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A kinetic study of the reversible piperidine and morpholine addition to α -nitrostilbene and to α -phenyl-substituted α -nitrostilbenes (4-Me, 4-Br, 3-NO₂, 4-NO₂) in 50% Me₂SO-50% water is reported. The reaction yields a zwitterionic adduct, PhCH(R₂NH⁺)C(Ar)NO₂⁻ (T_A[±]), which is in rapid equilibrium with the anion, PhCH(R₂N)C(Ar)NO₂⁻ (T_A⁻). Rate constants for addition (k_1) and its reverse (k_{-1}) as well as $K_1 = k_1/k_{-1}$ and the acidity constant of the zwitterion (pK_a^{\pm}) could be determined. The Hammett ρ values for all parameters are nearly the same for the piperidine and morpholine reactions, and β_{nuc} is virtually independent of the aryl substituent, indicating $p_{yy'} = \partial \beta_{nuc}/\partial \alpha = \partial \rho/\partial p K_{nuc} \approx 0$. The average ρ values are $\rho(k_1) = 0.90$, $\rho(k_{-1}) = 0.02$, $p(K_1) = 0.88$, $\rho(pK_a^{\pm}) = -1.02$, while the average β values are $\beta_{nuc} = 0.34$, $\beta_{1g} = -0.58$, $\beta_{eq} = 0.93$, $\beta_{nuc}^{n} = \beta_{nuc}/\beta_{eq} = 0.37$, and $\beta_{1g}^{n} = \beta_{1g}/\beta_{eq} = -0.63$. The almost equal magnitude of $\rho(k_1)$ and $\rho(K_1)(\alpha_{nuc}^{n} = \rho(k_1)/\rho(K_1) = 1.02)$ is reminiscent of Bordwell's observation of very large $\alpha_{CH} = \rho(k_1)/\rho(K_1)$ values in the deprotonation of phenylnitroalkanes and suggests an imbalanced transition state, i.e., one in which the delocalization of the negative charge into the nitro group has made little progress relative to bond formation. This lag in charge delocalization is not as pronounced as the $\alpha_{\text{nuc}}^{n} = \rho(k_{1})/\rho(K_{1}) = 1.02$ ratio might imply, though, because it is distorted by the effect of the positive charge on the amino nitrogen. After correcting for this effect one obtains $\alpha_{nuc}^{n}(corr) = 0.67$ and an imbalance of $\alpha_{nuc}^{n}(corr)$ $-\beta_{nuc}^{n} = 0.30$. The factors which render this imbalance smaller than that found in the deprotonation of the phenylnitroalkanes are discussed. Comparison with the reaction of amines with β -nitrostyrenes reveals a similarity in the imbalances but a substantial difference in the intrinsic rate constants for the two systems. Possible interpretations of these findings are offered.

Introduction

Nucleophilic additions to activated olefins (eq 1) show striking similarities to proton transfers involving activated carbon acids (eq 2) in their structure-reactivity behavior.

ArCH=CXY + Nu^ν
$$\stackrel{k_1}{\longleftrightarrow}$$
 ArCH(Nu^{ν+1})-CXY⁻ (1)

$$\operatorname{RCHXY} + \operatorname{B}^{\nu} \xrightarrow{k_{1}} \operatorname{RCXY}^{-} + \operatorname{BH}^{\nu+1}$$
(2)

For example, the intrinsic rate constants, k_0 (k_0 is $k_1 = k_{-1}$ for $K_1 = 1$)² display the same qualitative dependence on the activating substituents XY in both types of reactions; i.e., they decrease with increasing resonance stabilization and hydrogen-bonding solvation of the product carbanion.^{1,4-8}

It has been suggested that the rate retarding effect on k_0 is caused by the fact that, relative to bond formation, development of resonance and solvation in the incipient carbanion has made little progress at the transition state.^{7,9} This lag in the development of resonance and solvation manifests itself by "imbalances" in structure-reactivity coefficients such as Brønsted α and β values. For example, $\alpha_{\rm CH}$ which is the Brønsted α value obtained by varying a remote substituent in the carbon acid (eq 2) is often sig-

nificantly larger than the $\beta_{\rm B}$ value obtained by varying the $pK_{\rm a}$ of the base.¹⁰⁻¹³ The exalted value of $\alpha_{\rm CH}$ is generally understood to indicate a transition state in which the negative charge is largely localized on carbon, which is the equivalent of stating that resonance and solvation are poorly developed at the transition state.

As one would expect in the light of the above interpretation, the extent by which α_{CH} exceeds β_{B} increases with the degree of resonance and solvational stabilization in the product carbanion. In fact for nitroalkanes the situation is so extreme as to lead to α_{CH} values greater than unity, e.g., $\alpha = 1.54$ and 1.29 for the deprotonation of arylnitromethanes by OH⁻ or morpholine respectively,^{10a} in spite of "normal" $\beta_{\rm B}$ values of about 0.55. These extreme $\alpha_{\rm CH}$ values have led to the suggestion that there might actually be a tetrahedral intermediate (1),¹⁰ although a kinetic isotope effect study¹⁴ casts doubt on the existence of such an intermediate.



Even though fewer comparable data are available for nucleophilic additions to olefins (eq 1), it appears that similar imbalances occur in these reactions. If one regards the normalized β_{nuc} value $(\beta_{nuc}{}^n = \beta_{nuc}/\beta_{eq})$ as the analogue of β_B and $\alpha_{nuc}{}^n$ (defined as d log $k_1/d \log K_1$ by varying a remote substituent in the olefin) as the analogue of $\alpha_{\rm CH}$, the observation of $\alpha_{nuc}^n > \beta_{nuc}^n$ should then require the same interpretation as the finding of $\alpha_{CH} > \beta_B$. Values of

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⁽²⁾ For proton transfers, statistical factors³ are usually included and hence $k_0 = k_1/q = k_{-1}/p$ at $\Delta pK + \log (p/q) = 0$, with $\Delta pK = pK_a^{BH} - pK_a^{CH}$. (3) Bell, R. P. The Proton in Chemistry; Cornell University: Ithaca,

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 $\alpha_{nuc}{}^{n}$ exceeding $\beta_{nuc}{}^{n}$ have indeed been reported for the addition of aryloxide ions and amines to phenyl-substituted benzylidene Meldrum's acids,^{15,16} and of amines to substituted β -nitrostyrenes.⁴

The data pertaining to imbalances in nucleophilic addition reactions obtained so far are too limited to allow generalizations, though. This paper in which we report on the reaction of piperidine and morpholine with substituted α -nitrostyrenes (α -NS-Z, eq 3 below) is a step toward filling this gap.

