}H]*styrene* {[^{2}H](VI)}. This material, $\nu_{\max.}$ 2320 cm^{-1} (C–^{2}H), was prepared similarly from phenyl[^{2}H]acetylene.[42] N.m.r. (C$_6$D$_6$) showed >99% deuteriation.

Products.—The nitro-enamines were prepared by the following general procedure. The aniline (2 mol. equiv.) was added to (VI) (0·5 g) in acetonitrile (15 ml). After the completion of the reaction (0·5 h for p-anisidine, 24 h for p-chloroaniline) the solid anilinium hydrochloride was filtered off, the solution was evaporated, and the residue was crystallised from petroleum (b.p. 60—80°) or from carbon tetrachloride–petroleum; yields were >90%. Analytical data and the u.v. spectra are given in Table 4.

[35] R. B. Pritchard, C. E. Lough, D. J. Currie, and H. L. Holmes, *Canad. J. Chem.*, 1968, **46**, 775; C. E. Lough, D. J. Currie, and H. L. Holmes, *ibid.*, p. 771.

[36] C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, 1967, **89**, 2752.

[37] C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, 1967, **89**, 1721.

[38] (*a*) J. Crosby and C. J. M. Stirling, *J. Chem. Soc.* (*B*), 1970, 671; (*b*) Z. Rappoport, *ibid.*, 1971, 171.

[39] M. Fukuyama, P. W. K. Flanagan, F. T. Williams, jun., L. Frainier, S. A. Miller, and H. Schechter, *J. Amer. Chem. Soc.*, 1970, **92**, 4689; F. G. Bordwell, W. J. Boyle, jun., J. A. Hautala, and K. C. Yee, *ibid.*, 1969, **91**, 4002; F. G. Bordwell, and W. J. Boyle, jun., *ibid.*, 1972, **94**, 3907.

[40] Z. Rappoport, 'Handbook of Tables for Identification of Organic Compounds,' The Chemical Rubber Co., Ohio, 3rd edn., 1967.

[41] L. M. Long and H. D. Troutman, *J. Amer. Chem. Soc.*, 1949, **71**, 2471.

[42] D. S. Noyce and M. D. Schiavelli, *J. Amer. Chem. Soc.*, 1968, **90**, 1023.

Search for Deuterium Incorporation during the Reaction.—Aniline (0·2 g) was treated with (VI) in acetonitrile (10 ml)–D_2O (1 ml). After 2 h at room temperature the solvent was evaporated off and the i.r. spectrum (CCl_4) was taken before and after crystallisation of the enamine from petroleum (b.p. 60—80°). No C–^{2}H absorption in the enamine was observed.

A similar experiment with [^{2}H](VI) and aniline in dry acetonitrile showed no hydrogen incorporation from the aniline into the product (VII; Z = H).

Absence of Exchange in α-(p-*Methoxyanilino*)-β-*nitrostyrene.*—To α-(*p*-methoxyanilino)-β-nitrostyrene (VII; Z = *p*-MeO) in acetonitrile (5 ml), deuterium oxide (1 ml) was added. After 48 h, half the solvent was evaporated off; the i.r. spectrum of the residue showed no deuterium incorporation into the recovered (VII; Z = *p*-MeO). *p*-Anisidine (16 mg) was added to the other half, and the solvent was evaporated off after an additional 72 h at 25°. Again, the i.r. spectrum showed no deuterium incorporation into (VII; Z = *p*-MeO).

Reaction of (VI) *with Triethylamine in* MeCN–D_2O.—Triethylamine (0·3 ml) was added to (VI) (0·4 g) in acetonitrile (10 ml)–D_2O (1 ml). The mixture slowly turned red. After 50 min at room temperature the solvent was evaporated off; the i.r. spectrum (CCl_4) of the remaining solid showed no deuterium incorporation.

Kinetics.—The kinetics were followed spectrophotometrically in the thermostatted chamber of a Beckmann DU spectrophotometer. Initial rate constants were measured.

[4/1409 *Received*, 12*th July*, 1974]