The structure of the carbanion in the adduct T_A^{\pm} (eq 3) is quite similar to that of the carbanion formed in the deprotonation of phenylnitroalkanes which are the carbon acids that show the largest imbalances.¹⁰ Hence one might expect a relatively large and thus easily measurable imbalance for the addition to α -nitrostilbenes, as is also the case for amine addition to β -nitrostyrenes.⁴

A study of the α -nitrostilbenes offers another advantage because the phenyl group whose substituents (Z) are varied is attached to the carbanionic rather than the electrophilic carbon. This renders the interpretation of $\alpha_{nuc}{}^n$ more straightforward, because $\alpha_{nuc}{}^n$ should be strictly analogous to α_{CH} in proton transfers. In cases where the substituent variation occurs in the phenyl group attached to the electrophilic carbon (substituted β -nitrostyrenes and benzylidene Meldrum's acids), $\alpha_{nuc}{}^n$ may be affected by the degree of rehybridization of the electrophilic carbon at the transition state, particularly if this rehybridization were not synchronous with charge transfer from the nucleophile, and hence $\alpha_{nuc}{}^n$ may not be strictly comparable to α_{CH} .

Our report will also address problems such as the relationship between imbalances and intrinsic rate constants and provide an analysis of how other factors such as intramolecular hydrogen bonding and steric hindrance of π overlap probably affect the intrinsic rate constant of amine addition to α -nitrostilbenes.

Results

General Features. We studied the reaction of piperidine and morpholine with five α -nitrostilbenes (α -NS-Z with Z = 4-CH₃, H, 4-Br, 3-NO₂, and 4-NO₂) in 50% Me₂SO-50% water. As shown in the Experimental Section the configuration of all substrates was E. The reaction proceeds according to eq 3.



The T_{A}^{-} adducts were identified by their UV spectra $(\lambda_{max}: <250 \text{ nm}^{17} \text{ for } Z = 4\text{-}CH_3, H, 4\text{-}Br; 269 \text{ nm}$ ($\epsilon 1.35 \times 10^4$) for $Z = 3\text{-}NO_2$; 250 nm ($\epsilon 1.34 \times 10^4$) and 402 (5.19 $\times 10^3$) for $Z = 4\text{-}NO_2$), which are quite similar to those of the corresponding phenylnitroethane anions.¹⁸

Table I. Summary of Rate and Equilibrium Constants for Piperidine and Morpholine Addition to α -Nitrostilbenes in 50% Me₂SO-50% Water at 20 °C^a

			Z		
	4-CH ₃	н	4-Br	3-NO ₂	$4-NO_2$
		Piperie	dine		
k ₁ , M ⁻¹ s ⁻¹	88	117^{-}	203	512	575
k_{-1}, s^{-1}	2.30	2.60	2.50	2.24	2.30
K_1, M^{-1}	38	45	81	229	250
pK_a^{\pm}	9.87	9.73	9.47	8.94	8.92
$10^9 K_1 K_a^{\pm}$	5.1	8.4	27	260	300
		Morphe	oline		
$k_1, M^{-1} s^{-1}$	13.9	17.6	33.4	85	99
k_{-1}, s^{-1}	45.4	52	52	48	61°
K_1, M^{-1}	0.31	0.34	0.64	1.80	1.63
pK_a^{\pm}	7.43	7.26	7.00	6.55	6.48^{b}
$10^{9}K_{1}K_{2}^{\pm}$	12	19	64	510	540

 ${}^{a}\mu = 0.5 \text{ M}$ (KCl); error limits discussed in the text. b Assumed to be $pK_{a}^{\pm}(\text{pip}) - 2.44$, see text. c Calculated from inversion plot and estimated pK_{a}^{\pm} , see text.

If a solution of T_A^- is acidified shortly after generating the adduct, the recovery of the substrate is essentially quantitative. On a longer time scale T_A^- eventually decomposes to benzaldehyde and the corresponding arylnitromethane.

The kinetics of amine addition and its reverse were studied at 20 °C in a stopped-flow apparatus and monitored at 335 nm, near or at λ_{max} of the substrate [λ_{max} 326.5, 325, 326.5, 323.5 and 324 nm for Z = 4-CH₃, H, 4-Br, 3-NO₂ and 4-NO₂, respectively (with 10⁻⁴ ϵ 1.11, 1.19, 1.20, 1.35, and 1.44, respectively)]. With α -NS-4-NO₂ the reaction was also monitored at λ_{max} of the adduct (402 nm), with equal results. Pseudo-first-order conditions were used throughout, with substrate concentrations around 5 × 10⁻⁵ M. The ionic strength was maintained at 0.5 M with KCl.

Determination of Forward Rate Constants, k_1 . The kinetics of piperidine addition were measured at pH 11.65 and 12.08 and of morpholine addition at pH 9.02 and 9.43. At each pH the pseudo-first-order rate constants (k_{obsd}) were determined at five different amine concentrations in the range from 0.02 to 0.1 M free amine. The kinetic runs displayed excellent first-order characteristics except for the reactions with α -NS-4-NO₂, where the infinity line was slightly sloping, presumably due to the slow decomposition of T_A^- into benzaldehyde and (*p*-nitrophenyl)nitromethane mentioned before. Appropriate corrections were applied in evaluating k_{obsd} in this case.

The raw data are summarized in Tables S1–S4 (supplementary material).¹⁹ Plots of k_{obsd} vs. free amine concentration (not shown) were all linear with pH-independent slopes. This result is consistent with eq 3 for which k_{obsd} is given by eq 4.

$$k_{\rm obsd} = k_1 [R_2 NH] + k_{-1} \frac{a_{\rm H^+}}{K_{\rm a}^{\pm} + a_{\rm H^+}}$$
 (4)

In the piperidine reaction the intercepts $(k_{-1}a_{\rm H^+}/(K_{\rm a}^+ + a_{\rm H^+}))$ were too small to measure, but in the morpholine reaction they were significant except for the reaction of the 4-nitro derivative. The k_1 values are summarized in Table I.

Evaluation of k_{-1} **and** pK_a^{\pm} **.** Under the conditions conducive to the determination of k_1 the second term in eq 4 was either negligibly small or reduced to $k_{-1}a_{H^+}/K_a^{\pm}$ because of $K_a^{\pm} \gg a_{H^{\pm}}$. In order to determine k_{-1} and K_a^{\pm} ,

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Table II. β Values and log k_0 for Nucleophilic Addition of Morpholine and Piperidine to α -Nitrostilbenes

	2					
	4-CH ₃	Н	4-Br	3-NO ₂	4-NO ₂	average
$\beta_{\rm nuc} = d \log k_1 / d p K_{\rm a}^{\rm R_2 N H_2^+}$	0.35 ± 0.02	0.36 ± 0.02	0.34 ± 0.02	0.34 ± 0.02	0.33 ± 0.02	0.34
$\beta_{\rm lg} = {\rm d} \log k_{-1} / {\rm d} p K_{\rm s}^{\rm R_2 N H_2^+}$	-0.57 ± 0.04	-0.57 ± 0.04	-0.58 ± 0.04	-0.58 ± 0.04	-0.62 ± 0.06	-0.58
$\beta_{\rm ep} = d \log K_1 / d p K_{\rm e}^{\rm R_2 N H_2^+}$	0.92 🌰 0.06	0.93 ± 0.06	0.92 ± 0.04	0.92 ± 0.06	0.95 ± 0.08	0.93
$\beta_{\rm nuc}^{\rm n} = \beta_{\rm nuc} / \beta_{\rm ec}$	0.38 ± 0.06	0.39 ± 0.06	0.37 ± 0.06	0.37 ± 0.06	0.35 ± 0.08	0.37
$\beta_{l\sigma}^{n} = \beta_{l\sigma} / \beta_{s\sigma}$	-0.62 ± 0.06	-0.61 ± 0.06	-0.63 ± 0.06	-0.63 ± 0.06	-0.65 ± 0.08	-0.63
$\log k_0$	1.34 ± 0.06	1.43 ± 0.06	1.60 ± 0.06	1.84 ± 0.06	1.81 ± 0.06	
$p\breve{K}_{a}^{\pm}(pip) - pK_{a}^{\pm}(mor)$	2.44 ± 0.08	2.47 ± 0.08	2.47 ± 0.08	2.39 ± 0.08	2.44^{a}	2.44

^a Assumed value, see text.

the equilibrium was therefore approached in the direction $T_{A}^{-} \rightarrow \alpha$ -NS-Z. T_{A}^{-} was generated by adding substrate to a 0.04 M solution of piperidine or morpholine in 0.001 M KOH. This solution was then placed into the stopped-flow apparatus and mixed with a dilute buffer of low pH ("pH-jump"). The buffers included triethylamine (pH 9.67-10.67), Dabco (pH 8.50-9.29), N-methylmorpholine (pH 6.50-7.89), cacodylic acid (pH 7.39), acetic acid (pH 5.26-6.83), and chloroacetic acid (pH 3.71-4.19).

In these experiments the $k_1[R_2NH]$ term was often negligible and hence k_{-1} and K_a^{\pm} could be obtained from inversion plots according to eq 5. In those cases where $k_1[R_2NH]$ was not negligible, eq 5 was applied to $k_{obsd}^{corr} = k_{obsd} - k_1[R_2NH]$ instead of k_{obsd} . The k_{obsd} values are summarized in Tables S5 and S6.¹⁹ Figure 1 shows two representative inversion plots according to eq 5.

$$\frac{1}{k_{\rm obsd}} = \frac{1}{k_{-1}} + \frac{K_{\rm a}^{\pm}}{k_{-1}a_{\rm H^+}}$$
(5)

Consistent values of k_{-1} were obtained from the inversion plots (experiments in range near pK_a^{\pm}) and from experiments at $pH \ll pK_a^{\pm}$, where $k_{obsd} = k_{-1}$, except for α -NS-4-NO₂, where k_{-1} determined at very low pH was about 40% lower than at pH around pK_a^{\pm} . The reason for the small discrepancy is not known but it is not caused by protonation on the nitro group (aci form) since k_{-1} shows no additional decrease as the pH is lowered further. Two observations suggest that the k_{-1} values obtained at higher pH are more reliable: the spectrum of the recovered substrate solution at low pH indicated formation of minor quantities of an unidentified byproduct, and the k_{-1} values obtained at higher pH are more consistent with the structure-reactivity correlations (see Discussion section). Hence the latter are the values we have adopted.

The various k_{-1} and pK_a^{\pm} values are summarized in Table I. All rate and equilibrium constants are directly measured as described above except for the pK_a^{\pm} and k_{-1} of the morpholine adduct of α -NS-4-NO₂. In this case pK_a^{\pm} was calculated as $pK_a^{\pm}(\text{mor}) = pK_a^{\pm}(\text{pip}) -2.44$, with 2.44 being the average difference between $pK_a^{\pm}(\text{pip})$ and $pK_a^{\pm}(\text{mor})$ for the other substrates, and k_{-1} was obtained from k_{-1}/K_a^{\pm} measured at pH > pK_a^{\pm} (inversion plot). This method was chosen because a direct determination of $pK_a^{\pm}(\text{mor})$ would have to rely on measurements at quite low pH and would suffer from the same problem as k_{-1} determined at very low pH.

Discussion

Rate and equilibrium constants for eq 3 are summarized in Table I. The values for k_1 are considered the most accurate, with a conservatively estimated error limit of $\pm 5\%$ or better. For k_{-1} and K_1 we estimate error limits of $\pm 10\%$ and $\pm 15\%$, respectively, except for the reactions of α -NS-4-NO₂, where, due to the problems mentioned in the Results section, they are $\pm 15\%$ and $\pm 20\%$, respectively. For the pK_a^{\pm} values the likely errors are $\pm 0.04 \log$



Figure 1. Representative inversion plots according to eq 5. Reactions of morpholine adduct of α -NS-H (\blacksquare , top and right axes) and of piperidine adduct of α -NS-4-Br (\blacklozenge , bottom and left axes). Intercept = $1/k_{-1}$, slope = K_a^{\pm}/k_{-1} .

unit for all adducts except for those derived from α -NS-4-NO₂ where they are ± 0.06 unit.

Dependence on Amine. Several structure-reactivity parameters derived from the amine dependence of k_1 , k_{-1} , and K_1 are summarized in Table II. The various β values are, within experimental error, virtually independent of the phenyl substituent; the average values are $\beta_{nuc} = 0.34$, $\beta_{1g} = -0.58$, $\beta_{eq} = 0.93$, $\beta_{nuc}{}^n = 0.37$, and $\beta_{1g}{}^n = -0.63$. It is noteworthy that these β values are quite similar to the ones for morpholine/piperidine addition to β -nitrostyrene under the same reaction conditions ($\beta_{nuc} = 0.32$, $\beta_{1g} = -0.63$, $\beta_{eq} = 0.95$, $\beta_{nuc}{}^n = 0.34$, and $\beta_{1g}{}^n = -0.66$).⁴ The pK_a^{\pm} differences between the piperidine and mor-

The pK_a^{\pm} differences between the piperidine and morpholine adducts, $pK_a^{\pm}(pip) - pK_a^{\pm}(mor)$ are also included in Table II. These differences are, within experimental error, independent of the substituent, for an average of 2.44. This compares with a difference between the pK_a for pipH⁺ and morH⁺ of 2.28 in the same solvent.

Dependence on the Phenyl Substituent. In this and the following sections various types of α values will be used. For easy reference a summary of definitions is given in Table IV. Hammett plots for k_1 , k_{-1} and K_1 based on standard σ substituent constants are shown in Figure 2 for the piperidine reactions. Similar plots (not shown) were obtained for the morpholine reactions. Figure 3 shows Hammett plots of the pK_a^{\pm} values of the zwitterionic adducts. The respective ρ values are collected in Table III.



Figure 2. Hammett plots of k_1 , K_1 , and k_{-1} for piperidine addition to α -NS-Z (Z = 4-Me, H, 4-Br, 3-NO₂, 4-NO₂).



Figure 3. Hammett plots of pK_a^{\pm} of the piperidine and morpholine adducts of α -NS-Z (Z = 4-Me, H, 4-Br, 3-NO₂, 4-NO₂).

The following features are noteworthy:

(1) It was not necessary to use an exalted σ value (e.g., $\sigma^{-})^{20}$ to make α -NS-4-NO₂ fit on the Hammett plots for K_1 , k_1 , and k_{-1} . This indicates that the resonance effect of the *p*-nitro group on the arylnitromethane anion moiety is of minor importance. This is undoubtedly due to steric hindrance of π overlap between the carbanionic center and the α -aryl group in T_A^- ; it contrasts with the arylnitromethane anions whose pK_a values do correlate with σ^- rather than σ ;^{10a,25} see also ref 26. A steric effect can again be seen, though, with the arylnitroethane anions since their pK_a values only require a slightly exalted σ value for the *p*-nitro derivative.^{10a,18}

(2) The various ρ values are, within experimental error, virtually independent of the amine. In view of the virtual independence of the β values on the phenyl substituent (Table II) this result is not surprising; it is in fact required by virtue of the diagonal interaction coefficient p_{yy} ,²¹ which is defined by eq 6.

$$p_{yy'} = \frac{\partial^2 \log k_1}{\partial p K_{\text{nuc}} \partial \sigma} = \frac{\partial \beta_{\text{nuc}}}{\partial \sigma} = \frac{\partial \rho}{\partial p K_{\text{nuc}}} = \frac{\partial^2 \log k_1}{\partial \sigma \partial p K_{\text{nuc}}} \quad (6)$$

Table III. ρ and α_{nuc}^n Values

	······	Auc .	
	piperidine	morpholine	average
$\rho(k_1)$	0.87 ± 0.02	0.92 ± 0.03	0.90 ± 0.030
$\rho(k_{-1})$	-0.03 ± 0.03	0.07 ± 0.05	0.02 ± 0.05
$\rho(K_1)$	0.91 ± 0.04	0.85 ± 0.07	0.88 ± 0.07
$\rho(\mathbf{p}K_{\mathbf{a}}^{\pm})$	-1.04 ± 0.03^{a}	-1.00 ± 0.02^{a}	-1.02 ± 0.03^{a}
$\alpha_{\rm nuc}{}^{\rm n} = \rho(k_1) / \rho(K_1)$	0.96 ± 0.03^{b}	1.06 ± 0.07^{b}	1.01 ± 0.07^{b}

 ${}^{a}\rho(\mathbf{p}K_{a}^{*})$ is, within the limits of standard deviations, the same whether σ or σ^{0} is used. b Values given are obtained from plots of log k_{1} vs. log K_{1} .

Table IV. Definition of Various α Values

symbol	definition		
α _{CH}	d log k_1/d log K_1 (change in R, eq 2)		
$\alpha_{\rm nuc}^{\rm n} = \rho(k_1) / \rho(K_1)$	d log k_1/d log K_1 (change in Ar, eq 1, or change in Z, eq 3)		
$\alpha_{nuc}^{n}(corr)$	α_{nuc}^{n} corrected for effect of positive charge		
$\alpha_{\rm res, sol}$ or $\alpha_{\rm res, sol}$ NO ₂	progress of resonance and solvation at transition state (at nitro group)		
$\alpha_{\rm res}^{\rm Ph}$	progress of phenyl resonance at transition state		
$\alpha_{ m st}$	progress of steric effect at transition state		
α_{Hb}	progress of intramolecular hydrogen bonding at transition state		

(3) $\rho(k_1)$ and $\rho(K_1)$ are virtually the same while $\rho(k_{-1})$ is essentially zero, and hence $\alpha_{nuc}{}^n \approx 1.0$ (for definition see Table IV). This high $\alpha_{nuc}{}^n$ value is reminiscent of the results in the deprotonation of arylnitroalkanes, although $\alpha_{nuc}{}^n$ does not quite reach the α_{CH} values of 1.29–1.54 observed in these proton transfers.¹⁰

(4) The average $\rho(pK_a^{\pm})$ value (-1.02) is somewhat less negative than $\rho(pK_a^{\pm}) = -1.15$ for the amine adducts of β -nitrostyrene. This reduction must be due to the fact that the aryl group in the α -nitrostilbene adducts is one carbon further removed from the amine nitrogen in the β -nitrostyrene adducts. The difference between the $\rho(pK_a^{\pm})$ values for the α -nitrostilbene and β -nitrostyrene adducts actually seems small, probably because the less aqueous solvent²² tends to enhance the absolute value of $\rho(pK_a^{\pm})$ for the α -nitrostilbene adducts.

Imbalance. On the basis of the above results one might calculate an imbalance, $\alpha_{nuc}^n - \beta_{nuc}^n$ of ≈ 0.67 . However this value overestimates the "true" imbalance because the experimental $\alpha_{nuc}{}^n - \beta_{nuc}{}^n$ is distorted by the effect of the positive charge on the amine nitrogen. A similar distortion was found for the reaction of amines with substituted β -nitrostyrenes.⁴ It is caused by the fact that the ρ values (and hence α_{nuc}^{n}) measure the combined effect of negative and positive charge development. With the β -nitrostyrenes the distortion was particularly strong because the phenyl substituent is quite close to the site of positive charge and relatively remote from the site of negative charge. This manifests itself by very small $\rho(K_1)$ and $\rho(k_1)$ values (-0.06) and 0.27, respectively),⁴ indicating a near cancellation of the effects of the opposite charges. With the α -nitrostilbenes the substituent is much closer to the site of negative than to that of positive charge and hence the distorting effect of the positive charge should be smaller. This is borne out by the much larger $\rho(K_1) = 0.88$ and $\rho(k_1)$ = 0.90 values which show that here the influence of the negative charge clearly outweighs that of the positive charge.

In correcting α_{nuc}^n for the effect of the positive charge we follow the procedure developed before.⁴ We first correct for the contribution of the positive charge on $\rho(K_1)$ by expressing $\rho(K_1)$ as the sum of two terms (eq 7). $\rho_{eq}(C^{-})$

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$$\rho(K_1) = \rho_{eq}(C^-) + \rho_{eq}(NH^+) = 0.88$$
(7)

is the response to the negative charge, and $\rho_{\rm eq}(\rm NH^+)$ the response to the positive charge. $\rho_{eq}(NH^+)$ may be approximated by the ρ value for $pK_a^{\pm}(\rho(pK_a^{\pm}) = -1.02$, Table III). Solving eq 7 for $\rho_{eq}(C^{-})$ affords eq 8.

$$\rho_{\rm eq}(\rm C^{-}) = 0.88 + 1.02 = 1.90$$
(8)

In analogy to eq 7 we express $\rho(k_1)$ by eq 9.

$$\rho(k_1) = \rho_{\rm kin}(\rm C^-) + \rho_{\rm kin}(\rm NH^+) = 0.90 \tag{9}$$

The ratio $\rho_{\rm kin}(\rm NH^+)/\rho_{eq}(\rm NH^+)$ can be regarded as a measure of the progress of positive charge development on the amine nitrogen at the transition state, as seen by the phenyl substituent, while $\beta_{nuc}{}^n$ is assumed to measure the same process as seen by the amine substituent. Hence we set them equal and obtain

$$\rho_{\rm kin}(\rm NH^+) / \rho_{\rm eq}(\rm NH^+) = \beta_{\rm nuc}{}^{\rm n} = 0.37$$
 (10)

and

$$\rho_{\rm kin}(\rm NH^+) = 0.37(-1.02) = -0.38$$
(11)

Inserting into eq 9 leads to

$$\rho_{\rm kin}(\rm C^{-}) = 0.90 + 0.38 = 1.28 \tag{12}$$

and hence the corrected α_{nuc}^{n} is

$$\alpha_{\rm nuc}^{\rm n}({\rm corr}) = \rho_{\rm kin}({\rm C}^{-}) / \rho_{\rm eq}({\rm C}^{-}) = 1.28 / 1.90 = 0.67$$
 (13)

The difference $\alpha_{nuc}^{n}(corr) - \beta_{nuc}^{n} = 0.67 - 0.37$ (average value) = 0.30 may now be taken as a measure of the imbalance caused by the delayed development of resonance and solvation of the α -nitro group. It is noteworthy that this imbalance is comparable in size to that for the addition of piperidine and morpholine to β -nitrostyrene (0.26).⁴ This is a reasonable result and suggests that $\alpha_{nuc}^{n}(corr)$ in the β -nitrostyrene reactions is not significantly distorted by the possible nonsynchronicity between charge transfer and rehybridization discussed in the Introduction.

It appears then that the present study, along with three previous ones^{4,15,16} clearly establishes the presence of substantial imbalances in nucelophilic additions to activated olefins. On the other hand, it is also clear that these imbalances are much smaller than in the corresponding proton transfers, as seen by comparing $\alpha_{nuc}^{n}(corr) - \beta_{nuc}^{n}$ = 0.67 - 0.37 = 0.30 for amine addition to α -nitrostilbene with $\alpha_{CH} - \beta_B = 1.29 - 0.55 = 0.74$ for deprotonation of 1-arylnitroethanes by secondary aliphatic amines.^{10a}

One of the main reasons for this large difference probably lies in the different hybridizations of the carbon that bears the nitro group: in the nitroalkanes this carbon is sp³-hybridized, and it may largely retain this hybridization in the transition state (2). In the nitroolefins the carbon is sp²-hybridized, which facilitates π overlap with the nitro group and hence the shift of the negative charge into this group at the transition state (3).



Another factor likely to contribute to the difference in the imbalances is related to the absolute magnitude of $\beta_{\rm B}$ and β_{nuc}^{n} , respectively. This is best understood with reference to Figure 4, which is a schematic More O'Ferrall-Jencks diagram with separate axes for charge transfer (β = $\beta_{\rm B}$ or $\beta_{\rm nuc}$ ⁿ) and for the development of resonance and solvation ($\alpha_{res.sol}$). As can be seen from the figure, the



Figure 4. More O'Ferrall-Jencks diagrams showing separate axes for the degree of charge transfer ($\beta = \beta_B$ or β_{nuc} ⁿ) and for the development of resonance and solvation $(\alpha_{res,sol})$ for proton transfer (A) and nucleophilic addition (B). Curved reaction coordinates indicate a lag in the development of resonance and solvation behind charge transfer; dashed lines refer to a hypothetical reaction coordinate with no lag. $|\alpha_{res,sol} - \beta|$ is seen to depend both on degree of curvature in the reaction coordinate and on the magnitude of β .

extent by which resonance (and solvation) development lags behind charge transfer, as measured by $|\alpha_{res,sol} - \beta|$, not only depends on the extent by which the reaction coordinate deviates from the diagonal but also on the location of the transition state on the reaction coordinate, i.e., on the value of β . For the idealized symmetrical reaction coordinate shown in Figure 4 $|\alpha_{\rm res,sol} - \beta|$ goes through a maximum at a β value somewhat larger than 0.5, and approaches zero for $\beta \rightarrow 0$ and $\beta \rightarrow 1.0$.

Even though $\alpha_{res,sol} - \beta$ is not the same as $\alpha_{CH} - \beta_B$ or $\alpha_{nuc}^{n}(corr) - \beta_{nuc}^{n} (\alpha_{res,sol} - \beta \text{ is a negative number})$ these expressions are related because it is the lag in resonance (and solvation) development which is responsible for the imbalances measured by $\alpha_{\rm CH} - \beta_{\rm B}$ or $\alpha_{\rm nuc}{}^{\rm n}({\rm corr}) - \beta_{\rm nuc}{}^{\rm n}$. In a crude approximation we can therefore assume that $\alpha_{\rm CH}$ a crude approximation we can therefore assume that $\alpha_{\rm CH} - \beta_{\rm B}$ and $\alpha_{\rm nuc}{}^{\rm n}({\rm corr}) - \beta_{\rm nuc}{}^{\rm n}$ are roughly proportional to $|\alpha_{\rm res,sol} - \beta|$. Thus one would expect that $\alpha_{\rm CH} - \beta_{\rm B}$ for the proton transfer is larger than $\alpha_{\rm nuc}{}^{\rm n}({\rm corr}) - \beta_{\rm nuc}{}^{\rm n}$ for the addition reactions since $\beta_{\rm B} = 0.55$, but $\beta_{\rm nuc}{}^{\rm n}$ is only 0.37 for the α -nitrostilbenes and 0.26 for the β -nitrostyrenes.²³

Intrinsic Rate Constants. Intrinsic rate constants, k_0 , for the various α -nitrostilbenes are included in Table II. They were calculated from eq 14

$$\log k_0 = \log k_1 - \beta_{\text{nuc}}^n \log K_1 \tag{14}$$

where k_1 and K_1 refer to the same amine; this procedure is equivalent to our standard method⁸ of extrapolating or interpolating a plot of log k_1 vs. log K_1 , generated by varying the amine, to $\log K_1 = 0$.

The log k_0 values increase with increasing electronwithdrawing strength of the substituent. This increase is not due to any special feature of the electron-withdrawing substituents but merely a consequence of the fact that $\alpha_{\rm nuc}{}^{\rm n}$ $> \beta_{nuc}^{n}$. The change in log k_0 with substituent Z, relative

Soc. 1979, 101, 1295.

⁽²³⁾ On the basis of a simple central-force model used to calculate free energy changes and Brønsted exponents for proton transfer reactions, Bell²⁴ has suggested that now mey somewhat any transfer reactions, Bell²⁴ has suggested that α_{CH} may somewhat exceed β_B even in cases where there is no lag in the development of resonance or solvation at the transition state. We cannot speculate on how this effect, if it exists, would affect the relative magnitudes of $\alpha_{\rm CH} - \beta_{\rm B}$ and $\alpha_{\rm nuc}{}^{\rm n}({\rm corr}) - \beta_{\rm nuc}{}^{\rm n}$. (24) Bell, R. P. J. Chem. Soc., Faraday Trans. 1 1982, 78, 2593. (25) Keeffe, J. R.; Morey, J.; Palmer, C. A.; Lee, J. C. J. Am. Chem.

⁽²⁶⁾ A referee has pointed out that a comparison with α -cyanostilbenes where even σ^- for the *p*-nitro group is not exalted enough to correlate the equilibrium constants for methoxide ion addition²⁷ might be more relevant in demonstrating the steric effect.

⁽²⁷⁾ Stewart, R.; Kroeger, D. J. Can. J. Chem. 1967, 45, 2173.

to the unsubstituted compound, can be expressed by eq 15,⁹ with $\delta \log K_1(Z)$ being equivalent to $\log \{K_1(Z)/K_1(H)\}$. Note that the measured α_{nuc}^{n} rather than $\alpha_{nuc}^{n}(corr)$ is used in eq 15.

$$\delta \log k_0(Z) = (\alpha_{\text{nuc}}^n - \beta_{\text{nuc}}^n) \delta \log K_1(Z)$$
(15)

The log k_0 value for the parent α -nitrostilbene (1.43) is considerably lower than that for the piperidine/morpholine addition to β -nitrostyrene in the same solvent (2.55).⁴ A similar reduction is observed in comparing log k_0 for the deprotonation of phenylnitromethane (-0.25) with that of nitromethane (0.73).²⁸ In the proton transfer the reduction in log k_0 is most easily understood as the consequence of a lag in the development of the resonance effect of the phenyl group.²⁹ There is now ample experimental evidence⁷⁻⁹ as well as theoretical justification³⁰⁻³² which indicates that resonance development is generally late along the reaction coordinate and that this is the reason why k_0 for the formation of resonance-stabilized ions is reduced essentially in proportion to the degree of resonance stabilization of the product ion. Hence, on top of the strong k_0 -lowering effect of nitronate ion resonance (and solvation), there is the additional effect from the phenyl resonance. In keeping with a formalism developed earlier,^{7,9} the total reduction in k_0 , relative to a reference system for which there is no resonance stabilization of the carbanion, may be expressed by eq 16

$$\delta \log k_0 = \delta \log k_0^{\text{res}}(\text{NO}_2) + \log k_0^{\text{res}}(\text{Ph}) \quad (16)$$

with δlog

$$k_0^{\text{res}}(\text{NO}_2) = (\alpha_{\text{res,sol}}^{\text{NO}_2} - \beta_{\text{B}})\delta \log K_1^{\text{res}}(\text{NO}_2) \quad (17)$$

$$\delta \log k_0^{\text{res}}(\text{Ph}) = (\alpha_{\text{res}}^{\text{Ph}} - \beta_{\text{B}})\delta \log K_1^{\text{res}}(\text{Ph})$$
 (18)

In eqs 17 and 18 $\delta \log K_1^{\text{res}}(\text{NO}_2)$ and $\delta \log K_1^{\text{res}}(\text{Ph})$ represent the increased stability of the carbanion caused by the resonance (and solvation) effect of the nitro group and the resonance effect of the phenyl group, respectively. $\alpha_{\rm res sol}^{\rm NO_2}$ is the progress in the development of the nitro group resonance (and solvation) and corresponds to $\alpha_{res,sol}$ in Figure 4, α_{res}^{Ph} is the progress in the phenyl resonance development.

Since $\alpha_{\text{res,sol}}^{\text{NO}_2} < \beta_{\text{B}}$ and $\alpha_{\text{res}}^{\text{Ph}} < \beta_{\text{B}}$, $\delta \log k_0^{\text{res}}(\text{NO}_2)$ and $\delta \log k_0^{\text{res}}(\text{Ph})$ are both negative. Assuming that $\delta \log k_0^{\text{res}}(\text{Ph})$ $k_0^{\text{res}}(NO_2)$ for the deprotonation of phenylnitromethane is of comparable magnitude as for the deprotonation of nitromethane, the lower k_0 value for phenylnitromethane can then be understood as arising from the negative $\delta \log$ $k_0^{\text{res}}(\text{Ph})$ term in eq 16.

Can the lower k_0 value for amine addition to α -nitrostilbene as compared to β -nitrostyrene be explained in a similar way? It is tempting to do so, but closer scrutiny indicates that other factors come into play. For example, the strongly increased acidity of phenylnitromethane (pK_a) = 6.77) compared to nitromethane $(pK_a = 10.28)$ has no counterpart in the K_1 or $K_1K_a^{\pm}$ values for amine addition: K_1 for the piperidine adduct of α -nitrostilbene is 45 M⁻¹ and for the adduct of β -nitrostyrene 31.8 M⁻¹⁴; for $K_1K_3^{\pm}$ the value for α -nitrostilbene (8.4 \times 10⁻⁹) is even lower than that for β -nitrostyrene (1.58 \times 10⁻⁷).⁴ This lack of an enhancement of K_1 or $K_1 K_a^{\pm}$ as well as the failure of K_1 to correlate with σ^- mentioned earlier indicates that the

resonance effect of the phenyl group is either strongly reduced and/or that it is compensated for by other factors. The most likely state of affairs is that steric crowding prevents both the nitro and the phenyl group from achieving optimal π overlap in the α -nitrostilbene adducts.

Because of the reduced resonance effects of the phenyl and nitro groups in the α -nitrostilbene adducts, which imply reduced $\delta \log K_1^{\text{res}}(\text{NO}_2)$ and $\delta \log K_1^{\text{res}}(\text{Ph})$ values in eqs 17 and 18, respectively, $\delta \log k_0$ in eq 16 should be small. Hence one would expect that the change from β nitrostyrene to α -nitrostilbene reduces k_0 for nucleophilic addition less than the change from nitromethane to phenylnitromethane decreases k_0 for proton transfer. The fact that the observed reductions in k_0 are about the same or even slightly larger for the nucleophilic addition ($\Delta \log k_0$) = -1.12) than for the proton transfer ($\Delta \log k_0 = -0.98$) indicates that factors other than resonance must contribute to the lowering of k_0 with α -nitrostilbene.

Two such factors have recently been identified in the reaction of amines with benzylidene acetylacetone:¹ early development of steric hindrance to π overlap of the stabilizing groups attached to the carbanionic carbon and late development of intramolecular hydrogen bonding between the amine proton and an oxyanion in the adduct.

We have already discussed the evidence which points to steric hindrance to π overlap of the phenyl and nitro group of the α -nitrostilbene adducts. It is likely that this steric hindrance is already largely built into the substrate, as is clearly evident from molecular models, and thus development of the steric effect is indeed "early". The reduction in k_0 can then be expressed by eq 19, with $\delta \log \delta$

$$\delta \log k_0^{\rm st} = (\alpha_{\rm st} - \beta_{\rm nuc}^{\rm n}) \delta \log K_1^{\rm st}$$
(19)

 $K_1^{\rm st}$ (<0) being the reduction in the equilibrium constant caused by the steric effect and α_{st} (> β_{nuc} ⁿ) being the progress in the development of the steric effect at the transition state.

Intramolecular hydrogen bonding in the adducts of α -nitrostilbene is suggested by the p K_a^{\pm} values ($T_A^{\pm} \rightleftharpoons T_A^{-}$ + H^+) which are more than one pK unit higher than for the corresponding β -nitrostyrene adducts. For example, $pK_s^{\pm} = 9.73$ for the piperidine adduct of α -nitrostilbene, and $pK_a^{\pm} = 8.30$ for that of β -nitrostyrene. Development of this intramolecular hydrogen bond is likely to lag behind C-N bond formation because the donor and acceptor atoms may still be quite far apart in the transition state, and, probably more importantly, the acidity of the N-H proton and the basicity of the oxygen have not developed enough to give the hydrogen bond significant stability.

The decrease in k_0 caused by the lagging hydrogen bond is expressed by eq 20, with $\delta \log K_1^{\text{Hb}}$ (>0) being the increased stability of the adduct that results from hydrogen bonding and α_{Hb} ($<\beta_{nuc}^n$) measuring the development of the hydrogen bond at the transition state.

$$\delta \log k_0^{\text{Hb}} = (\alpha_{\text{Hb}} - \beta_{\text{nuc}}^{n}) \delta \log K_1^{\text{Hb}}$$
(20)

Conclusions. The kinetic behavior of amine addition to α -nitrostilbenes shows strong similarities to that of amine addition to β -nitrostyrenes but there also exist some subtle, though significant, differences.

(1) Both systems display large imbalances between $\beta_{nuc}{}^{n}$ and α_{nuc}^{n} . After correction for the effect of positive charge on the amine nitrogen the imbalance for the α -nitro-stilbenes, $(\alpha_{nuc}{}^{n}(corr) - \beta_{nuc}{}^{n} = 0.67 - 0.37 = 0.30)$ is quite similar to that for the β -nitrostyrenes $(\alpha_{nuc}{}^{n}(corr) - \beta_{nuc}{}^{n})$ = 0.51 - 0.25 = 0.26).

(2) The imbalances in the nucleophilic addition reactions are much smaller than the imbalances in the corresponding deprotonation of phenylnitroalkanes. This is probably

⁽²⁸⁾ Bernasconi, C. F.; Kliner, D. A.; Mullin, A., unpublished observations

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Table V. Predicted and Observed Shifts of Vinyl Proton of α -Nitrostilbenes^a

Z	$base(E)^d$	$base(Z)^d$	$\delta_{\text{calcd}}(E)^b$	$\delta_{\text{calcd}}(Z)^c$	δ_{obsd}
Н	5.20	5.70	8.22	7.51	8.21
4-Br	5.23	5.68	8.25	7.49	8.25
$4-CH_3$	5.18	5.69	8.20	7.50	8.20
$3-NO_2$	5.41	5.86	8.43	7.67	8.33
$4 - NO_2$	5.47	5.90	8.49	7.71	8.31

^a In ppm downfield from Me₄Si in CDCl₃. ^b $\delta_{calc}(E) = base + Z_{(gem Ph)} (=1.35)^{42} + Z_{(cis NO_2)} (=1.67)^{.43} \circ \delta_{cacl}(Z) base + Z_{(gem Ph)} (=-1.35)^{42} + Z_{(trans NO_2)} (=1.67)^{.43} d$ Reference 44.

mainly a consequence of the sp²-hybridization of the olefins which facilitates π overlap in the transition state and contrasts with the sp³-hybridization of the carbon acids. Thus, the reaction coordinate for nucleophilic addition (Figure 4) is closer to the diagonal than for proton transfer which reduces $|\alpha_{res,sol} - \beta|$. A contributing factor to the smaller imbalances may be lower $\beta_{nuc}{}^n$ values compared to β_B in the proton transfer which leads to further reduction in $|\alpha_{\text{res,sol}} - \beta|$ (Figure 4).

(3) The intrinsic rate constant for piperidine/morpholine addition to α -nitrostilbene (log $k_0 = 1.45$) is significantly lower than the already low value for β -nitrostyrene (log k_0 = 2.55). This reduction is very similar in magnitude to the reduction in k_0 observed when comparing the deprotonation of phenylnitromethane with that of nitromethane, but these reductions have different causes in the different reactions. In the proton transfer the reduction is probably a consequence of late development of the additional resonance introduced by the phenyl group, a factor that is minimal or nonexistent in the addition to α -nitrostilbenes because steric hindrance prevents π -overlap with the phenyl group. Rather, the reduction is attributed to early development of this steric hindrance and/or to a late development of intramolecular hydrogen bonding between the ammonio proton and the nitro group.

Experimental Section

Materials. The α -nitrostilbenes were prepared by condensation of the corresponding phenylnitromethanes and Nbenzylidinebutylamine according to the method of Robertson³³ and were recrystallized from ethanol/acetic acid: α -nitrostilbene, mp 73-74 °C (lit.³⁴ mp 74-75 °C); 4-methyl-α-nitrostilbene, mp 72-73.5 °C (lit.³⁵ 75-76 °C); 4-nitro-α-nitrostilbene, mp 117.5-118.5 °C (lit.³⁶ mp 122-123 °C).

4-Bromo- α -nitrostilbene is previously unreported: mp 101–103 °C; NMR δ 8.25 (s, 1 H, vinyl), 7.61, 7.18 (A₂B₂, 4 H, Ar), 7.15 (m, 5 H, Ar).

The 3-nitro- α -nitrostilbene prepared in the current study has mp 107-108 °C, which is substantially different from the value of 179-180 °C reported by Flürscheim and Holmes.³⁷ Fur-

(34) Freeman, J. P.; Stevens, T. E. J. Org. Chem. Soc. 1958, 23, 136.

thermore, these workers report the compound to be nearly colorless, whereas our material is distinctly yellow, as are the other α -nitrostilbenes. Since the NMR and UV-vis spectra of our compound are consistent with (E)-3-nitro- α -nitrostilbene, it seems likely that the previously reported material is a different compound.38

Substituted phenylnitromethanes used to make the stilbenes were in turn prepared by reaction of appropriately substituted benzyl bromides with AgNO2 or NaNO2, as described by Kornblum.40

Unsubstituted α -nitrostilbene was also prepared by the reaction of trans-stilbene and acetyl nitrate.41

Piperidine, morpholine, triethylamine, and N-methylmorpholine were refluxed over calcium hydride and distilled. Dabco was recrystallized from hexanes. Chloroacetic acid was recrystallized from petroleum ether. Cacodylic acid, acetic acid, and potassium chloride were used without further purification. KOH and HCl solutions were "Dilut-it" (Baker) diluted to appropriate volumes with deionized distilled water.

Stereochemistry of α -Nitrostilbenes. The stereochemistry of all the stilbenes was unambiguously determined to be E for all substrates by NMR spectroscopy. NMR spectra were obtained in CDCl₃ at 60 MHz on a Varian EM-360 spectrometer.

The shifts of the β -hydrogen for each substrate was compared to predicted values for both the E and Z terms. These were calculated by adding the chemical shift substituent constants for phenyl^{42} and nitro^{43} groups to the shifts of the corresponding hydrogens of the appropriate aryl-substituted styrenes.⁴⁴ The observed and predicted shifts are summarized in Table V.

Kinetics. All experiments were carried out in 50% Me₂SO-50% H₂O in a Durrum stopped-flow spectrophotometer with computerized data acquisition and analysis. Kinetics in the forward direction were evaluated by mixing a solution of the substrate $(1 \times 10^{-4} \text{ M})$ in 0.5 M KCl with the appropriate amine/amine hydrochloride solution. In pH-jump experiments the T_A^- species was generated by dissolving the substrate in 0.04 M of the amine and 0.001 M KOH; this was mixed with an appropriate acidic buffer in the stopped-flow apparatus to give the desired final pH. Reactions were monitored at 335 nm. Solution pH's were determined from mock mixing experiments using an Orion 611 digital pH meter standardized against 50% $Me_2SO-50\%$ H_2O buffers described by Hallé et al.

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Supplementary Material Available: Pseudo-first-order rate constants for morpholine and piperidine addition to α -nitrostilbenes and for decomposition of morpholine and piperidine adducts of α -nitrostilbenes (Tables S1–S6) (6 pages). Ordering information is given on any current masthead page.

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